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The thermodynamic tabulations previously published in four collections are extended by 227 new and revised tables. The JANAF Thermochemical Tables cover the thermodynamic properties over a wide temperature range with single phase tables for the crystal, liquid, and ideal gas state. In addition some multiphase tables are given. The properties given are heat capacity, entropy, Gibbs energy function, enthalpy, enthalpy of formation, Gibbs energy of formation, and the logarithm of the equilibrium constant for formation of each compound from the elements in their standard reference states. Each tabulation lists all pertinent input data and contains a critical evaluation of the literature upon which these values are based. Literature references are given.

Key words: critically evaluated data; enthalpy; entropy; equilibrium constant of formation; free energy of formation; Gibbs energy function; heat capacity; heat of formation; thermochemical tables.

Contents

1. Introduction

Since the inception of the JANAF Thermochemical Tables project in late 1959, the tables have been collected together to form eight publications [1–8].[1] The four early publications [5–8] are superseded by four more recent publications [1–4]. NSRDS-NBS 37 [1] includes all work through June 30, 1970. Tables generated in the period December 31, 1970 to June 30, 1976 are included in the 1974, 1975, and 1978 Supplement [2, 3, 4]. The 227 tables generated in the period December 31, 1976 to June 30, 1978 are combined in this article to provide additional tables which are to be used in conjunction with the four more recent publications [1, 2, 3, 4].

As of June 30, 1978, there are 1467 tabulations involving 42 elements and their compounds. The 42 elements are H, D, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Ti, V, Cr, Fe, Co, Ni, Cu, Br, Kr, Sr, Zr, Nb, Mo, I, Xe, Cs, Ba, Ta, W, Hg, and Pb.

The JANAF Thermochemical Tables are prepared following the procedures outlined in NSRDS-NBS 37 [1]. In our analyses of equilibrium data we give tabulations for the second and third law results and often list values (in units of eu (entropy units) or gibbs/mol) for the "drift." (The gibbs is defined as the thermochemical calorie per kelvin.) This is discussed briefly on page 5 in NSRDS-NBS 37 [1]. This drift actually refers to the difference, ΔS°_{298} (3rd law) $-$ ΔS°_{298} (2nd law). ΔS_{298} (2nd law) is not calculated, however, via the usual second law method or the Σ-method. It is instead derived from the slope of the assumed linear temperature dependence of the deviations from the mean of the third law heats of reaction. Our experience indicates that this method agrees closely, but no exactly, with the Σ-method. A detailed, general treatment of the analysis of equilibrium data is given by Freeman [9].

In the tabulations the Gibbs energy function and the enthalpy are referred to 298.15 K. Throughout the JANAF project we have striven for internal consistency. Internal and external reviews, however, do not always remove some minor discrepancies. In addition, changes in the nomenclature as adopted by Chemical Abstracts leave the tables with some out-dated chemical names. Changes in the atomic weights, the fundamental constants, and the temperature scale also cause minor internal inconsistencies. At present we are gradually converting each new or revised table to the 1977 atomic weights and the IPTS-68 temperature scale. This task is not easy and unambiguous, as the articles appearing in the literature do not always specify the standards used.

Finally, the JANAF Thermochemical Tables are presented in terms of the thermochemical calorie defined as 4.184 J. Values involving the calorie can be converted to the joule (for SI units) by multiplying by 4.184.

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[1] Figures in brackets indicate literature references.

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Two indices are provided in this article. The index in section 4 lists the tables which appear in this article. The list is alphabetical by name. Where applicable, the appropriate cross reference for the currently accepted Chemical Abstracts name is also included. The aim is to provide in this index any name which may be used so as to provide the reader an easier way to find the species of interest. The index in section 5 is the complete index for the JANAF Thermochemical Tables as of June 30, 1978. This complete index lists tables which are in NSRDS-NBS 37 [1], the 1974 Supplement [2], the 1975 Supplement [3], the 1978 Supplement [4], and this article. It should be emphasized that the tables in this article may be new (in which case there is no corresponding entry in the previous four publications [1, 2, 3, 4] or revised (in which case the table in this article supersedes the corresponding table in one of the previous four publications [1, 2, 3, 4]). The location of the most current table for a given species is best found by using the latest issue column in this index. This column refers to the year of publication of the five JANAF publications. The tables are arranged in this article in the same order as given in the complete index of section 5.

2. Acknowledgments

The JANAF Thermochemical Tables Project, as contained in this article, is sponsored by the Air Force Office of Scientific Research (Contract F44620-75-C-0048) and the U.S. Department of Energy, Pittsburgh Energy Technical Center Combustion Division (Contract EV-76-C-02-2984). The JANAF project since June 30, 1976, has been monitored by Dr. Joseph F. Masi, Captain Robert F. Sperlein, Dr. Leonard H. Caveny, and Mr. Francis E. Spencer, Jr. Their cooperation, direction, and encouragement are greatly appreciated. In Physicochemical Studies of The Dow Chemical Company, Daniel R. Stull was the project director from 1959–1969; followed by Harold Prophet from 1969 until his untimely death in late 1972. Malcolm W. Chase, Jr. is currently the project director with the principal contributors being P. A. Andreozzi, Carol A. Davies, Joseph R. Downey, Jr., Richard A. McDonald, Alan N. Syverud, Edward A. Valenzuela, and R. L. Vance. We thank the staff of Systems Research Laboratory of The Dow Chemical Company for their assistance in the production of these tables with special thanks to Betty Clark, Rhoda Toth, Dana Donley, Deborah Simpson, and Marge Sheets.

3. References

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[4] M. W. Chase, J. L. Curnutt, R. A. McDonald, and A. N. Syverud, JANAF Thermochemical Tables, 1978 Supplement, J. Phys. Chem. Ref. Data 7, 793 (1978).

[5] JANAF Thermochemical Tables, PB 168370, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1965 (obsolete).

[6] JANAF Thermochemical Tables, PB 168370-1, Information, Springfield, Virginia, 1966 (obsolete).

[7] JANAF Thermochemical Tables, PB 168370-2, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1967 (obsolete).

[8] JANAF Thermochemical Tables, PB 168370-3, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1968 (obsolete).

[9] R. D. Freeman, Bull. Chem. Thermodyn. 21, 505 (1973); High Temp. Sci. 11, 213 (179).

4. List of Tables in 1982 Supplement

5. Complete List of JANAF Thermochemical Tables

JANAF THERMOCHEMICAL TABLES - FILING ORDER

FORMULA	TABLE TITLE	LATEST ISSUE
Al	Aluminum (ref st)	1971
Al	Aluminum (c)	1971
Al	Aluminum (l)	1971
Al	Aluminum, monatomic (g)	1971
Al+	Aluminum, unipositive ion (g)	1971
$AlBO_2$	Aluminum boron dioxide (g)	1971
AlBr	Aluminum monobromide (g)	1974
$AlBr_3$	Aluminum tribromide (c)	1974
$AlBr_3$	Aluminum tribromide (l)	1974
$AlBr_3$	Aluminum tribromide (g)	1974
AlCl	Aluminum monochloride (g)	1971
AlCl+	Aluminum monochloride, unipos ion (g)	1978
AlClF	Aluminum chloride fluoride (g)	1978
AlClF+	Aluminum chloride fluoride, pos (g)	1978
$AlClF_2$	Aluminum chloride difluoride (g)	1978
AlClO	Aluminum oxychloride (c)	1971
AlClO	Aluminum oxychloride (g)	1971
$AlCl_2$	Aluminum dichloride (g)	1978
$AlCl_2+$	Aluminum dichloride, unipos ion (g)	1978
$AlCl_2-$	Aluminum dichloride, unineg ion (g)	1978
$AlCl_2F$	Aluminum dichloride fluoride (g)	1978
$AlCl_3$	Aluminum trichloride (c)	1971
$AlCl_3$	Aluminum trichloride (l)	1971
$AlCl_3$	Aluminum trichloride (g)	1971
$AlCl_4K$	Potassium tetrachloroaluminate (c)	1971
$AlCl_4Na$	Sodium tetrachloroaluminate (c)	1971
$AlCl_6K_3$	Tripotassium hexachloroaluminate (c)	1971
$AlCl_6Na_3$	Trisodium hexachloroaluminate (c)	1971
AlF	Aluminum monofluoride (g)	1978
AlF+	Aluminum monofluoride, unipos ion (g)	1978
AlFO	Aluminum fluoride oxide (g)	1978
AlF_2	Aluminum difluoride (g)	1978
AlF_2+	Aluminum difluoride, unipos ion (g)	1978
AlF_2-	Aluminum difluoride, unineg ion (g)	1978
AlF_2O	Aluminum difluoride oxide (g)	1978
AlF_2O-	Aluminum difluoride oxide neg ion (g)	1978
AlF_3	Aluminum trifluoride (c)	1971
AlF_3	Aluminum trifluoride (g)	1971
AlF_4-	Tetrafluoroaluminate, unineg ion (g)	1978
AlF_4Li	Lithium tetrafluoroaluminate (g)	1971
AlF_4Na	Sodium tetrafluoroaluminate (g)	1971
AlF_6K_3	Tripotassium hexafluoroaluminate (c)	1971
AlF_6Li_3	Trilithium hexafluoroaluminate (c)	1971
AlF_6Li_3	Trilithium hexafluoroaluminate (l)	1971
AlF_6Na_3	Cryolite (c)	1971
AlF_6Na_3	Cryolite (l)	1971
AlH	Aluminum monohydride (g)	1971
AlHO	Aluminum monoxyhydride (g)	1971
AlHO	Aluminum monohydroxide (g)	1971
AlHO+	Aluminum monohydroxide, pos ion (g)	1971
AlHO-	Aluminum monohydroxide, neg ion (g)	1971
$AlHO_2$	Aluminum dioxyhydride (g)	1971
AlH_4Li	Lithium aluminum hydride (c)	1971
AlI	Aluminum monoiodide (g)	1971
AlI_3	Aluminum triiodide (c)	1971
AlI_3	Aluminum triiodide (l)	1971
AlI_3	Aluminum triiodide (g)	1971
$AlLiO_2$	Lithium aluminate (c)	1974
$AlLiO_2$	Lithium aluminate (l)	1974
AlN	Aluminum nitride (c)	1971
AlN	Aluminum nitride (g)	1971
$AlNaO_2$	Sodium aluminate (c)	1971
AlO	Aluminum monoxide (g)	1978
AlO+	Aluminum monoxide, unipos ion (g)	1978
AlO-	Aluminum monoxide, unineg ion (g)	1978
AlO_2	Aluminum dioxide (g)	1978
AlO_2-	Aluminum dioxide, unineg ion (g)	1978
AlS	Aluminum sulfide (g)	1971
Al_2BeO_4	Beryllium aluminate (c)	1974
Al_2BeO_4	Beryllium aluminate (l)	1974
Al_2Br_6	Aluminum tribromide, dimeric (g)	1974
Al_2Cl_6	Aluminum trichloride, dimeric (g)	1971
$Al_2Cl_9K_3$	Potassium nonachloroaluminate (c)	1971
Al_2F_6	Aluminum trifluoride, dimeric (g)	1971
Al_2I_6	Aluminum triiodide, dimeric (g)	1971
Al_2MgO_4	Magnesium aluminate (c)	1974
Al_2MgO_4	Magnesium aluminate (l)	1974
Al_2O	Aluminum suboxide (g)	1978
Al_2O+	Aluminum suboxide, unipos ion (g)	1978
Al_2O_2	Aluminum monoxide, dimeric (g)	1978
Al_2O_2+	Dialuminum dioxide, unipos ion (g)	1978
Al_2O_3	Aluminum oxide, alpha (c)	1978
Al_2O_3	Aluminum oxide, delta (c)	1978
Al_2O_3	Aluminum oxide, gamma (c)	1978
Al_2O_3	Aluminum oxide, kappa (c)	1978
Al_2O_3	Aluminum oxide (l)	1978
Al_2O_5Si	Sillimanite (c)	1971
Al_2O_5Si	Andalusite (c)	1971
Al_2O_5Si	Kyanite (c)	1971
Al_6BeO_{10}	Aluminum beryllium oxide (c)	1974
Al_6BeO_{10}	Aluminum beryllium oxide (l)	1974
$Al_6O_{13}Si_2$	Mullite (c)	1971
Ar	Argon, monatomic (ref st)	1982
Ar+	Argon, unipos ion (g)	1982
B	Boron (ref st)	1971
B	Boron, beta-rhombohedral (c)	1971
B	Boron (l)	1971
B	Boron, monatomic (g)	1971
B+	Boron, unipositive ion (g)	1974
$BBeO_2$	Beryllium boron dioxide (g)	1971
BBr	Boron monobromide (g)	1971
BBrCl	Boron bromide chloride (g)	1971
$BBrCl_2$	Boron bromide dichloride (g)	1971
BBrF	Boron bromide fluoride (g)	1971
$BBrF_2$	Boron bromide difluoride (g)	1971
BBrO	Boron oxide bromide (g)	1971
BBr_2	Boron dibromide (g)	1971
BBr_2Cl	Boron dibromide chloride (g)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
BBr_2F	Boron dibromide fluoride (g)	1971
BBr_2H	Boron dibromide hydride (g)	1971
BBr_3	Boron tribromide (l)	1971
BBr_3	Boron tribromide (g)	1971
BCl	Boron monochloride (g)	1971
BCl^+	Boron monochloride, unipos ion (g)	1971
$BClF$	Boron chloride fluoride (g)	1971
$BClF_2$	Boron chloride difluoride (g)	1971
$BClO$	Boron oxide chloride (g)	1971
BCl_2	Boron dichloride (g)	1974
BCl_2^+	Boron dichloride, unipos ion (g)	1974
BCl_2^-	Boron dichloride, unineg ion (g)	1974
BCl_2F	Boron dichloride fluoride (g)	1971
BCl_2H	Boron dichloride hydride (g)	1971
BCl_3	Boron trichloride (g)	1971
BF	Boron monofluoride (g)	1971
BFO	Boron oxide fluoride (g)	1971
BF_2	Boron difluoride (g)	1974
BF_2^+	Boron difluoride, unipos ion (g)	1974
BF_2^-	Boron difluoride, unineg ion (g)	1974
BF_2H	Difluoroborane (g)	1971
BF_2HO	Boron hydroxide difluoride (g)	1971
BF_2O	Boron oxide difluoride (g)	1971
BF_3	Boron trifluoride (g)	1971
BF_4K	Potassium tetrafluoroborate (c)	1971
BF_4K	Potassium tetrafluoroborate (l)	1971
BF_4K	Potassium tetrafluoroborate (g)	1971
BH	Boron monohydride (g)	1971
BHO	Boron hydride oxide (g)	1978
BHO^+	Boron hydride oxide, unipos ion (g)	1978
BHO^-	Boron hydride oxide, unineg ion (g)	1978
BHO_2	Metaboric acid (c)	1971
BHO_2	Metaboric acid (g)	1971
BHS	Boron hydride sulfide (g)	1978
BHS^+	Boron hydride sulfide, unipos ion (g)	1978
BH_2	Boron dihydride (g)	1971
BH_2O_2	Boron dihydroxide (g)	1971
BH_3	Boron trihydride (g)	1971
BH_3O_3	Boric acid (c)	1971
BH_3O_3	Boric acid (g)	1971
BH_4K	Potassium tetrahydroborate (c)	1971
BH_4Li	Lithium tetrahydroborate (c)	1971
BH_4Na	Sodium tetrahydroborate (c)	1971
BI	Boron iodide (g)	1971
BI_2	Boron diiodide (g)	1971
BI_3	Boron triiodide (g)	1971
BKO_2	Potassium metaborate (c)	1974
BKO_2	Potassium metaborate (l)	1974
BKO_2	Potassium metaborate (g)	1974
$BLiO_2$	Lithium metaborate (c)	1974
$BLiO_2$	Lithium metaborate (l)	1974
$BLiO_2$	Lithium metaborate (g)	1974
BN	Boron nitride (c)	1971
BN	Boron nitride (g)	1971
$BNaO_2$	Sodium metaborate (c)	1974
$BNaO_2$	Sodium metaborate (l)	1974
$BNaO_2$	Sodium metaborate (g)	1974
BO	Boron monoxide (g)	1971
BO_2	Boron dioxide (g)	1971
BO_2^-	Boron dioxide, uninegative ion (g)	1971
BS	Boron monosulfide (g)	1974
BTi	Titanium monoboride (c)	1971
B_2	Boron, diatomic (g)	1971
B_2BeO_4	Beryllium diborate (g)	1971
$B_2Be_3O_6$	Triberyllium diborate (c)	1971
B_2Cl_4	Boron dichloride, dimeric (g)	1971
B_2F_4	Boron difluoride, dimeric (g)	1971
B_2F_4O	Diboron tetrafluoromonoxide (g)	1974
$B_2H_4O_4$	Boron dihydroxide, dimeric (c)	1971
$B_2H_4O_4$	Boron dihydroxide, dimeric (g)	1971
B_2H_6	Diborane (g)	1971
B_2Mg	Magnesium diboride (c)	1971
B_2O	Diboron monoxide (g)	1971
B_2O_2	Boron monoxide, dimeric (g)	1971
B_2O_3	Boron oxide (c)	1974
B_2O_3	Boron oxide (l)	1974
B_2O_3	Boron oxide (g)	1974
B_2O_4Pb	Lead diborate (c)	1971
B_2Ti	Titanium diboride (c)	1971
B_2Ti	Titanium diboride (l)	1971
B_2Zr	Zirconium diboride (c)	1971
B_2Zr	Zirconium diboride (l)	1971
$B_3Cl_3O_3$	Boron oxide chloride, trimeric (g)	1971
$B_3FH_2O_3$	Monofluoroboroxin (g)	1971
$B_3F_2HO_3$	Difluoroboroxin (g)	1971
$B_3F_3O_3$	Boron oxide fluoride, trimeric (c)	1971
$B_3F_3O_3$	Boron oxide fluoride, trimeric (g)	1971
$B_3H_3O_3$	Boroxin (c)	1971
$B_3H_3O_3$	Boroxin (g)	1971
$B_3H_3O_6$	Metaboric acid, trimeric (g)	1971
$B_3H_6N_3$	Borazine (g)	1971
$B_4K_2O_7$	Dipotassium tetraboron heptaoxide (c)	1971
$B_4K_2O_7$	Dipotassium tetraboron heptaoxide (l)	1971
$B_4Li_2O_7$	Dilithium tetraborate (c)	1971
$B_4Li_2O_7$	Dilithium tetraborate (l)	1971
B_4Mg	Magnesium tetraboride (c)	1971
$B_4Na_2O_7$	Disodium tetraborate (c)	1971
$B_4Na_2O_7$	Disodium tetraborate (l)	1971
B_4O_7Pb	Lead tetraborate (c)	1971
B_5H_9	Pentaborane (l)	1971
B_5H_9	Pentaborane (g)	1971
$B_6K_2O_{10}$	Dipotassium hexaborate (c)	1971
$B_6Li_2O_{10}$	Dilithium hexaborate (c)	1971
$B_6Na_2O_{10}$	Disodium hexaborate (c)	1971
$B_6O_{10}Pb$	Lead hexaborate (c)	1971
$B_8K_2O_{13}$	Dipotassium octaborate (c)	1971
$B_8K_2O_{13}$	Dipotassium octaborate (l)	1971
$B_8Li_2O_{13}$	Dilithium octaborate (c)	1971
$B_{10}H_{14}$	Decaborane (c)	1971
$B_{10}H_{14}$	Decaborane (l)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
$B_{10}H_{14}$	Decaborane (g)	1971
$B_{10}O_{17}Pb_2$	Dilead decaborate (c)	1971
Ba	Barium (ref st)	1974
Ba	Barium, alpha-beta-gamma (c)	1974
Ba	Barium (l)	1974
Ba	Barium, monatomic (g)	1974
$BaBr$	Barium monobromide (g)	1978
$BaBr_2$	Barium dibromide (c)	1978
$BaBr_2$	Barium dibromide (l)	1978
$BaBr_2$	Barium dibromide (g)	1978
$BaCl$	Barium monochloride (g)	1975
$BaCl_2$	Barium dichloride (c)	1975
$BaCl_2$	Barium dichloride (l)	1975
$BaCl_2$	Barium dichloride (g)	1975
BaF	Barium monofluoride (g)	1975
$BaF+$	Barium monofluoride, unipos ion (g)	1975
BaF_2	Barium difluoride (c)	1975
BaF_2	Barium difluoride (l)	1975
BaF_2	Barium difluoride (g)	1975
$BaHO$	Barium monohydroxide (g)	1978
$BaHO+$	Barium monohydroxide, unipos ion (g)	1978
BaH_2O_2	Barium dihydroxide, alpha (c)	1978
BaH_2O_2	Barium dihydroxide (l)	1978
BaH_2O_2	Barium dihydroxide (g)	1978
BaI	Barium monoiodide (g)	1978
BaI_2	Barium diiodide (c)	1978
BaI_2	Barium diiodide (l)	1978
BaI_2	Barium diiodide (g)	1978
BaO	Barium oxide (c)	1978
BaO	Barium oxide (l)	1978
BaO	Barium oxide (g)	1978
BaS	Barium monosulfide (c)	1982
BaS	Barium monosulfide (g)	1982
Be	Beryllium (ref st)	1971
Be	Beryllium (c)	1971
Be	Beryllium (l)	1971
Be	Beryllium, monatomic (g)	1971
$Be+$	Beryllium, unipositive ion (g)	1971
$BeBr$	Beryllium monobromide (g)	1978
$BeBr_2$	Beryllium dibromide (c)	1978
$BeBr_2$	Beryllium dibromide (g)	1978
$BeCl$	Beryllium monochloride (g)	1971
$BeCl+$	Beryllium monochloride, pos ion (g)	1971
$BeClF$	Beryllium chloride fluoride (g)	1971
$BeCl_2$	Beryllium dichloride, alpha (c)	1971
$BeCl_2$	Beryllium dichloride, beta (c)	1971
$BeCl_2$	Beryllium dichloride (l)	1971
$BeCl_2$	Beryllium dichloride (g)	1971
BeF	Beryllium monofluoride (g)	1974
BeF_2	Beryllium difluoride (c)	1971
BeF_2	Beryllium difluoride (l)	1971
BeF_2	Beryllium difluoride (g)	1971
BeF_3Li	Lithium trifluoroberyllate (c)	1974
BeF_3Li	Lithium trifluoroberyllate (l)	1974
BeF_3Li	Lithium beryllium fluoride (g)	1971
BeF_4Li_2	Dilithium tetrafluoroberyllate (c)	1974
BeF_4Li_2	Dilithium tetrafluoroberyllate (l)	1974
BeH	Beryllium monohydride (g)	1971
$BeH+$	Beryllium monohydride, unipos ion (g)	1971
$BeHO$	Beryllium monohydroxide (g)	1978
$BeHO+$	Beryllium monohydroxide, pos ion (g)	1978
BeH_2	Beryllium dihydride (g)	1971
BeH_2O_2	Beryllium dihydroxide, alpha (c)	1978
BeH_2O_2	Beryllium dihydroxide, beta (c)	1978
BeH_2O_2	Beryllium dihydroxide (g)	1978
BeI	Beryllium monoidide (g)	1978
BeI_2	Beryllium diiodide (c)	1978
BeI_2	Beryllium diiodide (l)	1978
BeI_2	Beryllium diiodide (g)	1978
BeN	Beryllium nitride (g)	1971
BeO	Beryllium oxide,alpha (c)	1978
BeO	Beryllium oxide,beta (c)	1978
BeO	Beryllium oxide (l)	1978
BeO	Beryllium oxide (g)	1978
BeO_4S	Beryllium sulfate, alpha (c)	1971
BeO_4S	Beryllium sulfate, beta (c)	1971
BeO_4S	Beryllium sulfate, gamma (c)	1971
BeO_4W	Beryllium tungstate (c)	1971
BeS	Beryllium monosulfide (c)	1982
BeS	Beryllium monosulfide (g)	1982
Be_2Cl_4	Beryllium dichloride, dimeric (g)	1971
Be_2F_2O	Diberyllium oxide difluoride (g)	1971
Be_2O	Diberyllium oxide (g)	1971
Be_2O_2	Beryllium oxide, dimeric (g)	1971
Be_2O_4Si	Beryllium orthosilicate (c)	1971
Be_3N_2	Beryllium nitride, alpha (c)	1971
Be_3N_2	Beryllium nitride (l)	1971
Be_3O_3	Beryllium oxide, trimeric (g)	1971
Be_4O_4	Beryllium oxide, tetrameric (g)	1971
Be_5O_5	Beryllium oxide, pentameric (g)	1971
Be_6O_6	Beryllium oxide, hexameric (g)	1971
Br	Bromine, monatomic (g)	1978
$BrCa$	Calcium monobromide (g)	1978
$BrCl$	Bromine monochloride (g)	1971
BrF	Bromine monofluoride (g)	1971
BrF_3	Bromine trifluoride (g)	1971
BrF_5	Bromine pentafluoride (g)	1971
BrF_5S	Sulfur bromide pentafluoride (g)	1982
BrH	Hydrogen bromide (g)	1971
BrH_3Si	Bromosilane (g)	1982
BrH_4N	Ammonium bromide (c)	1971
$BrHg$	Mercurous bromide (g)	1971
BrI	Iodine monobromide (g)	1971
BrK	Potassium bromide (c)	1971
BrK	Potassium bromide (l)	1971
BrK	Potassium bromide (g)	1971
$BrLi$	Lithium bromide (c)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
BrLi	Lithium bromide (l)	1971
BrLi	Lithium bromide (g)	1971
BrMg	Magnesium monobromide (g)	1978
BrN	Nitrogen bromide (g)	1971
BrNO	Nitrosyl bromide (g)	1971
BrNa	Sodium bromide (c)	1971
BrNa	Sodium bromide (l)	1971
BrNa	Sodium bromide (g)	1971
BrP	Phosphorus monobromide (g)	1971
BrPb	Lead monobromide (g)	1975
BrSi	Silicon monobromide (g)	1982
BrSr	Strontium monobromide (g)	1978
BrTi	Titanium monobromide (g)	1971
BrW	Tungsten monobromide (g)	1971
BrZr	Zirconium monobromide (g)	1971
Br_2	Bromine (ref st)	1971
Br_2	Bromine (l)	1971
Br_2	Bromine, diatomic (g)	1971
Br_2Ca	Calcium dibromide (c)	1978
Br_2Ca	Calcium dibromide (l)	1978
Br_2Ca	Calcium dibromide (g)	1978
Br_2Fe	Iron dibromide (c)	1971
Br_2Fe	Iron dibromide (l)	1971
Br_2Fe	Iron dibromide (g)	1971
Br_2H_2Si	Dibromosilane (g)	1982
Br_2Hg	Mercuric bromide (c)	1971
Br_2Hg	Mercuric bromide (l)	1971
Br_2Hg	Mercuric bromide (g)	1971
Br_2Hg_2	Mercurous bromide (c)	1971
Br_2K_2	Potassium bromide, dimeric (g)	1971
Br_2Li_2	Lithium bromide, dimeric (g)	1971
Br_2Mg	Magnesium dibromide (c)	1978
Br_2Mg	Magnesium dibromide (l)	1978
Br_2Mg	Magnesium dibromide (g)	1978
Br_2Mg+	Magnesium dibromide, unipos ion (g)	1978
Br_2Na_2	Sodium bromide, dimeric (g)	1971
Br_2Pb	Lead dibromide (c)	1975
Br_2Pb	Lead dibromide (l)	1975
Br_2Pb	Lead dibromide (g)	1975
Br_2Si	Silicon dibromide (g)	1982
Br_2Sr	Strontium dibromide (c)	1978
Br_2Sr	Strontium dibromide (l)	1978
Br_2Sr	Strontium dibromide (g)	1978
Br_2Ti	Titanium dibromide (c)	1971
Br_2Ti	Titanium dibromide (g)	1971
Br_2Zr	Zirconium dibromide (c)	1971
Br_2Zr	Zirconium dibromide (l)	1971
Br_2Zr	Zirconium dibromide (g)	1971
Br_3HSi	Tribromosilane (g)	1982
Br_3OP	Phosphoryl bromide (g)	1971
Br_3P	Phosphorus tribromide (g)	1971
Br_3PS	Thiophosphoryl bromide (g)	1971
Br_3Si	Silicon tribromide (g)	1982
Br_3Ti	Titanium tribromide (c)	1971

FORMULA	TABLE TITLE	LATEST ISSUE
Br_3Ti	Titanium tribromide (g)	1971
Br_3Zr	Zirconium tribromide (c)	1971
Br_3Zr	Zirconium tribromide (g)	1971
Br_4Fe_2	Iron dibromide, dimeric (g)	1971
Br_4Pb	Lead tetrabromide (g)	1975
Br_4Si	Silicon tetrabromide (l)	1982
Br_4Si	Silicon tetrabromide (g)	1982
Br_4Ti	Titanium tetrabromide (c)	1971
Br_4Ti	Titanium tetrabromide (l)	1971
Br_4Ti	Titanium tetrabromide (g)	1971
Br_4Zr	Zirconium tetrabromide (c)	1978
Br_4Zr	Zirconium tetrabromide (g)	1978
Br_5Nb	Niobium pentabromide (c)	1978
Br_5Nb	Niobium pentabromide (l)	1978
Br_5Nb	Niobium pentabromide (g)	1978
Br_5W	Tungsten pentabromide (c)	1971
Br_5W	Tungsten pentabromide (l)	1971
Br_5W	Tungsten pentabromide (g)	1971
Br_6W	Tungsten hexabromide (c)	1971
Br_6W	Tungsten hexabromide (g)	1971
C	Carbon (ref st)	1982
C	Carbon, monatomic (g)	1982
C+	Carbon, unipostive ion (g)	1982
C-	Carbon, uninegative ion (g)	1982
CAl	Aluminum carbide (g)	1971
CB	Boron carbide (g)	1971
CB_4	Tetraboron monocarbide (c)	1971
CB_4	Tetraboron monocarbide (l)	1971
CBe_2	Beryllium carbide (c)	1971
CBe_2	Beryllium carbide (l)	1971
CBr	Carbon monobromide (g)	1971
$CBrF_3$	Bromotrifluoromethane (g)	1971
CBrN	Cyanogen bromide (g)	1971
CBr_4	Carbon tetrabromide (g)	1971
CCl	Carbon monochloride (g)	1971
CClFO	Carbonyl chlorofluoride (g)	1971
$CClF_3$	Chlorotrifluoromethane (g)	1971
CClN	Cyanogen chloride (g)	1971
CClO	Carbonyl monochloride (g)	1971
CCl_2	Carbon dichloride (g)	1971
CCl_2F_2	Dichlorodifluoromethane (g)	1971
CCl_2O	Carbonyl chloride (g)	1971
CCl_3	Trichloromethyl (g)	1971
CCl_3F	Trichlorofluoromethane (g)	1971
CCl_4	Carbon tetrachloride (g)	1971
CCuN	Cuprous cyanide (c)	1974
CF	Carbon monofluoride (g)	1971
CF+	Carbon monofluoride, unipos ion (g)	1974
CFN	Cyanogen fluoride (g)	1971
CFO	Carbonyl monofluoride (g)	1971
CF_2	Carbon difluoride (g)	1971
CF_2+	Carbon difluoride, unipos ion (g)	1974
CF_2O	Carbonyl fluoride (g)	1971
CF_3	Trifluoromethyl (g)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE	FORMULA	TABLE TITLE	LATEST ISSUE
CF_3+	Trifluoromethyl, unipos ion (g)	1974	CP	Carbon phosphide (g)	1971
CF_3I	Trifluoriodomethane (g)	1971	CS	Carbon monosulfide (g)	1982
CF_4	Carbon tetrafluoride (g)	1971	CS_2	Carbon disulfide (g)	1982
CF_4O	Trifluoromethyl hypofluorite (g)	1971	CSi	Silicon carbide, alpha (c)	1971
CF_8S	CF3-SF5 (g)	1982	CSi	Silicon carbide, beta (c)	1971
CH	Methlylidyne (g)	1971	CSi	Silicon carbide (g)	1971
$CH+$	Methylidyne, unipositive ion (g)	1974	CSi_2	Disilicon carbide (g)	1971
$CHCl$	Monochloromethylene (g)	1971	CTa	Tantalum monocarbide (c)	1975
$CHClF_2$	Chlorodifluoromethane (g)	1971	CTa	Tantalum monocarbide (l)	1975
$CHCl_2F$	Dichlorofluoromethane (g)	1971	CTi	Titanium carbide (c)	1971
$CHCl_3$	Chloroform (g)	1971	CTi	Titanium carbide (l)	1971
CHF	Monofluoromethylene (g)	1971	CZr	Zirconium carbide (c)	1971
$CHFO$	Formyl fluoride (g)	1971	CZr	Zirconium carbide (l)	1971
CHF_3	Trifluoromethane (g)	1971			
CHN	Hydrogen cyanide (g)	1971	C_2	Carbon, diatomic (g)	1971
$CHNO$	Hydrogen isocyanate (g)	1974	C_2-	Dimeric carbon, uninegative ion (g)	1971
CHO	Formyl (g)	1974	C_2Be	Beryllium carbide (g)	1971
$CHO+$	Formyl, unipositive ion (g)	1974	C_2Cl_2	Dichloroacetylene (g)	1971
CHP	Methinophosphide (g)	1971	C_2Cl_4	Tetrachloroethylene (g)	1971
CH_2	Methylene (g)	1975	C_2Cl_6	Hexachloroethane (g)	1971
CH_2ClF	Chlorofluoromethane (g)	1971	C_2Cr_3	Trichromium dicarbide (c)	1975
CH_2Cl_2	Dichloromethane (g)	1971	C_2F_2	Difluoroacetylene (g)	1971
CH_2F_2	Difluoromethane (g)	1971	C_2F_3N	Trifluoroacetonitrile (g)	1971
CH_2O	Formaldehyde (g)	1971	C_2F_4	Tetrafluoroethylene (g)	1971
CH_3	Methyl (g)	1971	C_2F_6	Hexafluoroethane (g)	1971
CH_3Cl	Methyl chloride (g)	1974	C_2H	CCH radical (g)	1971
CH_3Cl_3Si	Trichloromethylsilane (g)	1971	C_2HCl	Chloroacetylene (g)	1971
CH_3F	Fluoromethane (g)	1971	C_2HF	Monofluoroacetylene (g)	1971
CH_3F_3Si	Trifluoromethylsilane (g)	1971	C_2H_2	Acetylene (g)	1971
CH_4	Methane (g)	1971	C_2H_4	Ethylene (g)	1971
CIN	Cyanogen iodide (g)	1971	C_2H_4O	Ethylene oxide (g)	1971
CKN	Potassium cyanide (c)	1971	$C_2K_2N_2$	Potassium cyanide, dimeric (g)	1971
CKN	Potassium cyanide (l)	1971	C_2Li_2	Lithium carbide (c)	1971
CKN	Potassium cyanide (g)	1971	C_2Mg	Magnesium carbide (c)	1971
CK_2O_3	Potassium carbonate (c)	1971	C_2N	CNC radical (g)	1971
CK_2O_3	Potassium carbonate (l)	1971	C_2N_2	Cyanogen (g)	1971
CLi_2O_3	Lithium carbonate (c)	1971	$C_2N_2Na_2$	Sodium cyanide, dimeric (g)	1971
CLi_2O_3	Lithium carbonate (l)	1971	C_2O	CCO radical (g)	1971
$CMgO_3$	Magnesium carbonate (c)	1971	C_2Si	Silicon dicarbide (g)	1971
CN	Cyano (g)	1971	C_3	Carbon, triatomic (g)	1971
$CN+$	Cyano, unipositive ion (g)	1974	C_3Al_4	Tetraluminum tricarbide (c)	1971
$CN-$	Cyano, uninegative ion (g)	1974	C_3Cr_7	Heptachromium tricarbide (c)	1975
$CNNa$	Sodium cyanide (c)	1971	C_3Mg_2	Magnesium carbide (c)	1971
$CNNa$	Sodium cyanide (l)	1971	C_3O_2	Carbon suboxide (g)	1971
$CNNa$	Sodium cyanide (g)	1971	C_4	Carbon, tetratomic (g)	1971
CNO	NCO radical (g)	1974	$C_4H_{12}Si$	Tetramethylsilane (g)	1971
CN_2	CNN radical (g)	1971	C_4N_2	Carbon subnitride (g)	1971
CN_2	NCN radical (g)	1974	C_4NiO_4	Nickel tetracarbonyl (l)	1982
CNa_2O_3	Sodium carbonate (c)	1971	C_4NiO_4	Nickel tetracarbonyl (g)	1982
CNa_2O_3	Sodium carbonate (l)	1971	C_5	Carbon, pentatomic (g)	1971
$C_{0.98}Nb$	Niobium monocarbide (c)	1975	C_5FeO_5	Iron pentacarbonyl (l)	1982
CO	Carbon monoxide (g)	1971	C_5FeO_5	Iron pentacarbonyl (g)	1982
COS	Carbon oxysulfide (g)	1971	C_6Cr_{23}	Chromium carbide (c)	1975
CO_2	Carbon dioxide (g)	1971			
CO_2-	Carbon dioxide, uninegative ion (g)	1971	Ca	Calcium (ref st)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
Ca	Calcium, alpha (c)	1971
Ca	Calcium, beta (c)	1971
Ca	Calcium (l)	1971
Ca	Calcium (g)	1971
Ca+	Calcium, unipositive ion (g)	1974
CaCl	Calcium monochloride (g)	1971
$CaCl_2$	Calcium chloride (c)	1971
$CaCl_2$	Calcium chloride (l)	1971
$CaCl_2$	Calcium chloride (g)	1971
CaF	Calcium monofluoride (g)	1971
CaF_2	Calcium difluoride (c)	1971
CaF_2	Calcium difluoride (l)	1971
CaF_2	Calcium difluoride (g)	1971
CaHO	Calcium monohydroxide (g)	1978
CaHO+	Calcium monohydroxide, unipos ion (g)	1978
CaH_2O_2	Calcium dihydroxide (c)	1978
CaH_2O_2	Calcium dihydroxide (g)	1978
CaI	Calcium monoiodide (g)	1978
CaI_2	Calcium diiodide (c)	1978
CaI_2	Calcium diiodide (l)	1978
CaI_2	Calcium diiodide (g)	1978
CaO	Calcium oxide (c)	1975
CaO	Calcium oxide (l)	1975
CaO	Calcium oxide (g)	1978
CaS	Calcium monosulfide (c)	1982
CaS	Calcium monosulfide (g)	1982
Ca_2	Calcium, diatomic (g)	1978
Cl	Chlorine, monatomic (g)	1974
Cl+	Chlorine, unipositive ion (g)	1971
Cl-	Chlorine, uninegative ion (g)	1971
ClCo	Cobalt monochloride (g)	1975
ClCs	Cesium chloride (c)	1971
ClCs	Cesium chloride (l)	1971
ClCs	Cesium chloride (g)	1971
ClCu	Copper monochloride (c)	1971
ClCu	Copper monochloride (l)	1971
ClCu	Copper monochloride (g)	1971
ClD	Deuterium chloride (g)	1982
ClF	Chlorine monofluoride (g)	1982
$ClFLi_2$	Lithium chlorofluoride (g)	1971
ClFMg	Magnesium chloride fluoride (g)	1971
$ClFO_2S$	Sulfuryl chloride fluoride (g)	1974
$ClFO_3$	Perchloryl fluoride (g)	1971
ClF_2OP	Phosphoryl difluorochloride (g)	1971
ClF_3	Chlorine trifluroide (g)	1971
ClF_3Si	Chlorotrifluorosilane (g)	1971
ClF_5	Chlorine pentafluoride (g)	1971
ClF_5S	Sulfur chloride pentafluoride (g)	1982
ClFe	Iron monochloride (g)	1971
ClH	Hydrogen chloride (g)	1971
ClHO	Hydrogen oxychloride (g)	1971
ClH_3Si	Chlorosilane (g)	1982
ClH_4N	Ammonium chloride (c)	1971
ClH_4NO_4	Ammonium perchlorate (c)	1971
ClHg	Mercurous chloride (g)	1971
ClI	Iodine monochloride (c)	1971
ClI	Iodine monochloride (l)	1971
ClI	Iodine monochloride (g)	1971
ClK	Potassium chloride (c)	1971
ClK	Potassium chloride (l)	1971
ClK	Potassium chloride (g)	1971
$ClKO_4$	Potassium perchlorate (c)	1971
ClLi	Lithium chloride (c)	1971
ClLi	Lithium chloride (l)	1971
ClLi	Lithium chloride (g)	1971
ClLiO	Lithium oxychloride (g)	1971
$ClLiO_4$	Lithium perchlorate (c)	1971
$ClLiO_4$	Lithium perchlorate (l)	1971
ClMg	Magnesium monochloride (g)	1971
ClMg+	Magnesium monochloride, pos ion (g)	1971
ClNO	Nitrosyl chloride (g)	1975
$ClNO_2$	Nitryl chloride (g)	1971
ClNa	Sodium chloride (c)	1971
ClNa	Sodium chloride (l)	1971
ClNa	Sodium chloride (g)	1971
$ClNaO_4$	Sodium perchlorate (c)	1971
ClNi	Nickel monochloride (g)	1982
ClO	Chlorine monoxide (g)	1971
ClOTi	Titanium oxychloride (g)	1971
ClO_2	Chlorine dioxide (g)	1971
ClP	Phosphorus monochloride (g)	1971
ClPb	Lead monochloride (g)	1975
ClPb+	Lead monochloride, unipos ion (g)	1975
ClS	Sulfur monochloride (g)	1982
ClS_2	Chlorosulfanyl radical (g)	1982
ClSi	Silicon monochloride (g)	1982
ClSr	Strontium monochloride (g)	1975
ClTi	Titanium monochloride (g)	1971
ClW	Tungsten monochloride (g)	1971
ClZr	Zirconium monochloride (g)	1971
Cl_2	Chlorine, diatomic (ref st)	1971
Cl_2Co	Cobalt dichloride (c)	1975
Cl_2Co	Cobalt dichloride (l)	1975
Cl_2Co	Cobalt dichloride (g)	1978
Cl_2Cs_2	Cesium chloride, dimeric (g)	1971
Cl_2Cu	Copper dichloride (c)	1971
Cl_2FOP	Phosphoryl fluorodichloride (g)	1971
Cl_2Fe	Iron dichloride (c)	1974
Cl_2Fe	Iron dichloride (l)	1974
Cl_2Fe	Iron dichloride (g)	1974
Cl_2H_2Si	Dichlorosilane (g)	1982
Cl_2Hg	Mercuric chloride (c)	1971
Cl_2Hg	Mercuric chloride (l)	1971
Cl_2Hg	Mercuric chloride (g)	1971
Cl_2Hg_2	Mercurous chloride (c)	1971
Cl_2K_2	Potassium chloride, dimeric (g)	1971
Cl_2Li_2	Lithium chloride, dimeric (g)	1971
Cl_2Mg	Magnesium dichloride (c)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
Cl_2Mg	Magnesium dichloride (l)	1971
Cl_2Mg	Magnesium dichloride (g)	1971
Cl_2MoO_2	Molybdenum dioxydichloride (g)	1971
Cl_2Na_2	Sodium chloride, dimeric (g)	1971
Cl_2Ni	Nickel dichloride (c)	1982
Cl_2Ni	Nickel dichloride (l)	1982
Cl_2Ni	Nickel dichloride (g)	1982
Cl_2O	Dichlorine monoxide (g)	1971
Cl_2OTi	Titanium oxydichloride (g)	1971
Cl_2O_2S	Sulfuryl chloride (g)	1974
Cl_2O_2W	Tungsten dioxydichloride (c)	1971
Cl_2O_2W	Tungsten dioxydichloride (g)	1971
Cl_2Pb	Lead dichloride (c)	1975
Cl_2Pb	Lead dichloride (l)	1975
Cl_2Pb	Lead dichloride (g)	1975
Cl_2Pb+	Lead dichloride, unipos ion (g)	1975
Cl_2S	Sulfur dichloride (l)	1982
Cl_2S	Sulfur dichloride (g)	1982
Cl_2S+	Sulfur dichloride, unipos ion (g)	1982
Cl_2S_2	Dichlorodisulfane (l)	1982
Cl_2S_2	Dichlorodisulfane (g)	1982
Cl_2Si	Silicon dichloride (g)	1982
Cl_2Sr	Strontium dichloride (c)	1975
Cl_2Sr	Strontium dichloride (l)	1975
Cl_2Sr	Strontium dichloride (g)	1975
Cl_2Ti	Titanium dichloride (c)	1971
Cl_2Ti	Titanium dichloride (g)	1971
Cl_2W	Tungsten dichloride (c)	1971
Cl_2W	Tungsten dichloride (g)	1971
Cl_2Zr	Zirconium dichloride (c)	1971
Cl_2Zr	Zirconium dichloride (l)	1971
Cl_2Zr	Zirconium dichloride (g)	1971
Cl_3Co	Cobalt trichloride (g)	1975
Cl_3Cu_3	Copper monochloride, trimeric (g)	1971
Cl_3FSi	Trichlorofluorosilane (g)	1971
Cl_3Fe	Iron trichloride (c)	1971
Cl_3Fe	Iron trichloride (l)	1971
Cl_3Fe	Iron trichloride (g)	1971
Cl_3HSi	Trichlorosilane (g)	1982
Cl_3Li_3	Lithium chloride, trimeric (g)	1971
Cl_3OP	Phosphoryl chloride (g)	1971
Cl_3P	Phosphorus trichloride (g)	1971
Cl_3PS	Thiophosphoryl chloride (g)	1971
Cl_3Si	Silicon trichloride (g)	1982
Cl_3Ti	Titanium trichloride (c)	1971
Cl_3Ti	Titanium trichloride (g)	1971
Cl_3Zr	Zirconium trichloride (c)	1971
Cl_3Zr	Zirconium trichloride (g)	1971
Cl_4Co_2	Cobalt dichloride, dimeric (g)	1975
Cl_4Fe_2	Iron dichloride, dimeric (g)	1974
Cl_4Mg_2	Magnesium dichloride, dimeric (g)	1971
Cl_4Mo	Molybdenum tetrachloride (c)	1971
Cl_4Mo	Molybdenum tetrachloride (l)	1971
Cl_4Mo	Molybdenum tetrachloride (g)	1971
Cl_4OW	Tungsten oxytetrachloride (c)	1971
Cl_4OW	Tungsten oxytetrachloride (l)	1971
Cl_4OW	Tungsten oxytetrachloride (g)	1971
Cl_4Pb	Lead tetrachloride (g)	1975
Cl_4Si	Silicon tetrachloride (g)	1974
Cl_4Ti	Titanium tetrachloride (g)	1971
Cl_4Ti	Titanium tetrachloride (c)	1971
Cl_4Ti	Titanium tetrachloride (l)	1971
Cl_4W	Tungsten tetrachloride (c)	1971
Cl_4W	Tungsten tetrachloride (g)	1971
Cl_4Zr	Zirconium tetrachloride (c)	1978
Cl_4Zr	Zirconium tetrachloride (g)	1978
Cl_5Mo	Molybdenum pentachloride (c)	1971
Cl_5Mo	Molybdenum pentachloride (l)	1971
Cl_5Mo	Molybdenum pentachloride (g)	1971
Cl_5Nb	Niobium pentachloride (c)	1978
Cl_5Nb	Niobium pentachloride (l)	1978
Cl_5Nb	Niobium pentachloride (g)	1978
Cl_5P	Phosphorus pentachloride (g)	1971
Cl_5Ta	Tantalum pentachloride (c)	1978
Cl_5Ta	Tantalum pentachloride (l)	1978
Cl_5Ta	Tantalum pentachloride (g)	1978
Cl_5W	Tungsten pentachloride (c)	1971
Cl_5W	Tungsten pentachloride (l)	1971
Cl_5W	Tungsten pentachloride (g)	1971
Cl_6Fe_2	Iron trichloride, dimeric (g)	1971
Cl_6Mo	Molybdenum hexachloride (c)	1971
Cl_6Mo	Molybdenum hexachloride (g)	1971
Cl_6W	Tungsten hexachloride, alpha (c)	1971
Cl_6W	Tungsten hexachloride, beta (c)	1971
Cl_6W	Tungsten hexachloride (l)	1971
Cl_6W	Tungsten hexachloride (g)	1971
$Cl_{10}W_2$	Tungsten pentachloride, dimeric (g)	1971
Co	Cobalt (ref st)	1971
Co	Cobalt (c)	1971
Co	Cobalt (l)	1971
Co	Cobalt, monatomic (g)	1971
Co+	Cobalt, unipositive ion (g)	1971
CoF_2	Cobalt difluoride (c)	1971
CoF_2	Cobalt difluoride (l)	1971
CoF_2	Cobalt difluoride (g)	1971
CoF_3	Cobalt trifluoride (c)	1974
CoO	Cobalt oxide (c)	1974
CoO_4S	Cobalt sulfate (c)	1974
Co_3O_4	Tricobalt tetraoxide (c)	1974
Cr	Chromium (ref st)	1975
Cr	Chromium (c)	1975
Cr	Chromium (l)	1975
Cr	Chromium, monatomic (g)	1975
CrN	Chromium mononitride (c)	1975
CrN	Chromium mononitride (g)	1975
CrO	Chromium monoxide (g)	1975
CrO_2	Chromium dioxide (g)	1975
CrO_3	Chromium trioxide (g)	1975

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FORMULA	TABLE TITLE	LATEST ISSUE
Cr_2N	Chromium subnitride (c)	1975
Cr_2O_3	Dichromium trioxide (c)	1975
Cr_2O_3	Dichromium trioxide (l)	1975
Cs	Cesium (ref st)	1971
Cs	Cesium (c)	1971
Cs	Cesium (l)	1971
Cs	Cesium, monatomic (g)	1971
Cs+	Cesium, unipositive ion (g)	1974
CsF	Cesium fluoride (c)	1971
CsF	Cesium fluoride (l)	1971
CsF	Cesium fluoride (g)	1971
CsHO	Cesium hydroxide (c)	1974
CsHO	Cesium hydroxide (l)	1974
CsHO	Cesium hydroxide (g)	1974
CsHO+	Cesium hydroxide, unipos ion (g)	1974
CsO	Cesium monoxide (g)	1971
Cs_2	Cesium, diatomic (g)	1971
Cs_2F_2	Cesium fluoride, dimeric (g)	1971
$Cs_2H_2O_2$	Cesium hydroxide, dimeric (g)	1974
Cs_2O	Dicesium monoxide (g)	1971
Cu	Copper (ref st)	1982
Cu	Copper (c)	1982
Cu	Copper (l)	1982
Cu	Copper, monatomic (g)	1982
Cu+	Copper, unipositive ion (g)	1982
CuF	Copper monofluoride (c)	1982
CuF	Copper monofluoride (g)	1982
CuF_2	Copper difluoride (c)	1982
CuF_2	Copper difluoride (l)	1982
CuF_2	Copper difluoride (g)	1982
CuH_2O_2	Copper dihydroxide (c)	1971
CuO	Copper monoxide (c)	1982
CuO	Copper monoxide (g)	1982
CuO_4S	Copper sulfate (c)	1971
Cu_2	Copper, diatomic (g)	1971
Cu_2O	Dicopper monoxide (c)	1982
Cu_2O	Dicopper monoxide (l)	1982
Cu_2O_5S	Copper oxide sulfate (c)	1971
D	Deuterium, monatomic (g)	1982
D+	Deuterium, unipositive ion (g)	1982
D-	Deuterium, uninegative ion (g)	1982
DF	Deuterium fluoride (g)	1982
DH	Deuterium hydride (g)	1982
DH+	Deuterium hydride, unipos ion (g)	1982
DH-	Deuterium hydride, unineg ion (g)	1982
DHO	Monodeutero-water (g)	1982
DN	Deutero-imidogen (g)	1982
DO	Deutero-hydroxyl (g)	1982
DS	Sulfur monodeuteride (g)	1982
D_2	Deuterium, diatomic (ref st)	1982
D_2+	Deuterium, diatomic, unipos ion (g)	1982
D_2-	Deuterium, diatomic, unineg ion (g)	1982
D_2N	Dideutero-amidogen (g)	1982
D_2N_2	Cis-dideutero-diimide (g)	1982
D_2O	Dideutero-water (g)	1982
D_2S	Deuterium sulfide (g)	1982
D_3N	Trideutero-ammonia (g)	1982
e-	Electron gas (ref st)	1982
F	Fluorine, monatomic (g)	1971
F-	Fluorine, uninegative ion (g)	1974
FFe	Iron monofluoride (g)	1971
FH	Hydrogen fluoride (g)	1982
FHO	Hypofluorous acid (g)	1975
FHO_3S	Fluorosulfuric acid (g)	1974
FH_3Si	Fluorosilane (g)	1978
FHg	Mercurous fluoride (g)	1971
FI	Iodine monofluoride (g)	1971
FK	Potassium fluoride (c)	1971
FK	Potassium fluoride (l)	1971
FK	Potassium fluoride (g)	1971
FLi	Lithium fluoride (c)	1971
FLi	Lithium fluoride (l)	1971
FLi	Lithium fluoride (g)	1971
FLiO	Lithium hypofluorite (g)	1971
FMg	Magnesium monofluoride (g)	1978
FMg+	Magnesium monofluoride, pos ion (g)	1978
FN	Nitrogen monofluoride (g)	1971
FNO	Nitrosyl fluoride (g)	1971
FNO_2	Nitryl fluoride (g)	1971
FNO_3	Fluorine nitrate (g)	1971
FNa	Sodium fluoride (c)	1971
FNa	Sodium fluoride (l)	1971
FNa	Sodium fluoride (g)	1971
FO	Fluorine monoxide (g)	1971
FOTi	Titanium oxyfluoride (g)	1971
FO_2	Monofluorine dioxide (g)	1971
FP	Phosphorus monofluoride (g)	1982
FP+	Phosphorus monofluoride, pos ion (g)	1982
FP-	Phosphorus monofluoride, neg ion (g)	1982
FPS	Phosphorus thiofluoride (g)	1971
FPb	Lead monofluoride (g)	1975
FS	Sulfur monofluoride (g)	1978
FS+	Sulfur monofluoride, unipos ion (g)	1978
FS-	Sulfur monofluoride, unineg ion (g)	1982
FSi	Silicon monofluoride (g)	1982
FSr	Strontium monofluoride (g)	1975
FSr+	Strontium monofluoride, unipos (g)	1975
FTi	Titanium monofluoride (g)	1971
FW	Tungsten monofluoride (g)	1971
FZr	Zirconium monofluoride (g)	1971
F_2	Fluorine, diatomic (ref st)	1982
F_2Fe	Iron difluoride (c)	1971
F_2Fe	Iron difluoride (l)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
F_2Fe	Iron difluoride (g)	1971
F_2HK	Potassium bifluoride (c)	1974
F_2HK	Potassium bifluoride (l)	1974
F_2H_2	Hydrogen fluoride, dimeric (g)	1982
F_2H_2Si	Difluorosilane (g)	1978
F_2Hg	Mercuric fluoride (c)	1971
F_2Hg	Mercuric fluoride (l)	1971
F_2Hg	Mercuric fluoride (g)	1971
F_2Hg_2	Mercurous fluoride (c)	1971
F_2K-	Potassium difluoride, neg ion (g)	1971
F_2K_2	Potassium fluoride, dimeric (g)	1971
F_2Li-	Lithium difluoride, neg ion (g)	1971
F_2Li_2	Lithium fluoride, dimeric (g)	1971
F_2Mg	Magnesium difluoride (c)	1978
F_2Mg	Magnesium difluoride (l)	1978
F_2Mg	Magnesium difluoride (g)	1978
F_2Mg+	Magnesium difluoride, unipos ion (g)	1978
F_2N	Nitrogen difluoride (g)	1971
F_2N_2	Difluorodiazine, cis- (g)	1971
F_2N_2	Difluorodiazine, trans- (g)	1971
F_2Na-	Sodium difluoride, unineg ion (g)	1971
F_2Na_2	Sodium fluoride, dimeric (g)	1971
F_2O	Oxygen difluoride (g)	1971
F_2OS	Thionyl fluoride (g)	1974
F_2OSi	Silicon oxydifluoride (g)	1971
F_2OTi	Titanium oxydifluoride (g)	1971
F_2O_2S	Sulfuryl fluoride (g)	1974
F_2P	Phosphorus difluoride (g)	1982
F_2P+	Phosphorus difluoride, pos ion (g)	1982
F_2P-	Phosphorus difluoride, neg ion (g)	1982
F_2Pb	Lead difluoride,alpha (c)	1975
F_2Pb	Lead difluoride,beta (c)	1975
F_2Pb	Lead difluoride (l)	1975
F_2Pb	Lead difluoride (g)	1975
F_2S	Sulfur difluoride (g)	1978
F_2S+	Sulfur difluoride, unipos ion (g)	1982
F_2S-	Sulfur difluoride, unineg ion (g)	1982
F_2S_2	Difluorodisulfane (g)	1978
F_2S_2	Thiothionyl fluoride (g)	1978
F_2Si	Silicon difluoride (g)	1982
F_2Sr	Strontium difluoride (c)	1975
F_2Sr	Strontium difluoride (l)	1975
F_2Sr	Strontium difluoride (g)	1975
F_2Ti	Titanium difluoride (g)	1971
F_2Zr	Zirconium difluoride (c)	1971
F_2Zr	Zirconium difluoride (l)	1971
F_2Zr	Zirconium difluoride (g)	1971
F_3Fe	Iron trifluoride (c)	1971
F_3Fe	Iron trifluoride (g)	1971
F_3HSi	Trifluorosilane (g)	1978
F_3H_3	Hydrogen fluoride cyclic trimeric (g)	1982
F_3Li_3	Lithium fluoride, trimeric (g)	1971
F_3N	Nitrogen trifluoride (g)	1982
F_3NO	Trifluoramine oxide (g)	1971
F_3OP	Phosphoryl fluoride (g)	1971

FORMULA	TABLE TITLE	LATEST ISSUE
F_3P	Phosphorus trifluoride (g)	1971
F_3PS	Thiophosphoryl fluoride (g)	1971
F_3S	Sulfur trifluoride (g)	1982
F_3S+	Sulfur trifluoride, unipos ion (g)	1982
F_3S-	Sulfur trifluoride, unineg ion (g)	1982
F_3Si	Silicon trifluoride (g)	1982
F_3Ti	Titanium trifluoride (c)	1971
F_3Ti	Titanium trifluoride (g)	1971
F_3Zr	Zirconium trifluoride (c)	1971
F_3Zr	Zirconium trifluoride (g)	1971
F_4H_4	Hydrogen fluoride cyclic tetramer (g)	1982
F_4Mg_2	Magnesium difluoride, dimeric (g)	1978
F_4MoO	Molybdenum oxytetrafluoride (g)	1971
F_4N_2	Tetrafluorohydrazine (g)	1971
F_4OW	Tungsten oxytetrafluoride (c)	1974
F_4OW	Tungsten oxytetrafluoride (l)	1974
F_4OW	Tungsten oxytetrafluoride (g)	1974
F_4Pb	Lead tetrafluoride (g)	1975
F_4S	Sulfur tetrafluoride (g)	1978
F_4S+	Sulfur tetrafluoride, unipos ion (g)	1982
F_4S-	Sulfur tetrafluoride, unineg ion (g)	1982
F_4Si	Silicon tetrafluoride (g)	1978
F_4Ti	Titanium tetrafluoride (c)	1971
F_4Ti	Titanium tetrafluoride (g)	1971
F_4Zr	Zirconium tetrafluoride (c)	1978
F_4Zr	Zirconium tetrafluoride (g)	1978
F_5H_5	Hydrogen fluoride cyclic pentamer (g)	1982
F_5I	Iodine pentafluoride (g)	1971
F_5P	Phosphorus pentafluoride (g)	1971
F_5S	Sulfur pentafluoride (g)	1982
F_5S+	Sulfur pentafluoride, unipos ion (g)	1982
F_5S-	Sulfur pentafluoride, unineg ion (g)	1982
F_6H_6	Hydrogen fluoride cyclic hexamer (g)	1982
F_6Mo	Molybdenum hexafluoride (l)	1971
F_6Mo	Molybdenum hexafluoride (g)	1971
F_6S	Sulfur hexafluoride (g)	1978
F_6S-	Sulfur hexafluoride, unineg ion (g)	1982
F_6W	Tungsten hexafluoride (l)	1971
F_6W	Tungsten hexafluoride (g)	1971
F_7H_7	Hydrogen fluoride cyclic septamer (g)	1982
F_7I	Iodine heptafluoride (g)	1971
$F_{10}S_2$	Disulfur decafluoride (g)	1982
Fe	Iron (ref st)	1982
Fe	Iron, alpha-delta (c)	1982
Fe	Iron, gamma (c)	1982
Fe	Iron (l)	1982
Fe	Iron, monatomic (g)	1982
Fe+	Iron, unipositive ion (g)	1982
Fe-	Iron, uninegative ion (g)	1982
FeH_2O_2	Iron dihydroxide (c)	1971
FeH_2O_2	Iron dihydroxide (g)	1971
FeH_3O_3	Iron trihydroxide (c)	1971
FeI_2	Iron diiodide (c)	1971
FeI_2	Iron diiodide (l)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
FeI_2	Iron diiodide (g)	1971
$Fe_{0.947}O$	Wustite (c)	1971
FeO	Iron oxide (c)	1971
FeO	Iron oxide (l)	1971
FeO	Iron oxide (g)	1971
FeO_4S	Iron sulfate (c)	1971
$Fe_{0.877}S$	Pyrrhotite (c)	1982
FeS	Troilite (c)	1982
FeS	Iron monosulfide (l)	1982
FeS	Iron monosulfide (g)	1982
FeS_2	Pyrite (c)	1982
FeS_2	Marcasite (c)	1982
Fe_2I_4	Iron diiodide, dimeric (g)	1971
Fe_2O_3	Hematite (c)	1971
$Fe_2O_{12}S_3$	Diiron trisulfate (c)	1971
Fe_3O_4	Magnetite (c)	1971
H	Hydrogen, monatomic (g)	1982
H+	Proton (g)	1982
H-	Hydrogen, uninegative ion (g)	1982
HHg	Mercury monohydride (g)	1971
HI	Hydrogen iodide (g)	1971
HI_3Si	Triiodosilane (g)	1982
HK	Potassium hydride (c)	1971
HK	Potassium hydride (g)	1971
HKO	Potassium hydroxide (c)	1974
HKO	Potassium hydroxide (l)	1974
HKO	Potassium hydroxide (g)	1974
HKO+	Potssium hydroxide, unipos ion (g)	1974
HLi	Lithium hydride (c)	1971
HLi	Lithium hydride (l)	1971
HLi	Lithium hydride (g)	1971
HLiO	Lithium hydroxide (c)	1974
HLiO	Lithium hydroxide (l)	1974
HLiO	Lithium hydroxide (g)	1974
HLiO+	Lithium hydroxide, unipos ion (g)	1974
HMg	Magnesium monohydride (g)	1971
HMgO	Magnesium monohydroxide (g)	1978
HMgO+	Magnesium monohydroxide, pos ion (g)	1978
HN	Imidogen (g)	1982
HNO	Nitroxyl (g)	1971
HNO_2	Nitrous acid, cis- (g)	1971
HNO_2	Nitrous acid, trans- (g)	1971
HNO_3	Nitric acid (g)	1971
HNa	Sodium hydride (c)	1971
HNa	Sodium hydride (g)	1971
HNaO	Sodium hydroxide (c)	1974
HNaO	Sodium hydroxide (l)	1974
HNaO	Sodium hydroxide (g)	1974
HNaO+	Sodium hydroxide, unipositive ion (g)	1974
HO	Hydroxyl (g)	1982
HO+	Hydroxyl, unipositive ion (g)	1974
HO-	Hydroxyl, uninegative ion (g)	1974
HOSr	Strontium monohydroxide (g)	1978
HOSr+	Strontium monohydroxide, pos ion (g)	1978

FORMULA	TABLE TITLE	LATEST ISSUE
HO_2	Hydroperoxyl (g)	1971
HP	Phosphorus monohydride (g)	1971
HPb	Lead monohydride (g)	1971
HS	Sulfur monohydride (g)	1982
HSi	Silicon monohydride (g)	1982
HSi+	Silicon monohydride, unipos ion (g)	1974
HZr	Zirconium hydride (g)	1971
H_2	Hydrogen, diatomic (ref st)	1982
H_2+	Hydrogen, diatomic, unipos ion (g)	1982
H_2-	Hydrogen, diatomic, unineg ion (g)	1982
H_2I_2Si	Diiodosilane (g)	1982
$H_2K_2O_2$	Potassium hydroxide, dimeric (g)	1974
$H_2Li_2O_2$	Lithium hydroxide, dimeric (g)	1974
H_2Mg	Magnesium hydride (c)	1971
H_2MgO_2	Magnesium dihydroxide (c)	1978
H_2MgO_2	Magnesium dihydroxide (g)	1978
H_2MoO_4	Molybdic acid (g)	1971
H_2N	Amidogen (g)	1982
H_2N_2	Diimide, cis- (g)	1971
$H_2Na_2O_2$	Sodium hydroxide, dimeric (g)	1974
H_2O	Water (g)	1971
H_2O_2	Hydrogen peroxide (g)	1971
H_2O_2Sr	Strontium dihydroxide (c)	1978
H_2O_2Sr	Strontium dihydroxide (l)	1978
H_2O_2Sr	Strontium dihydroxide (g)	1978
H_2O_4S	Sulfuric acid (l)	1982
H_2O_4S	Sulfuric acid (g)	1982
H_2O_4W	Tungstic acid (c)	1971
H_2O_4W	Tungstic acid (g)	1971
H_2P	Phosphorus hydride (g)	1971
H_2S	Hydrogen sulfide (g)	1982
H_2Ti	Titanium hydride (c)	1971
H_3ISi	Iodosilane (g)	1982
H_3N	Ammonia (g)	1982
H_3O+	Hydronium, unipositive ion (g)	1971
H_3O_4P	Orthophosphoric acid (c)	1974
H_3O_4P	Orthophosphoric acid (l)	1974
H_3P	Phosphine (g)	1971
H_4IN	Ammonium iodide (c)	1971
H_4N_2	Hydrazine (l)	1971
H_4N_2	Hydrazine (g)	1971
H_4O_5S	Sulfuric acid, monohydrate (l)	1982
H_4Si	Silane (g)	1978
H_6O_6S	Sulfuric acid, dihydrate (l)	1982
H_8O_7S	Sulfuric acid, trihydrate (l)	1982
$H_{10}O_8S$	Sulfuric acid, tetrahydrate (l)	1982
$H_{15}O_{11}S$	Sulfuric acid, hemihexahydrate (l)	1982
He	Helium, monatomic (ref st)	1982
He+	Helium, unipositive ion (g)	1982
Hg	Mercury (ref st)	1971
Hg	Mercury (l)	1971
Hg	Mercury, monatomic (g)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
HgI	Mercurous iodide (g)	1971
HgI_2	Mercuric iodide (c)	1971
HgI_2	Mercuric iodide (l)	1971
HgI_2	Mercuric iodide (g)	1971
HgO	Mercuric oxide (c)	1971
HgO	Mercury monoxide (g)	1971
Hg_2I_2	Mercurous iodide (c)	1971
Hg_2I_2	Mercurous iodide (l)	1971
I	Iodine, monatomic (g)	1978
IK	Potassium iodide (c)	1971
IK	Potassium iodide (l)	1971
IK	Potassium iodide (g)	1971
ILi	Lithium iodide (c)	1971
ILi	Lithium iodide (l)	1971
ILi	Lithium iodide (g)	1971
IMg	Magnesium monoiodide (g)	1978
INO	Nitrosyl iodide (g)	1971
INa	Sodium iodide (c)	1971
INa	Sodium iodide (l)	1971
IPb	Lead monoiodide (g)	1975
ISi	Silicon monoiodide (g)	1982
ISr	Strontium monoiodide (g)	1978
ITi	Titanium monoiodide (g)	1971
IZr	Zirconium monoiodide (g)	1971
I_2	Iodine (ref st)	1971
I_2	Iodine (l)	1971
I_2	Iodine, diatomic (g)	1971
I_2K_2	Potassium iodide, dimeric (g)	1971
I_2Li_2	Lithium iodide, dimeric (g)	1971
I_2Mg	Magnesium diiodide (c)	1978
I_2Mg	Magnesium diiodide (l)	1978
I_2Mg	Magnesium diiodide (g)	1978
I_2Pb	Lead diiodide (c)	1975
I_2Pb	Lead diiodide (l)	1975
I_2Pb	Lead diiodide (g)	1975
I_2Si	Silicon diiodide (g)	1982
I_2Sr	Strontium diiodide (c)	1978
I_2Sr	Strontium diiodide (l)	1978
I_2Sr	Strontium diiodide (g)	1978
I_2Ti	Titanium diiodide (c)	1971
I_2Ti	Titanium diiodide (g)	1971
I_2Zr	Zirconium diiodide (c)	1971
I_2Zr	Zirconium diiodide (l)	1971
I_2Zr	Zirconium diiodide (g)	1971
I_3Si	Silicon triiodide (g)	1982
I_3Ti	Titanium triiodide (c)	1971
I_3Ti	Titanium triiodide (g)	1971
I_3Zr	Zirconium triiodide (c)	1971
I_3Zr	Zirconium triiodide (g)	1971
I_4Pb	Lead tetraiodide (g)	1975
I_4Si	Silicon tetraiodide (c)	1978
I_4Si	Silicon tetraiodide (l)	1982
I_4Si	Silicon tetraiodide (g)	1982

FORMULA	TABLE TITLE	LATEST ISSUE
I_4Ti	Titanium tetraiodide (c)	1971
I_4Ti	Titanium tetraiodide (l)	1971
I_4Ti	Titanium tetraiodide (g)	1971
I_4Zr	Zirconium tetraiodide (c)	1978
I_4Zr	Zirconium tetraiodide (g)	1978
K	Potassium (ref st)	1971
K	Potassium (l)	1971
K	Potassium, monatomic (g)	1971
K^+	Potassium, unipositive ion (g)	1971
KO	Potassium monoxide (g)	1971
KO^-	Potassium monoxide, unineg ion (g)	1971
KO_2	Potassium superoxide (c)	1974
K_2	Potassium, diatomic (g)	1971
K_2O	Potassium oxide (c)	1971
K_2O_2	Potassium peroxide (c)	1971
K_2O_3Si	Potassium metasilicate (c)	1974
K_2O_3Si	Potassium metasilicate (l)	1974
K_2O_4S	Potassium sulfate, alpha (c)	1982
K_2O_4S	Potassium sulfate, beta (c)	1982
K_2O_4S	Potassium sulfate (l)	1982
K_2O_4S	Potassium sulfate (c,l)	1982
K_2O_4S	Potassium sulfate (g)	1982
K_2S	Dipotassium monosulfide (c)	1982
K_2S	Dipotassium monosulfide (l)	1982
Kr	Krypton, monatomic (ref st)	1982
Kr^+	Krypton, unipositive ion (g)	1982
Li	Lithium (ref st)	1971
Li	Lithium (c)	1971
Li	Lithium (l)	1971
Li	Lithium, monatomic (g)	1971
Li^+	Lithium, unipositive ion (g)	1971
LiN	Lithium nitride (g)	1971
$LiNO$	Lithium nitroxide (g)	1971
$LiNaO$	Lithium sodium oxide (g)	1971
LiO	Lithium monoxide (g)	1971
LiO^-	Lithium monoxide, uninegative ion (g)	1971
Li_2	Lithium, diatomic (g)	1971
Li_2O	Lithium oxide (c)	1971
Li_2O	Lithium oxide (l)	1971
Li_2O	Lithium oxide (g)	1971
Li_2O_2	Lithium peroxide (c)	1971
Li_2O_2	Lithium monoxide, dimeric (g)	1971
Li_2O_3Si	Lithium metasilicate (c)	1971
Li_2O_3Si	Lithium metasilicate (l)	1971
Li_2O_3Ti	Lithium metatitanate (c)	1971
Li_2O_3Ti	Lithium metatitanate (l)	1971
$Li_2O_5Si_2$	Lithium disilicate (c)	1971
$Li_2O_5Si_2$	Lithium disilicate (l)	1971
Li_3N	Lithium nitride (c)	1982
Mg	Magnesium (ref st)	1971
Mg	Magnesium (c)	1971

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FORMULA	TABLE TITLE	LATEST ISSUE
Mg	Magnesium (l)	1971
Mg	Magnesium, monatomic (g)	1971
Mg+	Magnesium, unipositive ion (g)	1974
MgN	Magnesium nitride (g)	1971
MgO	Magnesium oxide (c)	1978
MgO	Magnesium oxide (l)	1978
MgO	Magnesium oxide (g)	1978
MgO_3Si	Magnesium metasilicate (c)	1971
MgO_3Si	Magnesium metasilicate (l)	1971
MgO_3Ti	Magnesium metatitanate (c)	1971
MgO_3Ti	Magnesium metatitanate (l)	1971
MgO_4S	Magnesium sulfate (c)	1971
MgO_4S	Magnesium sulfate (l)	1971
MgO_4W	Magnesium tungstate (c)	1971
MgO_5Ti_2	Magnesium dititanate (c)	1971
MgO_5Ti_2	Magnesium dititanate (l)	1971
MgS	Magnesium monosulfide (c)	1982
MgS	Magnesium monosulfide (g)	1982
Mg_2	Magnesium, diatomic (g)	1978
Mg_2O_4Si	Magnesium orthosilicate (c)	1971
Mg_2O_4Si	Magnesium orthosilicate (l)	1971
Mg_2O_4Ti	Magnesium orthotitanate (c)	1971
Mg_2O_4Ti	Magnesium orthotitanate (l)	1971
Mg_2Si	Magnesium silicide (c)	1971
Mg_2Si	Magnesium silicide (l)	1971
Mg_3N_2	Magnesium nitride (c)	1971
$Mg_3O_8P_2$	Magnesium orthophosphate (c)	1971
$Mg_3O_8P_2$	Magnesium orthophosphate (l)	1971
Mo	Molybdenum (ref st)	1982
Mo	Molybdenum (c)	1982
Mo	Molybdenum (l)	1982
Mo	Molybdenum, monatomic (g)	1982
Mo+	Molybdenum, unipositive ion (g)	1982
Mo-	Molybdenum, uninegative ion (g)	1982
MoO	Molybdenum monoxide (g)	1971
MoO_2	Molybdenum dioxide (c)	1971
MoO_2	Molybdenum dioxide (g)	1971
MoO_3	Molybdenum trioxide (c)	1971
MoO_3	Molybdenum trioxide (l)	1971
MoO_3	Molybdenum trioxide (g)	1971
MoS_2	Molybdenum disulfide (c)	1982
Mo_2S_3	Dimolybdenum trisulfide (c)	1982
Mo_2S_3	Dimolybdenum trisulfide (l)	1982
Mo_2S_3	Dimolybdenum trisulfide (c,l)	1982
N	Nitrogen, monatomic (g)	1982
N+	Nitrogen, unipositive ion (g)	1982
N-	Nitrogen, uninegative ion (g)	1982
NO	Nitric oxide (g)	1971
NO+	Nitric oxide, unipositive ion (g)	1971
NO_2	Nitrogen dioxide (g)	1971
NO_2-	Nitrogen dioxide, uninegative ion (g)	1974
NO_3	Nitrogen trioxide (g)	1971
NP	Phosphorus nitride (g)	1971
NS	Sulfur nitride (g)	1971
NSi	Silicon nitride (g)	1971
NSi_2	Disilicon nitride (g)	1971
NTi	Titanium nitride (c)	1971
NTi	Titanium nitride (l)	1971
NV	Vanadium mononitride (c)	1975
NV	Vanadium mononitride (g)	1975
$N_{0.465}V$	Vanadium subnitride (c)	1975
NZr	Zirconium nitride (c)	1971
NZr	Zirconium nitride (l)	1971
NZr	Zirconium nitride (g)	1971
N_2	Nitrogen, diatomic (ref st)	1982
N_2+	Nitrogen, diatomic, unipos ion (g)	1982
N_2-	Nitrogen, diatomic, unineg ion (g)	1982
N_2O	Dinitrogen monoxide (g)	1971
N_2O+	Dinitrogen monoxide, unipos ion (g)	1974
N_2O_3	Dinitrogen trioxide (g)	1971
N_2O_4	Nitrogen tetroxide (c)	1971
N_2O_4	Dinitrogen tetroxide (l)	1971
N_2O_4	Nitrogen tetroxide (g)	1971
N_2O_5	Dinitrogen pentoxide (g)	1971
N_3	Azide (g)	1974
N_4Si_3	Silicon nitride, alpha (c)	1971
N_5P_3	Triphosphorus pentanitride (c)	1971
Na	Sodium (ref st)	1971
Na	Sodium (c)	1971
Na	Sodium (l)	1971
Na	Sodium, monatomic (g)	1971
Na+	Sodium, unipositive ion (g)	1971
NaO	Sodium monoxide (g)	1971
NaO-	Sodium monoxide, unineg ion (g)	1971
NaO_2	Sodium superoxide (c)	1971
Na_2	Sodium, diatomic (g)	1971
Na_2O	Disodium monoxide (c)	1971
Na_2O	Disodium monoxide (l)	1971
Na_2O_2	Disodium dioxide (c)	1971
Na_2O_3Si	Sodium metasilicate (c)	1971
Na_2O_3Si	Sodium metasilicate (l)	1971
Na_2O_4S	Sodium sulfate, v (c)	1982
Na_2O_4S	Sodium sulfate, iv (c)	1982
Na_2O_4S	Sodium sulfate, iii (c)	1982
Na_2O_4S	Sodium sulfate, i (c)	1982
Na_2O_4S	Sodium sulfate, delta (c)	1982
Na_2O_4S	Sodium sulfate (l)	1982
Na_2O_4S	Sodium sulfate (c,l)	1982
Na_2O_4S	Sodium sulfate (g)	1982
Na_2O_4W	Sodium tungstate (c)	1971
$Na_2O_5Si_2$	Sodium disilicate (c)	1971
$Na_2O_5Si_2$	Sodium disilicate (l)	1971
Na_2S	Disodium monosulfide (c)	1982
Na_2S	Disodium monosulfide (l)	1982
Nb	Niobium (ref st)	1975
Nb	Niobium (c)	1975

JANAF THERMOCHEMICAL TABLES - FILING ORDER

FORMULA	TABLE TITLE	LATEST ISSUE
Nb	Niobium (l)	1975
Nb	Niobium, monatomic (g)	1975
NbO	Niobium monoxide (c)	1975
NbO	Niobium monoxide (l)	1975
NbO	Niobium monoxide (g)	1975
NbO_2	Niobium dioxide (c)	1975
NbO_2	Niobium dioxide (l)	1975
NbO_2	Niobium dioxide (g)	1975
Nb_2O_5	Diniobium pentoxide (c)	1975
Nb_2O_5	Diniobium pentoxide (l)	1975
Ne	Neon, monatomic (ref st)	1982
Ne^+	Neon, unipositive ion (g)	1982
Ni	Nickel (ref st)	1982
Ni	Nickel (c)	1982
Ni	Nickel (l)	1982
Ni	Nickel (g)	1982
NiS	Nickel monosulfide (c)	1982
NiS	Nickel monosulfide (l)	1982
NiS	Nickel monosulfide (g)	1982
NiS_2	Nickel disulfide (c)	1982
NiS_2	Nickel disulfide (l)	1982
Ni_3S_2	Trinickel disulfide (c)	1982
Ni_3S_2	Trinickel disulfide (l)	1982
Ni_3S_4	Trinickel tetrasulfide (c)	1982
O	Oxygen, monatomic (g)	1982
O^+	Oxygen, unipositive ion (g)	1982
O^-	Oxygen, uninegative ion (g)	1982
OP	Phosphorus monoxide (g)	1974
OPb	Lead monoxide, red (c)	1974
OPb	Lead monoxide, yellow (c)	1974
OPb	Lead monoxide (l)	1974
OPb	Lead monoxide (g)	1974
OS	Sulfur monoxide (g)	1982
OS_2	Disulfur monoxide (g)	1971
OSi	Silicon monoxide (g)	1971
OSr	Strontium oxide (c)	1975
OSr	Strontium oxide (l)	1975
OSr	Strontium oxide (g)	1978
OTa	Tantalum monoxide (g)	1975
OTi	Titanium monoxide, alpha (c)	1975
OTi	Titanium monoxide, beta (c)	1975
OTi	Titanium monoxide (l)	1975
OTi	Titanium monoxide (g)	1975
OV	Vanadium monoxide (c)	1975
OV	Vanadium monoxide (l)	1975
OV	Vanadium monoxide (g)	1975
OW	Tungsten monoxide (g)	1971
OZr	Zirconium monoxide (g)	1971
O_2	Oxygen, diatomic (ref st)	1982
O_2^+	Oxygen, diatomic, unipositive ion (g)	1982
O_2^-	Oxygen, diatomic, uninegative ion (g)	1982

FORMULA	TABLE TITLE	LATEST ISSUE
O_2P	Phosphorus dioxide (g)	1971
O_2Pb	Lead dioxide (c)	1974
O_2S	Sulfur dioxide (g)	1971
O_2Si	Quartz (c)	1971
O_2Si	Cristobalite, low (c)	1971
O_2Si	Cristobalite, high (c)	1971
O_2Si	Silicon dioxide (l)	1971
O_2Si	Silicon dioxide (g)	1971
O_2Ta	Tantalum dioxide (g)	1975
O_2Ti	Titanium dioxide, anatase (c)	1975
O_2Ti	Titanium dioxide, rutile (c)	1975
O_2Ti	Titanium dioxide (l)	1975
O_2Ti	Titanium dioxide (g)	1975
O_2V	Vanadium dioxide (g)	1975
O_2W	Tungsten dioxide (c)	1971
O_2W	Tungsten dioxide (g)	1971
O_2Zr	Zirconium dioxide (c)	1971
O_2Zr	Zirconium dioxide (l)	1971
O_2Zr	Zirconium dioxide (g)	1971
O_3	Ozone (g)	1971
O_3PbSi	Lead metasilicate (c)	1971
O_3S	Sulfur trioxide (g)	1971
O_3Ti_2	Dititanium trioxide (c)	1975
O_3Ti_2	Dititanium trioxide (l)	1975
O_3V_2	Divanadium trioxide (c)	1975
O_3V_2	Divanadium trioxide (l)	1975
$O_{2.72}W$	Tungsten oxide (c)	1971
$O_{2.90}W$	Tungsten oxide (c)	1971
$O_{2.96}W$	Tungsten oxide (c)	1971
O_3W	Tungsten trioxide (c)	1971
O_3W	Tungsten trioxide (l)	1971
O_3W	Tungsten trioxide (g)	1971
O_4Pb_2Si	Lead orthosilicate (c)	1971
O_4Pb_3	Lead orthoplumbate (c)	1974
O_4SiZr	Zirconium orthosilicate (c)	1971
O_4V_2	Divanadium tetroxide (c)	1975
O_4V_2	Divanadium tetroxide (l)	1975
O_5Ta_2	Ditantalum pentoxide (c)	1975
O_5Ta_2	Ditantalum pentoxide (l)	1975
O_5Ti_3	Trititanium pentoxide, alpha (c)	1975
O_5Ti_3	Trititanium pentoxide, beta (c)	1975
O_5Ti_3	Trititanium pentoxide (l)	1975
O_5V_2	Divanadium pentoxide (c)	1975
O_5V_2	Divanadium pentoxide (l)	1975
O_6P_4	Phosphorus trioxide, dimeric (g)	1971
O_6W_2	Tungsten trioxide, dimeric (g)	1971
O_7Ti_4	Tetratitanium heptoxide (c)	1975
O_7Ti_4	Tetratitanium heptoxide (l)	1975
O_8W_3	Tritungsten octaoxide (g)	1971
O_9W_3	Tungsten trioxide, trimeric (g)	1971
$O_{10}P_4$	Diphosphorus pentoxide, dimeric (c)	1971
$O_{10}P_4$	Diphosphorus pentoxide, dimeric (g)	1971
$O_{12}W_4$	Tungsten trioxide, tetrameric (g)	1971
P	Phosphorus (ref st)	1971

JANAF THERMOCHEMICAL TABLES - FILING ORDER

FORMULA	TABLE TITLE	LATEST ISSUE
P	Phosphorus, red, V (c)	1971
P	Phosphorus, white (c)	1971
P	Phosphorus (l)	1971
P	Phosphorus, monatomic (g)	1971
PS	Monophosphorus monosulfide (g)	1971
P_2	Phosphorus, diatomic (g)	1971
P_4	Phosphorus, tetratomic (g)	1971
P_4S_3	Phosphorus sulfide (c)	1971
P_4S_3	Phosphorus sulfide (l)	1971
P_4S_3	Phosphorus sulfide (g)	1971
Pb	Lead (ref st)	1971
Pb	Lead (c)	1971
Pb	Lead (l)	1971
Pb	Lead, monatomic (g)	1971
PbS	Lead sulfide (c)	1975
PbS	Lead sulfide (l)	1975
PbS	Lead sulfide (g)	1975
Pb_2	Lead, diatomic (g)	1971
S	Sulfur (ref st)	1982
S	Sulfur, orthorhombic (c)	1982
S	Sulfur, monoclinic (c)	1982
S	Sulfur (l)	1982
S	Sulfur, monatomic (g)	1982
S+	Sulfur, monatomic, unipos ion (g)	1982
S-	Sulfur, monatomic, unineg ion (g)	1982
SSi	Silicon monosulfide (g)	1974
SSr	Strontium monosulfide (c)	1982
SSr	Strontium monosulfide (g)	1982
S_2	Sulfur, diatomic (g)	1982
S_2Si	Silicon disulfide (c)	1974
S_2Si	Silicon disulfide (l)	1974
S_3	Sulfur, triatomic (g)	1982
S_4	Sulfur, tetratomic (g)	1982
S_5	Sulfur, pentatomic (g)	1982
S_6	Sulfur, hexatomic (g)	1982
S_7	Sulfur, heptatomic (g)	1982
S_8	Sulfur, octatomic (g)	1982
Si	Silicon (ref st)	1971
Si	Silicon (c)	1971
Si	Silicon (l)	1971
Si	Silicon, monatomic (g)	1971
Si+	Silicon, unipositive ion (g)	1974
Si_2	Silicon, diatomic (g)	1971
Si_3	Silicon, triatomic (g)	1971
Sr	Strontium (ref st)	1974
Sr	Strontium, alpha-gamma (c)	1974
Sr	Strontium (l)	1974
Sr	Strontium, monatomic (g)	1974
Ta	Tantalum (ref st)	1975
Ta	Tantalum (c)	1975
Ta	Tantalum (l)	1975
Ta	Tantalum, monatomic (g)	1975
Ti	Titanium (ref st)	1971
Ti	Titanium, alpha (c)	1971
Ti	Titanium, beta (c)	1971
Ti	Titanium (l)	1971
Ti	Titanium, monatomic (g)	1971
Ti+	Titanium, unipositive ion (g)	1971
V	Vanadium (ref st)	1975
V	Vanadium (c)	1975
V	Vanadium (l)	1975
V	Vanadium, monatomic (g)	1975
W	Tungsten (ref st)	1971
W	Tungsten (c)	1971
W	Tungsten (l)	1971
W	Tungsten (g)	1971
W+	Tungsten, unipositive ion (g)	1971
Xe	Xenon, monatomic (ref st)	1982
Xe+	Xenon, unipositive ion (g)	1982
Zr	Zirconium (ref st)	1971
Zr	Zirconium, alpha (c)	1971
Zr	Zirconium, beta (c)	1971
Zr	Zirconium (l)	1971
Zr	Zirconium, monatomic (g)	1971
Zr+	Zirconium, unipositive ion (g)	1974

ARGON, MONATOMIC (AR) AR
(REFERENCE STATE - IDEAL GAS) GFW=39.948

	gibbs/mol			kcal/mol			
T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	0.000	0.000	0.000
100	4.968	31.556	41.400	-0.984	0.000	0.000	0.000
200	4.968	34.999	37.437	-0.488	0.000	0.000	0.000
298	4.968	36.983	36.983	0.000	0.000	0.000	0.000
300	4.968	37.013	36.983	0.009	0.000	0.000	0.000
400	4.968	38.443	37.178	0.506	0.000	0.000	0.000
500	4.968	39.551	37.546	1.003	0.000	0.000	0.000
600	4.968	40.457	37.958	1.500	0.000	0.000	0.000
700	4.968	41.223	38.371	1.996	0.000	0.000	0.000
800	4.968	41.886	38.770	2.493	0.000	0.000	0.000
900	4.968	42.471	39.149	2.990	0.000	0.000	0.000
1000	4.968	42.995	39.508	3.487	0.000	0.000	0.000
1100	4.968	43.468	39.847	3.984	0.000	0.000	0.000
1200	4.968	43.900	40.167	4.480	0.000	0.000	0.000
1300	4.968	44.298	40.469	4.977	0.000	0.000	0.000
1400	4.968	44.666	40.756	5.474	0.000	0.000	0.000
1500	4.968	45.009	41.028	5.971	0.000	0.000	0.000
1600	4.968	45.330	41.287	6.468	0.000	0.000	0.000
1700	4.968	45.631	41.534	6.964	0.000	0.000	0.000
1800	4.968	45.915	41.770	7.461	0.000	0.000	0.000
1900	4.968	46.183	41.995	7.958	0.000	0.000	0.000
2000	4.968	46.438	42.211	8.455	0.000	0.000	0.000
2100	4.968	46.681	42.418	8.952	0.000	0.000	0.000
2200	4.968	46.912	42.617	9.448	0.000	0.000	0.000
2300	4.968	47.133	42.809	9.945	0.000	0.000	0.000
2400	4.968	47.344	42.993	10.442	0.000	0.000	0.000
2500	4.968	47.547	43.171	10.939	0.000	0.000	0.000
2600	4.968	47.742	43.343	11.436	0.000	0.000	0.000
2700	4.968	47.929	43.510	11.932	0.000	0.000	0.000
2800	4.968	48.110	43.671	12.429	0.000	0.000	0.000
2900	4.968	48.284	43.827	12.926	0.000	0.000	0.000
3000	4.968	48.453	43.978	13.423	0.000	0.000	0.000
3100	4.968	48.615	44.125	13.920	0.000	0.000	0.000
3200	4.968	48.773	44.268	14.416	0.000	0.000	0.000
3300	4.968	48.926	44.407	14.913	0.000	0.000	0.000
3400	4.968	49.074	44.542	15.410	0.000	0.000	0.000
3500	4.968	49.218	44.674	15.907	0.000	0.000	0.000
3600	4.968	49.358	44.802	16.404	0.000	0.000	0.000
3700	4.968	49.494	44.927	16.900	0.000	0.000	0.000
3800	4.968	49.627	45.049	17.397	0.000	0.000	0.000
3900	4.968	49.756	45.168	17.894	0.000	0.000	0.000
4000	4.968	49.882	45.284	18.391	0.000	0.000	0.000
4100	4.968	50.004	45.398	18.888	0.000	0.000	0.000
4200	4.968	50.124	45.509	19.384	0.000	0.000	0.000
4300	4.968	50.241	45.618	19.881	0.000	0.000	0.000
4400	4.968	50.355	45.724	20.378	0.000	0.000	0.000
4500	4.968	50.467	45.828	20.875	0.000	0.000	0.000
4600	4.968	50.576	45.930	21.372	0.000	0.000	0.000
4700	4.968	50.683	46.030	21.868	0.000	0.000	0.000
4800	4.968	50.783	46.128	22.365	0.000	0.000	0.000
4900	4.968	50.890	46.224	22.862	0.000	0.000	0.000
5000	4.968	50.990	46.319	23.359	0.000	0.000	0.000
5100	4.968	51.089	46.411	23.855	0.000	0.000	0.000
5200	4.968	51.185	46.502	24.352	0.000	0.000	0.000
5300	4.968	51.280	46.591	24.849	0.000	0.000	0.000
5400	4.968	51.373	46.679	25.346	0.000	0.000	0.000
5500	4.968	51.464	46.765	25.843	0.000	0.000	0.000
5600	4.968	51.553	46.850	26.339	0.000	0.000	0.000
5700	4.968	51.641	46.933	26.836	0.000	0.000	0.000
5800	4.968	51.728	47.015	27.333	0.000	0.000	0.000
5900	4.968	51.813	47.096	27.830	0.000	0.000	0.000
6000	4.968	51.896	47.175	28.327	0.000	0.000	0.000

March 31, 1977

ARGON, MONATOMIC (Ar) (REFERENCE STATE - IDEAL GAS) GFW = 39.948

0 to 6000 K Ideal Gas

AR

Ground State Configuration $^1S_0$
$S^\circ_{298.15}$ = 36.983 ± 0.005 gibbs/mol
T_{tr} = 83.81 K
T_b = 87.30 K

ΔHf°_0 = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore (1). All predicted levels have been observed for n=3 and 4 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (2) has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 93,000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of proper fill and cutoff procedures (2).

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations (3). The tables agree within the estimated uncertainty with those by Hultgren et al. (4) and McBride et al. (5). The estimated uncertainty is due to uncertainties in the gram formula weight and fundamental constants which are based on the 1971 scale (6) and the 1973 values (7), respectively.

Phase Data

The triple point (T_{tr}) and boiling point (T_b) are taken from Hultgren et al. (4). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values of T_{tr} and T_b the reference state for argon is chosen to be the ideal gas at all temperatures down to 0 K. This may differ from the choice of other authors. The tables of Hultgren et al. (4), among others, use appropriate condensed states of argon as reference states and will differ from the present work at low temperatures.

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ARGON UNIPOSITIVE ION (Ar^+) Ar^+

(IDEAL GAS) GFW=39.94745

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	363.425		
100							
200							
298	5.015	39.745	39.745	0.000	364.909	362.598	-265.788
300	5.017	39.776	39.745	0.009	364.918	362.583	-264.138
400	5.120	41.233	39.943	0.516	365.424	361.729	-197.637
500	5.238	42.388	40.321	1.034	365.942	360.745	-157.680
600	5.334	43.352	40.748	1.563	366.471	359.657	-131.003
700	5.399	44.180	41.160	2.100	367.008	358.478	-111.920
800	5.434	44.903	41.601	2.641	367.550	357.223	-97.587
900	5.446	45.544	42.004	3.185	368.094	355.899	-86.423
1000	5.443	46.118	42.386	3.730	368.639	354.515	-77.478
1100	5.430	46.636	42.751	4.274	369.182	353.077	-70.149
1200	5.411	47.108	43.094	4.816	369.725	351.588	-64.032
1300	5.389	47.540	43.420	5.356	370.264	350.055	-58.849
1400	5.365	47.938	43.729	5.894	370.802	348.480	-54.400
1500	5.342	48.308	44.022	6.429	371.338	346.867	-50.538
1600	5.319	48.652	44.300	6.962	371.870	345.218	-47.154
1700	5.297	48.973	44.566	7.493	372.401	343.537	-44.164
1800	5.276	49.276	44.819	8.021	372.930	341.824	-41.502
1900	5.257	49.560	45.061	8.548	373.457	340.081	-39.118
2000	5.239	49.830	45.293	9.073	373.981	338.311	-36.968
2100	5.222	50.085	45.515	9.596	374.503	336.514	-35.021
2200	5.207	50.327	45.729	10.117	375.026	334.693	-33.248
2300	5.192	50.558	45.934	10.637	375.546	332.848	-31.627
2400	5.179	50.779	46.131	11.156	376.064	330.981	-30.140
2500	5.167	50.990	46.321	11.673	376.582	329.092	-28.769
2600	5.156	51.193	46.505	12.189	377.097	327.181	-27.502
2700	5.145	51.387	46.682	12.704	377.613	325.252	-26.327
2800	5.136	51.574	46.853	13.218	378.127	323.304	-25.235
2900	5.127	51.754	47.019	13.731	378.640	321.336	-24.216
3000	5.118	51.928	47.180	14.244	379.152	319.351	-23.264
3100	5.111	52.095	47.336	14.755	379.663	317.349	-22.373
3200	5.104	52.258	47.487	15.266	380.174	315.332	-21.536
3300	5.097	52.415	47.634	15.776	380.684	313.297	-20.749
3400	5.091	52.567	47.777	16.285	381.194	311.247	-20.007
3500	5.085	52.714	47.916	16.794	381.703	309.183	-19.306
3600	5.080	52.857	48.051	17.302	382.210	307.103	-18.643
3700	5.075	52.996	48.183	17.810	382.719	305.010	-18.016
3800	5.070	53.132	48.311	18.317	383.226	302.904	-17.421
3900	5.065	53.263	48.437	18.824	383.733	300.783	-16.855
4000	5.061	53.391	48.559	19.330	384.238	298.649	-16.317
4100	5.057	53.516	48.678	19.836	384.744	296.503	-15.805
4200	5.054	53.638	48.795	20.342	385.250	294.346	-15.316
4300	5.050	53.757	48.909	20.847	385.756	292.175	-14.850
4400	5.047	53.873	49.020	21.352	386.260	289.993	-14.404
4500	5.044	53.987	49.130	21.856	386.764	287.799	-13.977
4600	5.041	54.097	49.236	22.361	387.268	285.594	-13.569
4700	5.038	54.206	49.341	22.864	387.773	283.379	-13.177
4800	5.036	54.312	49.443	23.368	388.277	281.153	-12.801
4900	5.033	54.416	49.544	23.872	388.780	278.916	-12.440
5000	5.031	54.517	49.642	24.375	389.283	276.667	-12.093
5100	5.029	54.617	49.739	24.878	389.787	274.411	-11.759
5200	5.027	54.715	49.834	25.381	390.289	272.144	-11.438
5300	5.025	54.810	49.927	25.883	390.792	269.867	-11.128
5400	5.023	54.904	50.018	26.386	391.294	267.580	-10.829
5500	5.021	54.996	50.108	26.888	391.795	265.284	-10.541
5600	5.019	55.087	50.196	27.390	392.298	262.980	-10.263
5700	5.018	55.176	50.282	27.892	392.800	260.667	-9.994
5800	5.016	55.263	50.367	28.393	393.302	258.344	-9.735
5900	5.015	55.349	50.451	28.895	393.804	256.013	-9.483
6000	5.013	55.433	50.533	29.396	394.304	253.672	-9.240

March 31, 1977

ARGON UNIPOSITIVE ION (Ar^+) (IDEAL GAS) GFW = 39.94745

Ground State Configuration $^2P_{3/2}$
$S^\circ_{298.15}$ = 39.745 ± 0.005 gibbs/mol

ΔHf°_0 = 363.425 ± 0.001 kcal/mol Ar^+
$\Delta Hf^\circ_{298.15}$ = 364.909 ± 0.005 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	1431.41	2

Heat of Formation

The ionization limit of neutral argon (127109.9±0.1 cm^{-1}) reported by Moore (1) is adopted as ΔHf°_0 for Ar^+(g). The ionization limit is converted from cm^{-1} to kcal/mol using the factor, 1 cm^{-1} = 2.859144 x 10^{-3} kcal/mol, which is derived from the latest CODATA fundamental constants (2). The uncertainty in the ionization limit corresponds to an uncertainty of ±0.0003 kcal/mol in ΔHf°_0. The value of ΔHf°_{298} is derived from ΔHf°_0 using auxiliary JANAF data (3).

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights by Moore (4) is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (5) has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 108,000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore (1). The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight, fundamental constants, and energy of the $^2P_{1/2}$ state. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (5).

The thermodynamic functions reported here agree with those by Green et al. (6) and Hilsenrath et al. (7) within the limits of the uncertainty.

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BARIUM MONOSULFIDE (BaS) BaS

(CRYSTAL) GFW=169.39

T, K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-2.500	-110.594	-110.594	INFINITE
100	8.680	7.155	28.690	-2.153	-110.817	-110.419	241.318
200	11.140	14.143	19.800	-1.131	-110.796	-110.027	120.230
298	11.801	18.737	18.737	0.000	-110.800	-109.650	80.375
300	11.809	18.810	18.737	0.022	-110.800	-109.643	79.874
400	12.220	22.264	19.205	1.224	-111.420	-109.227	59.678
500	12.600	25.033	20.103	2.465	-112.030	-106.615	47.475
600	12.920	27.360	21.123	3.742	-112.714	-107.863	39.289
700	13.160	29.370	22.161	5.046	-113.122	-107.025	33.414
800	13.380	31.142	23.175	6.373	-126.589	-107.317	29.317
900	13.570	32.728	24.150	7.720	-126.614	-104.905	25.474
1000	13.780	34.169	25.081	9.088	-126.624	-102.493	22.400
1100	13.965	35.491	25.968	10.475	-128.618	-99.884	19.845
1200	14.150	36.714	26.813	11.881	-128.653	-97.270	17.715
1300	14.336	37.854	27.619	13.305	-128.650	-94.655	15.913
1400	14.520	38.923	28.389	14.748	-128.613	-92.041	14.368
1500	14.699	39.931	29.125	16.209	-128.548	-89.430	13.030
1600	14.880	40.885	29.830	17.688	-128.461	-86.826	11.860
1700	15.066	41.793	30.508	19.185	-128.355	-84.227	10.828
1800	15.250	42.660	31.159	20.701	-128.235	-81.635	9.912
1900	15.429	43.489	31.786	22.235	-128.106	-79.049	9.093
2000	15.610	44.285	32.391	23.787	-127.974	-76.470	8.356
2100	15.795	45.051	32.976	25.357	-127.843	-73.898	7.691
2200	15.980	45.790	33.542	26.946	-161.071	-70.107	6.964
2300	16.166	46.504	34.090	28.553	-160.760	-65.978	6.269
2400	16.350	47.196	34.622	30.179	-160.490	-61.864	5.633
2500	16.529	47.867	35.138	31.823	-160.260	-57.759	5.049
2600	16.710	48.519	35.640	33.485	-160.070	-53.663	4.511
2700	16.896	49.153	36.129	35.165	-159.918	-49.573	4.013
2800	17.080	49.771	36.605	36.864	-159.802	-45.489	3.551
2900	17.261	50.374	37.070	38.581	-159.717	-41.408	3.121
3000	17.440	50.962	37.523	40.316	-159.660	-37.329	2.719

Sept. 30, 1977

BARIUM MONOSULFIDE (BaS) (CRYSTAL) GFW = 169.39

ΔHf°_0 = −110.6 ± 0.5 kcal/mol BaS

$S^\circ_{298.15}$ = 18.7 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −110.8 ± 0.5 kcal/mol

Heat of Formation

Sabatier (1) measured the heat of solution of BaS in hydrochloric acid solution as ΔHr_{284} = −27.0±1.0 kcal/mol for $BaS(c) + 2\ HCl(100\ H_2O,aq) \rightarrow BaCl_2(100\ H_2O,aq) + H_2S(aq)$. We derive ΔHf°_{298}(BaS,c) = −111.0±2.0 kcal/mol based on the following auxiliary data: $\Delta Hf^\circ_{298}(HCl\cdot 100\ H_2O,aq)$ = −39.657 kcal/mol (2), $\Delta Hf^\circ_{298}(H_2S,aq)$ = −9.5 kcal/mol (2), and $\Delta Hf^\circ_{298}(BaCl_2\cdot 100\ H_2O,aq)$ = −207.803 kcal/mol (3). Mourlot (4) also measured the heat of solution of BaS in hydrochloric acid solution as ΔHr = −27.35±1.0 kcal/mol from which we calculate ΔHf°_{298}(BaS,c) = −110.6±2 kcal/mol using the same auxiliary data. The uncertainties quoted reflect the correction to 298.15 K and the ambiguity of the exact solution composition.

Our analyses of equilibrium studies of Okuno (5), Culver and Hamdorf (6), Nikonov (7), Schenck and Hammerschmidt (8), and Colin et al. (9), are listed below. The calculated 3rd law ΔHr° (298.15 K) may have an uncertainty of 0.5 kcal/mol since the JANAF free energy functions are partially based on the estimated C°_p data (above 300 K). Thus the heat of formation of BaS (c) derived from equilibrium studies is in good agreement with that derived from heat of solution studies (1, 4). We discount the studies of Nikonov (7) and of Colin et al. (9). More information is given in the SrS(c) table (10).

A weighted average, ΔHf°_{298}(BaS,c) = −110.8±0.5 kcal/mol, is adopted in the tabulation.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298} (kcal/mol) 2nd law	3rd law	ΔHf°_{298}[c] (BaS,c) kcal/mol
(5) Okuno (1935)	Equilibrium	A	973-1173	5	0.85±0.75	-6.27±0.81	-7.18±0.25	-110.29±1.0
(6) Culver (1955)	Equilibrium	B	1073-1373	Equation	-2.89	6.14	9.68±0.75	-111.23±2.5
(7) Nikonov (1961)	Vaporization	C	1400-1600	Equation	2.2	-106.38	-109.74±0.6	-100.7 ±4
(8) Schenck (1933)	Equilibrium	D	1355-1399	2	-11.4	52.6	68.31±0.7	-111.05±4.0
(9) Colin et al. (1964)	Mass Spec	E	1846-2120	10	-17.6±7.5	-59.4±15.0	-74.2 ±4.2	-118.6 ±12

[a] Reactions:
A) $BaSO_4(c) + 4CO(g) = BaS(c) + 4CO_2(g)$
B) $BaSO_4(c) + 4H_2(g) = BaS(c) + 4H_2O(g)$
C) $BaS(g) = BaS(c)$
D) $BaSO_4(c) + S_2(g) = BaS(c) + 2\ SO_2(g)$
E) $Ba(g) + 2\ S_2(g) = BaS(c) + 3\ S(g)$

[b] $\delta S = \Delta S_{298}$ (2nd law) − ΔS_{298} (3rd law)

[c] 3rd law ΔHr°_{298} is used to derive ΔHf°_{298}(BaS,c).

Heat Capacity and Entropy

King and Weller (11) measured the low temperature heat capacities from 54-296 K. Their smooth values are adopted in the tabulation. The entropy, S°_{298} = 18.7±0.2 gibbs/mol, is based on S°_{51} = 2.60 gibbs/mol as extrapolated by King and Weller using Debye and Einstein functions (θ_D = 159, θ_E = 267). The C°_p values above 300 K are estimated by graphical extrapolation combined with method B of Kubaschewski et al. (12).

Melting Data

Literature melting data for BaS(c) are not available. It has been reported (13, 14) that BaS melts above 2500 K but this value must be looked upon as a lower limit.

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BaS

BARIUM MONOSULFIDE (BaS) BAS

(IDEAL GAS) GFW=169.39

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-2.284	9.452	9.452	INFINITE
100	7.217	50.852	66.690	-1.584	9.582	5.611	-12.262
200	8.077	56.140	60.219	-0.816	9.349	1.720	-1.879
298	8.492	59.453	59.453	0.000	9.030	-1.960	1.437
300	8.497	59.506	59.453	0.016	9.024	-2.028	1.477
400	8.690	61.980	59.789	0.876	8.062	-5.630	3.076
500	8.793	63.431	60.429	1.751	7.086	-8.949	3.911
600	8.855	65.540	61.151	2.633	6.007	-12.050	4.389
700	8.896	66.908	61.878	3.521	5.183	-14.997	4.682
800	8.925	68.096	62.583	4.412	-8.720	-19.014	5.194
900	8.948	69.151	63.255	5.306	-9.198	-20.270	4.922
1000	8.966	70.095	63.893	6.202	-9.680	-21.475	4.693
1100	8.982	70.950	64.496	7.099	-12.164	-22.435	4.457
1200	8.997	71.732	65.067	7.998	-12.706	-23.344	4.252
1300	9.012	72.453	65.608	8.898	-13.227	-24.210	4.070
1400	9.029	73.121	66.121	9.800	-13.731	-25.036	3.908
1500	9.050	73.745	66.609	10.704	-14.223	-25.826	3.763
1600	9.080	74.330	67.073	11.611	-14.708	-26.584	3.631
1700	9.121	74.881	67.516	12.521	-15.189	-27.312	3.511
1800	9.178	75.404	67.940	13.435	-15.671	-28.011	3.401
1900	9.255	75.903	68.346	14.357	-16.154	-28.683	3.299
2000	9.356	76.380	68.736	15.287	-16.644	-29.330	3.205
2100	9.486	76.839	69.111	16.229	-17.141	-29.952	3.117
2200	9.649	77.284	69.472	17.186	-51.001	-29.324	2.913
2300	9.845	77.717	69.822	18.160	-51.323	-28.331	2.692
2400	10.078	78.141	70.159	19.156	-51.683	-27.324	2.488
2500	10.348	78.558	70.487	20.177	-52.076	-26.302	2.299
2600	10.654	78.970	70.805	21.227	-52.498	-25.262	2.123
2700	10.994	79.378	71.115	22.309	-52.944	-24.206	1.959
2800	11.365	79.784	71.418	23.426	-53.410	-23.133	1.806
2900	11.763	80.190	71.713	24.583	-53.885	-22.043	1.661
3000	12.183	80.596	72.002	25.780	-54.366	-20.937	1.525
3100	12.618	81.002	72.286	27.020	-54.845	-19.816	1.397
3200	13.063	81.410	72.565	28.304	-55.315	-18.678	1.276
3300	13.511	81.819	72.839	29.632	-55.770	-17.526	1.161
3400	13.954	82.229	73.109	31.006	-56.205	-16.361	1.052
3500	14.387	82.639	73.376	32.423	-56.616	-15.183	0.948
3600	14.802	83.051	73.639	33.882	-56.999	-13.993	0.849
3700	15.194	83.462	73.899	35.382	-57.353	-12.794	0.756
3800	15.558	83.872	74.156	36.920	-57.676	-11.586	0.666
3900	15.893	84.280	74.410	38.493	-57.967	-10.369	0.581
4000	16.186	84.686	74.662	40.097	-58.228	-9.145	0.500
4100	16.446	85.089	74.911	41.729	-58.459	-7.915	0.422
4200	16.667	85.488	75.158	43.385	-58.663	-6.679	0.348
4300	16.848	85.883	75.403	45.061	-58.843	-5.440	0.276
4400	16.992	86.272	75.646	46.753	-59.000	-4.195	0.208
4500	17.098	86.655	75.886	48.458	-59.138	-2.948	0.143
4600	17.169	87.031	76.124	50.172	-59.259	-1.697	0.081
4700	17.206	87.401	76.360	51.891	-59.368	-0.445	0.021
4800	17.213	87.763	76.594	53.612	-59.468	0.810	-0.037
4900	17.192	88.118	76.826	55.332	-59.561	2.066	-0.092
5000	17.146	88.465	77.055	57.049	-59.649	3.325	-0.145
5100	17.077	88.804	77.282	58.761	-59.735	4.585	-0.196
5200	16.990	89.135	77.507	60.464	-59.823	5.847	-0.246
5300	16.886	89.457	77.729	62.158	-59.913	7.111	-0.293
5400	16.768	89.772	77.950	63.841	-60.008	8.376	-0.339
5500	16.639	90.079	78.167	65.511	-60.109	9.645	-0.383
5600	16.502	90.377	78.383	67.169	-60.218	10.913	-0.426
5700	16.357	90.668	78.596	68.812	-60.336	12.184	-0.467
5800	16.208	90.951	78.806	70.440	-60.464	13.458	-0.507
5900	16.055	91.227	79.014	72.053	-60.603	14.733	-0.546
6000	15.901	91.495	79.220	73.651	-60.752	16.012	-0.583

Sept. 30, 1977

BARIUM MONOSULFIDE (BaS) (IDEAL GAS) GFW = 169.39

BAS

D_0° = 99.3 ± 3 kcal/mol
$S^\circ_{298.15}$ = 59.453 ± 0.10 gibbs/mol
Symmetry Number = 1

ΔHf_0° = 9.45 ± 3.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 9.03 ± 3.0 kcal/mol

Electronic and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(1, 2)	$X^1\Sigma^+$	0.0	1	2.5067	0.103160	0.000314	379.117	0.8828
(8)	$^3\Sigma^+$	[12000.]	3	[2.635]	[0.09339]	[0.000713]	[294.1]	[3.075]
(1, 8)	$^3\Pi$	[14000.]	6	[2.88]	[0.0784]	[0.0004]	[234.8]	[0.9]
(8)	$^1\Pi$	[14200.]	2	[2.88]	[0.0784]	[0.0004]	[234.8]	[0.9]
(1)	$A^1\Sigma^+$	14450.	1	2.635	0.09339	0.000713	294.06	3.075
(1)	$B^1\Sigma^+$	26997.74	1	2.7468	0.08591	0.000435	253.90	0.4373

Heat of Formation

The adopted value of the heat of formation, ΔHf°_{298}(BaS,g) = 9.03±3.0 kcal/mol, is based on the Knudsen mass-spectrometric study of Colin et al. (3). Our reanalysis of their ion intensity data is given below. Although the large drift would suggest a larger uncertainty in the derived quantities (ΔHf°, D_0°), our experience with related work on other alkaline earth sulfides and oxides by the same authors indicates that results derived from a third law analysis are preferred. Our value of the heat of formation is intermediate between ΔHf°_{298} = 7.3±5 kcal/mol obtained by Mills (6) (using different free energy functions) in a recent critical compilation and ΔHf°_{298} = 12.0 kcal/mol preferred by NBS (7). Using auxiliary JANAF data (8), and the recommended value for $D_0^\circ(S_2,g)$ = 100.69±0.01 kcal/mol (8), we calculate D_0°(BaS,g) = 99.3±3 kcal/mol. A linear Birge-Sponer extrapolation of the $X^1\Sigma^+$ ground state based on the data of Barrow et al. (1), after an ionic correction due to Hildenbrand (4) yields the dissociation energy of D_0° = 99.8 kcal/mol for the products Ba(^{1}S) + S(^{1}D). The $X^1\Sigma^+$ ground state cannot dissociate to ground state atoms. If the dissociation products are instead Ba(^{3}D) + S(^{3}P), analogous to the work of Field et al. (5) on BaO, the dissociation energy becomes D_0° = 100.4 kcal/mol. Both of these values are uncertain due to the very long vibrational extrapolation.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] Gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	ΔHr°_{298}/(kcal/mol) 3rd Law	ΔHf°_{298}[c] Kcal/mol	D_0° Kcal/mol
(3) Colin (1964)	Mass Spec	A	1846-2120	10	-2.5±4.9	-3.37±9.8	1.68±2.5	9.03±3.0	99.2±3.0

[a] Reactions: A) Ba(g) + S_2(g) = BaS(g) + S(g)

[b] δS = ΔSr°(2nd Law) - ΔSr°(3rd Law)

[c] 3rd law ΔHr°_{298} is used to derive ΔHf°_{298}(BaS,g).

Heat Capacity and Entropy

Electronic levels (T_{oo}) and vibrational-rotational constants of the observed states are from the optical study of Barrow et al. (1) and the microwave work of Tiemann et al. (2). Other low-lying electronic states and their vibrational-rotational constants are estimated in isoconfigurational groups by analogy with BaO (8) and from trends observed in the known states of the other alkaline-earth oxides and sulfides. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\varepsilon_i/T)$. Uncertainty in the energy and molecular constants for the estimated states may contribute as much as 2-3 gibbs/mol to S° at 3000 K. The molecular constants have been corrected to the natural isotopic abundances.

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BAS

BERYLLIUM MONOSULFIDE (BeS) BeS

(CRYSTAL) GFW=41.07218

	gibbs/mol			kcal/mol			
T, K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0							
100							
200							
298	8.130	8.850	8.850	0.000	-56.000	-55.675	40.810
300	8.200	8.901	8.850	0.015	-56.002	-55.672	40.557
400	10.170	11.547	9.198	0.940	-56.616	-55.527	30.338
500	11.400	13.957	9.913	2.022	-56.977	-55.215	24.134
600	12.200	16.110	10.770	3.204	-57.193	-54.839	19.975
700	12.750	18.033	11.672	4.452	-57.317	-54.437	16.996
800	13.180	19.764	12.577	5.750	-70.374	-55.218	15.085
900	13.540	21.338	13.465	7.086	-70.094	-53.339	12.952
1000	13.840	22.781	14.325	8.455	-69.809	-51.494	11.254
1100	14.094	24.112	15.155	9.852	-69.523	-49.675	9.869
1200	14.320	25.348	15.954	11.273	-69.242	-47.884	8.721
1300	14.522	26.502	16.721	12.716	-68.966	-46.115	7.753
1400	14.690	27.585	17.459	14.177	-68.699	-44.368	6.926
1500	14.807	28.603	18.168	15.651	-68.447	-42.639	6.212
1600	14.920	29.562	18.851	17.138	-70.965	-40.848	5.579
1700	15.024	30.469	19.508	18.635	-70.630	-38.976	5.011
1800	15.130	31.331	20.141	20.143	-70.293	-37.124	4.507
1900	15.241	32.152	20.751	21.661	-69.953	-35.290	4.059
2000	15.350	32.937	21.341	23.191	-69.609	-33.474	3.658
2100	15.455	33.688	21.911	24.731	-69.263	-31.676	3.297
2200	15.560	34.410	22.463	26.282	-68.914	-29.895	2.970
2300	15.665	35.104	22.998	27.843	-68.561	-28.127	2.673
2400	15.770	35.773	23.516	29.415	-68.205	-26.376	2.402
2500	15.875	36.418	24.020	30.997	-67.847	-24.643	2.154
2600	15.980	37.043	24.508	32.590	-67.483	-22.920	1.927
2700	16.085	37.648	24.984	34.193	-67.115	-21.214	1.717
2800	16.190	38.235	25.447	35.807	-137.772	-18.413	1.437
2900	16.295	38.805	25.898	37.431	-137.144	-14.160	1.067
3000	16.400	39.359	26.337	39.066	-136.508	-9.930	0.723

Sept. 30, 1977

BERYLLIUM MONOSULFIDE (BeS) (CRYSTAL) GFW = 41.07218

BeS

$\Delta Hf°_0$ = [-55.3 ± 2.5] kcal/mol

$S°_{298.15}$ = [8.85 ± 1.0] gibbs/mol

$\Delta Hf°_{298.15}$ = -56.0 ± 2.1 kcal/mol

Heat of Formation

Von Wartenberg (1) has measured the heat of solution of Be and BeS in H_2SO_4. The difference between these two heats gives $\Delta Hr°_{353}$ = -51.35±2.1 kcal/mol for the reaction Be(c) + H_2S(g) = BeS(c) + H_2(g). Using auxiliary JANAF (2) data we calculate $\Delta Hf°_{298}$(BeS,c) = -56.0±2.1 kcal/mol. This is in agreement with the value for the heat of formation preferred by NBS (3).

Heat Capacity and Entropy

No low-temperature heat capacity or high-temperature enthalpy measurements have been reported. We estimate $C_{p298}°$ = 8.13 gibbs/mol from the reaction BeO(c,α) + MgS(c) = MgO(c) + BeS(c) by assuming $\Delta C_p°$ = 0 (2). Comparison of this value with $C_p°$ data for all the alkaline earth oxides and sulfides (2) suggests that our estimate is reasonable. $C_p°$ data above 298.15 K are estimated graphically by comparison with α, β-BeO (2).

Several methods of estimation predict that the value of $S°_{298}$ should lie near 8.85 gibbs/mol. A graphical comparison of the standard entropies for other alkaline-earth oxides and sulfides suggest values for $S°_{298}$ in the range 9-10 gibbs/mol while additive entropy constants (4) give 6.8 (Kelly's) and 9.3 (Latimer's) gibbs/mol. Literature estimates have included (in gibbs/mol) 7.4 (5), 8.0 (6), and 8.4 (7). We adopt $S°_{298}$ = 8.85±1.0 gibbs/mol based on cation increments for a series of beryllium and magnesium compounds.

Melting Data

No literature melting data are available. BeO and BeS have a different crystal structure (cubic, zincblende type) than the remaining alkaline-earth oxides and sulfides (cubic, NaCl type).

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BERYLLIUM MONOSULFIDE (BeS) BeS

(IDEAL GAS) GFW=41.07218

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.098	62.424	62.424	INFINITE
100	6.957	42.532	56.568	-1.404	62.944	59.003	-128.950
200	7.043	47.369	50.895	-0.705	63.112	54.970	-60.067
298	7.358	50.234	50.234	0.000	63.000	50.987	-37.374
300	7.365	50.279	50.234	0.014	62.997	50.912	-37.089
400	7.737	52.450	50.527	0.769	62.213	46.941	-25.647
500	8.039	54.211	51.093	1.559	61.560	43.195	-18.880
600	8.264	55.697	51.740	2.374	60.977	39.578	-14.416
700	8.431	56.984	52.399	3.209	60.440	36.054	-11.257
800	8.565	58.119	53.045	4.059	46.935	31.408	-8.580
900	8.691	59.135	53.666	4.922	46.742	29.480	-7.159
1000	8.834	60.058	54.260	5.798	46.534	27.572	-6.026
1100	9.014	60.908	54.826	6.690	46.315	25.687	-5.103
1200	9.247	61.702	55.366	7.603	46.088	23.821	-4.338
1300	9.541	62.453	55.883	8.541	45.859	21.975	-3.694
1400	9.896	63.173	56.378	9.513	45.637	20.146	-3.145
1500	10.307	63.869	56.854	10.522	45.424	18.332	-2.671
1600	10.759	64.549	57.314	11.576	42.473	16.611	-2.269
1700	11.237	65.215	57.759	12.675	42.410	14.997	-1.928
1800	11.722	65.871	58.192	13.823	42.387	13.385	-1.625
1900	12.195	66.518	58.613	15.019	42.405	11.774	-1.354
2000	12.639	67.155	59.024	16.261	42.461	10.160	-1.110
2100	13.042	67.781	59.426	17.546	42.552	8.543	-0.889
2200	13.391	68.396	59.820	18.868	42.672	6.920	-0.687
2300	13.683	68.999	60.206	20.222	42.818	5.294	-0.503
2400	13.912	69.586	60.585	21.602	42.982	3.660	-0.333
2500	14.082	70.157	60.956	23.002	43.158	2.016	-0.176
2600	14.194	70.712	61.321	24.417	43.344	0.368	-0.031
2700	14.253	71.249	61.679	25.839	43.531	-1.289	0.104
2800	14.266	71.767	62.030	27.266	-27.313	-1.844	0.144
2900	14.240	72.268	62.374	28.691	-26.884	-0.941	0.071
3000	14.181	72.750	62.712	30.113	-26.461	-0.055	0.004
3100	14.095	73.213	63.043	31.527	-26.048	0.816	-0.058
3200	13.989	73.659	63.368	32.931	-25.647	1.679	-0.115
3300	13.862	74.085	63.686	34.324	-25.261	2.527	-0.167
3400	13.730	74.500	63.998	35.704	-24.892	3.362	-0.216
3500	13.597	74.896	64.304	37.071	-24.539	4.187	-0.261
3600	13.454	75.277	64.604	38.423	-24.206	5.005	-0.304
3700	13.311	75.644	64.897	39.762	-23.891	5.810	-0.343
3800	13.168	75.997	65.185	41.086	-23.597	6.609	-0.380
3900	13.027	76.337	65.466	42.396	-23.322	7.403	-0.415
4000	12.893	76.665	65.742	43.692	-23.068	8.186	-0.447
4100	12.761	76.982	66.013	44.974	-22.835	8.962	-0.478
4200	12.635	77.288	66.277	46.244	-22.621	9.736	-0.507
4300	12.515	77.584	66.537	47.501	-22.429	10.506	-0.534
4400	12.401	77.870	66.791	48.747	-22.257	11.269	-0.560
4500	12.292	78.148	67.040	49.982	-22.105	12.029	-0.584
4600	12.190	78.417	67.285	51.206	-21.974	12.786	-0.607
4700	12.093	78.678	67.525	52.420	-21.863	13.539	-0.630
4800	12.002	78.931	67.760	53.625	-21.773	14.292	-0.651
4900	11.917	79.178	67.990	54.821	-21.702	15.043	-0.671
5000	11.837	79.418	68.216	56.008	-21.651	15.795	-0.690
5100	11.761	79.652	68.438	57.188	-21.620	16.543	-0.709
5200	11.691	79.879	68.656	58.361	-21.608	17.288	-0.727
5300	11.625	80.101	68.870	59.526	-21.617	18.038	-0.744
5400	11.564	80.318	69.080	60.686	-21.644	18.785	-0.760
5500	11.507	80.530	69.286	61.839	-21.690	19.534	-0.776
5600	11.453	80.737	69.489	62.987	-21.755	20.285	-0.792
5700	11.403	80.939	69.688	64.130	-21.837	21.038	-0.807
5800	11.356	81.137	69.884	65.268	-21.938	21.794	-0.821
5900	11.312	81.330	70.076	66.401	-22.058	22.545	-0.835
6000	11.272	81.520	70.265	67.530	-22.195	23.300	-0.849

Sept. 30, 1977

BERYLLIUM MONOSULFIDE (BeS) (IDEAL GAS) GFW = 41.07218

D_0° = [80 ± 15] kcal/mol
$S^\circ_{298.15}$ = 50.23 ± 0.10
Symmetry Number = 1

ΔHf_0° = [62.4 ± 15] kcal/mol BeS
$\Delta Hf^\circ_{298.15}$ = [63 ± 15] kcal/mol

Electronic and Molecular Constants

Source	State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(1)	$X^1\Sigma^+$	0.0	1	1.7415	0.79059	0.00664	997.94	6.137
(1, 2, 7)	$^3\Pi$	[6600.]	6	[1.9075]	[0.6590]	[0.00605]	[762.46]	[4.12]
(1)	$A^1\Pi$	7842.9	2	1.9075	0.6590	0.00605	762.46	4.12
(1)	$^1\Delta$	[13048.4]	2	[2.000]	[0.5997]	[0.0069]	[671.6]	[5.48]
(1, 2)	$^3\Sigma^+$	[21000.]	3	[1.8137]	[0.72894]	[0.00604]	[851.35]	[4.85]
(1)	$B^1\Sigma^+$	25868.6	1	1.8137	0.72894	0.00604	851.35	4.85

Heat of Formation

No experimental data are available on BeS(g). We estimate D_0°(BeS,g) by the method of Hauge and Margrave (1) based on data involving known bond energies and force constants of the gaseous diatomic oxides and sulfides. Based on dissociation energies of the alkaline earth monoxides, taken from Srivastava (2), dissociation energies of the alkaline earth sulfides and force constants calculated from JANAF data (3), we calculate D_0°(BeS,g) = 80±10 kcal/mol A normal linear-Birge-Sponer extrapolation of the ground state yields D_0°(BeS,g) = 115 kcal/mol. After correcting for ionic character (8) and for excited state products D_0°(BeS,g) = 76 kcal/mol. These values are very uncertain. See the discussion of MgS(g) (3). We adopt D_0°(BeS,g) = 80±15 kcal/mol. Using auxiliary JANAF data (3), we calculate ΔHf°_{298}(BeS,g) = 63±15 kcal/mol.

Heat Capacity and Entropy

The spectroscopic constants of the observed states taken from Cheetham et al. (4) are corrected to account for the natural abundances of the elements. Other low-lying electronic states and their vibrational-rotational constants are estimated in isoconfigurational groups by analogy with BeO (5) and from trends observed in the known states of the other alkaline-earth oxides and sulfides (3). Uncertainty in the energy and molecular constants for the estimated states may contribute as much as 2-3 gibbs/mol to the entropy above 3000 K.

The splitting between the $A^1\Pi$ and a $^3\Pi$ states, ∿1200 cm^{-1}, is based on trends in the triplet-singlet splitting observed by Field (6) for the alkaline-earth oxides. The Hartree-Fock calculations of Verhaegen and Richards (7) support this. Their theoretical singlet-triplet splitting should be reasonably accurate even though the absolute energies are biased. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r and Q_v in the partition function $Q = Q_t \Sigma_i Q_r^i Q_v^i g_i \exp(-c_2 \epsilon_i/T)$.

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SULFUR BROMIDE PENTAFLUORIDE ($BrSF_5$) BrF_5S
(IDEAL GAS) GFW=206.95602

T, K	gibbs/mol Cp°	S°	−(G°−H°₂₉₈)/T	kcal/mol H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-4.645	-227.899	-227.899	INFINITE
100	11.271	60.411	98.068	-3.766	-229.255	-224.180	489.938
200	19.409	70.733	81.879	-2.229	-230.447	-218.603	238.875
298	25.591	79.719	79.719	0.000	-232.510	-212.462	155.737
300	25.683	79.878	79.720	0.047	-232.524	-212.338	154.686
400	29.607	87.851	80.780	2.828	-236.886	-204.802	111.897
500	32.012	94.737	82.900	5.919	-237.186	-196.747	85.997
600	33.536	100.718	85.382	9.202	-237.278	-188.647	68.714
700	34.544	105.968	87.956	12.609	-237.237	-180.544	56.368
800	35.238	110.629	90.504	16.100	-250.109	-173.652	47.439
900	35.733	114.810	92.977	19.650	-249.625	-164.121	39.853
1000	36.098	118.594	95.352	23.242	-249.126	-154.648	33.798
1100	36.373	122.048	97.624	26.866	-248.615	-145.226	28.853
1200	36.586	125.223	99.794	30.515	-248.097	-135.849	24.741
1300	36.754	128.156	101.864	34.182	-247.574	-126.515	21.269
1400	36.888	130.887	103.841	37.864	-247.053	-117.223	18.299
1500	36.998	133.436	105.730	41.559	-246.532	-107.968	15.731
1600	37.088	135.826	107.537	45.263	-246.013	-98.748	13.488
1700	37.163	138.077	109.268	48.976	-245.495	-89.557	11.513
1800	37.226	140.203	110.928	52.695	-244.984	-80.402	9.762
1900	37.279	142.217	112.522	56.421	-244.472	-71.269	8.198
2000	37.325	144.131	114.055	60.151	-243.969	-62.170	6.793
2100	37.365	145.953	115.531	63.886	-243.467	-53.091	5.525
2200	37.399	147.692	116.954	67.624	-242.971	-44.037	4.375
2300	37.429	149.355	118.327	71.365	-242.481	-35.006	3.326
2400	37.456	150.949	119.653	75.110	-241.993	-25.995	2.367
2500	37.479	152.478	120.935	78.856	-241.511	-17.005	1.487
2600	37.500	153.948	122.177	82.605	-241.033	-8.034	0.675
2700	37.519	155.364	123.380	86.356	-240.561	0.918	-0.074
2800	37.535	156.729	124.547	90.109	-240.093	9.853	-0.769
2900	37.550	158.046	125.680	93.863	-239.629	18.773	-1.415
3000	37.563	159.319	126.780	97.619	-239.173	27.672	-2.016
3100	37.576	160.551	127.849	101.376	-238.717	36.563	-2.578
3200	37.587	161.745	128.890	105.134	-238.268	45.434	-3.103
3300	37.597	162.901	129.903	108.893	-237.823	54.293	-3.596
3400	37.606	164.024	130.890	112.653	-237.383	63.138	-4.058
3500	37.615	165.114	131.853	116.414	-236.949	71.970	-4.494
3600	37.622	166.174	132.791	120.176	-236.518	80.791	-4.905
3700	37.629	167.205	133.708	123.939	-236.092	89.598	-5.292
3800	37.636	168.208	134.602	127.702	-235.670	98.396	-5.659
3900	37.642	169.186	135.477	131.466	-235.254	107.183	-6.006
4000	37.648	170.139	136.331	135.231	-234.844	115.956	-6.335
4100	37.653	171.069	137.167	138.996	-234.438	124.722	-6.648
4200	37.658	171.976	137.985	142.761	-234.037	133.477	-6.945
4300	37.662	172.862	138.786	146.527	-233.641	142.224	-7.228
4400	37.667	173.728	139.571	150.294	-233.251	150.960	-7.498
4500	37.671	174.575	140.339	154.060	-232.868	159.686	-7.755
4600	37.674	175.403	141.092	157.828	-232.487	168.407	-8.001
4700	37.678	176.213	141.831	161.595	-232.112	177.120	-8.236
4800	37.681	177.006	142.556	165.363	-231.746	185.819	-8.460
4900	37.684	177.783	143.267	169.131	-231.382	194.517	-8.676
5000	37.687	178.545	143.965	172.900	-231.025	203.203	-8.882
5100	37.690	179.291	144.650	176.669	-230.672	211.886	-9.080
5200	37.692	180.023	145.323	180.438	-230.328	220.558	-9.270
5300	37.695	180.741	145.985	184.207	-229.988	229.228	-9.452
5400	37.697	181.445	146.635	187.977	-229.654	237.887	-9.628
5500	37.699	182.137	147.274	191.747	-229.324	246.546	-9.797
5600	37.701	182.816	147.903	195.517	-229.004	255.192	-9.959
5700	37.703	183.484	148.521	199.287	-228.687	263.837	-10.116
5800	37.705	184.139	149.130	203.057	-228.375	272.476	-10.267
5900	37.706	184.784	149.728	206.828	-228.070	281.110	-10.413
6000	37.708	185.418	150.318	210.598	-227.773	289.734	-10.553

Dec. 31, 1977

SULFUR BROMIDE PENTAFLUORIDE ($BrSF_5$) (IDEAL GAS) GFW = 206.95602

ΔHa_0° = [413.6 ± 16] kcal/mol
$S^\circ_{298.15}$ = [79.7 ± 0.5] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf_0° = [-227.9 ± 14] kcal/mol BrF_5S
$\Delta Hf^\circ_{298.15}$ = [-232.5 ± 14] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
848(1)	621(1)	580(2)
694(1)	[325](1)	423(2)
597(1)	502(1)	225(2)
279(1)	892(2)	

Point Group = C_{4v} σ = 4
Bond Distances: S-F = 1.597 Å S-Br = 2.1902 Å
Bond Angles: Br-S-F* = [92°] F*-S-F* = 90°
(* - equatorial)
Product of Moments of Inertia: $I_AI_BI_C$ = [1.64712 x 10^{-112}] g^3 cm^6

Heat of Formation

The adopted value of ΔHf° equal to -227.9±14 kcal/mol is calculated at 0 K from a S-Br bond energy of 41.4±10 kcal/mol by combining D_0° with JANAF heats of formation (1) for SF_5 and Br. We estimate the strength of the S-Br bond in $BrSF_5$ from bond energy correlations. In the case of related sulfur chlorine molecules, we calculate that the ratio of the S-Cl bond strength in $ClSF_5$ (1) is 1.1 times the mean S-Cl bond energy in $SOCl_2$ (2). Assuming that this relationship holds for $BrSF_5$ and $SOBr_2$, we obtain the adopted value for $D_0^\circ(SF_5\text{-}Br)$ from $\bar{D}_0^\circ(SOBr\text{-}Br)$ = 37.6 kcal/mol (2).

The heat of atomization (ΔHa_0°) and mean S-F bond energy ($\bar{D}_0^\circ$) are calculated to be 413.6±16 kcal/mol and 74.4 kcal/mol, respectively. The latter value is identical with that found for $ClSF_5$, indicating that the sulfur fluorine bonding is very similar in these two molecules. This conclusion is supported by spectroscopic data (1, 3, and 4).

Heat Capacity and Entropy

Microwave (3) and vibrational spectroscopic (4) measurements indicate that $BrSF_5$ is a symmetrical top molecule possessing C_{4v} symmetry. We adopt the structural parameters proposed by Neuvar and Jache (3) from an analysis of the observed rotational spectrum. The adopted bond lengths were calculated assuming that the Br-S-F* bond angle was 92° which was estimated from the value (91.6°) for the Cl-S-F* angle in $ClSF_5$ reported by Kewley et al. (5). A more plausible value for the Cl-S-F* angle is 90.7±0.2° (1), indicating that the bond lengths reported by Neuvar and Jache (3) may be slightly biased. We place the values of S°_{298} and $I_AI_BI_C$ in brackets to emphasize this uncertainty.

The vibrational frequencies are based on the infrared and laser-excited Raman spectra of $BrSF_5$ recorded under matrix (argon) isolation conditions by Smardzewski et al. (4). We adjust their reported frequencies for a matrix effect which is estimated as 5 cm^{-1} from gas phase (1) and argon-matrix (4) spectral data for $ClSF_5$. Evidence available for $ClSF_5$ (1) indicates that ν_6 = 220 cm^{-1} by Smardzewski et al. (4) should be reassigned. We believe that this Raman band is the low frequency mode ν_{11} (S-Br wag) and that ν_6 has not been resolved. We estimate ν_6 = 325 cm^{-1} from the force-field value for $ClSF_5$ (1).

The principal moments of inertia are: $I_A = 3.1900 \times 10^{-38}$ g cm^2 and $I_B = I_C = 7.1857 \times 10^{-38}$ g cm^2.

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BROMOSILANE (SiH_3Br) BRH3SI

(IDEAL GAS) GFW=111.0137

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.813	-14.778	-14.778	INFINITE
100	8.143	52.046	72.197	-2.015	-15.517	-16.329	35.686
200	10.096	58.194	63.779	-1.117	-16.390	-16.825	18.386
298	12.635	62.704	62.704	0.000	-18.700	-16.673	12.222
300	12.680	62.782	62.704	0.023	-18.722	-16.660	12.137
400	14.823	66.736	63.229	1.403	-23.010	-15.122	8.263
500	16.505	70.231	64.286	2.973	-23.474	-13.094	5.723
600	17.876	73.366	65.543	4.694	-23.815	-10.985	4.001
700	19.019	76.210	66.867	6.540	-24.053	-8.825	2.755
800	19.977	78.814	68.200	8.451	-24.209	-6.640	1.814
900	20.779	81.215	69.514	10.530	-24.299	-4.436	1.077
1000	21.450	83.440	70.797	12.643	-24.338	-2.227	0.487
1100	22.010	85.511	72.041	14.817	-24.339	-0.016	0.003
1200	22.480	87.447	73.245	17.042	-24.311	2.194	-0.400
1300	22.875	89.263	74.408	19.310	-24.266	4.401	-0.740
1400	23.210	90.970	75.531	21.615	-24.211	6.604	-1.031
1500	23.494	92.582	76.615	23.951	-24.153	8.805	-1.283
1600	23.737	94.106	77.661	26.312	-24.098	10.998	-1.502
1700	23.945	95.551	78.671	28.697	-36.037	13.298	-1.710
1800	24.125	96.925	79.647	31.100	-35.934	16.196	-1.966
1900	24.282	98.234	80.591	33.521	-35.829	19.090	-2.196
2000	24.419	99.483	81.505	35.956	-35.723	21.978	-2.402
2100	24.539	100.677	82.389	38.404	-35.618	24.860	-2.587
2200	24.644	101.821	83.247	40.863	-35.515	27.736	-2.755
2300	24.738	102.919	84.079	43.333	-35.412	30.610	-2.909
2400	24.821	103.973	84.886	45.811	-35.314	33.481	-3.049
2500	24.896	104.988	85.670	48.297	-35.220	36.341	-3.177
2600	24.962	105.966	86.432	50.790	-35.127	39.205	-3.295
2700	25.022	106.909	87.173	53.289	-35.039	42.059	-3.404
2800	25.076	107.820	87.894	55.794	-34.955	44.913	-3.506
2900	25.125	108.701	88.596	58.304	-34.873	47.768	-3.600
3000	25.169	109.554	89.281	60.819	-34.796	50.612	-3.687
3100	25.210	110.380	89.948	63.338	-34.722	53.457	-3.769
3200	25.246	111.180	90.599	65.860	-34.654	56.303	-3.845
3300	25.280	111.958	91.235	68.387	-34.590	59.146	-3.917
3400	25.311	112.713	91.855	70.916	-34.529	61.982	-3.984
3500	25.340	113.447	92.462	73.449	-34.475	64.822	-4.048
3600	25.366	114.161	93.055	75.984	-126.385	69.914	-4.244
3700	25.390	114.857	93.635	78.522	-126.243	75.366	-4.452
3800	25.412	115.534	94.202	81.062	-126.103	80.814	-4.648
3900	25.433	116.194	94.757	83.604	-125.972	86.257	-4.834
4000	25.452	116.839	95.301	86.149	-125.845	91.697	-5.010
4100	25.470	117.467	95.834	88.695	-125.724	97.131	-5.178
4200	25.487	118.081	96.357	91.243	-125.608	102.567	-5.337
4300	25.502	118.681	96.869	93.792	-125.497	107.997	-5.489
4400	25.517	119.268	97.371	96.343	-125.392	113.424	-5.634
4500	25.531	119.841	97.864	98.895	-125.293	118.852	-5.772
4600	25.543	120.403	98.348	101.449	-125.197	124.280	-5.905
4700	25.555	120.952	98.823	104.004	-125.109	129.704	-6.031
4800	25.567	121.490	99.290	106.560	-125.024	135.121	-6.152
4900	25.577	122.017	99.749	109.117	-124.945	140.543	-6.268
5000	25.587	122.534	100.199	111.676	-124.870	145.954	-6.380
5100	25.597	123.041	100.642	114.235	-124.802	151.376	-6.487
5200	25.605	123.538	101.078	116.795	-124.738	156.787	-6.590
5300	25.614	124.026	101.506	119.356	-124.678	162.206	-6.689
5400	25.622	124.505	101.927	121.918	-124.625	167.611	-6.784
5500	25.629	124.975	102.342	124.480	-124.576	173.024	-6.875
5600	25.636	125.437	102.751	127.043	-124.533	178.433	-6.964
5700	25.643	125.891	103.153	129.607	-124.495	183.849	-7.049
5800	25.650	126.337	103.548	132.172	-124.462	189.256	-7.131
5900	25.656	126.775	103.938	134.737	-124.435	194.662	-7.211
6000	25.661	127.207	104.323	137.303	-124.412	200.065	-7.287

Dec. 31, 1976

BROMOSILANE (SiH_3Br) (IDEAL GAS) GFW = 111.0137

Point Group C_{3v}
$S^\circ_{298.15}$ = 62.70 ± 0.05 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = [-14.78 ± 4] kcal/mol BRH3SI
$\Delta Hf^\circ_{298.15}$ = [-18.7 ± 4] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2200 (1)	2209.2(2)
930.3(1)	946.3(2)
430.6(1)	632.6(2)

Bond Distances: Si-H = 1.486 ± 0.008 Å Si-Br = 2.210 Å σ = 3
Bond Angles: H-Si-H = 110.42° ± 0.5° H-Si-Br = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_AI_BI_C = 3.7987 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

ΔHf°_{298} is estimated by linear interpolation between the values (1) of $SiBr_4(g)$ and $SiH_4(g)$. The only experimental ΔHf° for $SiHBr_3(g)$ appears to be too uncertain to justify a nonlinear interpolation such as that adopted for SiH_3Cl (1). Normally we would seek a comparison with ΔHf° values of CH_nBr_{4-n}. These were recently reviewed by Kudchadker and Kudchadker (2). They adopted a cubic variation of ΔHf° with n, based on ΔHf° values of $CHBr_3$ and CBr_4 selected by Wagman et al. (3). We presume that Wagman's values are calculated rather than experimental. Uncertainty in these values (4-6) precludes their use as a comparison for SiH_nBr_{4-n}. We conclude, as did Hunt and Sirtl (15), that the available data justify only linear interpolation of ΔHf°.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley et al. (7) for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structural determinations (8). The principal moments of inertia are $I_A = 0.9970 \times 10^{-39}$ and $I_B = I_C = 19.5193 \times 10^{-39}$ g cm^2.

Vibrational frequencies are from gas-phase infrared spectra (9) measured with a grating spectrometer by Buerger et al. Assignments were based on analysis of band contours and rotational fine structure. These results supersede Shimanouchi's selected frequencies (10) which derive from lower resolution spectra. The new data agree with unpublished data cited by Ball et al. (11).

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3Br (12). SiH_3Br has several high-lying electronic absorptions and a diffuse band with a maximum at ~52000 cm^{-1} (13). Comparison (12, 13) with CH_3Br (12, 14) suggests that the lowest excited state in SiH_3Br is near 40000 cm^{-1}. Contributions due to excited states should be unimportant.

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BRH3SI

SILICON MONOBROMIDE (SIBR) BRSI
(IDEAL GAS) GFW=107.990

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.400	57.543	57.543	INFINITE
100	7.305	49.950	66.935	-1.698	57.846	53.586	-117.113
200	8.756	55.493	59.943	-0.890	57.788	49.337	-53.913
298	9.257	59.107	59.107	0.000	56.244	45.486	-33.269
300	9.260	59.165	59.108	0.017	56.236	45.319	-33.015
400	9.327	61.842	59.472	0.948	52.540	42.437	-23.186
500	9.298	63.921	60.162	1.880	52.486	39.917	-17.448
600	9.259	65.613	60.934	2.807	52.402	37.410	-13.626
700	9.229	67.038	61.707	3.732	52.294	34.919	-10.902
800	9.209	68.269	62.452	4.654	52.168	32.445	-8.864
900	9.196	69.353	63.159	5.574	52.027	29.989	-7.282
1000	9.189	70.321	63.828	6.493	51.873	27.549	-6.021
1100	9.187	71.197	64.459	7.412	51.705	25.124	-4.992
1200	9.189	71.996	65.054	8.331	51.528	22.715	-4.137
1300	9.193	72.732	65.617	9.250	51.339	20.324	-3.416
1400	9.198	73.413	66.150	10.169	51.141	17.943	-2.801
1500	9.206	74.048	66.655	11.089	50.932	15.579	-2.270
1600	9.214	74.643	67.136	12.010	50.713	13.229	-1.807
1700	9.223	75.201	67.594	12.932	38.492	10.999	-1.414
1800	9.234	75.729	68.032	13.855	38.310	9.387	-1.140
1900	9.244	76.228	68.450	14.779	38.128	7.786	-0.896
2000	9.256	76.703	68.851	15.704	37.945	6.194	-0.677
2100	9.267	77.155	69.236	16.630	37.765	4.610	-0.480
2200	9.280	77.586	69.605	17.557	37.584	3.035	-0.301
2300	9.292	77.999	69.961	18.486	37.404	1.469	-0.140
2400	9.305	78.395	70.305	19.416	37.225	-0.088	0.008
2500	9.319	78.775	70.636	20.347	37.047	-1.640	0.144
2600	9.332	79.141	70.956	21.280	36.869	-3.184	0.268
2700	9.347	79.493	71.266	22.213	36.693	-4.723	0.382
2800	9.362	79.833	71.566	23.149	36.517	-6.251	0.488
2900	9.377	80.162	71.856	24.086	36.342	-7.776	0.586
3000	9.394	80.480	72.139	25.024	36.169	-9.295	0.677
3100	9.411	80.788	72.413	25.965	35.996	-10.808	0.762
3200	9.429	81.088	72.679	26.907	35.825	-12.313	0.841
3300	9.448	81.378	72.938	27.850	35.655	-13.815	0.915
3400	9.468	81.660	73.191	28.796	35.486	-15.312	0.984
3500	9.489	81.935	73.437	29.744	35.319	-16.805	1.049
3600	9.511	82.203	73.676	30.694	-56.807	-16.034	0.973
3700	9.535	82.464	73.910	31.646	-56.872	-14.901	0.880
3800	9.560	82.718	74.139	32.601	-56.934	-13.765	0.792
3900	9.586	82.967	74.362	33.558	-56.996	-12.629	0.708
4000	9.613	83.210	74.580	34.518	-57.056	-11.491	0.628
4100	9.642	83.448	74.794	35.481	-57.114	-10.354	0.552
4200	9.673	83.680	75.002	36.447	-57.169	-9.212	0.479
4300	9.704	83.908	75.207	37.416	-57.221	-8.069	0.410
4400	9.738	84.132	75.407	38.388	-57.271	-6.925	0.344
4500	9.772	84.351	75.604	39.363	-57.318	-5.777	0.281
4600	9.809	84.566	75.796	40.342	-57.361	-4.632	0.220
4700	9.846	84.778	75.985	41.325	-57.402	-3.484	0.162
4800	9.885	84.985	76.170	42.312	-57.440	-2.339	0.107
4900	9.926	85.189	76.352	43.302	-57.473	-1.189	0.053
5000	9.967	85.390	76.531	44.297	-57.503	-0.043	0.002
5100	10.010	85.588	76.707	45.296	-57.530	1.109	-0.048
5200	10.055	85.783	76.879	46.299	-57.552	2.258	-0.095
5300	10.100	85.975	77.049	47.306	-57.569	3.410	-0.141
5400	10.147	86.164	77.216	48.319	-57.584	4.558	-0.184
5500	10.195	86.351	77.381	49.336	-57.594	5.710	-0.227
5600	10.243	86.535	77.542	50.358	-57.600	6.862	-0.268
5700	10.293	86.717	77.702	51.385	-57.602	8.016	-0.307
5800	10.344	86.896	77.859	52.416	-57.599	9.167	-0.345
5900	10.396	87.073	78.013	53.453	-57.593	10.314	-0.382
6000	10.448	87.249	78.166	54.496	-57.582	11.463	-0.418

Dec. 31, 1976

SILICON MONOBROMIDE (SiBr) (IDEAL GAS) GFW = 107.990

D_0^o = 77.3 ± 10.3 kcal/mol
$S^o_{298.15}$ = 59.11 ± 0.05 gibbs/mol
Symmetry Number = 1

ΔHf^o_0 = 57.5 ± 11.0 kcal/mol BrSi
$\Delta Hf^o_{298.15}$ = 56.2 ± 11.0 kcal/mol

Electronic Levels and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(5)	X $^2\Pi_{1/2}$	0	2	2.210	0.1669	0.0019	423.2	1.5
(5)	$^2\Pi_{3/2}$	419.2	2	2.210	0.1669	0.0019	423.2	1.5
(6)	A $^2\Sigma$	20937.6	2	[2.210]	[0.1669]	[0.0019]	249.6	0.5
(1)	B' $^2\Delta$	23920	4	[2.210]	[0.1669]	[0.0019]	394	4
(5)	B $^2\Sigma$	33572.7	2	2.132	0.1793	[0.0019]	573.6	4.0
(10)	C $^2\Pi$	41057	4	[2.210]	[0.1669]	[0.0019]	529.2	2.0

Heat of Formation

Kuznetsova and Kuzyakov (1) suggested a value of D_0^o = 85.8±11.4 kcal/mol based on linear Birge-Sponer extrapolations of the ground state and B' $^2\Delta$ state vibrational data. We correct this value for the ionic character of the bond according to Hildenbrand (2) and obtain D_0^o = 77.3±10.3. With auxiliary JANAF data (3) this yields ΔHf^o_0 = 57.5 kcal/mol and ΔHf^o_{298} = 56.2 kcal/mol as the adopted values. Tandon and Tandon (4) obtained D_0^o = 85.3 kcal/mol from a theoretical treatment based on Sutherland's potential function in good agreement with the adopted value. The value of D_0^o may be compared to the average (per bond) heats of atomization of 80.58 and 77.89 kcal/mol for $SiBr_2$(g) and $SiBr_4$(g), respectively (3).

Heat Capacity and Entropy

Molecular constant data for the ground state are from Mishra and Khanna (5). The vibrational data is in good agreement with data from Rao and Haranath (6), Kuznetsova et al. (7), and Jevons and Bashford (8). Data for the A $^2\Sigma$ and B' $^2\Delta$ states are from Rao and Haranath (6) and Kuznetsova and Kuzyakov (1), respectively. The B $^2\Sigma$ state data are from Mishra and Khanna (5) and the vibrational data agree well with Jevons and Bashford (8). Slightly different values for the rotational constants for both this state and the ground state have been obtained by Kuznetsova and Kuzyakov (9). Data for the C $^2\Pi$ state is from Oldershaw and Robinson (10) who also reported data for several higher states; these are not included due to uncertainties in their assignments and degeneracies. Splittings of 18 and 12 cm^{-1} for the B' $^2\Delta$ and C $^2\Pi$ states (1, 10), respectively, have not been included in our calculations. The $^4\Sigma$ state observed for SiF and SiI has not been observed for SiBr. It is expected to lie near 24,000 cm^{-1} by analogy with SiF and SiI (3) which is very near the B' $^2\Delta$ state. This raises the possibility that this state *may have been missed, or the* $^2\Delta$ *state misassigned, due to the large number of lines in this region* (1). A high resolution re-examination of this region of the spectrum is desirable to clarify the situation. We have assigned an uncertainity of ±0.05 gibbs/mol to S^o_{298} in view of these uncertainties. All molecular constant data has been corrected to the natural abundances of Si and Br assuming the observed data was for $^{28}Si\ ^{79}Br$. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant (A = 419.2 cm^{-1}). This approximation gives slightly biased results at low temperature: the stated uncertainty in S^o_{298} should account for this.

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DIBROMOSILANE (SiH_2BR_2) BR_2H_2SI

(IDEAL GAS) GFW=189.9098

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.411	-40.259	-40.259	INFINITE
100	9.851	60.677	86.054	-2.538	-40.877	-43.127	94.254
200	12.885	68.387	75.426	-1.408	-41.802	-45.038	49.215
298	15.665	74.077	74.077	0.000	-45.500	-46.092	33.787
300	15.710	74.174	74.077	0.029	-45.526	-46.096	33.581
400	17.689	78.982	74.719	1.705	-53.291	-44.710	24.429
500	19.092	83.088	75.992	3.548	-53.574	-42.531	18.590
600	20.161	86.667	77.480	5.513	-53.765	-40.303	14.680
700	21.017	89.842	79.023	7.573	-53.885	-38.049	11.879
800	21.717	92.695	80.557	9.711	-53.949	-35.783	9.775
900	22.293	95.288	82.052	11.912	-53.970	-33.509	8.137
1000	22.770	97.662	83.496	14.166	-53.958	-31.236	6.827
1100	23.167	99.851	84.884	16.464	-53.923	-28.966	5.755
1200	23.498	101.882	86.217	18.797	-53.872	-26.698	4.862
1300	23.775	103.774	87.496	21.161	-53.812	-24.436	4.108
1400	24.009	105.544	88.722	23.551	-53.747	-22.179	3.462
1500	24.207	107.208	89.900	25.962	-53.685	-19.926	2.903
1600	24.377	108.776	91.031	28.391	-53.628	-17.678	2.415
1700	24.522	110.258	92.119	30.837	-65.567	-15.326	1.970
1800	24.648	111.663	93.166	33.295	-65.467	-12.375	1.502
1900	24.757	112.999	94.175	35.766	-65.364	-9.426	1.084
2000	24.852	114.271	95.148	38.246	-65.263	-6.485	0.709
2100	24.935	115.486	96.088	40.736	-65.161	-3.549	0.369
2200	25.009	116.648	96.996	43.233	-65.062	-0.619	0.061
2300	25.074	117.761	97.875	45.737	-64.964	2.309	-0.219
2400	25.132	118.829	98.726	48.247	-64.869	5.235	-0.477
2500	25.183	119.856	99.551	50.763	-64.777	8.150	-0.713
2600	25.229	120.845	100.351	53.284	-64.686	11.068	-0.930
2700	25.271	121.798	101.128	55.809	-64.599	13.977	-1.131
2800	25.308	122.717	101.882	58.338	-64.516	16.887	-1.318
2900	25.342	123.606	102.616	60.870	-64.435	19.796	-1.492
3000	25.373	124.466	103.330	63.406	-64.357	22.695	-1.653
3100	25.401	125.298	104.026	65.945	-64.282	25.596	-1.804
3200	25.427	126.105	104.703	68.486	-64.211	28.496	-1.946
3300	25.450	126.888	105.364	71.030	-64.144	31.392	-2.079
3400	25.471	127.648	106.008	73.576	-64.079	34.283	-2.204
3500	25.491	128.387	106.637	76.124	-64.020	37.177	-2.321
3600	25.509	129.105	107.251	78.675	-155.924	42.324	-2.569
3700	25.526	129.804	107.851	81.226	-155.774	47.829	-2.825
3800	25.542	130.485	108.438	83.780	-155.626	53.332	-3.067
3900	25.556	131.149	109.012	86.335	-155.485	58.828	-3.297
4000	25.569	131.796	109.573	88.891	-155.348	64.320	-3.514
4100	25.582	132.427	110.123	91.448	-155.216	69.807	-3.721
4200	25.593	133.044	110.661	94.007	-155.087	75.296	-3.918
4300	25.604	133.646	111.189	96.567	-154.962	80.780	-4.106
4400	25.614	134.235	111.706	99.128	-154.842	86.260	-4.285
4500	25.624	134.811	112.213	101.690	-154.726	91.739	-4.455
4600	25.632	135.374	112.711	104.253	-154.613	97.218	-4.619
4700	25.641	135.926	113.199	106.816	-154.507	102.694	-4.775
4800	25.649	136.465	113.678	109.381	-154.403	108.160	-4.925
4900	25.656	136.994	114.148	111.946	-154.303	113.632	-5.068
5000	25.663	137.513	114.610	114.512	-154.207	119.094	-5.206
5100	25.669	138.021	115.064	117.079	-154.116	124.563	-5.338
5200	25.675	138.520	115.511	119.646	-154.028	130.025	-5.465
5300	25.681	139.009	115.949	122.214	-153.943	135.492	-5.587
5400	25.687	139.489	116.381	124.782	-153.865	140.944	-5.704
5500	25.692	139.960	116.805	127.351	-153.789	146.406	-5.818
5600	25.697	140.423	117.223	129.920	-153.719	151.862	-5.927
5700	25.702	140.878	117.634	132.490	-153.652	157.324	-6.032
5800	25.706	141.325	118.039	135.061	-153.589	162.778	-6.134
5900	25.710	141.764	118.437	137.632	-153.531	168.229	-6.232
6000	25.714	142.197	118.829	140.203	-153.477	173.675	-6.326

Dec. 31, 1976

DIBROMOSILANE (SiH_2Br_2) (IDEAL GAS) GFW = 189.9098

Point Group [C_{2v}]
$S°_{298.15}$ = [74.08 ± 0.3] gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = [-40.26 ± 4] kcal/mol
$\Delta Hf°_{298.15}$ = [-45.5 ± 4] kcal/mol

BR_2H_2SI

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2206(1)	2232(1)
942(1)	556(1)
407(1)	843(1)
122(1)	471(1)
688(1)	

Bond Distances: Si-H = [1.49] Å Si-Br = [2.19] Å σ = [2]
Bond Angles: H-Si-H = [111°] Br-Si-Br = [110°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [6.3612 x 10^{-113}] g^3 cm^6

Heat of Formation

$\Delta Hf°_{298}$ is estimated by linear interpolation between the values (1) of $SiBr_4(g)$ and $SiH_4(g)$. The only experimental ΔHf° for $SiHBr_3(g)$ appears to be too uncertain to justify a nonlinear interpolation such as that adopted for SiH_3Cl (1). Normally we would seek a comparison with ΔHf° values of CH_nBr_{4-n}. These were recently reviewed by Kudchadker and Kudchadker (2). They adopted a cubic variation of ΔHf° with n, based on ΔHf° values of $CHBr_3$ and CBr_4 selected by Wagman et al. (3). We presume that Wagman's values are calculated rather than experimental. Uncertainty in these values (4 - 6) precludes their use as a comparison for SiH_nBr_{4-n}. We conclude, as did Hunt and Sirtl (7), that the available data justify only linear interpolation of ΔHf°.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3Br, $SiHBr_3$ and the chlorosilanes (1). Bond distances are assumed to be intermediate between those of SiH_3Br and $SiHBr_3$ (1). The principal moments of inertia are I_A = 7.9742 x 10^{-39}, I_B = 85.901 x 10^{-39} and I_C = 92.865 x 10^{-39} g cm^2.

Vibrational frequencies are those selected by Shimanouchi (8) based on gas-phase infrared spectra (9) and liquid-phase Raman spectra (10). Gas-phase frequencies are adopted except for ν_4 = 122 cm^{-1} and infrared inactive ν_5 = 686 cm^{-1}.

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2 (1).

References

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BR_2H_2SI

SILICON DIBROMIDE ($SiBr_2$) BR2SI
(IDEAL GAS) GFW=187.8935

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.195	-9.067	-9.067	INFINITE
100	9.926	60.435	83.622	-2.319	-8.923	-13.588	29.695
200	11.893	67.978	74.072	-1.219	-9.275	-18.133	19.815
298	12.820	72.924	72.924	0.000	-12.500	-22.053	16.165
300	12.831	73.003	72.924	0.024	-12.518	-22.112	16.108
400	13.258	76.761	73.434	1.331	-19.958	-23.788	12.997
500	13.479	79.745	74.408	2.469	-20.047	-24.735	10.812
600	13.605	82.215	75.509	4.023	-20.149	-25.664	9.348
700	13.683	84.318	76.621	5.388	-20.262	-26.575	8.297
800	13.735	86.149	77.700	6.759	-20.387	-27.469	7.504
900	13.771	87.769	78.731	8.135	-20.521	-28.345	6.883
1000	13.797	89.221	79.708	9.513	-20.667	-29.206	6.383
1100	13.817	90.537	80.634	10.894	-20.823	-30.054	5.971
1200	13.831	91.740	81.510	12.276	-20.989	-30.885	5.625
1300	13.843	92.848	82.340	13.660	-21.165	-31.703	5.330
1400	13.852	93.874	83.128	15.045	-21.351	-32.506	5.074
1500	13.860	94.830	83.876	16.430	-21.549	-33.297	4.851
1600	13.866	95.725	84.589	17.817	-21.756	-34.073	4.654
1700	13.871	96.566	85.269	19.204	-33.967	-34.730	4.465
1800	13.875	97.358	85.919	20.591	-34.141	-34.770	4.222
1900	13.879	98.109	86.541	21.979	-34.315	-34.799	4.003
2000	13.882	98.821	87.137	23.367	-34.491	-34.821	3.805
2100	13.886	99.498	87.710	24.755	-34.667	-34.833	3.625
2200	13.889	100.144	88.261	26.144	-34.844	-34.838	3.461
2300	13.892	100.762	88.791	27.533	-35.022	-34.833	3.310
2400	13.896	101.353	89.302	28.922	-35.201	-34.819	3.171
2500	13.900	101.920	89.795	30.312	-35.380	-34.801	3.042
2600	13.905	102.466	90.272	31.702	-35.560	-34.773	2.923
2700	13.911	102.990	90.734	33.093	-35.740	-34.742	2.812
2800	13.917	103.496	91.181	34.484	-35.922	-34.699	2.708
2900	13.925	103.985	91.614	35.876	-36.103	-34.652	2.611
3000	13.935	104.457	92.034	37.269	-36.284	-34.601	2.521
3100	13.946	104.914	92.442	38.664	-36.465	-34.541	2.435
3200	13.959	105.357	92.839	40.059	-36.646	-34.474	2.354
3300	13.974	105.787	93.225	41.455	-36.828	-34.405	2.279
3400	13.990	106.204	93.600	42.854	-37.007	-34.330	2.207
3500	14.009	106.610	93.966	44.254	-37.187	-34.248	2.139
3600	14.030	107.005	94.323	45.655	-129.328	-31.905	1.937
3700	14.053	107.390	94.671	47.060	-129.405	-29.198	1.725
3800	14.078	107.765	95.011	48.466	-129.483	-26.488	1.523
3900	14.105	108.131	95.342	49.875	-129.560	-23.776	1.332
4000	14.134	108.488	95.667	51.287	-129.635	-21.065	1.151
4100	14.165	108.838	95.984	52.702	-129.709	-18.352	0.978
4200	14.198	109.180	96.294	54.120	-129.780	-15.635	0.814
4300	14.233	109.514	56.597	55.542	-129.848	-12.914	0.656
4400	14.270	109.842	96.895	56.967	-129.915	-10.194	0.506
4500	14.308	110.163	97.186	58.396	-129.978	-7.469	0.363
4600	14.348	110.478	97.471	59.828	-130.039	-4.747	0.226
4700	14.389	110.787	97.752	61.265	-130.097	-2.020	0.094
4800	14.431	111.090	98.026	62.706	-130.152	0.701	-0.032
4900	14.475	111.388	58.296	64.152	-130.202	3.430	-0.153
5000	14.519	111.681	98.561	65.601	-130.250	6.156	-0.269
5100	14.565	111.969	98.821	67.055	-130.295	8.885	-0.381
5200	14.611	112.252	99.076	68.514	-130.335	11.614	-0.488
5300	14.657	112.531	99.328	69.978	-130.370	14.347	-0.592
5400	14.704	112.805	99.575	71.446	-130.404	17.073	-0.691
5500	14.751	113.076	99.818	72.918	-130.434	19.807	-0.787
5600	14.798	113.342	100.057	74.396	-130.460	22.539	-0.880
5700	14.846	113.604	100.292	75.878	-130.483	25.275	-0.969
5800	14.893	113.863	100.524	77.365	-130.502	28.008	-1.055
5900	14.940	114.118	100.752	78.857	-130.518	30.736	-1.139
6000	14.986	114.369	100.977	80.353	-130.531	33.466	-1.219

Dec. 31, 1976; Dec. 31, 1977

SILICON DIBROMIDE ($SiBr_2$) (IDEAL GAS) GFW = 187.8935

ΔHa°_0 = 172.1 ± 5.0 kcal/mol
$S^\circ_{298.15}$ = [72.92 ± 0.5] gibbs/mol

ΔHf°_0 = -9.1 ± 4.0 kcal/mol BR2SI
$\Delta Hf^\circ_{298.15}$ = -12.5 ± 4.0 kcal/mol

Electronic Levels and Quantum Weights

state	ε_i, cm^{-1}	g_i
$[^1A_1]$	0	[1]
$[^3B_1]$	[20000]	[3]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
402 (1)
[120](1)
398.9(1)

Point Group: C_{2v} σ = 2
Bond Distance: Si-Br = [2.19] Å
Bond Angle: Br-Si-Br = 109° ± 3°
Product of the Moments of Inertia: $I_AI_BI_C$ =[4.9111 x 10^{-113}] g^3 cm^6

Heat of Formation

The equilibrium reaction Si(c) + $SiBr_4$(g) = 2 $SiBr_2$(g) was studied by Schäfer et al. (1) and Wolf and Herbst (2). Both investigators used a flow technique in an argon atmosphere. A second and third law analysis of their results (reported only in equation form) is summarized below. As in the case of $SiCl_2$ (3), there is acceptable agreement between these two studies. Using the mean ΔHr°_{298} from the third law results and auxiliary data (3), we calculate and adopt ΔHf°_{298} = -12.5 kcal/mol for $SiBr_2$(g).

		ΔHr°_{298}, kcal/mol		Drift
Source	Range	2nd Law	3rd Law	gibbs/mol
Schäfer et al. (1)	1320-1475 K	71.61	73.26	1.18
Wolf and Herbst (2)	1200-1550 K	77.33	75.21	-1.54

The adopted heat of formation leads to a ΔHa°_0 value which implies that the average bond energy is roughly 10% larger in $SiBr_2$(g) than in SiBr(g) or $SiBr_4$(g) (3).

Heat Capacity and Entropy

Maass, Hauge, and Margrave (4) observed the infrared spectra of $SiBr_2$ in nitrogen and argon matrices in the Si-Br stretching region. Attempts to observe the bending fundamental in the region between 90 cm^{-1} and 150 cm^{-1} were unsuccessful. Maass et al. (4) measured and assigned ν_1 and ν_3. The bond angle was calculated to be 109±3° from the isotopic splittings due to three silicon isotopes. The authors also assumed ν_2 = 120 cm^{-1}. This bending frequency is consistent with the analogous $SiBr_2$ "bending mode" in SiH_2Br_2 (3). We adopt the frequencies and bond angles as suggested by Maass et al. (4).

We assume the Si-Br bond distance to be the same as that in SiH_2Br_2 (3). By observing the trends in SiF_2 and $SiCl_2$ (3), we assume a $^1A_1$ ground electronic state and a $^3B_1$ excited state at ~20000 cm^{-1}. Additional support for this assignment comes from the luminescense spectrum of a glow discharge in $SiBr_4$ vapors observed by Kuznetsova and Kuzyokov (5). They stated that the complex spectral structure of the 16800-23500 cm^{-1} band could be attributable to the oscillation and deformation of the nonlinear $SiBr_2$ molecule. The inclusion of this triplet electronic state increases the entropy by 0.004 gibbs/mol at 3000 K. The principal moments of inertia are calculated to be I_A = 6.415 x 10^{-39}, I_B = 84.349 x 10^{-39}, and I_C = 90.764 x 10^{-39} g cm^2.

References

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2. E. Wolf and C. Herbst, Z. Anorg. Allg. Chem. 347, 113 (1966).
3. JANAF Thermochemical Tables: $SiBr_4$(g), SiBr(g), and SiH_2Br_2(g), 12-31-76; Si(g), 3-31-67; Br(g), 6-30-74; $SiCl_2$(g) and SiF_2(g), 12-31-77.
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TRIBROMOSILANE ($SiHBr_3$)

(IDEAL GAS) GFW=268.8059

Br_3HSi

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-4.260	-66.090	-66.090	INFINITE
100	12.840	65.843	98.411	-3.257	-66.533	-69.876	152.713
200	16.674	75.987	84.843	-1.771	-67.386	-72.905	79.666
298	19.218	83.158	83.158	0.000	-72.400	-74.928	54.924
300	19.255	83.277	83.159	0.036	-72.429	-74.943	54.596
400	20.832	89.051	83.935	2.046	-83.633	-73.489	40.152
500	21.844	93.816	85.449	4.183	-83.714	-70.942	31.009
600	22.557	97.865	87.189	6.405	-83.742	-68.385	24.909
700	23.095	101.384	88.971	8.689	-83.733	-65.826	20.552
800	23.518	104.497	90.721	11.021	-83.699	-63.271	17.285
900	23.857	107.287	92.409	13.390	-83.645	-60.719	14.745
1000	24.132	109.815	94.025	15.790	-83.578	-58.175	12.714
1100	24.358	112.126	95.567	18.215	-83.504	-55.639	11.055
1200	24.545	114.254	97.037	20.660	-83.425	-53.109	9.672
1300	24.700	116.225	98.438	23.123	-83.347	-50.585	8.504
1400	24.831	118.060	99.775	25.599	-83.271	-48.068	7.504
1500	24.941	119.777	101.052	28.088	-83.202	-45.557	6.638
1600	25.035	121.390	102.273	30.587	-83.141	-43.049	5.880
1700	25.116	122.910	103.443	33.095	-95.080	-40.438	5.199
1800	25.185	124.348	104.565	35.610	-94.980	-37.228	4.520
1900	25.245	125.711	105.642	38.131	-94.879	-34.020	3.913
2000	25.297	127.007	106.678	40.658	-94.781	-30.821	3.368
2100	25.343	128.243	107.676	43.191	-94.681	-27.626	2.875
2200	25.383	129.423	108.638	45.727	-94.585	-24.436	2.428
2300	25.419	130.552	109.566	48.267	-94.490	-21.248	2.019
2400	25.450	131.634	110.463	50.810	-94.397	-18.063	1.645
2500	25.479	132.674	111.331	53.357	-94.307	-14.887	1.301
2600	25.504	133.674	112.171	55.906	-94.217	-11.710	0.984
2700	25.527	134.637	112.986	58.458	-94.131	-8.542	0.691
2800	25.547	135.565	113.775	61.011	-94.048	-5.371	0.419
2900	25.566	136.462	114.542	63.567	-93.966	-2.204	0.166
3000	25.583	137.329	115.288	66.124	-93.887	0.955	-0.070
3100	25.598	138.168	116.012	68.684	-93.810	4.116	-0.290
3200	25.612	138.981	116.717	71.244	-93.736	7.277	-0.497
3300	25.625	139.769	117.404	73.806	-93.666	10.430	-0.691
3400	25.636	140.535	118.073	76.369	-93.596	13.582	-0.873
3500	25.647	141.278	118.726	78.933	-93.531	16.735	-1.045
3600	25.657	142.001	119.362	81.498	-185.430	22.140	-1.344
3700	25.666	142.704	119.983	84.064	-185.271	27.904	-1.648
3800	25.674	143.388	120.590	86.631	-185.116	33.665	-1.936
3900	25.682	144.055	121.184	89.199	-184.965	39.421	-2.209
4000	25.690	144.706	121.764	91.768	-184.817	45.169	-2.468
4100	25.696	145.340	122.331	94.337	-184.672	50.914	-2.714
4200	25.703	145.959	122.886	96.907	-184.530	56.660	-2.948
4300	25.708	146.564	123.430	99.478	-184.391	62.403	-3.172
4400	25.714	147.155	123.962	102.049	-184.256	68.140	-3.385
4500	25.719	147.733	124.484	104.620	-184.124	73.877	-3.588
4600	25.724	148.298	124.996	107.193	-183.993	79.610	-3.782
4700	25.728	148.852	125.497	109.765	-183.868	85.343	-3.968
4800	25.733	149.393	125.990	112.338	-183.745	91.063	-4.146
4900	25.737	149.924	126.473	114.912	-183.624	96.790	-4.317
5000	25.740	150.444	126.947	117.486	-183.506	102.509	-4.481
5100	25.744	150.954	127.413	120.060	-183.393	108.229	-4.638
5200	25.747	151.454	127.870	122.634	-183.281	113.945	-4.789
5300	25.751	151.944	128.320	125.209	-183.171	119.665	-4.934
5400	25.753	152.426	128.762	127.784	-183.067	125.370	-5.074
5500	25.756	152.898	129.196	130.360	-182.964	131.085	-5.209
5600	25.759	153.362	129.624	132.936	-182.866	136.792	-5.339
5700	25.762	153.818	130.044	135.512	-182.770	142.505	-5.464
5800	25.764	154.266	130.458	138.088	-182.677	148.211	-5.585
5900	25.766	154.707	130.865	140.665	-182.589	153.911	-5.701
6000	25.768	155.140	131.266	143.241	-182.503	159.606	-5.814

Dec. 31, 1976

TRIBROMOSILANE ($SiHBr_3$) (IDEAL GAS) GFW = 268.8059

Point Group C_{3v}

$S^\circ_{298.15}$ = 83.16 ± 0.1 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = [-66.09 ± 4] kcal/mol Br_3HSi

$\Delta Hf^\circ_{298.15}$ = [-72.4 ± 4] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2239.2(1)	774. (2)
362. (1)	483.5(2)
168.5(1)	116.8(2)

Bond Distances: Si-H = 1.494 Å Si-Br = 2.170 Å σ = 3

Bond Angles: H-Si-Br = 107.51° Br-Si-Br = 111.36°

Product of the Moments of Inertia: $I_AI_BI_C = 1.31197 \times 10^{-111}\ g^3\ cm^6$

Heat of Formation

ΔHf°_{298} is estimated by linear interpolation between the values (1) of $SiBr_4$(g) and SiH_4(g). In adopting linear estimates for SiH_nBr_{4-n} (n=1,2,3), we dismiss the solution calorimetry of Wolf et al. (2) because of possible negative bias. These authors reported ΔHf°_{298}(g) = -69.3±2.0 kcal/mol derived from enthalpies of solution in dilute aqueous NaOH. Wagman et al. (3) changed this value to -75.9 kcal/mol due to revised auxiliary data, especially ΔHf°(Na_2SiO_3,c,soln). The calorimetric result is 3.5 kcal/mol more negative than our linear estimate. This could imply a cubic variation of ΔHf°(SiH_nBr_{4-n}) with n, such as we adopt for the chlorosilanes (1). We tentatively reject this hypothesis because the solution results (2) for $SiHCl_3$(g), $SiCl_4$(g), $SiBr_4$(ℓ) and SiI_4(c) are also more negative than our adopted values (1). It is conceivable that the hydrolysis reactions did not proceed to equal degrees in the different calorimetric studies. We conclude, as did Hunt and Sirtl (4), that the available data justify only linear interpolation of ΔHf°.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Mitzlaff et al. (5) for eight isotopic forms of $SiHBr_3$ and $SiDBr_3$. Structural parameters are presumably substitutional (r_s) values. The principal moments of inertia are $I_A = I_B = 87.730 \times 10^{-39}$ and $I_C = 170.462 \times 10^{-39}\ g\ cm^2$.

Vibrational frequencies are from gas-phase infrared spectra of Buerger and Cichon (6). Assignments are based on band contour analysis and are consistent with Shimanouchi's values (7) derived from liquid-phase Raman spectra (8).

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2 (1).

References

1. JANAF Thermochemical Tables: Br_4Si(ℓ,g), Br_2H_2Si(g), BrH_3Si(g), ClH_3Si(g), Cl_2H_2Si(g), Cl_3HSi(g) 12-31-76; H_4Si(g), I_4Si(c) 6-30-76.
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Br_3HSi

SILICON TRIBROMIDE (SIBR3) BR3SI
(IDEAL GAS) GFW=267.7975

T, K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0	0.000	0.000	INFINITE	-4.151	-42.800	-42.800	INFINITE
100	12.833	67.192	98.678	-3.149	-42.863	-47.560	103.941
200	16.200	77.238	85.637	-1.680	-43.432	-52.052	56.879
298	17.825	84.050	84.050	0.000	-48.206	-55.652	40.794
300	17.845	84.160	84.050	0.033	-48.232	-55.698	40.575
400	18.629	89.414	84.761	1.861	-59.270	-55.921	30.553
500	19.042	93.620	86.126	3.747	-59.253	-55.086	24.078
600	19.282	97.115	87.675	5.664	-59.236	-54.254	19.762
700	19.432	100.099	89.242	7.600	-59.224	-53.425	16.680
800	19.532	102.701	90.765	9.549	-59.220	-52.598	14.369
900	19.602	105.006	92.222	11.506	-59.222	-51.769	12.571
1000	19.652	107.074	93.605	13.469	-59.233	-50.940	11.133
1100	19.690	108.949	94.916	15.436	-59.254	-50.111	9.956
1200	19.718	110.663	96.158	17.406	-59.283	-49.278	8.975
1300	19.741	112.242	97.335	19.379	-59.322	-48.442	8.144
1400	19.759	113.706	98.453	21.354	-59.371	-47.604	7.431
1500	19.773	115.070	99.516	23.331	-59.432	-46.761	6.813
1600	19.785	116.346	100.528	25.309	-59.502	-45.914	6.271
1700	19.795	117.546	101.494	27.288	-71.576	-44.956	5.779
1800	19.803	118.678	102.418	29.268	-71.613	-43.390	5.268
1900	19.810	119.749	103.302	31.248	-71.650	-41.819	4.810
2000	19.816	120.765	104.150	33.230	-71.690	-40.249	4.398
2100	19.821	121.732	104.964	35.211	-71.729	-38.677	4.025
2200	19.826	122.654	105.748	37.194	-71.771	-37.103	3.686
2300	19.830	123.535	106.502	39.177	-71.813	-35.525	3.376
2400	19.833	124.379	107.229	41.160	-71.857	-33.944	3.091
2500	19.836	125.189	107.932	43.143	-71.902	-32.365	2.829
2600	19.839	125.967	108.611	45.127	-71.949	-30.782	2.587
2700	19.841	126.716	109.267	47.111	-71.996	-29.201	2.364
2800	19.843	127.438	109.903	49.095	-72.046	-27.612	2.155
2900	19.845	128.134	110.520	51.080	-72.096	-26.024	1.961
3000	19.847	128.807	111.119	53.064	-72.148	-24.436	1.780
3100	19.849	129.457	111.700	55.049	-72.202	-22.844	1.610
3200	19.850	130.088	112.265	57.034	-72.256	-21.248	1.451
3300	19.851	130.699	112.814	59.019	-72.313	-19.656	1.302
3400	19.853	131.291	113.349	61.004	-72.370	-18.060	1.161
3500	19.854	131.867	113.870	62.990	-72.429	-16.461	1.028
3600	19.855	132.426	114.377	64.975	-164.452	-12.605	0.765
3700	19.856	132.970	114.872	66.960	-164.414	-8.388	0.495
3800	19.856	133.499	115.356	68.946	-164.378	-4.170	0.240
3900	19.857	134.015	115.828	70.932	-164.346	0.046	-0.003
4000	19.858	134.518	116.289	72.918	-164.314	4.258	-0.233
4100	19.859	135.008	116.739	74.903	-164.286	8.468	-0.451
4200	19.859	135.487	117.180	76.889	-164.257	12.683	-0.660
4300	19.860	135.954	117.611	78.875	-164.230	16.898	-0.859
4400	19.860	136.411	118.033	80.861	-164.206	21.110	-1.049
4500	19.861	136.857	118.447	82.847	-164.182	25.324	-1.230
4600	19.861	137.294	118.852	84.833	-164.159	29.535	-1.403
4700	19.862	137.721	119.249	86.820	-164.139	33.749	-1.569
4800	19.862	138.139	119.638	88.806	-164.121	37.952	-1.728
4900	19.863	138.549	120.020	90.792	-164.103	42.166	-1.881
5000	19.863	138.950	120.394	92.778	-164.086	46.373	-2.027
5100	19.863	139.343	120.762	94.765	-164.072	50.581	-2.168
5200	19.864	139.729	121.123	96.751	-164.058	54.790	-2.303
5300	19.864	140.107	121.478	98.737	-164.045	59.002	-2.433
5400	19.864	140.479	121.826	100.724	-164.035	63.205	-2.558
5500	19.865	140.843	122.168	102.710	-164.026	67.417	-2.679
5600	19.865	141.201	122.505	104.697	-164.019	71.623	-2.795
5700	19.865	141.553	122.836	106.683	-164.014	75.836	-2.908
5800	19.865	141.898	123.162	108.670	-164.010	80.045	-3.016
5900	19.865	142.238	123.482	110.656	-164.009	84.247	-3.121
6000	19.866	142.572	123.798	112.643	-164.010	88.449	-3.222

Dec. 31, 1977

SILICON TRIBROMIDE ($SiBr_3$) (IDEAL GAS) GFW = 267.7975

ΔHa_0° = [234 ± 15] kcal/mol
$S_{298.15}^\circ$ = [84.05 ± 2.0] gibbs/mol
Ground State Quantum Weight = [2]

ΔHf_0° = [-42.8 ± 15] kcal/mol
$\Delta Hf_{298.15}^\circ$ = [-48.2 ± 15] kcal/mol

BR3SI

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[362](1)
[168](1)
[483.5](2)
[116.8](2)

Point Group: [C_{3v}] σ = [3]
Bond Distance: Si-Br = [2.17] Å
Bond Angle: Br-Si-Br = [111.36°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [12.9052×10^{-112}] g^3 cm^6

Heat of Formation

The heat of formation of $SiBr_3$(g) is based on an assumed average bond energy of 78±5 kcal/mol (1). This average bond energy is that of $SiBr_4$(g), i.e. $\Delta Ha_0^\circ(SiBr_4,g)/4$. The rationale for this assumption is based on the same relationship existing for the silicon chloride and fluoride species (1).

Heat Capacity and Entropy

The molecular structure is assumed to be identical to the $SiBr_3$ group in $SiHBr_3$ (1). From this structure we estimate the following principal moments of inertia: $I_A = I_B = 87.01 \times 10^{-39}$, and $I_C = 170.46 \times 10^{-39}$g cm^2. The vibrational frequencies are assumed to be those of the $SiBr_3$ group in $SiHBr_3$(g).

References

1. JANAF Thermochemical Tables: $SiCl_3$(g) and SiF_3(g), 12-31-77; $SiBr_4$(g) and $SiHBr_3$(g), 12-31-76.

SILICON TETRABROMIDE ($SiBr_4$)
(LIQUID) GFW=347.702

BR_4SI

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	35.000	66.500	66.500	0.000	-109.300	-106.090	77.766
300	35.000	66.717	66.501	0.065	-109.310	-106.069	77.271
400	35.000	76.785	67.873	3.565	-122.797	-102.156	55.815
500	35.000	84.595	70.466	7.065	-121.607	-97.134	42.457
600	35.000	90.977	73.369	10.565	-120.451	-92.349	33.638
700	35.000	96.372	76.279	14.065	-119.322	-87.756	27.399
800	35.000	101.046	79.090	17.565	-118.214	-83.323	22.763

Dec. 31, 1976

SILICON TETRABROMIDE ($SiBr_4$) (LIQUID) GFW = 347.702

$S°_{298.15}$ = [66.5 ± 0.3] gibbs/mol
T_m = 278.4 ± 1.0 K
T_b = 425.60 K [f = 1]

$ΔHf°_{298.15}$ = -109.3 ± 2.0 kcal/mol
ΔHm° = unknown
ΔHv° = 8.583 kcal/mol

BR_4SI

Heat of Formation

Schäfer and Heine (1) measured the heat of solution of Si(c) in an HF solution containing AgF. For the overall reaction $SiBr_4(ℓ)$ + 4Ag(c) = Si(c) + 4AgBr(c), they reported $ΔHr°_{298}$ = +13.3±1.1 kcal/mol. Using auxiliary data for AgBr(2), we calculate $ΔHf°_{298}$ = -109.3 kcal/mol for $SiBr_4(ℓ)$. We adopt this value and assign an uncertainty of ±2.0 kcal/mol

Wolf et al. (3) studied the heats of solution of $SiBr_4(ℓ)$ and $Na_2SiO_3(c)$ in caustic solution. The net reaction of interest, $SiBr_4(ℓ)$ + 6NaOH(c) = $Na_2SiO_3(c)$ + 4NaBr(c) + $3H_2O(ℓ)$, yielded $ΔHr°_{298}$ = -199.32 kcal/mol based on the appropriate combination of results from five solution studies. Using current auxiliary data (4, 5), we update this value to $ΔHr°_{298}$ = -198.06 kcal/mol and calculate $ΔHf°_{298}$ = -114.8 kcal/mol for $SiBr_4(ℓ)$. This data is suspect due to uncertainties in the conversion of data from Na_2SiO_3 (calorimetric solution) to $Na_2SiO_3(c)$. The final state of the calorimetric solution is not well defined or well known and thus large uncertainties result.

Heat Capacity and Entropy

The heat capacity from 25°-100°C was determined calorimetrically within 2% by Sladkov (6). The constant value of 35.0 gibbs/mol is extrapolated to 800 K. The entropy at 298.15 K is chosen so as to bring the 2nd and 3rd law analysis of the vapor pressure data into agreement.

Melting Data

Pohland (7) reported the melting point of $SiBr_4$ to be 5.2°C (±1°C). No data is available on the heat of melting.

Vaporization Data

T_b is calculated as that temperature for which ΔGr° = 0 for the process $SiBr_4(ℓ)$ = $SiBr_4(g)$. ΔHv° is calculated as the difference between the ΔHf° values for the ideal gas and the liquid at T_b. Normal boiling points reported in the literature are 426.0 K (7) and 426.6 K (8), and 427.8 K (766 mm Hg, 9). The normal boiling point (p = 760 mm) should be slightly lower than our calculated T_b which corresponds to f = 760 mm. Refer to the $SiBr_4(g)$ table for a possible explanation of this discrepancy.

References

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BR_4SI

SILICON TETRABROMIDE ($SiBr_4$) BR4SI
(IDEAL GAS) GFW=347.702

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-5.333	-92.146	-92.146	INFINITE
100	16.895	68.586	109.729	-4.114	-92.327	-96.520	210.945
200	21.147	81.770	92.709	-2.188	-93.024	-100.461	109.779
298	23.185	90.643	90.643	0.000	-99.300	-103.288	75.712
300	23.211	90.786	90.643	0.043	-99.332	-103.312	75.263
400	24.215	97.617	91.568	2.420	-113.942	-101.634	55.530
500	24.749	103.084	93.343	4.871	-113.801	-98.573	43.086
600	25.061	107.626	95.355	7.362	-113.654	-95.541	34.801
700	25.257	111.505	97.392	9.879	-113.508	-92.535	28.891
800	25.387	114.887	99.372	12.412	-113.367	-89.550	24.464
900	25.478	117.883	101.266	14.955	-113.232	-86.579	21.024
1000	25.544	120.571	103.064	17.506	-113.105	-83.623	18.276
1100	25.594	123.008	104.768	20.063	-112.987	-80.682	16.030
1200	25.631	125.236	106.382	22.625	-112.876	-77.750	14.160
1300	25.661	127.289	107.912	25.189	-112.777	-74.826	12.579
1400	25.684	129.192	109.365	27.757	-112.686	-71.911	11.226
1500	25.703	130.964	110.747	30.326	-112.608	-69.002	10.054
1600	25.719	132.624	112.063	32.897	-112.540	-66.096	9.028
1700	25.732	134.183	113.319	35.470	-124.475	-63.089	8.111
1800	25.743	135.654	114.519	38.044	-124.373	-59.482	7.222
1900	25.752	137.046	115.668	40.618	-124.273	-55.877	6.427
2000	25.760	138.368	116.771	43.194	-124.175	-52.282	5.713
2100	25.767	139.625	117.829	45.770	-124.077	-48.690	5.067
2200	25.772	140.823	118.847	48.347	-123.982	-45.104	4.481
2300	25.778	141.969	119.828	50.925	-123.888	-41.519	3.945
2400	25.782	143.066	120.773	53.503	-123.796	-37.937	3.455
2500	25.786	144.119	121.686	56.081	-124.706	-34.363	3.004
2600	25.790	145.130	122.569	58.660	-123.617	-30.790	2.588
2700	25.793	146.104	123.422	61.239	-123.530	-27.225	2.204
2800	25.796	147.042	124.249	63.818	-123.447	-23.656	1.846
2900	25.798	147.947	125.051	66.398	-123.363	-20.094	1.514
3000	25.800	148.822	125.829	68.978	-123.281	-16.537	1.205
3100	25.803	149.668	126.584	71.558	-123.203	-12.978	0.915
3200	25.804	150.487	127.319	74.139	-123.124	-9.421	0.643
3300	25.806	151.281	128.033	76.719	-123.050	-5.873	0.389
3400	25.808	152.051	128.728	79.300	-122.975	-2.324	0.149
3500	25.809	152.799	129.405	81.881	-122.904	1.225	-0.077
3600	25.810	153.527	130.065	84.462	-214.796	7.027	-0.427
3700	25.812	154.234	130.709	87.043	-214.628	13.186	-0.779
3800	25.813	154.922	131.337	89.624	-214.464	19.342	-1.112
3900	25.814	155.593	131.950	92.205	-214.303	25.494	-1.429
4000	25.815	156.246	132.549	94.787	-214.143	31.636	-1.729
4100	25.816	156.884	133.135	97.368	-213.987	37.775	-2.014
4200	25.816	157.506	133.708	99.950	-213.831	43.916	-2.285
4300	25.817	158.113	134.269	102.532	-213.677	50.054	-2.544
4400	25.818	158.707	134.817	105.113	-213.527	56.186	-2.791
4500	25.819	159.287	135.355	107.695	-213.377	62.316	-3.026
4600	25.819	159.854	135.881	110.277	-213.229	68.441	-3.252
4700	25.820	160.410	136.397	112.859	-213.084	74.567	-3.467
4800	25.820	160.953	136.903	115.441	-212.942	80.677	-3.673
4900	25.821	161.486	137.399	118.023	-212.800	86.797	-3.871
5000	25.821	162.007	137.886	120.605	-212.660	92.908	-4.061
5100	25.822	162.519	138.364	123.187	-212.524	99.017	-4.243
5200	25.822	163.020	138.834	125.769	-212.388	105.124	-4.418
5300	25.823	163.512	139.295	128.352	-212.252	111.233	-4.587
5400	25.823	163.995	139.748	130.934	-212.122	117.329	-4.749
5500	25.823	164.469	140.193	133.516	-211.992	123.434	-4.905
5600	25.824	164.934	140.630	136.099	-211.865	129.529	-5.055
5700	25.824	165.391	141.061	138.681	-211.741	135.629	-5.200
5800	25.824	165.840	141.484	141.263	-211.618	141.724	-5.340
5900	25.825	166.281	141.901	143.846	-211.498	147.809	-5.475
6000	25.825	166.716	142.311	146.428	-211.381	153.891	-5.605

Dec. 31, 1976

SILICON TETRABROMIDE (*$SiBr_4$*) (IDEAL GAS) GFW = 347.702

ΔHa°_0 = 311.54 ± 4.0 kcal/mol
$S^\circ_{298.15}$ = 90.64 ± 0.2 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -92.1 ± 4.0 kcal/mol BR4SI
$\Delta Hf^\circ_{298.15}$ = -99.3 ± 4.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
246.7(1)	494 (3)
84.8(2)	133.6(3)

Point Group: Td σ = 12
Bond Distance: *Si-Br = 2.15 ± 0.02 Å*
Bond Angle: Br-Si-Br = 109.47122°
Product of the Moments of Inertia: $I_A I_B I_C = 4.3742 \times 10^{-111}$ g^3 cm^6

Heat of Formation

Pohland (1) has studied the vaporization of $SiBr_4$ from 260-426 K (0.8-755.5 mm Hg). This vapor pressure data (20 points) is corrected for vapor non-ideality by means of the equation ΔG°/T = -R ln p - Bp/T. The Berthelot equation of state and *critical constants* T_c = 656 *K and Pc* = 41.3 *atm as suggested in the review article* by Lapidus et al. (2) are used to calculate B. The recent study on orthobaric densities by Nisel'son et al. (3) reported Tc = 663K. The use of this latter value does not signficantly affect the results.

A second and third law analysis of this corrected data (1) yields ΔHv°_{298} = 10.0 kcal/mol. The entropy of the liquid at 298.15 K is adjusted so as to bring the second and third law results into agreement. This treatment suggests that the five lowest pressure data points (260-345K, 0.8-60.3 mm Hg) are biased. These five points are not included *in the above analysis*. Any vapor pressure equation used to represent this data will be significantly altered in neglecting these five data points.

We adopt ΔHv°_{298} = 10.0 kcal/mol which leads to ΔHf°_{298} = -99.3 kcal/mol (4). Using auxiliary data (4), we calculate ΔHa°_0 ($SiBr_4$,g) = 311.54 kcal/mol. This value is 4.03 times the dissociation energy of SiBr(g) (4).

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark and Rippon (5), who recorded the Raman spectra in the vapor phase (*210°C*). *The spectral data were interpreted in terms of a tetrahedral structure. This structure* is consistent with the electron diffraction data of Lister and Sutton (6), Yamasaki et al. (7), and Spitzer et al. (8), which suggested a tetrahedral structure with a Si-Br bond distance of 2.15±0.02 Å. We adopt this bond distance. The individual moments of inertia are $I_A = I_B + I_C = 16.354 \times 10^{-38}$ g cm^2.

Shimanouchi, in a recent compilation of molecular vibrational frequencies (9), suggested somewhat different values (249, 90, 487, 137 cm^{-1}) based on earlier infrared and Raman studies by Trumpy (10), Delwaulle (11), *Radhakrishnan* (12), *and* Long et al. (13). These frequencies would lead to a S°_{298} value of 90.3 gibbs/mol. Much literature has been published on the inter-relationships between force constants and vibrational frequencies. Since the majority of this work was published prior to the Clark and Rippon study (5), it will not be further discussed or referenced. The same situation exists for temperature dependent thermochemical tabulations of $SiBr_4$(g).

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BR4SI

CARBON(C) C

(REFERENCE STATE - GRAPHITE) GFW=12.011

T, K	gibbs/mol Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	kcal/mol $H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-0.251	0.000	0.000	0.000
100	.400	0.228	2.597	-0.237	0.000	0.000	0.000
200	1.196	0.737	1.531	-0.159	0.000	0.000	0.000
298	2.036	1.372	1.372	0.000	0.000	0.000	0.000
300	2.051	1.385	1.372	0.004	0.000	0.000	0.000
400	2.824	2.083	1.462	0.248	0.000	0.000	0.000
500	3.495	2.787	1.657	0.565	0.000	0.000	0.000
600	4.026	3.474	1.903	0.942	0.000	0.000	0.000
700	4.430	4.126	2.174	1.366	0.000	0.000	0.000
800	4.739	4.739	2.457	1.825	0.000	0.000	0.000
900	4.977	5.311	2.743	2.312	0.000	0.000	0.000
1000	5.165	5.845	3.026	2.819	0.000	0.000	0.000
1100	5.316	6.345	3.306	3.343	0.000	0.000	0.000
1200	5.441	6.813	3.579	3.881	0.000	0.000	0.000
1300	5.546	7.253	3.845	4.431	0.000	0.000	0.000
1400	5.635	7.667	4.103	4.990	0.000	0.000	0.000
1500	5.713	8.059	4.354	5.558	0.000	0.000	0.000
1600	5.782	8.430	4.597	6.132	0.000	0.000	0.000
1700	5.843	8.782	4.833	6.714	0.000	0.000	0.000
1800	5.899	9.118	5.062	7.301	0.000	0.000	0.000
1900	5.950	9.438	5.284	7.893	0.000	0.000	0.000
2000	5.997	9.745	5.499	8.491	0.000	0.000	0.000
2100	6.042	10.038	5.708	9.093	0.000	0.000	0.000
2200	6.083	10.320	5.912	9.699	0.000	0.000	0.000
2300	6.123	10.592	6.109	10.309	0.000	0.000	0.000
2400	6.160	10.853	6.301	10.924	0.000	0.000	0.000
2500	6.196	11.105	6.489	11.541	0.000	0.000	0.000
2600	6.231	11.349	6.671	12.163	0.000	0.000	0.000
2700	6.265	11.585	6.848	12.788	0.000	0.000	0.000
2800	6.297	11.813	7.022	13.416	0.000	0.000	0.000
2900	6.329	12.035	7.191	14.047	0.000	0.000	0.000
3000	6.360	12.250	7.356	14.682	0.000	0.000	0.000
3100	6.391	12.459	7.517	15.319	0.000	0.000	0.000
3200	6.420	12.662	7.675	15.960	0.000	0.000	0.000
3300	6.450	12.860	7.829	16.603	0.000	0.000	0.000
3400	6.478	13.053	7.980	17.250	0.000	0.000	0.000
3500	6.507	13.241	8.127	17.899	0.000	0.000	0.000
3600	6.535	13.425	8.272	18.551	0.000	0.000	0.000
3700	6.563	13.604	8.414	19.206	0.000	0.000	0.000
3800	6.590	13.780	8.553	19.863	0.000	0.000	0.000
3900	6.617	13.951	8.689	20.524	0.000	0.000	0.000
4000	6.644	14.119	8.822	21.187	0.000	0.000	0.000
4100	6.671	14.284	8.954	21.853	0.000	0.000	0.000
4200	6.698	14.445	9.083	22.521	0.000	0.000	0.000
4300	6.724	14.603	9.209	23.192	0.000	0.000	0.000
4400	6.751	14.758	9.333	23.866	0.000	0.000	0.000
4500	6.777	14.910	9.456	24.542	0.000	0.000	0.000
4600	6.803	15.059	9.576	25.221	0.000	0.000	0.000
4700	6.828	15.205	9.694	25.903	0.000	0.000	0.000
4800	6.854	15.349	9.810	26.587	0.000	0.000	0.000
4900	6.880	15.491	9.925	27.274	0.000	0.000	0.000
5000	6.905	15.630	10.038	27.963	0.000	0.000	0.000
5100	6.931	15.767	10.149	28.655	0.000	0.000	0.000
5200	6.956	15.902	10.258	29.349	0.000	0.000	0.000
5300	6.982	16.035	10.366	30.046	0.000	0.000	0.000
5400	7.007	16.166	10.472	30.746	0.000	0.000	0.000
5500	7.032	16.294	10.577	31.448	0.000	0.000	0.000
5600	7.057	16.421	10.680	32.152	0.000	0.000	0.000
5700	7.082	16.546	10.782	32.859	0.000	0.000	0.000
5800	7.107	16.670	10.882	33.568	0.000	0.000	0.000
5900	7.132	16.792	10.981	34.280	0.000	0.000	0.000
6000	7.157	16.912	11.079	34.995	0.000	0.000	0.000

Mar. 31, 1961; Mar. 31, 1978

CARBON (C) (REFERENCE STATE - GRAPHITE, Spectroscopic-Grade Acheson) GFW = 12.011

C

$S^\circ_{298.15}$ = 1.372 ± 0.05 cal/(mol K)

ΔHf°_0 = 0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Heat of Formation

ΔHf° is zero by definition for the adopted standard reference state of Acheson spectroscopic graphite, i.e. artificial graphite of spectroscopic grade which is graphitized near 2600°C in an Acheson-type electric furnace. This standard state was adopted by CODATA (1) in order to be more consistent with the samples used in determining ΔHf°_{298} of $CO_2(g)$. CODATA (1) cites references which show the effects of various graphite samples on $\Delta Hf^\circ(CO_2)$. Their assigned uncertainty (1) of ±0.031 kcal/mol for $\Delta Hf^\circ(CO_2)$ is a rough measure of the deviations of various high purity graphites from our standard state. Larger deviations occur in carbon samples which are impure or less completely graphitized or which have much disorder or high surface area. Gross deviations (up to several kcal/mol) have been found for other carbons; e.g., many "glassy" carbons appear to be more stable than graphite at elevated temperatures due to large ΔSf values (2) which compensate for positive values of ΔHf.

Heat Capacity and Entropy

S°_{298} and $(H^\circ_0-H^\circ_{298})$ are the values selected by CODATA (1) based on Cp° (13-301 K) of CS-grade Acheson graphite measured by DeSorbo and Tyler (3). DeSorbo's later study (3) gave minor corrections to Cp° and more information on his sample. Due to differences in Cp° of various graphites, we increase the uncertainty of S°_{298} from ±0.029 (1) to ±0.05 cal/(mol K). The entropy extrapolation below 13 K was given (3) as 0.0041 cal/(mol K). Properties tabulated at 100 and 200 K are from our smoothing of the data (3). Cp° above 298 K is based on enthalpy data of McDonald (4) and West and Ishihara (5) and on Cp° data of Cezairliyan et al. (6, 7). Deviations of the enthalpy data from our table are -0.3 to +0.6% (4, omitting 341 and 1037 K) and 0.0 to -0.6% (5). Deviations of the Cp° equations (6, 7) from our table are much less than the estimated uncertainties of 3% (6) and 3 to 5% (7). The selected studies (4-7) show reasonable agreement in their regions of overlap even though they involve different grades of graphite. Together, they yield mutually consistent data extending up to 3800 K.

Discrepancies in other Cp data are of concern since no single type of graphite has been accurately measured over the whole temperature range. At all temperatures the many studies show unusually large differences, some of which are due to deviations of the graphite samples from our chosen standard state. For example, the Cp of natural (Ceylon) graphite (3) was found to be ~9% lower from 200 to 300 K, yielding values of S_{298} and $(H_{298}-H_0)$ which are lower by 0.08 cal/(mol K) and 21 cal/mol, respectively. Lutkov et al. (8) reported similar differences in Cp among two graphites and one pyrolytic carbon. Discrepancies are even larger below 30 K (9, 10) and above 3000 K (6, 10-15).

If there were a large bias in our Cp° at 300-1500 K or above 3000 K, it could affect the interpretation of data on vaporization and melting. New studies of various graphites by laser flash (16) and differential scanning calorimetry (17) tend to confirm our Cp° at 350-950 K, where the largest deviations (~3%) are roughly equal to the experimental error. More controversial are Cp (12) and enthalpy (13) studies which gave Cp curves that rise very rapidly near 3500 K. Recent pulse-heating data (7), however, gave a slowly rising Cp° which is linear up to 3800 K. Four Cp° studies (6, 7, 12, 14) and an enthalpy study (15) agree satisfactorily below 3500 K, so the discrepancy must be due to temperature-dependent differences in experimental methods or graphite samples. This is a region where some graphites degrade rapidly with emission of particles, leading to possible bias in Cp data. Moreover, Whittaker has proposed (18) that graphite is metastable in this region and slowly transforms to carbynes. If this is the case, then very rapid measurements (7) should yield Cp° data which are different and more appropriate to graphite. The rapidly rising enthalpy data (13) could be explained by Whittaker's proposal or by differences in the various graphite samples (13).

Sublimation Data

See the tables for C(g), $C_2(g)$, $C_3(g)$, $C_4(g)$, etc. The most abundant species is C_3. Recent analyses gave sublimation temperature values (corresponding to 1 atm total pressure of all carbon species) of 3895-4020 K (19) from carbon arc data, ≤4070 K (20) from mass-loss data at 0.1-11 atm, and ~3915 K (21) from extrapolation of mass-spectrometric data at low pressure. Earlier values for this controversial point (see below) were summarized by Palmer (22).

Melting Data and Phase Data

Controversy surrounds the solid-liquid-vapor triple point which recent studies place either at ~4000 K and ~1 atm (18, carbyne form) or at 4130±30 K and 120±10 atm (23, pyrolytic graphite). We doubt the latter triple point because the temperature is displaced by 400 to 800 kelvins from the sublimation curves (19-22 and ref. cited therein). The nature of the observed phenomenon (22-24) has been questioned (18) as well as the measurement of temperature (18, 19, 24). Also controversial is Whittaker's proposal (18) that several carbyne forms are more stable than graphite above 2600 K. Evidence includes X-ray data which were interpreted (18) to indicate slow forward transitions, graphite → carbynes, but rapid reverse transitions. These transitions might explain discrepancies observed in various Cp curves but alternative explanations are possible. We retain graphite as the reference state at all temperatures; this arbitrary choice avoids the need to switch phases at the proposed transition point, sublimation point or melting point, all of which are subject to change.

References

C

See C(g).

CARBON, MONATOMIC (C) C
(IDEAL GAS) GFW=12.011

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.562	169.979	169.979	INFINITE
100	5.084	32.283	42.202	-0.992	170.535	167.330	-365.693
200	4.996	35.769	38.216	-0.489	170.960	163.953	-179.157
298	4.981	37.760	37.761	0.000	171.290	160.441	-117.605
300	4.980	37.791	37.761	0.009	171.295	160.373	-116.830
400	4.975	39.223	37.956	0.507	171.549	156.693	-85.612
500	4.972	40.333	38.324	1.004	171.729	152.956	-66.856
600	4.971	41.240	38.737	1.501	171.849	149.190	-54.342
700	4.970	42.006	39.151	1.999	171.923	145.407	-45.397
800	4.970	42.669	39.550	2.495	171.960	141.616	-38.687
900	4.969	43.255	39.930	2.992	171.970	137.821	-33.467
1000	4.969	43.778	40.289	3.489	171.960	134.028	-29.291
1100	4.969	44.252	40.628	3.986	171.933	130.236	-25.875
1200	4.970	44.684	40.948	4.483	171.892	126.447	-23.029
1300	4.970	45.082	41.251	4.980	171.839	122.661	-20.621
1400	4.972	45.451	41.538	5.477	171.777	118.881	-18.558
1500	4.975	45.794	41.810	5.975	171.707	115.104	-16.770
1600	4.978	46.115	42.070	6.472	171.630	111.334	-15.207
1700	4.983	46.417	42.316	6.970	171.546	107.568	-13.829
1800	4.990	46.702	42.552	7.469	171.458	103.807	-12.604
1900	4.998	46.972	42.778	7.968	171.365	100.052	-11.508
2000	5.008	47.228	42.994	8.469	171.268	96.300	-10.523
2100	5.019	47.473	43.201	8.970	171.167	92.554	-9.632
2200	5.031	47.707	43.401	9.472	171.063	88.813	-8.823
2300	5.045	47.931	43.593	9.976	170.957	85.077	-8.084
2400	5.061	48.146	43.778	10.482	170.848	81.345	-7.407
2500	5.077	48.353	43.957	10.988	170.737	77.619	-6.785
2600	5.094	48.552	44.130	11.497	170.624	73.896	-6.211
2700	5.112	48.745	44.297	12.007	170.509	70.177	-5.680
2800	5.130	48.931	44.460	12.519	170.393	66.463	-5.188
2900	5.149	49.111	44.617	13.033	170.276	62.754	-4.729
3000	5.168	49.286	44.770	13.549	170.157	59.048	-4.302
3100	5.187	49.456	44.918	14.067	170.038	55.347	-3.902
3200	5.206	49.621	45.063	14.586	169.916	51.649	-3.527
3300	5.224	49.781	45.203	15.108	169.795	47.955	-3.176
3400	5.243	49.938	45.340	15.631	169.671	44.264	-2.845
3500	5.261	50.090	45.474	16.156	169.547	40.578	-2.534
3600	5.279	50.238	45.604	16.683	169.422	36.895	-2.240
3700	5.296	50.383	45.731	17.212	169.296	33.215	-1.962
3800	5.313	50.525	45.855	17.743	169.170	29.540	-1.699
3900	5.329	50.663	45.977	18.275	169.041	25.866	-1.449
4000	5.345	50.798	46.096	18.809	168.912	22.197	-1.213
4100	5.360	50.930	46.212	19.344	168.781	18.530	-0.988
4200	5.374	51.059	46.326	19.881	168.650	14.868	-0.774
4300	5.388	51.186	46.437	20.419	168.517	11.208	-0.570
4400	5.401	51.310	46.547	20.958	168.382	7.551	-0.375
4500	5.414	51.432	46.654	21.499	168.247	3.898	-0.189
4600	5.426	51.551	46.759	22.041	168.110	0.247	-0.012
4700	5.437	51.668	46.862	22.584	167.971	-3.401	0.158
4800	5.448	51.782	46.964	23.128	167.831	-7.046	0.321
4900	5.458	51.895	47.063	23.674	167.690	-10.688	0.477
5000	5.468	52.005	47.161	24.220	167.547	-14.326	0.626
5100	5.477	52.113	47.257	24.767	167.402	-17.963	0.770
5200	5.486	52.220	47.351	25.315	167.256	-21.596	0.908
5300	5.494	52.324	47.444	25.864	167.108	-25.226	1.040
5400	5.502	52.427	47.536	26.414	166.958	-28.854	1.168
5500	5.509	52.528	47.625	26.965	166.807	-32.479	1.291
5600	5.516	52.627	47.714	27.516	166.654	-36.101	1.409
5700	5.523	52.725	47.801	28.068	166.499	-39.720	1.523
5800	5.529	52.821	47.887	28.621	166.343	-43.335	1.633
5900	5.535	52.916	47.971	29.174	166.184	-46.949	1.739
6000	5.540	53.009	48.054	29.728	166.023	-50.561	1.842

Mar. 31, 1961; Mar. 31, 1978

CARBON, MONATOMIC (C) (IDEAL GAS) GFW = 12.011

Ground State Configuration $^3P_0$
$S^\circ_{298.15}$ = 37.760 ± 0.005 cal/(mol K)

ΔHf°_0 = 169.979 ± 0.11 kcal/mol C
$\Delta Hf^\circ_{298.15}$ = 171.29 ± 0.11 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.00	1	60333.43	1
16.40	3	60352.63	3
43.40	5	60393.14	5
10192.63	5	61981.82	3
21648.01	1	64086.92	7
33735.20	5	64090.95	5
		64089.85	3

Heat of Formation

ΔHf°_{298} = 171.29±0.11 kcal/mol is the value selected by CODATA (1) based on D°_0(CO) = 89595±30 cm^{-1} (256.165±0.086 kcal/mol) from Douglas and Møller (2). The conversion factor used by CODATA (1) corresponds to the negligibly different value of 256.163 kcal/mol; this yields the adopted ΔHf° when combined with ΔHf°_0(CO) = -27.201±0.041 and ΔHf°_0(O) = 58.982±0.024 kcal/mol (1, 3). According to Krupenie (4) it is most likely that the atomic dissociation products are in their ground states as assumed in the adopted D°_0(CO).

The enthalpy of sublimation, ΔHs° = ΔHf°, is confirmed by Knudsen-effusion mass-spectrometric data of Wachi and Gilmartin (5) for graphite. They obtained absolute pressures from calibrations using gold and cobalt; pressures from the latter were higher by 8.74%. Our third-law analyses yield ΔHs°_{298} = 171.22±0.61 and 170.78±0.61 kcal/mol from gold and cobalt, respectively. Second-law values are ΔHs°_{298} = 172.5±3.3 kcal/mol and ΔSs°(2nd law) - ΔSs°(3rd law) = 0.5±1.2 (gold) and 0.7±1.2 (cobalt) cal/(mol K). The data consisted of 14 points in the range 2509-2753 K. None of the other studies of C(g) over pure graphite included calibrations for conversion of ion intensities to absolute pressures.

Heat Capacity and Entropy

The atomic energy levels are from Moore (6). S°_{298} and $(H^\circ_0-H^\circ_{298})$ are the same as the values selected by CODATA (1). Observed and predicted levels above 64091 cm^{-1} are omitted since they do not change the thermodynamic functions at 6000 K. At 14000 K the BETHE-FILL cut-off method would yield a Gibbs-energy function ∿0.1 cal/(mol K) larger than either the present cut-off method or the TEMPER method (7).

References For C(g)

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C

CARBON, MONATOMIC UNIPOSITIVE ION (C^+) C^+

(IDEAL GAS) GFW=12.010451

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.589	429.648		
100							
200							
298	5.013	36.939	36.939	0.000	432.467	420.375	-308.139
300	5.012	36.970	36.939	0.009	432.481	420.300	-306.184
400	4.992	38.409	37.135	0.509	433.234	416.124	-227.357
500	4.983	39.522	37.506	1.008	433.913	411.767	-179.981
600	4.979	40.430	37.920	1.506	434.531	407.280	-148.350
700	4.976	41.197	38.334	2.004	435.101	402.691	-125.724
800	4.974	41.861	38.735	2.501	435.636	398.025	-108.734
900	4.973	42.447	39.115	2.999	436.143	393.292	-95.503
1000	4.972	42.971	39.475	3.496	436.631	388.505	-84.907
1100	4.971	43.445	39.815	3.993	437.101	383.670	-76.227
1200	4.971	43.877	40.136	4.490	437.556	378.792	-68.987
1300	4.970	44.275	40.439	4.987	438.000	373.877	-62.854
1400	4.970	44.644	40.726	5.484	438.435	368.928	-57.591
1500	4.970	44.986	40.999	5.981	438.861	363.948	-53.026
1600	4.969	45.307	41.258	6.478	439.281	358.941	-49.028
1700	4.969	45.608	41.505	6.975	439.692	353.906	-45.497
1800	4.969	45.892	41.741	7.472	440.099	348.848	-42.355
1900	4.969	46.161	41.967	7.969	440.501	343.769	-39.542
2000	4.969	46.416	42.183	8.466	440.896	338.667	-37.007
2100	4.969	46.658	42.390	8.963	441.288	333.546	-34.712
2200	4.969	46.890	42.590	9.460	441.675	328.405	-32.624
2300	4.969	47.110	42.782	9.956	442.059	323.249	-30.715
2400	4.969	47.322	42.966	10.453	442.438	318.074	-28.964
2500	4.969	47.525	43.145	10.950	442.815	312.886	-27.352
2600	4.969	47.720	43.317	11.447	443.187	307.681	-25.863
2700	4.968	47.907	43.483	11.944	443.555	302.461	-24.482
2800	4.968	48.088	43.645	12.441	443.920	297.229	-23.199
2900	4.968	48.262	43.801	12.938	444.283	291.984	-22.004
3000	4.968	48.431	43.952	13.434	444.642	286.726	-20.888
3100	4.968	48.594	44.100	13.931	444.999	281.457	-19.842
3200	4.968	48.751	44.242	14.428	445.351	276.175	-18.862
3300	4.968	48.904	44.381	14.925	445.702	270.883	-17.940
3400	4.968	49.052	44.517	15.422	446.048	265.580	-17.071
3500	4.968	49.197	44.648	15.919	446.393	260.268	-16.252
3600	4.968	49.336	44.777	16.415	446.735	254.945	-15.477
3700	4.968	49.473	44.902	16.912	447.073	249.612	-14.744
3800	4.968	49.605	45.024	17.409	447.410	244.271	-14.049
3900	4.968	49.734	45.143	17.906	447.743	238.921	-13.389
4000	4.968	49.860	45.259	18.403	448.073	233.563	-12.761
4100	4.968	49.983	45.373	18.900	448.401	228.196	-12.164
4200	4.969	50.102	45.484	19.396	448.726	222.821	-11.594
4300	4.969	50.219	45.593	19.893	449.049	217.438	-11.051
4400	4.969	50.333	45.699	20.390	449.369	212.049	-10.532
4500	4.969	50.445	45.804	20.887	449.687	206.652	-10.036
4600	4.969	50.554	45.906	21.384	450.002	201.248	-9.561
4700	4.969	50.661	46.006	21.881	450.313	195.835	-9.106
4800	4.970	50.766	46.104	22.378	450.623	190.418	-8.670
4900	4.970	50.868	46.200	22.875	450.930	184.994	-8.251
5000	4.971	50.969	46.294	23.372	451.235	179.564	-7.849
5100	4.971	51.067	46.387	23.869	451.536	174.127	-7.462
5200	4.972	51.164	46.478	24.366	451.836	168.685	-7.090
5300	4.973	51.258	46.567	24.863	452.133	163.237	-6.731
5400	4.974	51.351	46.655	25.361	452.427	157.783	-6.386
5500	4.975	51.443	46.741	25.858	452.720	152.324	-6.053
5600	4.976	51.532	46.826	26.356	453.009	146.859	-5.731
5700	4.977	51.620	46.909	26.853	453.297	141.390	-5.421
5800	4.979	51.707	46.991	27.351	453.583	135.917	-5.121
5900	4.980	51.792	47.072	27.849	453.866	130.437	-4.832
6000	4.982	51.876	47.151	28.347	454.146	124.952	-4.551

Mar. 31, 1978

CARBON, MONATOMIC UNIPOSITIVE ION (C^+) (IDEAL GAS) GFW = 12.010451

Ground State Configuration $^2P^\circ_{1/2}$ ΔHf°_0 = 429.648 ± 0.11 kcal/mol C^+

$S^\circ_{298.15}$ = 36.939 ± 0.005 cal/(mol K) $\Delta Hf^\circ_{298.15}$ = [432.467] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0.00	2
63.42	4
43003.3	2
43025.3	4
43053.6	6

Heat of Formation

ΔHf°_0 is obtained from $\Delta Hf^\circ_0(C, g)$ = 169.979±0.11 kcal/mol (1, 2) using the spectroscopic value of IP(C, g) = 90820.42±0.1 cm^{-1} (259.6686±0.0003 kcal/mol) from Moore (3). Rosenstock et al. (4) summarize other data for the ionization potential.

$\Delta Hf^\circ_{298}(C^+, g)$ is obtained from $\Delta Hf^\circ(C, g)$ by using IP(C) with JANAF (1) enthalpies ($H^\circ_0-H^\circ_{298}$) for C(g), C^+(g) and e^-(g). $\Delta Hr^\circ_{298}(C \rightarrow C^+ + e^-)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (4). ΔHf°_{298} should be changed by -1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

Electronic energy levels are taken from Moore (3). Observed (3) and predicted (5) levels above 43054 cm^{-1} are omitted since their effect on the Gibbs-energy function is detectable only above 20000 K.

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CARBON, MONATOMIC UNINEGATIVE ION (C^-) C^-
(IDEAL GAS) GFW=12.011549

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	140.856		
100							
200							
298	4.968	36.155	36.155	0.000	140.605	131.721	-96.553
300	4.968	36.186	36.155	0.009	140.601	131.666	-95.918
400	4.968	37.615	36.350	0.506	140.357	128.723	-70.330
500	4.968	38.724	36.718	1.003	140.040	125.850	-55.008
600	4.968	39.630	37.130	1.500	139.663	123.046	-44.819
700	4.968	40.396	37.544	1.996	139.239	120.310	-37.562
800	4.968	41.059	37.942	2.493	138.780	117.637	-32.136
900	4.968	41.644	38.322	2.990	138.293	115.022	-27.931
1000	4.969	42.168	38.681	3.487	137.786	112.464	-24.579
1100	4.970	42.641	39.020	3.984	137.262	109.957	-21.846
1200	4.973	43.074	39.340	4.481	136.725	107.499	-19.578
1300	4.978	43.472	39.642	4.978	136.175	105.085	-17.666
1400	4.987	43.841	39.929	5.477	135.618	102.714	-16.034
1500	5.001	44.186	40.202	5.976	135.052	100.383	-14.626
1600	5.021	44.509	40.461	6.477	134.482	98.091	-13.398
1700	5.047	44.814	40.703	6.980	133.907	95.834	-12.320
1800	5.080	45.104	40.944	7.487	133.330	93.611	-11.366
1900	5.121	45.379	41.170	7.997	132.751	91.421	-10.516
2000	5.168	45.643	41.388	8.511	132.170	89.260	-9.754
2100	5.223	45.897	41.596	9.031	131.591	87.128	-9.067
2200	5.284	46.141	41.797	9.556	131.014	85.026	-8.446
2300	5.350	46.377	41.991	10.088	130.439	82.948	-7.882
2400	5.421	46.606	42.179	10.626	129.865	80.895	-7.366
2500	5.496	46.829	42.360	11.172	129.297	78.867	-6.894
2600	5.574	47.046	42.537	11.725	128.731	76.860	-6.461
2700	5.653	47.258	42.707	12.287	128.172	74.876	-6.061
2800	5.733	47.465	42.874	12.856	127.616	72.912	-5.691
2900	5.814	47.668	43.036	13.433	127.065	70.968	-5.348
3000	5.893	47.866	43.193	14.019	126.519	69.043	-5.030
3100	5.971	48.061	43.347	14.612	125.978	67.136	-4.733
3200	6.047	48.252	43.497	15.213	125.442	65.247	-4.456
3300	6.120	48.439	43.644	15.821	124.910	63.374	-4.197
3400	6.190	48.623	43.788	16.437	124.382	61.517	-3.954
3500	6.256	48.803	43.929	17.059	123.858	59.675	-3.726
3600	6.319	48.980	44.067	17.688	123.338	57.849	-3.512
3700	6.377	49.154	44.202	18.323	122.822	56.037	-3.310
3800	6.430	49.325	44.334	18.963	122.308	54.240	-3.119
3900	6.480	49.492	44.464	19.609	121.796	52.454	-2.939
4000	6.525	49.657	44.592	20.259	121.286	50.683	-2.769
4100	6.565	49.819	44.718	20.914	120.778	48.924	-2.608
4200	6.602	49.977	44.841	21.572	120.272	47.179	-2.455
4300	6.633	50.133	44.962	22.234	119.766	45.444	-2.310
4400	6.661	50.286	45.082	22.898	119.259	43.721	-2.172
4500	6.685	50.436	45.199	23.566	118.754	42.010	-2.040
4600	6.705	50.583	45.314	24.235	118.247	40.310	-1.915
4700	6.721	50.727	45.428	24.907	117.741	38.622	-1.796
4800	6.733	50.869	45.540	25.579	117.232	36.943	-1.682
4900	6.743	51.008	45.650	26.253	116.722	35.275	-1.573
5000	6.749	51.144	45.759	26.928	116.211	33.619	-1.469
5100	6.753	51.278	45.866	27.603	115.698	31.972	-1.370
5200	6.753	51.409	45.971	28.278	115.182	30.336	-1.275
5300	6.752	51.538	46.075	28.954	114.664	28.709	-1.184
5400	6.748	51.664	46.177	29.629	114.142	27.091	-1.096
5500	6.742	51.788	46.278	30.303	113.617	25.484	-1.013
5600	6.733	51.909	46.377	30.977	113.091	23.887	-0.932
5700	6.724	52.028	46.475	31.650	112.560	22.299	-0.855
5800	6.712	52.145	46.572	32.321	112.025	20.721	-0.781
5900	6.699	52.260	46.668	32.992	111.487	19.151	-0.709
6000	6.685	52.372	46.762	33.661	110.944	17.589	-0.641

Sept. 30, 1965; Mar. 31, 1978

CARBON, MONATOMIC UNINEGATIVE ION (C^-) (IDEAL GAS) GFW = 12.011549

Ground State Configuration ${}^4S_{3/2}$
$S^\circ_{298.15}$ = 36.155 ± 0.005 cal/(mol K)

ΔHf°_0 = 140.856 ± 0.12 kcal/mol C^-
$\Delta Hf^\circ_{298.15}$ = [140.605] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	4
9920	10

Heat of Formation

ΔHf°_0 is calculated from $\Delta Hf^\circ_0(C, g)$ = 169.979±0.11 kcal/mol (1) using the electron affinity EA(C) = 1.2629±0.0003 eV (10185.9±2.4 cm^{-1} or 29.123±0.007 kcal/mol). Feldmann (2) determined this EA from the photodetachment threshold observed during interaction of a tunable laser with a beam of C^- ions. Hotop and Lineberger (3) reviewed earlier data and selected EA = 1.268±0.005 eV. This value was calculated using EA(C) − EA(O) = −0.194 eV from unpublished data of Bennett and Hall measured by laser-photodetachment electron spectroscopy.

$\Delta Hf^\circ_{298}(C^-)$ is obtained from $\Delta Hf^\circ(C)$ by using EA(C) with JANAF (1) enthalpies ($H^\circ_0-H^\circ_{298}$) for $C^-(g)$, C(g) and $e^-(g)$. $\Delta Hr^\circ_{298}(C^- \rightarrow C + e^-)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (4). ΔHf°_{298} should be changed by +1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

Electronic energy levels are from the laser photodetachment study of Feldmann (2). He found that the $C^-({}^2D)$ state has a binding energy of 0.033±0.001 eV (266±8 cm^{-1}) relative to ground state $C({}^3P_0)$. The electronic energy of 9920 cm^{-1} is the difference in binding energy between ground and excited states. Spin-orbit splitting of the ${}^2D$ state was not resolved (2) but has been estimated (3) to be 3 cm^{-1}. We neglect this splitting because its effect is negligible. $C^-({}^2D)$ binding energies obtained by other methods (3, 5) are in satisfactory agreement.

Note that we include the excited state even though its binding energy is only 266 cm^{-1}. If this state were omitted, the Gibbs-energy function would change by −0.001 (1700 K), −0.042 (3000 K) and −0.414 (6000 K).

References

1. JANAF Thermochemical Tables: C(g), 3-31-78; e^-(g), 3-31-77.
2. D. Feldmann, Chem. Phys. Lett. 47, 338 (1977).
3. H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
4. H. M. Rosenstock et al., J. Phys. Chem. Ref. Data 6, Suppl. 1, I-28 (1977).
5. V. A. Oparin et al., Sov. Phys.-JETP 39, 989 (1974).

C^-

TRIFLUOROMETHYLSULFUR PENTAFLUORIDE (CSF_8) CF_8S
(IDEAL GAS) GFW=196.05822

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-5.756	-406.400	-406.400	INFINITE
100	13.328	66.434	113.970	-4.754	-408.356	-398.399	870.689
200	24.492	79.112	93.411	-2.860	-409.733	-387.844	423.811
298	33.275	90.629	90.629	0.000	-410.385	-376.940	276.300
300	33.412	90.835	90.629	0.062	-410.393	-376.733	274.446
400	39.469	101.336	92.020	3.726	-411.149	-365.447	199.668
500	43.498	110.606	94.830	7.888	-411.459	-353.984	154.724
600	46.218	118.793	98.155	12.383	-411.517	-342.480	124.747
700	48.100	126.067	101.633	17.104	-411.412	-330.981	103.335
800	49.440	132.582	105.101	21.985	-424.198	-320.704	87.611
900	50.420	138.465	108.487	26.980	-423.613	-307.799	74.743
1000	51.155	143.817	111.756	32.060	-423.004	-294.965	64.464
1100	51.717	148.720	114.897	37.205	-422.374	-282.191	56.065
1200	52.156	153.240	117.906	42.400	-421.732	-269.475	49.077
1300	52.506	157.429	120.787	47.634	-421.083	-256.812	43.173
1400	52.787	161.330	123.546	52.899	-420.435	-244.201	38.121
1500	53.017	164.980	126.188	58.189	-419.787	-231.637	33.749
1600	53.208	168.408	128.720	63.501	-419.139	-219.114	29.929
1700	53.367	171.639	131.151	68.830	-418.493	-206.630	26.564
1800	53.501	174.693	133.486	74.173	-417.858	-194.189	23.577
1900	53.616	177.589	135.731	79.529	-417.221	-181.776	20.909
2000	53.714	180.342	137.894	84.896	-416.598	-169.405	18.511
2100	53.799	182.965	139.978	90.272	-415.977	-157.059	16.345
2200	53.873	185.469	141.989	95.655	-415.364	-144.743	14.379
2300	53.938	187.865	143.932	101.046	-414.760	-132.457	12.586
2400	53.995	190.162	145.811	106.443	-414.161	-120.195	10.945
2500	54.045	192.367	147.629	111.845	-413.571	-107.958	9.438
2600	54.090	194.488	149.391	117.252	-412.989	-95.745	8.048
2700	54.130	196.530	151.099	122.663	-412.415	-83.553	6.763
2800	54.166	198.499	152.757	128.077	-411.851	-71.385	5.572
2900	54.198	200.401	154.367	133.496	-411.292	-59.234	4.464
3000	54.227	202.238	155.933	138.917	-410.746	-47.107	3.432
3100	54.254	204.017	157.455	144.341	-410.202	-34.990	2.467
3200	54.278	205.740	158.937	149.768	-409.670	-22.898	1.564
3300	54.300	207.410	160.381	155.197	-409.145	-10.817	0.716
3400	54.320	209.032	161.788	160.628	-408.629	1.245	-0.080
3500	54.338	210.607	163.161	166.060	-408.125	13.291	-0.830
3600	54.355	212.138	164.500	171.495	-407.625	25.325	-1.537
3700	54.370	213.627	165.808	176.931	-407.136	37.344	-2.206
3800	54.385	215.077	167.085	182.369	-406.653	49.352	-2.838
3900	54.398	216.490	168.334	187.808	-406.180	61.346	-3.438
4000	54.410	217.867	169.555	193.249	-405.717	73.327	-4.006
4100	54.422	219.211	170.750	198.690	-405.262	85.299	-4.547
4200	54.432	220.523	171.920	204.133	-404.817	97.258	-5.061
4300	54.442	221.804	173.065	209.577	-404.379	109.207	-5.550
4400	54.451	223.055	174.187	215.021	-403.953	121.145	-6.017
4500	54.460	224.279	175.286	220.467	-403.536	133.073	-6.463
4600	54.468	225.476	176.365	225.913	-403.128	144.994	-6.889
4700	54.475	226.648	177.422	231.361	-402.725	156.908	-7.296
4800	54.483	227.795	178.459	236.808	-402.341	168.807	-7.686
4900	54.489	228.918	179.478	242.257	-401.958	180.704	-8.060
5000	54.495	230.019	180.478	247.706	-401.590	192.589	-8.418
5100	54.501	231.098	181.460	253.156	-401.226	204.473	-8.762
5200	54.507	232.157	182.424	258.607	-400.878	216.343	-9.093
5300	54.512	233.195	183.373	264.057	-400.538	228.211	-9.410
5400	54.517	234.214	184.305	269.509	-400.206	240.070	-9.716
5500	54.522	235.214	185.221	274.961	-399.884	251.926	-10.010
5600	54.526	236.197	186.123	280.413	-399.576	263.773	-10.294
5700	54.530	237.162	187.010	285.866	-399.274	275.616	-10.568
5800	54.534	238.110	187.883	291.319	-398.981	287.454	-10.831
5900	54.538	239.042	188.742	296.773	-398.699	299.290	-11.086
6000	54.542	239.959	189.588	302.227	-398.430	311.114	-11.332

Dec. 31, 1977

TRIFLUOROMETHYLSULFUR PENTAFLUORIDE (CSF_8) (IDEAL GAS) GFW = 196.05822

ΔHa_0° = [788.6 ± 19] kcal/mol
$S^\circ_{298.15}$ = [90.6 ± 0.5] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf_0° = [-406.4 ± 15] kcal/mol CF_8S
$\Delta Hf^\circ_{298.15}$ = [-410.4 ± 15] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1168(1)	Free Rotation	591(2)
883(1)	627(1)	558(2)
755(1)	319(1)	425(2)
692(1)	501(1)	290(2)
612(1)	1256(2)	220(2)
325(1)	903(2)	

Point Group = C_{4v} σ (Overall) = 12
Bond Distances: C-F = [1.32] Å S-F = [1.56] Å C-S = 1.92 Å
Bond Angles: S-C-F = [109.5°] F*-S-F* = 90°
F*-S-C = [90°] F**-S-C = 180°
(* - *equatorial* ** - *axial*)
Product of Moments of Inertia: $I_AI_BI_C$ = [2.6591 x 10^{-112}] g^3 cm^6
Reduced Moment of Inertia: I_{red} = [9.9216 x 10^{-39}] g cm^2

Heat of Formation

We adopt $D_0^\circ(CF_3-SF_5)$ = 80±10 kcal/mol from which ΔHf° is calculated to be -406.4±15 kcal/mol at 0 K by combining D_0° with $\Delta Hf_0^\circ(CF_3,g)$ = -111.7±1.0 kcal/mol and $\Delta Hf_0^\circ(SF_5,g)$ = -214.7±3.6 kcal/mol (1). We estimate that the D_0°(C-S) in CF_3SF_5 lies between the C-C bond energy in C_2F_6 (95.7 kcal/mol, 1) and the S-S bond energy in S_2F_{10} (58.4 kcal/mol, 1). A comparison of the C-C, S-S, and C-S bond lengths and the corresponding stretching frequencies for C_2F_6, S_2F_{10}, and CF_3SF_5 indicates that D_0°(C-S) should be intermediate between those for C-C and S-S. We calculate the heat of atomization (ΔHa_0°) and ΔHf° value at 298.15 K as 788.6±19 kcal/mol and -410.385±15 kcal/mol, respectively.

Heat Capacity and Entropy

The microwave spectrum of CSF_8 observed by Kisliuk and Silvey (2) shows that the molecule is a symmetric rotor comprised of CF_3 and SF_5 groups joined by a C-S bond. The infrared (3, 4) and Raman (4) spectra obey the selection rules predicted for the point group C_{4v}. We estimate all structural data except for the C-S bond length by analogy with the CF_3 structure in C_2F_6 and the SF_5 structure in S_2F_{10} (1). We select a value for the C-S bond length which when combined with the estimated data reproduces the experimentally determined moment of inertia ($I_A = I_B$ = 7.656 x 10^{-38} g cm^2, 2) within experimental error. The principal moment of inertia about the symmetry axis is I_c = 4.5966 x 10^{-38} g cm^2.

The vibrational frequencies are rounded values taken from the gas phase infrared and liquid phase Raman study of Griffiths (4). The infrared data are supported by results obtained in an earlier study (3). Griffiths (4) assigned the Raman band at 262 cm^{-1} to the b_1 SF_2 out-of-plane deformation mode (ν_9) by analogy with his assigment for $ClSF_5$ (ν_6 = 271 cm^{-1}). More recent information (1) on $ClSF_5$ indicates that the 271 cm^{-1} Raman band is the low-frequency SF_5 rocking fundamental ν_{11}. By analogy with this new assignment for $ClSF_5$, we assign the infrared band observed at 290 cm^{-1} by Griffiths (4) to the SF_5 rocking fundamental (ν_{16}). The Raman band at 319 cm^{-1} is believed to be ν_9 since it is close to the values (332 cm^{-1} and 317 cm^{-1}) predicted for the analogous deformation mode (ν_6) in $ClSF_5$ (1) by force field calculations. We assume that the internal rotation about the C-S bond is unrestricted based on spectroscopic evidence (3, 4) which indicates that the barrier is very small. Kisliuk and Silvey (2) have derived a potential barrier of 219 cm^{-1} (0.63 kcal/mol) from satellite lines observed in their microwave spectrum; however, these lines are probably due to the CF_3 rocking mode (ν_{17}) rather than the torsional vibration (ν_7), as indicated by Eggers et al. (3). The overall symmetry number is calculated as the product of the external (σ) and internal (η) symmetry numbers with η assumed equal to 12.

References

1. JANAF Thermochemical Tables: CF_3(g) and C_2F_6(g), 6-30-69; SF_5(g), S_2F_{10}(g), and $ClSF_5$(g), 12-31-77.
2. P. Kisliuk and G. A. Silvey, J. Chem. Phys. 20, 517 (1952).
3. D. F. Eggers, Jr., H. E. Wright, and D. W. Robinson, J. Chem. Phys. 35, 1045 (1961).
4. J. E. Griffiths, Spectrochim. Acta, 23A, 2145 (1967).

CF_8S

CARBON MONOSULFIDE (CS)
(IDEAL GAS) GFW=44.071

CS

T, °K	gibbs/mol Cp°	S°	-(G°-H°298)/T	kcal/mol H°-H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.061	66.224	66.224	INFINITE
100	6.956	42.666	56.531	-1.387	66.740	62.791	-137.231
200	6.975	47.490	50.942	-0.690	66.966	58.736	-64.184
298	7.122	50.297	50.297	0.000	67.000	54.684	-40.085
300	7.126	50.341	50.297	0.013	66.999	54.608	-39.782
400	7.401	52.427	50.579	0.739	66.380	50.509	-27.597
500	7.690	54.110	51.122	1.454	65.878	46.599	-20.368
600	7.938	55.535	51.742	2.276	65.425	42.786	-15.585
700	8.137	56.774	52.374	3.080	65.004	39.071	-12.199
800	8.293	57.871	52.954	3.902	51.542	34.126	-9.323
900	8.415	58.855	53.591	4.737	51.452	31.954	-7.759
1000	8.511	59.747	54.163	5.564	51.352	29.793	-6.511
1100	8.588	60.562	54.708	6.439	51.241	27.641	-5.492
1200	8.651	61.312	55.228	7.301	51.123	25.502	-4.645
1300	8.703	62.006	55.723	8.169	50.997	23.372	-3.929
1400	8.746	62.653	56.195	9.041	50.866	21.253	-3.318
1500	8.782	63.258	56.646	9.918	50.731	19.141	-2.789
1600	8.813	63.825	57.077	10.797	50.592	17.040	-2.328
1700	8.840	64.361	57.490	11.680	50.452	14.947	-1.922
1800	8.864	64.867	57.886	12.565	50.308	12.862	-1.562
1900	8.885	65.346	58.266	13.453	50.164	10.788	-1.241
2000	8.904	65.803	58.631	14.342	50.017	8.718	-0.953
2100	8.921	66.238	58.983	15.234	49.870	6.657	-0.693
2200	8.936	66.653	59.323	16.126	49.719	4.602	-0.457
2300	8.951	67.050	59.650	17.021	49.569	2.556	-0.243
2400	8.964	67.432	59.966	17.917	49.417	0.515	-0.047
2500	8.976	67.798	60.272	18.814	49.265	-1.520	0.133
2600	8.988	68.150	60.569	19.712	49.110	-3.548	0.298
2700	8.999	68.490	60.856	20.611	48.955	-5.573	0.451
2800	9.009	68.817	61.134	21.512	48.800	-7.589	0.592
2900	9.020	69.133	61.405	22.413	48.642	-9.599	0.723
3000	9.030	69.439	61.667	23.316	48.484	-11.604	0.845
3100	9.041	69.736	61.923	24.219	48.326	-13.604	0.959
3200	9.051	70.023	62.172	25.124	48.166	-15.600	1.065
3300	9.062	70.301	62.414	26.025	48.005	-17.593	1.165
3400	9.074	70.572	62.650	26.936	47.844	-19.575	1.258
3500	9.086	70.835	62.880	27.844	47.681	-21.560	1.346
3600	9.099	71.091	63.104	28.753	47.519	-23.535	1.429
3700	9.114	71.341	63.324	29.664	47.355	-25.505	1.507
3800	9.129	71.584	63.538	30.576	47.192	-27.471	1.580
3900	9.146	71.822	63.747	31.490	47.028	-29.434	1.649
4000	9.165	72.053	63.952	32.406	46.865	-31.389	1.715
4100	9.186	72.280	64.152	33.323	46.701	-33.347	1.778
4200	9.209	72.502	64.349	34.243	46.537	-35.294	1.837
4300	9.234	72.719	64.541	35.165	46.373	-37.243	1.893
4400	9.262	72.931	64.729	36.090	46.210	-39.186	1.946
4500	9.292	73.140	64.914	37.017	46.047	-41.125	1.997
4600	9.325	73.344	65.095	37.946	45.886	-43.060	2.046
4700	9.362	73.545	65.272	38.883	45.728	-44.992	2.092
4800	9.402	73.743	65.447	39.821	45.569	-46.921	2.136
4900	9.445	73.937	65.618	40.743	45.413	-48.843	2.178
5000	9.491	74.128	65.786	41.710	45.259	-50.767	2.219
5100	9.541	74.317	65.952	42.661	45.106	-52.689	2.258
5200	9.596	74.502	66.114	43.618	44.958	-54.603	2.295
5300	9.654	74.686	66.274	44.581	44.814	-56.516	2.330
5400	9.716	74.867	66.432	45.549	44.672	-58.424	2.365
5500	9.782	75.046	66.587	46.524	44.534	-60.333	2.397
5600	9.852	75.223	66.739	47.505	44.400	-62.238	2.429
5700	9.926	75.398	66.890	48.454	44.271	-64.146	2.459
5800	10.005	75.571	67.038	49.451	44.148	-66.045	2.489
5900	10.088	75.743	67.184	50.495	44.030	-67.943	2.517
6000	10.175	75.913	67.328	51.505	43.919	-69.841	2.544

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1976

CARBON MONOSULFIDE (CS) (IDEAL GAS) GFW = 44.071

D_0° = 169.1 ± 6 kcal/mol
$S^\circ_{298.15}$ = 50.30 ± 0.01 gibbs/mol

ΔHf_0° = 66.2 ± 6 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 67.0 ± 6 kcal/mol

CS

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$a^3\Pi$	27509	2
	27590	2
	27607	2
$a(^3\Pi)$	38613.9	6
$A^1\Pi$	38797.6	2
$a'^3\Sigma^+$	38851.8	3
$c^3\Sigma^-$	39160.8	3
$(^1\Delta)$	39170	2
$(^1\Delta)$	39950	2

ω_e = 1285.08 cm^{-1} $\omega_e x_e$ = 6.46 cm^{-1} σ = 1
B_e = 0.820046 cm^{-1} α_e = 0.005922 cm^{-1} r_e = 1.5349 Å

Heat of Formation

Several values have been proposed for the heat of formation or the dissociation energy of CS(g) (1 - 17). Many of these have been summarized by Hubin-Franksin et al. (16) although distinction was not made between ΔHf_0° and ΔHf°_{298}. The values proposed or derivable for ΔHf°_{298} vary from ≤32 kcal/mol (electron impact of COS, 16) to 77±4 kcal/mol (photodissociation of COS, 15). We give more weight to the equilibrium measurements - - ΔHf°_{298} = 69 kcal/mol derived from (3), 58±5 and 60±6 kcal/mol (5), 55±1 kcal/mol (7), and 70±2 kcal/mol (11) (lack of data prohibits a complete re-analysis of these values) - - and adopt ΔHf°_{298}(CS, g) = 67±6 kcal/mol. This leads to ΔHf_0° = 66.2±6 kcal/mol and to D_0° = 169.1±6 kcal/mol for the process CS(g) = C(g) + S(g), using JANAF values for the heats of formation of C(g) and S(g) (18).

Heat Capacity and Entropy

The molecular constants and electronic levels are those compiled by Rosen (19) except that the value of $\omega_3 x_e$ = 8.46 cm^{-1} given by Rosen (19) and by Suchard (20) appears to be a transcription error for the original $\omega_e x_e$ = 6.46 cm^{-1} by Lagerqvist, et al. (4).

The microwave spectra of carbon monosulfide have been critically reviewed by Lovas and Krupenie (21). Their derived rotational constants are in agreement with those adopted.

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CARBON DISULFIDE (CS_2)
(IDEAL GAS) GFW=76.131

T, °K	gibbs/mol Cp°	S°	−(G°−H°$_{298}$)/T	kcal/mol H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.554	27.754	27.754	INFINITE
100	7.408	47.007	65.516	-1.851	28.115	24.028	-52.514
200	9.476	52.777	57.809	-1.006	28.096	19.933	-21.782
298	10.914	56.852	56.852	0.000	27.950	15.955	-11.695
300	10.935	56.919	56.852	0.020	27.946	15.881	-11.569
400	11.873	60.202	57.293	1.164	26.646	11.934	-6.520
500	12.546	62.927	58.155	2.386	25.673	8.369	-3.658
600	13.053	65.262	59.150	3.667	24.862	4.987	-1.817
700	13.442	67.305	60.172	4.993	24.163	1.779	-0.556
800	13.743	69.120	61.179	6.353	-2.586	-3.910	1.068
900	13.980	70.753	62.154	7.739	-2.563	-4.078	0.990
1000	14.169	72.236	63.089	9.147	-2.543	-4.247	0.928
1100	14.322	73.594	63.983	10.572	-2.527	-4.421	0.878
1200	14.448	74.846	64.837	12.011	-2.512	-4.591	0.836
1300	14.553	76.006	65.652	13.461	-2.501	-4.763	0.801
1400	14.643	77.088	66.430	14.921	-2.491	-4.937	0.771
1500	14.720	78.101	67.175	16.389	-2.483	-5.116	0.745
1600	14.787	79.053	67.888	17.864	-2.474	-5.290	0.723
1700	14.846	79.952	68.571	19.346	-2.464	-5.467	0.703
1800	14.899	80.802	69.228	20.834	-2.455	-5.645	0.685
1900	14.947	81.609	69.858	22.326	-2.445	-5.819	0.669
2000	14.991	82.376	70.465	23.823	-2.435	-5.998	0.655
2100	15.031	83.109	71.050	25.324	-2.425	-6.177	0.643
2200	15.068	83.809	71.614	26.829	-2.415	-6.355	0.631
2300	15.103	84.479	72.159	28.337	-2.405	-6.534	0.621
2400	15.135	85.123	72.686	29.849	-2.394	-6.713	0.611
2500	15.166	85.741	73.196	31.364	-2.381	-6.894	0.603
2600	15.195	86.337	73.690	32.882	-2.370	-7.075	0.595
2700	15.222	86.911	74.169	34.403	-2.357	-7.259	0.588
2800	15.249	87.465	74.634	35.927	-2.344	-7.442	0.581
2900	15.275	88.000	75.086	37.453	-2.332	-7.623	0.574
3000	15.299	88.519	75.525	38.982	-2.320	-7.803	0.568
3100	15.323	89.021	75.952	40.513	-2.305	-7.986	0.563
3200	15.346	89.508	76.368	42.046	-2.294	-8.170	0.558
3300	15.369	89.980	76.773	43.582	-2.280	-8.359	0.554
3400	15.391	90.439	77.169	45.120	-2.267	-8.537	0.549
3500	15.412	90.886	77.554	46.660	-2.256	-8.730	0.545
3600	15.433	91.320	77.931	48.202	-2.242	-8.913	0.541
3700	15.454	91.743	78.298	49.747	-2.231	-9.096	0.537
3800	15.474	92.156	78.657	51.293	-2.218	-9.281	0.534
3900	15.494	92.558	79.009	52.842	-2.206	-9.468	0.531
4000	15.513	92.950	79.352	54.392	-2.194	-9.648	0.527
4100	15.532	93.334	79.689	55.944	-2.182	-9.839	0.524
4200	15.551	93.708	80.018	57.498	-2.172	-10.022	0.522
4300	15.570	94.074	80.341	59.054	-2.162	-10.213	0.519
4400	15.589	94.433	80.657	60.612	-2.153	-10.400	0.517
4500	15.607	94.783	80.967	62.172	-2.144	-10.586	0.514
4600	15.625	95.126	81.271	63.734	-2.135	-10.775	0.512
4700	15.643	95.463	81.569	65.297	-2.126	-10.964	0.510
4800	15.661	95.792	81.862	66.862	-2.120	-11.153	0.508
4900	15.678	96.115	82.150	68.429	-2.113	-11.335	0.506
5000	15.696	96.432	82.432	69.998	-2.108	-11.528	0.504
5100	15.713	96.743	82.710	71.568	-2.105	-11.718	0.502
5200	15.730	97.048	82.983	73.141	-2.100	-11.904	0.500
5300	15.747	97.348	83.251	74.714	-2.097	-12.093	0.499
5400	15.764	97.643	83.515	76.290	-2.095	-12.277	0.497
5500	15.781	97.932	83.774	77.867	-2.095	-12.468	0.495
5600	15.797	98.217	84.030	79.446	-2.096	-12.654	0.494
5700	15.814	98.496	84.281	81.027	-2.098	-12.850	0.493
5800	15.831	98.771	84.528	82.609	-2.101	-13.036	0.491
5900	15.847	99.042	84.772	84.193	-2.104	-13.227	0.490
6000	15.863	99.309	85.012	85.778	-2.110	-13.411	0.489

June 30, 1961; Dec. 31, 1976

CARBON DISULFIDE (CS_2)   (IDEAL GAS)   GFW = 76.131

ΔHa_0° = 273.33 ± 0.66 kcal/mol
$S^\circ_{298.15}$ = 56.85 ± 0.02 gibbs/mol
Ground State Quantum Weight = 1

ΔHf_0° = 27.75 ± 0.20 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 27.95 ± 0.20 kcal/mol

Vibrational Frequencies, Degeneracies, and Anharmonicity and Rotational Constants

ν, cm^{-1}	x_{ii}, cm^{-1}	x_{ij}, cm^{-1}	α_i, cm^{-1}
657.98 (1)	x_{11} = -0.83	x_{12} = -1.75	α_1 = 0.0002144
395.93 (2)	x_{22} = 0.82	x_{23} = -6.49	α_2 = 0.0007130
1535.35 (1)	x_{33} = -6.54	x_{13} = -7.59	α_3 = -0.0002148

B_e = 0.109277 cm^{-1} g_{22} = -0.74
D_o = 1.05 x 10^{-8} cm^{-1}
Bond Distance: C-S = 1.553 Å
Bond Angle: S-C-S = 180°
Point Group $D_{\infty h}$ σ = 2

Heat of Formation

Good, Lacina, and Mc Cullough (1) have determined $\Delta Hf^\circ_{298}(CS_2, \ell)$ = 21.37±0.17 kcal/mol by rotating bomb combustion calorimetry. They combined this with an unpublished measurement of ΔHv°_{298} = 6.61±0.02 kcal/mol to obtain $\Delta Hf^\circ_{298}(CS_2,g)$ = 27.98± 0.19 kcal/mol. We adopt ΔHv°_{298} = 6.578±0.003 kcal/mol determined by Waddington et al. (2) by vapor flow calorimetry and obtain the adopted $\Delta Hf^\circ_{298}(CS_2, g)$ = 27.95±0.20 kcal/mol.

The resulting ΔHf_0° (CS_2, g) = 27.75±0.20 kcal/mol leads to ΔHa_0° = 273.33±0.66 kcal/mol for the process $CS_2(g) = C(g) + 2\,S(g)$. Auxiliary data are from the JANAF Tables (12).

Heat Capacity and Entropy

The fundamental ground state vibrational frequencies are those from a re-analysis of infra-red and Raman spectra by Guenther and Stoicheff, referenced by Kleman (3) as a private communication. Several sets of anharmonicity constants and/or rotational constants have been published (2, 4-9). Some are corrected for Fermi resonance to some degree in some manner (6, 7, 9), others are not (2, 4). We adopt the x_{ii}, x_{ij}, α_i, and g_{22} terms determined from the least-square estimates of the force constants in the general quartic force field by Giguere et al. (9). The rotational constants B_e and D_o are from McBride and Gordon (7). The bond distance, r_e, is a rounded average of 1.5529±0.0005 Å (4) and 1.5523±0.0005 Å (5) and is consistent with the adopted B_e. The bond angle of 180° is from Cross and Brockway (10).

Waddington et al. (2) have measured Cp° of carbon disulfide gas in the 325.65-502.25 K range. At 325.65 K, the value calculated by Waddington et al. (2), where Fermi resonance was not considered explicitly, is approximately 0.03% lower than the observed value; at 300 K, the present table is higher than the table calculated by Waddington et al. (2) by about 0.3%. At 502.25 K, the present table is approximately 0.6% higher (0.074 gibbs/mole) than the measured value of 12.484 gibbs/mol. The value calculated by Waddington et al. (2) is 0.2% higher (0.025 gibbs/mole) than the observed value. At 6000 K, the value of Cp° in the present table is approximately 1.1% higher (0.17 gibbs/mol) than the value calculated with the anharmonicity constants used by Waddington et al. (2).

The tabulated functions have been generated by the NASA-Lewis computer program (11). We adopt these functions directly for 0 to 298.15 K and reproduce the functions at higher temperatures by integration of Cp°.

The allowed error of ±0.02 gibbs/mol for S°_{298} includes the values calculated using other anharmonicity correction constants (2, 6, 7).

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NICKEL TETRACARBONYL $(Ni(CO)_4)$ C_4NiO_4
(LIQUID) GFW=170.7416

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	48.600	76.377	76.377	0.000	−151.000	−140.785	103.197
300	48.620	76.677	76.378	0.090	−150.963	−140.722	102.515
400	49.940	90.845	78.300	5.018	−149.084	−137.597	75.179
500	51.260	102.131	81.975	10.078	−147.463	−134.918	58.972
600	52.580	111.593	86.143	15.270	−146.072	−132.542	48.278
700	53.900	119.798	90.378	20.594	−144.794	−130.388	40.708

March 31, 1978

NICKEL TETRACARBONYL $(Ni(CO)_4)$ (LIQUID) GFW = 170.7416

$S^\circ_{298.15}$ = [76.4 ± 3.0] gibbs/mol
Tm = 253.86 ± 0.1 K
Tb = 315.4 ± 0.2 K (P = 1 atm)

$\Delta Hf^\circ_{298.15}$ = −151.0 ± 2.0 kcal/mol
ΔHm° = 3.306 ± 0.005 kcal/mol
ΔHv° = [6.999] kcal/mol C_4NiO_4

Heat of Formation

The adopted heat of formation is a weighted average based on heat of combustion data of Smagina and Ormont (1) and Fischer et al. (2). *The results of Smagina and Ormont* (1) *have been recalculated along the lines indicated by* Sykes (3), using recent values of ΔHf(NiO,c) (4) and other auxiliary data (5). Their corrected value of $\Delta Hf^\circ_{298}(Ni(CO)_4,\ell)$ is −150.3±3.0 kcal/mol (average of 3 determinations using Pt fuse). Fischer et al. (2) made two sets of determinations yielding the following values of $\Delta Hf^\circ_{298}(Ni(CO)_4,\ell)$; −150.3±0.5 kcal/mol (average of 5 determinations using benzoic acid fuse) and −152.3±0.5 kcal/mol (average of 4 determinations using Pt fuse). Fischer et al. (2) mention that the difference in their two sets of values may be due to hydration effects but a more likely explanation is higher uncertainties in the percentage combustion, as suggested by Sykes (3). Therefore, we adopt an uncertainty of ±2.0 kcal/mol.

Heat Capacity and Entropy

We adopt the smooth values of Cp° (90-270 K) reported by Spice et al. (6). Values above 270 K are based on a linear extrapolation of liquid Cp° values from 255-270 K. The Cp° data reported by Duncan and Murray (7) were calculated from gas phase Cp° data via a poorly defined procedure and show large deviations from the adopted Cp°.

The value of S°_{298} is difficult to assess because of the lack of Cp° data below 90 K. The adopted value of S°_{298} is chosen so as to get the best agreement between second and third law analysis of the consistent vapor pressure data of Suginuma and Satozaki (8), Walsh (9), and Baev (10). This treatment results in a value of $S^\circ_{90}(c)$ = 23.95 gibbs/mol. Spice et al. (6) had estimated a value of $S^\circ_{90}(c)$ = 20.6 gibbs/mol based on comparisons (at 90 and 120 K) with a "standard" heat capacity curve.

Melting Data

The adopted values of Tm and ΔHm° are those reported by Spice et al. (6). The value of ΔHm° is the mean of three *calorimetrically determined values. Walsh* (9) *reported a value of Tm approximately 2 K higher than* the adopted value and also reported that Tm is very sensitive to purity of the $Ni(CO)_4$. However, we find the purity determinations of Spice et al. (6) more compelling than those of Walsh (9).

Vaporization Data

The normal boiling point, Tb = 315.4±0.2 K, is based on the vapor pressure measurements of Suginuma and Satozaki (8), Walsh (9) and Baev (10); fugacity corrections have not been made. See $Ni(CO)_4(g)$ table (5) for analysis of ΔHv°.

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NICKEL TETRACARBONYL (Ni(CO)$_4$) C_4NiO_4
(IDEAL GAS) GFW=170.7416

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-7.288	-144.770	-144.770	INFINITE
100	20.191	68.528	127.172	-5.864	-144.911	-143.217	312.997
200	30.586	85.990	102.410	-3.284	-144.487	-141.645	154.781
298	35.681	99.282	99.282	0.000	-143.780	-140.394	102.910
300	35.745	99.503	99.283	0.066	-143.767	-140.374	102.261
400	38.331	110.175	100.721	3.782	-143.100	-139.345	76.134
500	40.031	118.920	103.512	7.704	-142.617	-138.466	60.523
600	41.388	126.342	106.714	11.777	-142.345	-137.664	50.143
700	42.543	132.811	109.990	15.975	-142.193	-136.896	42.740
800	43.532	138.558	113.208	20.280	-142.058	-136.150	37.194
900	44.372	143.735	116.317	24.676	-141.986	-135.420	32.884
1000	45.082	148.448	119.298	29.150	-141.956	-134.689	29.436
1100	45.680	152.774	122.147	33.689	-141.970	-133.962	26.615
1200	46.185	156.771	124.868	38.283	-142.020	-133.232	24.265
1300	46.612	160.485	127.467	42.923	-142.106	-132.497	22.274
1400	46.975	163.953	129.950	47.603	-142.226	-131.753	20.567
1500	47.284	167.204	132.327	52.316	-142.382	-131.002	19.087
1600	47.550	170.265	134.603	57.058	-142.569	-130.235	17.789
1700	47.778	173.154	136.787	61.825	-142.798	-129.460	16.643
1800	47.980	175.891	138.884	66.613	-147.160	-128.496	15.601
1900	48.153	178.490	140.901	71.420	-147.439	-127.450	14.660
2000	48.308	180.964	142.842	76.243	-147.736	-126.392	13.811
2100	48.442	183.324	144.714	81.081	-148.046	-125.318	13.042
2200	48.564	185.580	146.521	85.931	-148.370	-124.227	12.341
2300	48.671	187.742	148.266	90.793	-148.710	-123.121	11.699
2400	48.769	189.815	149.955	95.665	-149.066	-122.000	11.110
2500	48.856	191.808	151.589	100.546	-149.439	-120.866	10.566
2600	48.935	193.726	153.173	105.436	-149.829	-119.718	10.063
2700	49.006	195.574	154.710	110.333	-150.230	-118.548	9.596
2800	49.072	197.357	156.201	115.237	-150.650	-117.367	9.161
2900	49.131	199.080	157.650	120.147	-151.090	-116.173	8.755
3000	49.187	200.747	159.059	125.063	-151.542	-114.961	8.375
3100	49.238	202.360	160.430	129.984	-152.013	-113.736	8.018
3200	49.286	203.924	161.765	134.911	-242.560	-111.333	7.604
3300	49.330	205.442	163.066	139.841	-242.667	-107.231	7.101
3400	49.371	206.915	164.334	144.776	-242.787	-103.125	6.629
3500	49.410	208.347	165.571	149.715	-242.925	-99.017	6.183
3600	49.446	209.739	166.778	154.658	-243.075	-94.903	5.761
3700	49.480	211.094	167.958	159.605	-243.241	-90.786	5.362
3800	49.512	212.414	169.111	164.554	-243.424	-86.664	4.984
3900	49.542	213.701	170.238	169.507	-243.618	-82.535	4.625
4000	49.571	214.956	171.340	174.463	-243.828	-78.400	4.284
4100	49.599	216.180	172.419	179.421	-244.057	-74.261	3.958
4200	49.625	217.375	173.475	184.382	-244.301	-70.117	3.649
4300	49.650	218.543	174.509	189.346	-244.560	-65.968	3.353
4400	49.674	219.685	175.523	194.312	-244.835	-61.812	3.070
4500	49.697	220.802	176.517	199.281	-245.124	-57.645	2.800
4600	49.719	221.894	177.492	204.252	-245.437	-53.482	2.541
4700	49.740	222.964	178.448	209.225	-245.760	-49.301	2.292
4800	49.761	224.011	179.386	214.200	-246.105	-45.120	2.054
4900	49.781	225.037	180.307	219.177	-246.467	-40.929	1.825
5000	49.801	226.043	181.212	224.156	-246.846	-36.729	1.605
5100	49.820	227.030	182.101	229.137	-247.244	-32.523	1.394
5200	49.838	227.997	182.974	234.120	-247.664	-28.309	1.190
5300	49.856	228.947	183.833	239.104	-248.105	-24.088	0.993
5400	49.873	229.879	184.677	244.091	-248.566	-19.857	0.804
5500	49.890	230.794	185.507	249.079	-249.048	-15.615	0.620
5600	49.906	231.693	186.324	254.069	-249.554	-11.368	0.444
5700	49.922	232.577	187.127	259.060	-250.082	-7.107	0.273
5800	49.938	233.445	187.919	264.053	-250.636	-2.843	0.107
5900	49.954	234.299	188.697	269.048	-251.212	1.438	-0.053
6000	49.969	235.139	189.464	274.044	-251.817	5.724	-0.208

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NICKEL TETRACARBONYL (Ni(CO)$_4$) (IDEAL GAS) GFW = 170.7416

Point Group T_d
$S^\circ_{298.15}$ = 99.3 ± 2.0 gibbs/mol
Tb = 315.4 ± 0.2 K (P = 1 atm)
Ground State Quantum Weight = 1

ΔHf°_0 = −144.77 ± 2.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −143.78 ± 2.5 kcal/mol
ΔHv° = [6.999] kcal/mol C_4NiO_4

Vibrational Frequencies, Quantum Weights, and Anharmonicities

ν, cm^{-1}	g_i	ν, cm^{-1}	g_i	x_{ij}, cm^{-1}
2132.4	1	458.9	3	x_{11} = −2.6
370.8	1	423.1	3	x_{15} = −11.0
380	2	79	3	x_{55} = −5.0
62	2	300	3	g_{55} = −4.5
2057.8	3			All others = 0

Bond Distances: Ni-C = 1.82±0.03 Å C-O = 1.15±0.02 Å σ = 12
Bond Angles: C-Ni-C = 109.4712° Ni-C-O = 180°
Product of the Moments of Inertia: $I_AI_BI_C$ = 5.14154 x $10^{-112}g^3\ cm^6$

Heat of Formation

The value of ΔHf°_{298}(g) is obtained from ΔHf°_{298}(ℓ) (1) by addition of the heat of vaporization, ΔHv°_{298} = 7.22±1.5 kcal/mol. The adopted value of the heat of vaporization is selected from our third law analysis of the vaporization data given below and is based primarily on the data of Suginuma and Satozaki (2), Baev (3) and Walsh (4). The uncertainty has been increased above that indicated in the table below to account for uncertainties in the free energy functions of the liquid and gas. Fugacity corrections have not been applied but they are expected to be within the stated uncertainty. The heat of vaporization at the boiling point, ΔHv°, is the difference between ΔHf°(g) and ΔHf°(ℓ) at the boiling point.

Data for the equilibrium Ni(c) + 4 CO(g) $\rightleftarrows$ Ni(CO)$_4$(g) have been reviewed by Kipnis (7). The data show considerable scatter and this has been attributed to differences in chemical potential of nickel (sheet or powder) used in the reaction (7, 8). Values of ΔHf°_{298} derived from these studies are less negative than the adopted value by several kcal/mol and are less reliable due to uncertainty in the chemical potential of nickel.

Source	No. Pts.	Range T, K	ΔHv°_{298}, kcal/mol		gibbs/mol	$-\Delta Hf^\circ_{298}$ kcal/mol
			Second Law	Third Law		
Suginuma (2)	20	273-298	7.209±0.024	7.217±0.005	0.026±0.084	143.78±2.5
Suginuma (2)	18	273-307	7.285±0.015	7.224±0.005	-0.208±0.052	143.78±2.5
Baev (3)	33[†]	285-312	7.146±0.013	7.216±0.006	0.231±0.043	143.78±2.5
Walsh (4)	5	273-308	7.233±0.031	7.222±0.005	-0.037±0.105	143.78±2.5
Anderson (5)	9	253-316	6.933±0.025	7.209±0.043	0.961±0.086	143.79±2.5
Mittasch (6)	8	275-313	7.284±0.075	7.264±0.016	-0.068±0.255	143.74±2.5

[†] Point at 281.94 K rejected by statistical test.

Heat Capacity and Entropy

The adopted vibrational data, including anharmonicity, are from Jones et al. (9). The largest uncertainty in these assignments is in the frequency of the MCO bending vibration, ν_3. Jones et al. (9) chose 380 cm^{-1} based on a study of the spectra of substituted carbonyls by Bigorgne and Bouquet (10). Ross et al. (11) summarized values of S°_{298} (96.2 to 99.8 gibbs/mol) obtained from various frequency assignments; most of this variation is due to alternate assignments for ν_3.

The adopted molecular structure data are from the electron diffraction study of Brockway and Cross (12) which conclusively indicates a tetrahedral structure. Moment of inertia calculations based on the adopted bond distances and angles yield $I_A=I_B=I_C$= 8.01120 x 10^{-38} g cm^2.

The thermodynamic functions, including the effects of available vibrational anharmonicities, are calculated using the computer program of McDowell (13). Compared to a harmonic oscillator calculation using the same data the present results are identical at 298.15 K, while at 6000 K the entropy is 0.333 gibbs/mol higher.

References

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13. R. E. McDowell, QCPE #269, Quantum Chemistry Program Exchange, Indiana University (1974).

C_4NiO_4

IRON PENTACARBONYL $(Fe(CO)_5)$ C_5FeO_5

(LIQUID) GFW=195.899

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	55.876	80.564	80.564	0.000	-183.100	-166.601	122.120
300	55.876	80.909	80.565	0.103	-183.060	-166.500	121.293
400	55.876	96.984	82.756	5.691	-181.096	-161.286	88.121
500	55.876	109.452	86.895	11.279	-179.602	-156.515	68.412
600	55.876	119.640	91.529	16.866	-178.525	-152.004	55.367
700	55.876	128.253	96.176	22.454	-177.797	-147.646	46.097

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IRON PENTACARBONYL $(Fe(CO)_5)$ (LIQUID) GFW = 195.899

$S^\circ_{298.15}$ = 80.6 ± 1.0 cal/(mol K)
Tm = 253.1 ± 0.1 K
Tb = 377 ± 3 K (P = 1 atm)

$\Delta Hf^\circ_{298.15}$ = -183.1 ± 1.7 kcal/mol
ΔHm° = 3.161 ± 0.003 kcal/mol
ΔHv° = [8.061] kcal/mol

C_5FeO_5

Heat of Formation

The adopted heat of formation is based on the heat of combustion measurements of Cotton et al. (1). The average energy of combustion reported by these authors is -386.86±1.7 kcal/mol which yields a value of ΔHc°_{298} = -385.82±1.7 kcal/mol. Using auxiliary JANAF data (2) we calculate the adopted value of ΔHf°_{298} = -183.1±1.7 kcal/mol. Earlier combustion work by Roth (3) and Mittasch (4) appears less reliable due to incomplete characterization of products.

Heat Capacity and Entropy

The adopted heat capacity is derived by merging the Cp° data of Leadbetter and Spice (5) (22 - 287 K) with Cp° data derived from the enthalpy measurements of Welty et al. (6) (302 - 387 K). Leadbetter and Spice report a small anomaly in Cp°(c) near 230 K which they attribute to the presence of a small amount of impurity; therefore we have smoothed through this anomaly. The heat capacity (5) and enthalpy data (6) of the liquid merge smoothly and yield a constant Cp° = 55.876 cal/(mol K) from the melting point to 387 K. We assume Cp° remains constant at this value above this temperature.

The adopted value of S°_{298} is obtained by the appropriate integration of Cp° data assuming S°_{25} = 3.49±1.0 cal/(mol K). S°_{25} is obtained by using a single Debye function with 18 degrees of freedom and θ_D = 155 K as suggested by Leadbetter and Spice (5). The uncertainty in this procedure is rather large since a single Debye function fits the observed Cp° data quite poorly.

Melting Data

The adopted values of Tm and ΔHm° are those reported by Leadbetter and Spice (5). The value of Tm agrees well with that listed by Brynestad (7). For ΔHm° the only other value is ΔHm° = 3250±40 cal/mol reported by Mittasch (4). This is much less precise than the adopted value which is an average of two determinations.

Vaporization Data

The adopted boiling point is based on the vapor pressure data of Trautz and Badstubner (8) and Baev (9); fugacity corrections have not been made. See the heat of formation section of the $Fe(CO)_5(g)$ table (2) for details of the selected value of ΔHv°.

References

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C_5FeO_5

IRON PENTACARBONYL (FE(CO)$_5$) C_5FeO_5

(IDEAL GAS) GFW=195.899

T, K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-7.922	-174.362	-174.362	INFINITE
100	21.712	71.454	135.797	-6.434	-174.781	-171.319	374.412
200	33.302	90.124	108.488	-3.673	-174.572	-167.894	183.463
298	40.799	104.966	104.966	0.000	-173.960	-164.736	120.753
300	40.902	105.219	104.967	0.076	-173.948	-164.680	119.968
400	45.179	117.623	106.629	4.398	-173.249	-161.695	88.345
500	48.000	128.024	109.896	9.064	-172.677	-158.875	69.443
600	50.148	136.973	113.680	13.976	-172.276	-156.155	56.878
700	51.889	144.838	117.581	19.080	-172.030	-153.490	47.921
800	53.326	151.864	121.435	24.343	-171.921	-150.851	41.210
900	54.514	158.216	125.174	29.737	-171.960	-148.221	35.992
1000	55.499	164.012	128.773	35.239	-172.196	-145.570	31.814
1100	56.318	169.341	132.222	40.831	-172.670	-142.880	28.387
1200	57.000	174.272	135.523	46.498	-173.029	-140.160	25.526
1300	57.573	178.857	138.682	52.228	-173.013	-137.424	23.103
1400	58.057	183.142	141.706	58.010	-173.029	-134.685	21.025
1500	58.467	187.162	144.604	63.837	-173.080	-131.947	19.224
1600	58.819	190.947	147.383	69.701	-173.161	-129.200	17.648
1700	59.121	194.522	150.052	75.599	-173.508	-126.447	16.256
1800	59.383	197.909	152.617	81.524	-173.741	-123.671	15.015
1900	59.611	201.126	155.087	87.474	-177.379	-120.712	13.885
2000	59.811	204.188	157.466	93.445	-177.745	-117.723	12.864
2100	59.988	207.111	159.761	99.435	-178.128	-114.713	11.938
2200	60.144	209.905	161.977	105.442	-178.526	-111.683	11.094
2300	60.284	212.582	164.119	111.464	-178.944	-108.634	10.322
2400	60.409	215.150	166.193	117.498	-179.387	-105.572	9.614
2500	60.521	217.619	168.201	123.545	-179.840	-102.483	8.959
2600	60.623	219.994	170.147	129.602	-180.321	-99.382	8.354
2700	60.715	222.284	172.036	135.669	-180.819	-96.260	7.792
2800	60.800	224.494	173.870	141.745	-181.335	-93.119	7.268
2900	60.877	226.629	175.653	147.829	-181.871	-89.956	6.779
3000	60.948	228.694	177.387	153.920	-182.433	-86.781	6.322
3100	61.013	230.693	179.074	160.018	-183.007	-83.581	5.892
3200	61.074	232.631	180.718	166.123	-266.849	-78.673	5.373
3300	61.130	234.511	182.320	172.233	-267.006	-72.786	4.820
3400	61.183	236.337	183.882	178.349	-267.199	-66.902	4.300
3500	61.232	238.111	185.406	184.469	-267.412	-61.007	3.809
3600	61.278	239.837	186.894	190.595	-267.653	-55.105	3.345
3700	61.321	241.516	188.348	196.725	-267.922	-49.200	2.906
3800	61.362	243.152	189.768	202.859	-268.214	-43.282	2.489
3900	61.400	244.747	191.158	208.997	-268.537	-37.362	2.094
4000	61.437	246.302	192.517	215.139	-268.884	-31.428	1.717
4100	61.471	247.819	193.847	221.284	-269.260	-25.489	1.359
4200	61.504	249.301	195.150	227.433	-269.657	-19.535	1.016
4300	61.536	250.749	196.426	233.585	-270.085	-13.575	0.690
4400	61.566	252.164	197.677	239.740	-270.540	-7.604	0.378
4500	61.595	253.547	198.903	245.898	-271.020	-1.620	0.079
4600	61.623	254.902	200.106	252.059	-271.530	4.369	-0.208
4700	61.650	256.227	201.286	258.223	-272.069	10.372	-0.482
4800	61.675	257.525	202.444	264.389	-272.633	16.388	-0.746
4900	61.700	258.797	203.581	270.558	-273.227	22.413	-1.000
5000	61.725	260.044	204.698	276.729	-273.850	28.454	-1.244
5100	61.748	261.267	205.795	282.903	-274.501	34.507	-1.479
5200	61.771	262.466	206.874	289.079	-275.180	40.575	-1.705
5300	61.793	263.643	207.934	295.257	-275.893	46.652	-1.924
5400	61.814	264.798	208.976	301.437	-276.639	52.742	-2.135
5500	61.835	265.932	210.001	307.620	-277.413	58.849	-2.338
5600	61.856	267.047	211.010	313.804	-278.217	64.969	-2.536
5700	61.876	268.142	212.003	319.991	-279.056	71.108	-2.726
5800	61.895	269.218	212.980	326.180	-279.926	77.260	-2.911
5900	61.915	270.276	213.942	332.370	-280.832	83.427	-3.090
6000	61.933	271.317	214.890	338.562	-281.777	89.605	-3.264

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Point Group D_{3h}
$S^\circ_{298.15}$ = 105.0 ± 3.0 cal/(mol K)
Tb = 377 ± 3 K (P = 1 atm)
Ground State Quantum Weight = 1

ΔHf°_0 = -174.36 ± 1.7 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -173.96 ± 1.7 kcal/mol
ΔHv° = [8.061] kcal/mol

C_5FeO_5

Vibrational Frequencies, Quantum Weights, and Anharmonicities

ν, cm^{-1}	g_i	ν, cm^{-1}	g_i	ν, cm^{-1}	g_i	x_{ij}, cm^{-1}	x_{ij}, cm^{-1}
2120.7	1	618.8	1	474.3	2	$x_{1,1}$ = -2.2	$x_{1,6}$ = -11.9
2041.7	1	429.0	1	104.9	2	$x_{2,10}$ = -6.9	$x_{1,10}$ = -7.2
442.8	1	100	1	74.3	2	$x_{6,6}$ = -7.7	$x_{2,6}$ = -14.1
413.4	1	2013.3	2	488	2	$x_{10,10}$ = -5.6	$x_{2,2}$ = $x_{6,10}$ = -2.0
383	1	645.0	2	375	2	$x_{1,2}$ = -9.3	all others = 0
2034.0	1	542.5	2	97.3	2		

Bond Distances: Fe-C_{eq} = 1.833±0.004 Å Fe-C_{ax} = 1.806±0.005 Å C-O = 1.145±0.003 Å σ = 6
Bond Angles: Fe-C-O = 180° C_{ax}-Fe-C_{ax} = 180° C_{eq}-Fe-C_{eq} = 120° C_{ax}-Fe-C_{eq} = 90°
Product of the Moments of Inertia: $I_AI_BI_C = 9.94833 \times 10^{-112}\ g^3cm^6$

Heat of Formation

The adopted value of ΔHf°_{298}(g) is obtained from ΔHf°_{298}(ℓ)(1) by addition of the heat of vaporization, ΔHv°_{298} = 9.14±1.2 kcal/mol. The adopted value of the heat of vaporization is selected from our third law analysis of the vaporization data below and is based primarily on the data of Trautz and Badstubner (2) and Baev (3). The uncertainty has been increased above that indicated in the table below to account for uncertainties in the free energy functions of the liquid and gas. Fugacity corrections have not been made but they are expected to be well within the stated uncertainty. The heat of vaporization at the boiling point, ΔHv°, is calculated from the difference between ΔHf°(g) and ΔHf°(ℓ) at the boiling point.

Source	No. Pts	Range T, K	ΔHv°_{298}, kcal/mol Second Law	ΔHv°_{298}, kcal/mol Third Law	Drift cal/(mol K)	$-\Delta Hf^\circ_{298}$ kcal/mol
Trautz (2)	69	320-377	9.727±0.004	9.138±0.049	-1.688±0.011	173.96±1.7
Baev (3)	28	266-353	9.215±0.041	9.141±0.036	-0.224±0.125	173.96±1.7
Leadbetter (4)	16	293-306	9.754±0.095	9.219±0.017	-1.780±0.317	173.88±1.7
Gilbert (5)	12	254-306	9.207±0.106	9.241±0.042	0.121±0.381	173.86±1.7
Eyber (6)	13	258-293	9.505±0.014	9.247±0.025	-0.936±0.052	173.85±1.7
Dewar (7)	7	266-351	7.195±0.550	8.977±0.440	5.915±1.816	174.12±1.8

Heat Capacity and Entropy

The selected vibrational data, including anharmonicity, are from Jones et al. (8). The largest uncertainty in these assignments is for ν_9; Jones estimates it to lie at 100±15 cm^{-1}. The uncertainty in this assignment coupled with unknown anharmonicities for the low frequency vibrational modes lead to rather large uncertainties in the thermal functions. Following the arguments of Jones we estimate an uncertainty of ±3.0 cal/(mol K) in S°_{298}.

The adopted molecular structure data are from the electron diffraction data of Beagley et al. (9) which clearly indicate that the Fe-C axial bond is shorter than the Fe-C equatorial bond. Moment of inertia calculations based on the adopted bond distances and angles yield $I_A = 9.078946 \times 10^{-38}\ g\ cm^2$ and $I_B=I_C= 1.046785 \times 10^{-37} g\ cm^2$. The electron diffraction study of Almenningen et al. (10) is in excellent agreement with the adopted data although a slightly smaller difference between the axial and equatorial Fe-C bond lengths is indicated. This would lead to an insignificant difference in S°_{298}.

The thermodynamic functions, including the effects of available vibrational anharmonicities, are calculated using the computer program of McDowell (11). Compared to a harmonic oscillator calculation using the same data the present results are identical at 298.15 K, while at 6000 K the entropy is 0.407 cal/(mol K) higher.

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1. JANAF Thermochemical Tables: Fe(CO)$_5$(ℓ) 3-31-78.
2. M. Trautz and W. Badstubner, Z. Electrokhem. 35, 799 (1929).
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C_5FeO_5

CALCIUM MONOSULFIDE (CaS)   CaS

(CRYSTAL) GFW=72.14

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.151	-112.826	-112.826	INFINITE
100	6.201	3.460	22.614	-1.915	-112.988	-112.654	246.202
200	10.087	9.228	14.533	-1.061	-113.069	-112.281	122.693
298	11.339	13.528	13.528	0.000	-113.100	-111.888	82.015
300	11.340	13.598	13.528	0.021	-113.101	-111.881	81.504
400	11.760	16.921	13.978	1.177	-113.682	-111.446	60.890
500	12.070	19.579	14.841	2.369	-114.075	-110.844	48.449
600	12.320	21.803	15.821	3.589	-114.362	-110.168	40.128
700	12.510	23.717	16.816	4.831	-114.573	-109.452	34.172
800	12.670	25.398	17.785	6.090	-128.067	-109.877	30.017
900	12.800	26.898	18.716	7.363	-128.085	-107.602	26.129
1000	12.930	28.253	19.603	8.650	-128.147	-105.323	23.018
1100	13.046	29.491	20.447	9.949	-128.253	-103.036	20.471
1200	13.150	30.631	21.248	11.259	-130.186	-100.585	18.319
1300	13.239	31.687	22.011	12.578	-130.042	-98.125	16.496
1400	13.320	32.671	22.738	13.906	-129.892	-95.675	14.935
1500	13.381	33.592	23.431	15.241	-129.739	-93.236	13.584
1600	13.460	34.458	24.094	16.583	-129.583	-90.808	12.404
1700	13.566	35.277	24.727	17.935	-129.420	-88.389	11.363
1800	13.670	36.056	25.335	19.296	-166.146	-85.300	10.357
1900	13.774	36.798	25.919	20.669	-165.747	-80.819	9.296
2000	13.870	37.507	26.481	22.051	-165.343	-76.360	8.344
2100	13.954	38.185	27.022	23.442	-164.935	-71.921	7.485
2200	14.040	38.836	27.545	24.842	-164.523	-67.501	6.706
2300	14.129	39.462	28.049	26.250	-164.108	-63.100	5.996
2400	14.220	40.066	28.537	27.668	-163.691	-58.718	5.347
2500	14.316	40.646	29.010	29.094	-163.273	-54.353	4.751
2600	14.410	41.211	29.469	30.531	-162.853	-50.004	4.203
2700	14.530	41.757	29.914	31.976	-162.436	-45.672	3.697
2800	14.590	42.286	30.346	33.431	-162.020	-41.354	3.228
2900	14.680	42.799	30.767	34.894	-161.610	-37.052	2.792
3000	14.770	43.299	31.176	36.367	-161.206	-32.764	2.387

Dec. 31, 1971; Sept. 30, 1977

CALCIUM MONOSULFIDE (CaS)   (CRYSTAL)   GFW = 72.14

ΔHf°_0 = -112.8 ± 0.7 kcal/mol   CaS

$S^\circ_{298.15}$ = 13.5 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -113.1 ± 0.7 kcal/mol

T_m = [2798] K

Heat of Formation

Sabatier (1), Mourlot (2), and von Wartenberg (3), all measured the heat of solution of CaS in hydrochloric acid solution. Sabatier determined $\Delta Hr^\circ_{283.8}$ = -26.3±1.0 kcal/mol while Mourlot determined ΔHr°_{291} = -26.7±1.0 kcal/mol for CaS(c) + 2HCl(100 H_2O,aq) → $CaCl_2$(100 H_2O,aq) + H_2S(aq). We derive ΔHf°_{298}(CaS,c) = -112.7±2.0 kcal/mol and ΔHf°_{298}(CaS,c) = -112.3±2.0 kcal/mol respectively, based on the following auxiliary data: ΔHf°_{298}(HCl·100 H_2O,aq) = -39.657 kcal/mol (4), ΔHf°_{298}(H_2S,aq) = -9.5 kcal/mol (4), and ΔHf°_{298}($CaCl_2$·100 H_2O,aq) = -208.849 kcal/mol (5). Von Wartenberg measured $\Delta Hr_{293.15}$ = -20.6±0.4 kcal/mol for CaS(c) + 2HCl(30 H_2O,aq) → $CaCl_2$(30 H_2O,aq) + H_2S(g). We derive ΔHf°_{298}(CaS,c) = -113.9±0.6 kcal/mol based on the following auxiliary data: ΔHf°_{298}(HCl·30 H_2O,aq) = -39.357 kcal/mol (4), ΔHf°_{298}(H_2S,g) = -4.90 kcal/mol (4, 18), and ΔHf°_{298}($CaCl_2$·30 H_2O, aq) = -208.33 kcal/mol (5).

Our analyses of equilibrium and mass spectrometric studies are given below.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr_{298}/(kcal/mol) 2nd law	3rd law	ΔHf°_{298}[c] (CaS,c) kcal/mol
(6) Nikonov (1961)	Vap. Press.	A	1400 - 1700	Equation	-3.94	112.3	118.39±1.0	-88.9±30
(7) Filipovska (1975)	Equilibrium	B	1019 - 1704	15	1.06±0.1	15.6±0.1	14.14±0.5	-113.01±0.8
(8) Rosenquist (1951)	Equilibrium	B	1031 - 1698	12	1.01±0.2	15.4±0.3	14.02±0.5	-112.89±0.8
(9) Uno (1951)	Equilibrium	B	1173 - 1373	Equation	0.18	14.3	14.04±1.0	-112.91±1.0
(9) Uno (1951)	Equilibrium	C	926 - 1026	Equation	0.03	-23.02	-23.06±1.0	-113.31±2.0
(10) Schenck (1933)	Equilibrium	D	1124 - 1348	6	5.5±0.6	-51.2±0.8	-58.0±1.0	-111.98±2.0
(11) Zawadzki (1932)	Equilibrium	D	1173 - 1393	10	7.3±3.2	-76.3±4.2	-66.8±1.6	-103.2±4
(11) Zawadzki (1932)	Equilibrium	E	1173 - 1393	10	-0.95±5	254.06±6.5	255.2±1.9	-117.9±4
(12) Sander (1968)	Equilibrium	C	1400 - 1650	7	-2.8±0.3	17.3±0.5	22.3±0.5	-114.04±0.6
(13) Berkowitz (1963)	Mass Spec.	F	1709	1			212.5±10	-103.4±10
(14) Colin et al. (1964)	Mass Spec.	G	1849 - 2155	7	-11.8±2.0	-1.4±4.0	22.0±2.0	-116.3±8

[a] Reactions:
A) CaS(c) = CaS(g)
B) CaS(c) + H_2O(g) = CaO(c) + H_2S(g)
C) CaS(c) + 0.5SO_2(g) = CaO(c) + 0.5S_2(g)
D) CaS(c) + 2SO_2(g) = $CaSO_4$(c) + S_2(g)
E) CaS(c) + 3$CaSO_4$(c) = 4CaO(c) + 4SO_2(g)
F) CaS(c) = Ca(g) + S(g)
G) CaS(c) + 3S(g) = Ca(g) + 2S_2(g)

[b] $\delta S = \Delta S_{298}$(2nd law) - ΔS_{298}(3rd law)

[c] 3rd law ΔHr°_{298} is used to derive ΔHf°_{298}(CaS,c)

The calculated 3rd-law ΔHr°_{298} may have an uncertainty of 0.5 kcal/mol since the JANAF free energy functions are partially based on the estimated Cp°data (above 300 K). The results of the majority of the equilibrium studies, (7, 8, 9, 10, 11, 12), are in very good agreement with the heat of solution (1, 2, 3) studies within combined experimental errors. The mass spectrometric studies (13, 14) are not as reliable in condensed phase equilibrium as they are in gas phase equilibrium (18). A weighted average, ΔHf°_{298}(CaS,c) = -113.1±0.7 kcal/mol is adopted in the tabulation.

Heat Capacity and Entropy

Anderson (15) measured the low temperature heat capacities of CaS(c) from 58.1 - 294.9 K in an isothermal calorimeter. We have smoothed his Cp°data by a polynomial curve fitting technique and obtain S°_{298} = 13.5±0.3 gibbs/mol based on S°_{60} = 1.192 gibbs/mol. The value of S°_{60} is calculated from the combination of Debye and Einstein functions (θ_D=284 and θ_E=369). The Cp° values above 300 K are estimated by graphical extrapolation combined with a variant of method B of Kubaschewski et al. (16).

Melting Data

The melting point of CaS(c) is given as 2525°C (17).

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CaS

CALCIUM MONOSULFIDE (CaS) CaS

(IDEAL GAS) GFW=72.14

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.237	29.728	29.728	INFINITE
100	7.076	47.207	62.601	-1.539	30.028	25.987	-56.794
200	7.826	52.337	56.311	-0.795	29.837	22.003	-24.044
298	8.318	55.564	55.564	0.000	29.540	18.219	-13.355
300	8.325	55.615	55.564	0.015	29.533	18.148	-13.221
400	8.580	58.049	55.894	0.862	28.643	14.428	-7.883
500	8.721	59.980	56.525	1.728	27.924	10.954	-4.788
600	8.807	61.578	57.238	2.604	27.293	7.622	-2.776
700	8.869	62.941	57.958	3.488	26.724	4.389	-1.370
800	8.924	64.129	58.656	4.378	12.861	0.067	-0.018
900	8.992	65.183	59.324	5.273	12.465	-1.509	0.366
1000	9.097	66.136	59.958	6.177	12.020	-3.039	0.664
1100	9.257	67.010	60.560	7.095	11.533	-4.521	0.898
1200	9.489	67.825	61.132	8.031	9.226	-5.806	1.057
1300	9.801	68.596	61.677	8.995	9.015	-7.050	1.185
1400	10.192	69.336	62.197	9.994	8.836	-8.278	1.292
1500	10.651	70.055	62.697	11.036	8.696	-9.496	1.383
1600	11.163	70.758	63.179	12.126	8.600	-10.705	1.462
1700	11.704	71.451	63.646	13.269	8.554	-11.910	1.531
1800	12.252	72.136	64.098	14.467	-28.335	-12.433	1.510
1900	12.781	72.812	64.539	15.719	-28.057	-11.557	1.329
2000	13.270	73.481	64.969	17.022	-27.732	-10.697	1.169
2100	13.704	74.139	65.390	18.371	-27.366	-9.854	1.025
2200	14.069	74.785	65.803	19.760	-26.965	-9.029	0.897
2300	14.359	75.417	66.207	21.182	-26.536	-8.223	0.781
2400	14.574	76.033	66.604	22.630	-26.089	-7.437	0.677
2500	14.715	76.631	66.993	24.095	-25.632	-6.669	0.583
2600	14.789	77.210	67.375	25.571	-25.173	-5.920	0.498
2700	14.803	77.768	67.750	27.051	-24.721	-5.188	0.420
2800	14.766	78.306	68.117	28.529	-24.282	-4.472	0.349
2900	14.687	78.823	68.477	30.002	-23.862	-3.772	0.284
3000	14.574	79.319	68.831	31.466	-23.467	-3.086	0.225
3100	14.436	79.795	69.177	32.916	-23.103	-2.413	0.170
3200	14.279	80.251	69.516	34.352	-22.772	-1.751	0.120
3300	14.110	80.687	69.848	35.772	-22.479	-1.099	0.073
3400	13.934	81.106	70.173	37.174	-22.226	-0.455	0.029
3500	13.754	81.507	70.491	38.558	-22.016	0.182	-0.011
3600	13.575	81.892	70.802	39.925	-21.850	0.814	-0.049
3700	13.398	82.262	71.107	41.273	-21.731	1.442	-0.085
3800	13.226	82.617	71.405	42.604	-21.659	2.067	-0.119
3900	13.059	82.958	71.697	43.919	-21.635	2.690	-0.151
4000	12.900	83.287	71.983	45.216	-21.660	3.314	-0.181
4100	12.747	83.603	72.262	46.499	-21.732	3.940	-0.210
4200	12.603	83.909	72.536	47.766	-21.854	4.568	-0.238
4300	12.466	84.204	72.804	49.020	-22.025	5.198	-0.264
4400	12.338	84.489	73.066	50.260	-22.243	5.834	-0.290
4500	12.217	84.765	73.323	51.487	-22.510	6.475	-0.314
4600	12.103	85.032	73.575	52.703	-22.821	7.123	-0.338
4700	11.997	85.291	73.821	53.908	-23.178	7.778	-0.362
4800	11.897	85.543	74.063	55.103	-23.580	8.440	-0.384
4900	11.804	85.787	74.300	56.288	-24.024	9.111	-0.406
5000	11.718	86.025	74.532	57.464	-24.508	9.793	-0.428
5100	11.637	86.256	74.759	58.632	-25.032	10.485	-0.449
5200	11.562	86.481	74.983	59.792	-25.594	11.186	-0.470
5300	11.491	86.701	75.202	60.944	-26.192	11.899	-0.491
5400	11.426	86.915	75.417	62.090	-26.824	12.623	-0.511
5500	11.365	87.124	75.628	63.230	-27.486	13.360	-0.531
5600	11.309	87.328	75.835	64.363	-28.180	14.108	-0.551
5700	11.256	87.528	76.038	65.491	-28.900	14.871	-0.570
5800	11.207	87.723	76.238	66.614	-29.647	15.645	-0.590
5900	11.161	87.914	76.434	67.733	-30.417	16.433	-0.609
6000	11.119	88.102	76.627	68.847	-31.210	17.233	-0.628

Sept. 30, 1977

CALCIUM MONOSULFIDE (CaS) (IDEAL GAS) GFW = 72.14

D_0^o = 78.7 ± 2 kcal/mol
$S^o_{298.15}$ = 55.564 ± 0.10 gibbs/mol
Symmetry Number = 1

ΔHf_0^o = 29.73 ± 2.0 kcal/mol CaS
$\Delta Hf^o_{298.15}$ = 29.54 ±2.0 kcal/mol

Electronic and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, A°	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(3)	$X^1\Sigma^+$	0.0	1	2.3178	0.17667	0.000837	462.23	1.76
(4)	$^3\Pi$	[6800.]	6	[2.63]	[0.137]	[0.0006]	[330]	[1.5]
(4)	$^1\Pi$	[7200.]	2	[2.63]	[0.137]	[0.0006]	[330]	[1.5]
(3, 4)	$^3\Sigma^+$	[14000.]	3	[2.3864]	[0.16666]	[0.000605]	[409.04]	[0.818]
(3)	$A^1\Sigma^+$	15194.44	1	2.3864	0.16666	0.000605	409.04	0.818

Heat of Formation

The adopted value for the heat of formation, $\Delta Hf^o_{298}(CaS,g)$ = 29.54±2 kcal/mol, is based on the Knudsen mass spectrometric studies analyzed below. The two independent studies are in very good agreement and we have adopted the average value. Our value is intermediate between ΔHf^o_{298} = 32 kcal/mol obtained by NBS (5) and ΔHf^o_{298} = 27.9±5 kcal/mol obtained by Mills (6) in a recent critical compilation. Using auxiliary JANAF data (4) and a recommended value for $D_0^o(S_2,g)$ = 100.69±0.01 kcal/mol (4), we calculate $D_0^o(CaS,g)$ = 78.7±2 kcal/mol.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] Gibbs/mol	ΔHr^o_{298}/(kcal/mol) 2nd law	ΔHr^o_{298}/(kcal/mol) 3rd law	ΔHf^o_{298}[c] Kcal/mol	D_0^o Kcal/mol
(1) Colin (1964)	Mass Spec	A	2058-2319	9	2.83±3.5	28.36±7.5	22.32±1.6	29.72±1.7	78.6±2
(2) Marquart (1967)	Mass Spec	A	1709-1962	2	0.22	22.37	21.97±2	29.37±2	78.9±2

[a] Reactions: A) $Ca(g) + S_2(g) = CaS(g) + S(g)$

[b] $\delta S = \Delta S_{298}$(2nd law) - ΔS_{298}(3rd law)

[c] 3rd law ΔHr^o_{298} is used to derive $\Delta Hf^o_{298}(CaS,g)$

Heat Capacity and Entropy

Electronic levels (T_{oo}) and vibrational-rotational constants for the observed states are from the optical study of Blues and Barrow (3). Other low-lying electronic states and their vibrational-rotational constants are estimated in isoconfigurational groups by analogy with CaO (4) and from trends observed in the known states of the other alkaline-earth oxides and sulfides (4). Uncertainty in the energy and constants for the estimated states may contribute as much as 2-3 gibbs/mol to S° at 3000 K. The molecular constants have been corrected to the natural isotopic abundances. The thermodynamic functions are calculated using first order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\varepsilon_i/T)$.

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CaS

DEUTERIUM CHLORIDE (DCL) CLD
(IDEAL GAS) GFW=37.4671

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.070	-22.259	-22.259	INFINITE
100	6.958	38.436	52.231	-1.379	-22.245	-22.485	49.139
200	6.961	43.259	46.677	-0.684	-22.265	-22.718	24.825
298	6.972	46.040	46.040	0.000	-22.310	-22.932	16.809
300	6.972	46.083	46.040	0.013	-22.311	-22.936	16.708
400	7.028	48.095	46.314	0.712	-22.376	-23.134	12.640
500	7.149	49.675	46.834	1.421	-22.444	-23.316	10.191
600	7.316	50.993	47.420	2.144	-22.508	-23.484	8.554
700	7.501	52.135	48.014	2.885	-22.562	-23.643	7.381
800	7.682	53.148	48.593	3.644	-22.607	-23.794	6.500
900	7.850	54.063	49.151	4.420	-22.644	-23.940	5.813
1000	7.999	54.898	49.685	5.213	-22.672	-24.083	5.263
1100	8.130	55.666	50.194	6.020	-22.696	-24.223	4.813
1200	8.244	56.379	50.680	6.838	-22.715	-24.361	4.437
1300	8.343	57.043	51.144	7.668	-22.732	-24.497	4.118
1400	8.429	57.664	51.588	8.507	-22.745	-24.632	3.845
1500	8.504	58.248	52.013	9.353	-22.758	-24.767	3.609
1600	8.570	58.799	52.420	10.207	-22.769	-24.900	3.401
1700	8.628	59.320	52.810	11.067	-22.780	-25.032	3.218
1800	8.680	59.815	53.186	11.932	-22.791	-25.165	3.055
1900	8.727	60.286	53.547	12.803	-22.801	-25.296	2.910
2000	8.768	60.734	53.896	13.678	-22.811	-25.427	2.779
2100	8.806	61.163	54.232	14.556	-22.822	-25.559	2.660
2200	8.841	61.574	54.556	15.439	-22.833	-25.689	2.552
2300	8.872	61.967	54.870	16.324	-22.845	-25.818	2.453
2400	8.901	62.346	55.173	17.213	-22.857	-25.946	2.363
2500	8.928	62.709	55.468	18.105	-22.871	-26.075	2.279
2600	8.953	63.060	55.753	18.999	-22.885	-26.203	2.203
2700	8.976	63.398	56.030	19.895	-22.901	-26.330	2.131
2800	8.998	63.725	56.299	20.794	-22.918	-26.456	2.065
2900	9.019	64.041	56.560	21.695	-22.937	-26.583	2.003
3000	9.039	64.348	56.815	22.598	-22.957	-26.709	1.946
3100	9.058	64.644	57.063	23.503	-22.978	-26.834	1.892
3200	9.075	64.932	57.304	24.409	-23.002	-26.958	1.841
3300	9.092	65.212	57.540	25.318	-23.027	-27.081	1.793
3400	9.109	65.483	57.769	26.228	-23.053	-27.202	1.749
3500	9.125	65.748	57.993	27.139	-23.082	-27.325	1.706
3600	9.140	66.005	58.212	28.053	-23.112	-27.445	1.666
3700	9.154	66.255	58.426	28.967	-23.144	-27.565	1.628
3800	9.169	66.500	58.636	29.883	-23.178	-27.685	1.592
3900	9.183	66.738	58.840	30.801	-23.213	-27.802	1.558
4000	9.196	66.971	59.041	31.720	-23.251	-27.920	1.525
4100	9.209	67.198	59.237	32.640	-23.289	-28.036	1.494
4200	9.222	67.420	59.429	33.562	-23.329	-28.152	1.465
4300	9.235	67.637	59.617	34.485	-23.370	-28.267	1.437
4400	9.247	67.850	59.802	35.409	-23.413	-28.378	1.410
4500	9.259	68.058	59.983	36.334	-23.457	-28.492	1.384
4600	9.271	68.261	60.161	37.261	-23.502	-28.603	1.359
4700	9.283	68.461	60.336	38.188	-23.548	-28.713	1.335
4800	9.294	68.656	60.507	39.117	-23.595	-28.823	1.312
4900	9.306	68.848	60.675	40.047	-23.643	-28.931	1.290
5000	9.317	69.036	60.840	40.978	-23.691	-29.039	1.269
5100	9.328	69.221	61.003	41.910	-23.740	-29.144	1.249
5200	9.339	69.402	61.163	42.844	-23.789	-29.249	1.229
5300	9.350	69.580	61.320	43.778	-23.839	-29.355	1.210
5400	9.360	69.755	61.475	44.714	-23.889	-29.459	1.192
5500	9.371	69.927	61.627	45.650	-23.939	-29.560	1.175
5600	9.382	70.096	61.776	46.588	-23.989	-29.663	1.158
5700	9.392	70.262	61.924	47.527	-24.039	-29.766	1.141
5800	9.402	70.425	62.069	48.466	-24.089	-29.863	1.125
5900	9.413	70.586	62.212	49.407	-24.138	-29.964	1.110
6000	9.423	70.744	62.353	50.349	-24.187	-30.061	1.095

July 31, 1972 (NBS); June 30, 1977

DEUTERIUM CHLORIDE (DCl) (IDEAL GAS) GFW = 37.4671

D_0° = 103.38 ± 0.05 kcal/mol
$S^\circ_{298.15}$ = 46.04 gibbs/mol
Symmetry Number = 1

ΔHf_0° = -22.26 ± 0.05 kcal/mol CLD
$\Delta Hf^\circ_{298.15}$ = -22.31 ± 0.05 kcal/mol

Electronic States and Molecular Constants

State	ε_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0	1	2144.0	26.90	5.4444	0.1121	1.2746
$B^1\Pi$	75160	2	2199.0	[26.9]	5.1793	[0.1121]	
$V^1\Sigma^+$	76520	1	684.6	[26.9]	1.555	[0.1121]	2.43
$C^1\Pi$	77525	2	2114.1	[26.9]	4.9605	[0.1121]	

Heat of Formation (Provisional-evaluation incomplete)

The heat of formation was calculated from the selected value of ΔHf°_{298} of HCl(g) given by JANAF (1), the appropriate *thermal functions (see H_2, D_2, DCl tables, and HCl (1)) and zero point energies. The zero point energies of H_2(g) and D_2(g)* are taken from Herzberg and Monfile (2). The zero point energies of HCl(g) and DCl(g), including the Dunham correction, were calculated from the molecular constants taken from Rosen (3).

Heat Capacity and Entropy

The vibrational and rotational constants at the respective electronic levels were taken from Rosen (3) and were adjusted to Cl^{35} = 75.4% and Cl^{37} = 24.6%.

The National Bureau of Standards prepared this table (4) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (4), we recalculate the table in terms of 1973 fundamental constants (5), 1975 atomic weights (6), and current JANAF reference states for the elements.

References

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CLD

CHLORINE MONOFLUORIDE (ClF)

(IDEAL GAS) GFW=54.4514

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.129	-11.998	-11.998	INFINITE
100	6.961	44.227	58.567	-1.434	-11.998	-12.128	26.506
200	7.200	49.101	52.748	-0.730	-12.007	-12.257	13.393
298	7.668	52.062	52.062	0.000	-12.020	-12.377	9.072
300	7.676	52.110	52.062	0.014	-12.020	-12.379	9.018
400	8.067	54.375	52.369	0.802	-12.032	-12.497	6.828
500	8.333	56.205	52.959	1.623	-12.039	-12.612	5.512
600	8.513	57.742	53.631	2.466	-12.046	-12.726	4.635
700	8.638	59.064	54.315	3.324	-12.051	-12.839	4.008
800	8.729	60.224	54.983	4.193	-12.056	-12.951	3.538
900	8.797	61.256	55.623	5.069	-12.060	-13.062	3.172
1000	8.850	62.186	56.234	5.952	-12.065	-13.174	2.879
1100	8.893	63.031	56.814	6.839	-12.069	-13.285	2.639
1200	8.929	63.807	57.365	7.730	-12.073	-13.395	2.440
1300	8.960	64.523	57.888	8.625	-12.077	-13.505	2.270
1400	8.986	65.188	58.386	9.522	-12.082	-13.615	2.125
1500	9.010	65.808	58.860	10.422	-12.087	-13.724	2.000
1600	9.032	66.391	59.313	11.324	-12.092	-13.833	1.890
1700	9.052	66.939	59.746	12.228	-12.096	-13.941	1.792
1800	9.072	67.457	60.160	13.134	-12.101	-14.050	1.706
1900	9.092	67.948	60.557	14.042	-12.106	-14.157	1.628
2000	9.114	68.415	60.938	14.953	-12.111	-14.266	1.559
2100	9.138	68.860	61.305	15.865	-12.115	-14.374	1.496
2200	9.167	69.286	61.658	16.780	-12.119	-14.481	1.439
2300	9.202	69.694	61.999	17.699	-12.122	-14.588	1.386
2400	9.245	70.086	62.327	18.621	-12.122	-14.695	1.338
2500	9.299	70.465	62.645	19.548	-12.120	-14.802	1.294
2600	9.366	70.831	62.953	20.481	-12.113	-14.909	1.253
2700	9.449	71.186	63.252	21.422	-12.102	-15.017	1.216
2800	9.550	71.531	63.541	22.372	-12.083	-15.125	1.181
2900	9.672	71.868	63.823	23.333	-12.055	-15.235	1.148
3000	9.818	72.199	64.096	24.307	-12.017	-15.346	1.118
3100	9.989	72.523	64.363	25.297	-11.964	-15.457	1.090
3200	10.189	72.843	64.623	26.306	-11.896	-15.571	1.063
3300	10.417	73.160	64.877	27.336	-11.809	-15.687	1.039
3400	10.677	73.475	65.125	28.390	-11.699	-15.805	1.016
3500	10.969	73.789	65.368	29.472	-11.564	-15.929	0.995
3600	11.293	74.102	65.606	30.585	-11.400	-16.055	0.975
3700	11.650	74.417	65.840	31.732	-11.205	-16.187	0.956
3800	12.037	74.732	66.070	32.916	-10.974	-16.326	0.939
3900	12.456	75.050	66.296	34.141	-10.705	-16.469	0.923
4000	12.902	75.371	66.519	35.408	-10.395	-16.621	0.908
4100	13.375	75.696	66.739	36.722	-10.041	-16.782	0.895
4200	13.870	76.024	66.956	38.084	-9.640	-16.951	0.882
4300	14.384	76.356	67.171	39.457	-9.190	-17.131	0.871
4400	14.914	76.693	67.383	40.961	-8.690	-17.319	0.860
4500	15.454	77.034	67.594	42.480	-8.138	-17.523	0.851
4600	15.999	77.380	67.803	44.052	-7.532	-17.738	0.843
4700	16.546	77.730	68.011	45.680	-6.873	-17.966	0.835
4800	17.088	78.084	68.217	47.361	-6.162	-18.211	0.829
4900	17.621	78.442	68.422	49.097	-5.398	-18.468	0.824
5000	18.139	78.803	68.626	50.885	-4.582	-18.744	0.819
5100	18.639	79.167	68.829	52.724	-3.715	-19.034	0.816
5200	19.115	79.533	69.031	54.612	-2.802	-19.343	0.813
5300	19.565	79.902	69.233	56.546	-1.843	-19.672	0.811
5400	19.984	80.272	69.434	58.524	-0.842	-20.017	0.810
5500	20.370	80.642	69.634	60.542	0.199	-20.381	0.810
5600	20.720	81.012	69.834	62.597	1.276	-20.766	0.810
5700	21.034	81.382	70.033	64.685	2.385	-21.171	0.812
5800	21.311	81.750	70.232	66.802	3.524	-21.592	0.814
5900	21.549	82.116	70.431	68.946	4.687	-22.036	0.816
6000	21.749	82.480	70.628	71.111	5.870	-22.498	0.819

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965;
July 31, 1972 (NBS); June 30, 1977

CHLORINE MONOFLUORIDE (ClF) (IDEAL GAS) GFW = 54.4514

D°_0 = 58.98 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 52.062 gibbs/mol

Symmetry Number = 1

ΔHf°_0 = -12.00 ± 0.1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -12.02 ± 0.1 kcal/mol

Electronic States and Molecular Constants

State	ε_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0	1	784.49	6.201	0.51409	0.004329	1.6281
$A^3\Pi_0$	18721	6	312.74	2.207	0.37026	0.01390	1.92

Heat of Formation

The selected value, ΔHf°_{298}(ClF) = -12.02±0.1 kcal/mol, is based on spectroscopic data. Three studies of the visible absorption bands of ClF, by Wahrhaftig (1), by Schmitz and Schumacher (2), and by Stricker (3) agree in indicating a band convergence limit at 21,514±10 cm^{-1}. Assignment of this limit to Cl($^2P_{1/2}$) + F($^2P_{3/2}$) is supported by the dissociative ionization threshold for ClF reported by Dibeler et al. (4) whose ion-pair threshold, when reassigned to a hot band, corroborates this choice. From this assignment it follows that D°_0(ClF) = 58.98±0.02 kcal/mol.

Combining this value with $D^\circ_0(F_2)$ = 36.7±0.2 kcal/mol, reported by Berkowitz et al. (5), and with $D^\circ_0(Cl_2)$ = 57.177±0.006 kcal/mol, given by Douglas et al. (6), one obtains ΔHf°_0(ClF) = -12.0±0.1 kcal/mol.

Calorimetric values for ΔHf°_{298}, which bracket the selected value, are as follows: -11.6 kcal/mol, Wicke (7); -11.7 kcal/mol, Wicke and Friz (8); -14.34 and -15.0 kcal/mol, Schmitz and Schumacher (9); and -14.4±0.8 kcal/mol, Nuttall and Armstrong (10).

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels are taken from Rosen (11) and are adjusted to Cl^{35} = 75.4% and Cl^{37} = 24.6%. The value of α_e listed for the ground state by Rosen (11) has been divided by 10 to agree with the original data (12). The National Bureau of Standards prepared this table (13) by critical analysis of data existing in 1972 but used the incorrect value (11) for α_e of the ground state. Using the correct molecular constants and ΔHf° selected by NBS (13), we recalculate the table in terms of 1973 fundamental constants (14), 1975 atomic weights (15), and current JANAF reference states for the elements. The thermodynamic functions of this table may be biased at temperatures above about 3000 K due to the neglect of rotational cut-off.

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SULFUR CHLORIDE PENTAFLUORIDE ClF_5S
(IDEAL GAS) GFW=162.50502

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-4.411	-245.288	-245.288	INFINITE
100	10.148	58.261	93.974	-3.571	-246.697	-239.793	524.060
200	18.415	67.780	78.529	-2.150	-247.782	-232.421	253.975
298	24.938	76.439	76.439	0.000	-248.300	-224.754	164.747
300	25.036	76.593	76.439	0.046	-248.306	-224.608	163.625
400	29.168	84.411	77.477	2.773	-249.017	-216.653	118.372
500	31.701	91.214	79.560	5.827	-249.339	-208.524	91.145
600	33.305	97.146	82.008	9.083	-249.448	-200.348	72.976
700	34.367	102.365	84.551	12.470	-249.420	-192.165	59.996
800	35.099	107.005	87.073	15.946	-262.302	-185.192	50.592
900	35.621	111.171	89.523	19.483	-261.827	-175.579	42.636
1000	36.006	114.944	91.879	23.065	-261.335	-166.024	36.284
1100	36.296	118.390	94.135	26.681	-260.830	-156.517	31.097
1200	36.521	121.559	96.290	30.322	-260.317	-147.057	26.782
1300	36.698	124.489	98.348	33.984	-259.799	-137.638	23.139
1400	36.840	127.214	100.314	37.661	-259.282	-128.262	20.022
1500	36.955	129.760	102.193	41.351	-258.765	-118.921	17.327
1600	37.050	132.148	103.991	45.051	-258.249	-109.616	14.973
1700	37.129	134.397	105.714	48.760	-257.734	-100.339	12.899
1800	37.196	136.521	107.367	52.477	-257.226	-91.098	11.061
1900	37.253	138.534	108.955	56.199	-256.717	-81.879	9.418
2000	37.301	140.446	110.482	59.927	-256.217	-72.693	7.943
2100	37.343	142.267	111.953	63.659	-255.718	-63.528	6.611
2200	37.379	144.005	113.370	67.395	-255.225	-54.388	5.403
2300	37.411	145.667	114.739	71.135	-254.738	-45.270	4.302
2400	37.439	147.260	116.061	74.877	-254.254	-36.173	3.294
2500	37.464	148.789	117.340	78.623	-253.775	-27.096	2.369
2600	37.486	150.258	118.578	82.370	-253.301	-18.037	1.516
2700	37.505	151.674	119.777	86.120	-252.834	-8.998	0.728
2800	37.523	153.038	120.941	89.871	-252.372	0.025	-0.002
2900	37.538	154.355	122.071	93.624	-251.914	9.031	-0.681
3000	37.553	155.628	123.168	97.379	-251.464	18.018	-1.313
3100	37.566	156.859	124.235	101.135	-251.016	26.957	-1.903
3200	37.577	158.052	125.273	104.892	-250.576	35.956	-2.456
3300	37.588	159.209	126.284	108.650	-250.141	44.905	-2.974
3400	37.598	160.331	127.269	112.409	-249.711	53.840	-3.461
3500	37.607	161.421	128.229	116.169	-249.288	62.759	-3.919
3600	37.615	162.480	129.166	119.931	-248.869	71.670	-4.351
3700	37.622	163.511	130.081	123.692	-248.457	80.568	-4.759
3800	37.629	164.514	130.974	127.455	-248.048	89.455	-5.145
3900	37.636	165.492	131.846	131.218	-247.646	98.333	-5.510
4000	37.642	166.445	132.699	134.982	-247.251	107.198	-5.857
4100	37.647	167.374	133.534	138.747	-246.860	116.054	-6.186
4200	37.652	168.282	134.350	142.512	-246.475	124.901	-6.499
4300	37.657	169.168	135.150	146.277	-246.096	133.739	-6.797
4400	37.662	170.034	135.933	150.043	-245.722	142.569	-7.081
4500	37.666	170.880	136.700	153.809	-245.355	151.387	-7.352
4600	37.670	171.708	137.452	157.576	-244.991	160.201	-7.611
4700	37.673	172.518	138.190	161.343	-244.633	169.007	-7.859
4800	37.677	173.311	138.913	165.111	-244.284	177.801	-8.095
4900	37.680	174.088	139.623	168.879	-243.936	186.594	-8.322
5000	37.683	174.849	140.320	172.647	-243.596	195.374	-8.540
5100	37.686	175.596	141.004	176.415	-243.258	204.154	-8.748
5200	37.688	176.327	141.677	180.184	-242.930	212.922	-8.949
5300	37.691	177.045	142.337	183.953	-242.606	221.685	-9.141
5400	37.693	177.750	142.986	187.722	-242.287	230.441	-9.326
5500	37.696	178.442	143.625	191.491	-241.972	239.195	-9.505
5600	37.698	179.121	144.253	195.261	-241.665	247.939	-9.676
5700	37.700	179.788	144.870	199.031	-241.362	256.678	-9.841
5800	37.702	180.444	145.478	202.801	-241.063	265.415	-10.001
5900	37.704	181.088	146.076	206.571	-240.772	274.145	-10.155
6000	37.705	181.722	146.665	210.342	-240.487	282.869	-10.303

Dec. 31, 1977

SULFUR CHLORIDE PENTAFLUORIDE ($ClSF_5$) (IDEAL GAS) GFW = 162.50502

ΔHa_0° = 431.8 ± 4.5 kcal/mol
$S_{298.15}^\circ$ = 76.4 ± 0.3 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf_0° = -245.2 ± 2.5 kcal/mol
$\Delta Hf_{298.15}^\circ$ = -248.3 ± 2.5 kcal/mol

ClF_5S

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
855(1)	625(1)	579(2)
707(1)	[332](1)	441(2)
602(1)	505(1)	287(2)
402(1)	909(2)	

Point Group = C_{4v} σ = 4
Bond Distances: S-F* = 1.566 ± 0.003 Å S-F** = 1.588 ± 0.009 Å
S-Cl = 2.047 ± 0.003 Å
Bond Angles: Cl-S-F* = 90.7 ± 0.2° F*-S-F* = 90°
(* - equatorial ** - axial)
Product of Moments of Inertia: $I_AI_BI_C = 6.6573 \times 10^{-113}$ g^3 cm^6

Heat of Formation

Leach and Roberts (1) have reported calorimetric measurements on the heat of hydrolysis of liquid sulfur chloride pentafluoride in aqueous caustic. Reevaluation of their data using more recent auxiliary heats of formation (2) for aqueous NaOH, Na_2SO_4, NaCl, and NaF leads to $\Delta Hf_{298}^\circ(ClSF_5,\ell)$ = -252.9±2.0 kcal/mol. The adopted value for the gas is obtained from that for the liquid by addition of the heat of vaporization at 298.15 K. We estimate a value for ΔHv_{298}° equal to 4.6±0.5 kcal/mol from ΔHv = 5.19 kcal/mol reported by Griffiths (3) from an analysis of vapor pressure data. We assume that the reported ΔHv value refers to a boiling temperature of 251.85 K, and we estimate the ΔCp° of vaporization as -12 gibbs/mol. Earlier vapor pressure measurements (4) lead to a lower value (3.9 kcal/mol) for ΔHv_{298}°; however, we believe the earlier vapor pressure data are less reliable than the measurements of Griffiths (3).

Electron-impact studies by Harland and Thynne (5) on SF_6 and $ClSF_5$ have provided information on the appearance potentials (AP) for the formation of SF_5^+ and SF_5^- from these neutral molecules. Our analysis of their AP data (5) leads to ΔHf° values which are more than 15 kcal/mol different than the adopted result.

The heat of atomization (ΔHa_0°) and S-Cl bond dissociation energy are calculated to be 431.8±4.5 kcal/mol and 59.6±6.0 kcal/mol, respectively. The latter value appears reasonable when compared with the mean value for the S-Cl bond strength in SCl_2 (63.8 kcal/mol).

Heat Capacity and Entropy

The structural parameters are taken from a study by Marsden and Bartell (6) who established the C_{4v} *structure of* $ClSF_5$ *by a* simultaneous least-squares analysis of electron diffraction and microwave spectroscopic data. The microwave data were based on the measurements of Kewley et al. (7). We use r_g distances to calculate the principal moments of inertia of $I_A = 3.0943 \times 10^{-38}$ and $I_B = I_C = 4.6384 \times 10^{-38}$ g cm^2.

The vibrational spectrum of $ClSF_5$ has been studied using various spectroscopic techniques (3, 8, 9). The observed vibrational frequencies show good agreement, but conflicting assignments have been reported. Griffiths (3) has argued that the fundamentals assigned as ν_6 = 396 cm^{-1} and ν_{11} = 270 cm^{-1} by Cross et al. (8) should be reversed. A recent Raman study (9) of $ClSF_5$ isolated in an argon matrix has identified the band at 395 cm^{-1} as the Cl component of the S-Cl stretching frequency (ν_4). A comparison of the vibrational spectra of $ClSF_5$ and $ClSeF_5$ (10) and results from two force field studies (6, 11) suggest that the low-frequency SF_5 bending mode (ν_{11}) should lie in the range 270-290 cm^{-1}. We adopt ν_{11} = 287 cm^{-1} which was observed in the gas phase infrared spectra by Griffiths (3). As suggested by others (10, 11), we believe that the SF_2 out-of-plane deformation (ν_6) has not been resolved, and we use an estimated value (332 cm^{-1}) calculated from a general valency-force field (11). An independent force-field calculation (6) supports this value (ν_6 = 317 cm^{-1}). All other fundamentals are rounded values taken from the gas phase infrared and liquid phase Raman study of Griffiths (3).

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ClF_5S

CHLOROSILANE (SIH$_3$CL) CLH$_3$SI

(IDEAL GAS) GFW=66.5627

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.734	-31.732	-31.732	INFINITE
100	8.021	49.639	69.025	-1.939	-32.487	-31.444	68.720
200	9.646	55.576	60.940	-1.073	-33.170	-30.156	32.953
298	12.212	59.906	59.906	0.000	-33.900	-28.519	20.905
300	12.259	59.982	59.907	0.023	-33.913	-28.486	20.752
400	14.498	63.828	60.416	1.365	-34.534	-26.579	14.522
500	16.260	67.260	61.448	2.906	-35.012	-24.532	10.723
600	17.688	70.355	62.679	4.606	-35.365	-22.402	8.160
700	18.872	73.173	63.979	6.436	-35.612	-20.219	6.313
800	19.859	75.760	65.293	8.374	-35.776	-18.010	4.920
900	20.683	78.148	66.590	10.402	-35.872	-15.781	3.832
1000	21.370	80.364	67.858	12.506	-35.917	-13.547	2.961
1100	21.943	82.428	69.090	14.672	-35.923	-11.309	2.247
1200	22.422	84.359	70.283	16.891	-35.900	-9.072	1.652
1300	22.826	86.170	71.436	19.154	-35.859	-6.839	1.150
1400	23.166	87.874	72.550	21.454	-35.807	-4.608	0.719
1500	23.456	89.483	73.625	23.786	-35.752	-2.380	0.347
1600	23.703	91.004	74.664	26.144	-35.700	-0.159	0.022
1700	23.915	92.448	75.668	28.525	-47.642	2.169	-0.279
1800	24.098	93.820	76.639	30.926	-47.542	5.095	-0.619
1900	24.258	95.128	77.578	33.344	-47.439	8.017	-0.922
2000	24.397	96.375	78.487	35.777	-47.336	10.934	-1.195
2100	24.519	97.569	79.367	38.223	-47.234	13.844	-1.441
2200	24.626	98.712	80.221	40.680	-47.133	16.750	-1.664
2300	24.721	99.809	81.049	43.148	-47.034	19.652	-1.867
2400	24.806	100.863	81.853	45.624	-46.938	22.552	-2.054
2500	24.881	101.877	82.633	48.108	-46.849	25.441	-2.224
2600	24.949	102.854	83.392	50.600	-46.759	28.334	-2.382
2700	25.010	103.797	84.131	53.098	-46.676	31.218	-2.527
2800	25.065	104.707	84.849	55.602	-46.597	34.102	-2.662
2900	25.114	105.588	85.549	58.111	-46.522	36.986	-2.787
3000	25.159	106.440	86.232	60.625	-46.452	39.860	-2.904
3100	25.200	107.266	86.897	63.143	-46.385	42.735	-3.013
3200	25.238	108.066	87.546	65.664	-46.326	45.611	-3.115
3300	25.272	108.843	88.180	68.190	-46.271	48.486	-3.211
3400	25.303	109.598	88.799	70.719	-46.220	51.354	-3.301
3500	25.332	110.332	89.403	73.251	-46.177	54.223	-3.386
3600	25.359	111.046	89.995	75.785	-138.100	59.349	-3.603
3700	25.383	111.741	90.573	78.322	-137.970	64.833	-3.830
3800	25.406	112.419	91.139	80.862	-137.844	70.312	-4.044
3900	25.427	113.079	91.693	83.403	-137.727	75.788	-4.247
4000	25.447	113.723	92.236	85.947	-137.615	81.262	-4.440
4100	25.465	114.351	92.768	88.493	-137.509	86.729	-4.623
4200	25.482	114.965	93.289	91.040	-137.409	92.198	-4.798
4300	25.498	115.565	93.800	93.589	-137.314	97.662	-4.964
4400	25.512	116.151	94.301	96.139	-137.226	103.125	-5.122
4500	25.526	116.725	94.793	98.691	-137.143	108.587	-5.274
4600	25.539	117.286	95.276	101.245	-137.064	114.050	-5.419
4700	25.551	117.835	95.750	103.799	-136.993	119.510	-5.557
4800	25.563	118.373	96.216	106.355	-136.925	124.964	-5.690
4900	25.573	118.901	96.674	108.912	-136.862	130.423	-5.817
5000	25.583	119.417	97.123	111.469	-136.804	135.869	-5.939
5100	25.593	119.924	97.566	114.028	-136.751	141.331	-6.056
5200	25.602	120.421	98.000	116.588	-136.702	146.780	-6.169
5300	25.611	120.909	98.428	119.149	-136.658	152.235	-6.278
5400	25.619	121.388	98.849	121.710	-136.620	157.679	-6.382
5500	25.626	121.858	99.263	124.272	-136.586	163.129	-6.482
5600	25.633	122.320	99.670	126.835	-136.557	168.578	-6.579
5700	25.640	122.773	100.072	129.399	-136.532	174.030	-6.673
5800	25.647	123.219	100.467	131.963	-136.514	179.477	-6.763
5900	25.653	123.658	100.856	134.528	-136.499	184.922	-6.850
6000	25.659	124.089	101.240	137.094	-136.488	190.367	-6.934

Dec. 31, 1960; Dec. 31, 1976

CHLOROSILANE (SiH$_3$Cl) (IDEAL GAS) GFW = 66.5627

Point Group C_{3v}
$S°_{298.15}$ = 59.91 ± 0.05 gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = [-31.7 ± 2] kcal/mol CLH$_3$SI
$\Delta Hf°_{298.15}$ = [-33.9 ± 2] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2201 (1)	2211 (2)
945 (1)	952 (2)
551 (1)	663 (2)

Bond Distances: Si-H = 1.486±0.008 Å Si-Cl = 2.049 Å σ = 3
Bond Angles: H-Si-H = 110.42°±0.5° H-Si-Cl = 108.5°±0.5°
Product of the Moments of Inertia: $I_AI_BI_C = 1.60126 \times 10^{-115}$ g^{3}cm^6

Heat of Formation

$\Delta Hf°_{298}$ is estimated from values for SiCl$_4$, SiHCl$_3$ and SiH$_4$ (1). Data for SiHCl$_3$ (1) suggest that ΔHf° shows minor deviations from linearity in the chlorosilanes. We assume that ΔHf° has a cubic variation with a constant third difference of -1.5 kcal/mol. ΔHf° values of the chloromethanes yield an almost constant third difference of about -2.5 kcal/mol (2, 3, 1). This approximation corresponds to Allen's bond additivity scheme involving near-neighbor interactions taken two and three at a time (2). Our adopted ΔHf° is 0.4 kcal/mol more negative than that estimated by linear interpolation between SiCl$_4$ and SiH$_4$.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley et al. (4) for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structures obtained by various methods (5). The principal moments of inertia are $I_A = 0.9970 \times 10^{-39}$ and $I_B = I_C = 12.6729 \times 10^{-39}$ g cm^2.

Shimanouchi (6) selected vibrational frequencies from gas-phase infrared spectra of SiH$_3$X (X=F,Cl,Br) observed by Newman et al. (7). These authors' assignments for SiH$_3$F and SiH$_3$Br have been modified slightly by new data (1) obtained at higher resolution. Unpublished gas-phase frequencies of SiH$_3$X from the thesis of Robiette were quoted by Ball et al. (8). These are more consistent with the new data for SiH$_3$F and SiH$_3$Br, so we adopt them for SiH$_3$Cl. Monfils also obtained partially resolved spectra of SiH$_3$Cl; his final paper (9) is not available to us.

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH$_3$Cl (10). Electronic absorption bands of SiH$_3$Cl were observed at ≥67000 cm^{-1} (11) and the absorption maximum in the lowest transition was estimated to be at ~62000 cm^{-1} (12). Contributions of these high-lying states would be negligible.

References

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NICKEL MONOCHLORIDE (NiCl) CLNI
(IDEAL GAS) GFW=94.153

T, K	gibbs/mol Cp°	S°	$-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.262	43.479	43.479	INFINITE
100	7.133	51.692	67.329	-1.564	43.708	40.974	-89.548
200	7.956	56.894	60.936	-0.808	43.649	38.250	-41.797
298	8.471	60.176	60.176	0.000	43.500	35.631	-26.118
300	8.479	60.228	60.176	0.016	43.497	35.583	-25.922
400	8.835	62.718	60.513	0.882	43.296	32.973	-18.015
500	9.115	64.721	61.161	1.780	43.058	30.420	-13.296
600	9.327	66.403	61.898	2.703	42.763	27.919	-10.169
700	9.475	67.852	62.647	3.643	42.471	25.471	-7.952
800	9.572	69.124	63.379	4.596	42.243	23.057	-6.299
900	9.630	70.255	64.081	5.556	42.010	20.673	-5.020
1000	9.662	71.272	64.750	6.521	41.766	18.315	-4.003
1100	9.679	72.194	65.386	7.488	41.505	15.982	-3.175
1200	9.689	73.036	65.989	8.457	41.228	13.673	-2.490
1300	9.700	73.812	66.561	9.426	40.932	11.390	-1.915
1400	9.715	74.531	67.105	10.397	40.615	9.129	-1.425
1500	9.738	75.202	67.623	11.369	40.277	6.891	-1.004
1600	9.772	75.832	68.116	12.345	39.920	4.677	-0.639
1700	9.817	76.426	68.588	13.324	39.541	2.486	-0.320
1800	9.875	76.988	69.039	14.309	35.044	0.489	-0.059
1900	9.944	77.524	69.472	15.300	34.649	-1.419	0.163
2000	10.025	78.036	69.887	16.298	34.259	-3.308	0.361
2100	10.116	78.527	70.287	17.305	33.879	-5.177	0.539
2200	10.215	79.000	70.672	18.321	33.506	-7.028	0.698
2300	10.321	79.457	71.044	19.348	33.144	-8.862	0.842
2400	10.433	79.898	71.404	20.386	32.791	-10.680	0.973
2500	10.548	80.326	71.753	21.435	32.448	-12.485	1.091
2600	10.666	80.742	72.090	22.495	32.116	-14.275	1.200
2700	10.785	81.147	72.418	23.568	31.795	-16.054	1.299
2800	10.903	81.542	72.737	24.652	31.483	-17.820	1.391
2900	11.020	81.926	73.047	25.749	31.183	-19.576	1.475
3000	11.134	82.302	73.350	26.856	30.893	-21.322	1.553
3100	11.244	82.669	73.644	27.975	30.612	-23.057	1.626
3200	11.351	83.027	73.932	29.105	-59.725	-23.627	1.614
3300	11.452	83.378	74.213	30.245	-59.592	-22.501	1.490
3400	11.548	83.722	74.488	31.395	-59.451	-21.379	1.374
3500	11.639	84.058	74.756	32.555	-59.302	-20.263	1.265
3600	11.724	84.387	75.019	33.723	-59.145	-19.148	1.162
3700	11.803	84.709	75.277	34.899	-58.982	-18.039	1.066
3800	11.876	85.025	75.529	36.083	-58.813	-16.936	0.974
3900	11.944	85.334	75.777	37.274	-58.639	-15.835	0.887
4000	12.006	85.637	76.019	38.472	-58.462	-14.740	0.805
4100	12.062	85.934	76.258	39.675	-58.280	-13.650	0.728
4200	12.114	86.226	76.491	40.884	-58.096	-12.564	0.654
4300	12.160	86.511	76.721	42.098	-57.910	-11.482	0.584
4400	12.202	86.791	76.947	43.316	-57.722	-10.403	0.517
4500	12.239	87.066	77.169	44.538	-57.534	-9.331	0.453
4600	12.272	87.335	77.387	45.764	-57.345	-8.262	0.393
4700	12.301	87.600	77.601	46.992	-57.158	-7.197	0.335
4800	12.327	87.859	77.812	48.224	-56.971	-6.136	0.279
4900	12.350	88.113	78.020	49.458	-56.786	-5.078	0.226
5000	12.370	88.363	78.224	50.694	-56.603	-4.025	0.176
5100	12.387	88.608	78.425	51.932	-56.422	-2.974	0.127
5200	12.401	88.849	78.624	53.171	-56.245	-1.927	0.081
5300	12.414	89.085	78.819	54.412	-56.073	-0.886	0.037
5400	12.424	89.317	79.011	55.654	-55.904	0.154	-0.006
5500	12.433	89.545	79.200	56.897	-55.741	1.191	-0.047
5600	12.440	89.769	79.387	58.140	-55.583	2.224	-0.087
5700	12.445	89.990	79.571	59.384	-55.432	3.253	-0.125
5800	12.450	90.206	79.753	60.629	-55.285	4.284	-0.161
5900	12.453	90.419	79.932	61.874	-55.147	5.309	-0.197
6000	12.456	90.628	80.108	63.120	-55.017	6.332	-0.231

Sept. 30, 1977

NICKEL MONOCHLORIDE (NiCl) (IDEAL GAS) GFW = 94.153

D_0° = 87.4 ± 2.2 kcal/mol
$S^\circ_{298.15}$ = [60.2 ± 3] gibbs/mol

ΔHf°_0 = 43.5 ± 1.0 kcal/mol CLNI
$\Delta Hf^\circ_{298.15}$ = 43.5 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i	g_i
0	[6]
[1507]	[4]
[8394]	[10]
[9330]	[8]
[10116]	[6]
[10664]	[4]
[13550]	[8]
[14996]	[6]
[23108]	[6]
[23796]	[4]
[24788]	[4]
[24836]	[2]
[25036]	[6]
[29071]	[4]
[29593]	[2]
[32500]	[10]
[32524]	[8]

ω_e = [424] cm^{-1}
B_e = [0.167] cm^{-1}
$\omega_e x_e$ = [2] cm^{-1}
α_e = [0.002] cm^{-1}
σ = 1
r_e = [2.137] Å

Heat of Formation

The adopted value of ΔHf°_{298} is based on our third law analysis of unpublished mass spectrometry data (7 points, 1400-1540 K) of Hildenbrand (1) for the reaction $Ni(g) + NiCl_2(g) = 2NiCl(g)$. Our analysis of this data yields second and third law values for ΔHf°_{298} of 43.0±1.3 kcal/mol and 43.5±1.0 kcal/mol, respectively, with a drift of 0.64±1.17 gibbs/mol. These values are in good agreement with a value of ΔHf°_{298} = 42.9±5.4 kcal/mol based on the dissociation energy of 88±5 kcal/mol reported by Bulewicz et al. (2) using flame photometry. Additional studies include an analysis by Rao and Dadape (3) of the equilibrium $NiCl_2(g) + Ni(c) \rightarrow 2NiCl(g)$ by the flow method. Our analysis of their data (10 points, 1243-1298 K) using auxiliary JANAF data (4) yields the following values for ΔHf°_{298}; 36.9±1.6 kcal/mol (second law) and 28.5±0.8 kcal/mol (third law) with a very large drift of -12.85±2.42 gibbs/mol. The large drift probably indicates an experimental problem such as lack of equilibrium or the presence of side reactions. Other studies on the heat of formation are summarized by Rao and Dadape (3) and are not considered here since the uncertainties in these studies are very large.

Heat Capacity and Entropy

The 18 observed band systems of NiCl(g) are adequately summarized by Suchard (5). All of these systems have been observed in emission only and the electronic states giving rise to these transitions have not been assigned. The only rotational analysis by Rao and Rao (6) indicates that the upper and lower states are $^2\Delta_{5/2}$ states but the lower state is not definitely identified with the ground state. In view of these difficulties we have chosen to use the electronic energy levels and quantum weights of $Ni^+(g)$ (7) as an approximation to those of NiCl(g). This approximation generally gives upper limit values for the thermal functions; we estimate an uncertainty of ±3 gibbs/mol for S°_{298}.

Molecular constant data for the ground state are assigned assuming that the lower state of the G band system represents the ground state (5, 6). While this assignment is not certain, the molecular constant data for most of the observed systems are fairly similar (5) so no gross errors will be introduced if this assignment proves incorrect. On this basis the adopted values of B_e and ω_e are from Rao and Rao (6) and Rao et al. (8), respectively, while $\omega_e x_e$ and α_e are our best estimates.

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CLNI

SULFUR MONOCHLORIDE (SCL) CLS
(IDEAL GAS) GFW=67.513

T, K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.347	37.200	37.200	INFINITE
100	7.220	47.801	64.272	-1.647	37.388	35.164	-76.851
200	8.456	53.202	57.504	-0.861	37.418	32.924	-35.977
298	8.973	56.696	56.696	0.000	37.396	30.720	-22.518
300	8.977	56.751	56.696	0.017	37.395	30.679	-22.349
400	9.100	59.355	57.050	0.922	36.786	28.472	-15.556
500	9.116	61.398	57.722	1.833	36.331	26.442	-11.558
600	9.108	63.050	58.476	2.744	35.952	24.502	-8.925
700	9.099	64.453	59.232	3.655	35.623	22.620	-7.062
800	9.091	65.667	59.962	4.564	22.330	19.585	-5.350
900	9.087	66.738	60.657	5.473	22.355	19.242	-4.673
1000	9.085	67.695	61.313	6.382	22.372	18.894	-4.129
1100	9.085	68.561	61.934	7.290	22.385	18.546	-3.685
1200	9.087	69.352	62.519	8.199	22.393	18.197	-3.314
1300	9.090	70.079	63.073	9.108	22.396	17.846	-3.000
1400	9.094	70.753	63.598	10.017	22.395	17.497	-2.731
1500	9.099	71.380	64.096	10.926	22.389	17.147	-2.498
1600	9.104	71.968	64.570	11.837	22.380	16.798	-2.294
1700	9.110	72.520	65.021	12.747	22.367	16.450	-2.115
1800	9.117	73.041	65.453	13.659	22.350	16.101	-1.955
1900	9.124	73.534	65.865	14.571	22.331	15.756	-1.812
2000	9.131	74.002	66.260	15.483	22.308	15.411	-1.684
2100	9.138	74.448	66.640	16.397	22.283	15.066	-1.568
2200	9.145	74.873	67.004	17.311	22.254	14.723	-1.463
2300	9.153	75.283	67.355	18.226	22.224	14.382	-1.367
2400	9.160	75.669	67.694	19.141	22.191	14.042	-1.279
2500	9.168	76.044	68.020	20.058	22.156	13.702	-1.198
2600	9.176	76.403	68.336	20.975	22.120	13.365	-1.123
2700	9.185	76.750	68.641	21.893	22.081	13.029	-1.055
2800	9.193	77.084	68.937	22.812	22.040	12.695	-0.991
2900	9.201	77.407	69.223	23.732	21.997	12.361	-0.932
3000	9.210	77.719	69.501	24.652	21.953	12.029	-0.876
3100	9.219	78.021	69.771	25.574	21.907	11.699	-0.825
3200	9.228	78.314	70.034	26.496	21.859	11.370	-0.777
3300	9.237	78.598	70.289	27.419	21.810	11.044	-0.731
3400	9.247	78.874	70.537	28.344	21.760	10.719	-0.689
3500	9.257	79.142	70.779	29.269	21.707	10.393	-0.649
3600	9.267	79.403	71.015	30.195	21.654	10.072	-0.611
3700	9.278	79.657	71.245	31.122	21.599	9.751	-0.576
3800	9.289	79.904	71.470	32.051	21.544	9.431	-0.542
3900	9.300	80.146	71.689	32.980	21.487	9.113	-0.511
4000	9.312	80.381	71.904	33.911	21.428	8.797	-0.481
4100	9.324	80.612	72.113	34.842	21.369	8.482	-0.452
4200	9.337	80.836	72.318	35.776	21.310	8.168	-0.425
4300	9.350	81.056	72.519	36.710	21.248	7.855	-0.399
4400	9.364	81.271	72.716	37.646	21.187	7.546	-0.375
4500	9.378	81.482	72.908	38.583	21.124	7.235	-0.351
4600	9.393	81.688	73.097	39.521	21.062	6.928	-0.329
4700	9.408	81.890	73.282	40.461	20.999	6.622	-0.308
4800	9.424	82.089	73.463	41.403	20.934	6.315	-0.288
4900	9.440	82.283	73.641	42.346	20.870	6.013	-0.268
5000	9.456	82.474	73.816	43.291	20.806	5.710	-0.250
5100	9.473	82.661	73.987	44.237	20.742	5.410	-0.232
5200	9.491	82.846	74.156	45.186	20.678	5.110	-0.215
5300	9.508	83.026	74.322	46.135	20.613	4.810	-0.198
5400	9.527	83.204	74.484	47.087	20.547	4.512	-0.183
5500	9.545	83.379	74.645	48.041	20.483	4.217	-0.168
5600	9.564	83.552	74.802	48.996	20.418	3.921	-0.153
5700	9.584	83.721	74.957	49.954	20.354	3.626	-0.139
5800	9.603	83.888	75.110	50.913	20.290	3.335	-0.126
5900	9.623	84.052	75.260	51.874	20.225	3.042	-0.113
6000	9.644	84.214	75.408	52.838	20.160	2.752	-0.100

June 30, 1978

SULFUR MONOCHLORIDE (SCl) (IDEAL GAS) GFW = 67.513

D_0° = [57.1 ± 4.0] kcal/mol
$S^\circ_{298.15}$ = [56.7 ± 0.6] cal/(mol K)

ΔHf_0° = [37.2 ± 4.0] kcal/mol CLS
$\Delta Hf^\circ_{298.15}$ = [37.4 ± 4.0] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[400]	[2]
[25000]	[4]

ω_e = [536] cm^{-1}
B_e = [0.24060] cm^{-1}
$\omega_e x_e$ = [2.08] cm^{-1}
α_e = [0.00126] cm^{-1}
σ = 1
r_e = [2.04] Å

Heat of Formation

The adopted results are ΔHf_0°(SCl, g) = 37.2±4.0 kcal/mol and D_0°(S-Cl) = 57.1±4.0 kcal/mol. We calculate ΔHf° from an estimated value for the primary bond dissociation energy of SCl_2 of 69.7±3.0 kcal/mol, using auxiliary heat of formation data from JANAF (1). The value of D_0°(SCl-Cl) is obtained from the relationship D_0°(SCl-Cl)/ΔHa_0°(SCl_2) = 0.55±0.03 with ΔHa_0°(SCl_2) = 126.8±0.9 kcal/mol (1). The value of the ratio is taken to be the mean of three values calculated (1) for SF_2(0.53±0.05), $SiCl_2$(0.57±0.01), and SiF_2(0.54±0.03). Converting ΔHf° to 298.15 K, we obtain ΔHf°_{298}(SCl, g) = 37.4 kcal/mol which is in reasonable agreement with the previous estimates made by Mills (35±5, 2), McBride et al. (32.0, 3), and Benson (36.5±2, 4).

Perona et al. (5) have measured the hydrogen chloride infrared emission from reactions involving H and D atoms with SCl_2. From the observed highest vibrational level of HCl, they estimated an upper limit to D_0°(SCl-Cl) of $\leq$ 58 kcal/mol. From this result, we calculate ΔHf_0°(SCl, g) $\leq$ 25.5 kcal/mol and D_0°(SCl) $\geq$ 68.8 kcal/mol. We note that the results from this study predict that D_0°(S-Cl) > D_0°(SCl-Cl) which is inconsistent with established trends in the bond dissociation energies (1) for other mono- and dihalides, such as the silicon chlorides, silicon fluorides, and sulfur fluorides. Factors which can influence the D_0° values estimated from infrared chemiluminescence studies have been discussed by Perona et al. (5). It seems likely that their estimate of D_0° may be too low due to the formation of some HCl in higher vibrational levels by an energy exchange mechanism rather than what is actually produced by the H/SCl_2 chemical reaction. For these reasons, we believe that the ΔHf_0° value (19±3 kcal/mol) recently reported by Takacs (6) based primarily on his analysis of the chemiluminscence work of Perona et al. (5) is suspect. The results adopted here predict D_0°(SCl-Cl) > D_0°(S-Cl) by roughly 13 kcal/mol which seems reasonable by comparison with bond energy data (1) for other halide systems.

Heat Capacity and Entropy

We estimate the S-Cl bond length to lie between those for SCl_2 and S_2Cl_2 (1). The value of B_e is calculated from the adopted r_e. We use Badger's rule (7) to estimate a value for ω_e. The equation is written as $\omega_e^2 = 3.159 \times 10^6/\mu(r_e-d_{ij})^3$, and we use molecular data (1) for SiCl to determine the constant d_{ij} = 1.172. The value of x_e is estimated from the expression $x_e\mu^{1/2}$ = 0.01595 calculated from data for SiCl (1). By analogy with SiCl, SiF, and SF, we expect the ground state electronic configuration for SCl to be $^2\Pi$. The ground state splitting (400 cm^{-1}) and doublet pi state at 25000 cm^{-1} are estimated from those observed for SF (1).

McBride et al. (3) have previously estimated thermal functions over an extended temperature range (0-6000 K), using molecular data similar to ours. Their entropies are consistently higher than our values by 0.6 cal/(mol K) at 298.15 K and 0.3 cal/(mol K) at 4000 K. The difference at 298.15 K arises primarily from the electronic contribution caused by treating the ground state as a single level (3) with a quantum weight of 4. We believe that the uncertainty in S°_{298} should not exceed ±0.6 cal/(mol K). Their estimate of $\omega_e x_e$ = 5.85 cm^{-1} (3), obtained assuming a linear Birge-Sponer relation, seems rather high in comparison with similar data (1) for SiCl, SiF, and SF.

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CLS

CHLOROSULFANYL RADICAL (S_2CL) CLS$_2$
(IDEAL GAS) GFW=99.573

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.981	19.000	19.000	INFINITE
100	9.111	58.255	79.763	-2.151	19.154	16.185	-35.371
200	10.989	65.166	70.880	-1.143	19.013	13.255	-14.484
298	12.178	69.799	69.799	0.000	18.776	10.478	-7.680
300	12.194	69.875	69.799	0.023	18.771	10.426	-7.595
400	12.829	73.479	70.287	1.277	17.411	7.731	-4.224
500	13.179	76.383	71.225	2.579	16.408	5.420	-2.369
600	13.386	78.806	72.292	3.908	15.591	3.304	-1.204
700	13.518	80.880	73.374	5.254	14.897	1.312	-0.410
800	13.606	82.691	74.428	6.610	-11.709	-2.982	0.815
900	13.668	84.297	75.437	7.974	-11.668	-1.891	0.459
1000	13.713	85.740	76.396	9.343	-11.634	-0.808	0.177
1100	13.746	87.048	77.306	10.716	-11.604	0.273	-.054
1200	13.772	88.246	78.169	12.092	-11.580	1.352	-.246
1300	13.792	89.349	78.987	13.470	-11.563	2.428	-.408
1400	13.808	90.371	79.764	14.851	-11.550	3.505	-.547
1500	13.821	91.325	80.503	16.232	-11.546	4.580	-.667
1600	13.832	92.217	81.208	17.615	-11.549	5.655	-.772
1700	13.841	93.056	81.880	18.998	-11.558	6.731	-.865
1800	13.848	93.847	82.523	20.383	-11.575	7.806	-.948
1900	13.855	94.596	83.139	21.768	-11.596	8.885	-1.022
2000	13.860	95.307	83.730	23.154	-11.624	9.964	-1.089
2100	13.865	95.983	84.297	24.540	-11.657	11.043	-1.149
2200	13.869	96.628	84.843	25.927	-11.697	12.124	-1.204
2300	13.872	97.245	85.369	27.314	-11.740	13.210	-1.255
2400	13.876	97.835	85.876	28.701	-11.789	14.295	-1.302
2500	13.879	98.402	86.366	30.089	-11.843	15.382	-1.345
2600	13.882	98.946	86.840	31.477	-11.900	16.473	-1.385
2700	13.884	99.470	87.298	32.865	-11.961	17.565	-1.422
2800	13.887	99.975	87.742	34.254	-12.026	18.661	-1.457
2900	13.890	100.462	88.172	35.643	-12.096	19.757	-1.489
3000	13.893	100.933	88.589	37.032	-12.169	20.855	-1.519
3100	13.897	101.389	88.995	38.421	-12.245	21.957	-1.548
3200	13.900	101.830	89.389	39.811	-12.324	23.062	-1.575
3300	13.904	102.258	89.773	41.201	-12.406	24.169	-1.601
3400	13.909	102.673	90.146	42.592	-12.491	25.279	-1.625
3500	13.914	103.077	90.510	43.983	-12.579	26.390	-1.648
3600	13.920	103.469	90.864	45.375	-12.670	27.506	-1.670
3700	13.927	103.850	91.210	46.767	-12.764	28.623	-1.691
3800	13.934	104.222	91.548	48.160	-12.860	29.742	-1.711
3900	13.943	104.584	91.877	49.554	-12.959	30.865	-1.730
4000	13.952	104.937	92.199	50.949	-13.060	31.990	-1.748
4100	13.963	105.281	92.514	52.344	-13.163	33.118	-1.765
4200	13.974	105.618	92.822	53.741	-13.268	34.248	-1.782
4300	13.987	105.947	93.124	55.139	-13.376	35.380	-1.798
4400	14.000	106.269	93.419	56.539	-13.486	36.517	-1.814
4500	14.015	106.583	93.708	57.939	-13.598	37.653	-1.829
4600	14.031	106.892	93.991	59.342	-13.710	38.795	-1.843
4700	14.048	107.194	94.269	60.746	-13.826	39.937	-1.857
4800	14.067	107.490	94.541	62.151	-13.944	41.081	-1.870
4900	14.086	107.780	94.808	63.559	-14.063	42.230	-1.884
5000	14.107	108.065	95.071	64.969	-14.182	43.379	-1.896
5100	14.128	108.344	95.328	66.380	-14.303	44.533	-1.908
5200	14.151	108.619	95.581	67.794	-14.426	45.688	-1.920
5300	14.175	108.888	95.830	69.211	-14.549	46.845	-1.932
5400	14.200	109.154	96.074	70.629	-14.676	48.002	-1.943
5500	14.226	109.414	96.314	72.051	-14.800	49.167	-1.954
5600	14.254	109.671	96.550	73.475	-14.927	50.330	-1.964
5700	14.281	109.924	96.783	74.902	-15.054	51.495	-1.974
5800	14.310	110.172	97.012	76.331	-15.182	52.666	-1.984
5900	14.340	110.417	97.237	77.764	-15.312	53.835	-1.994
6000	14.370	110.658	97.458	79.199	-15.442	55.009	-2.004

June 30, 1978

CHLOROSULFANYL RADICAL (S_2Cl) (IDEAL GAS) GFW = 99.573

ΔHa°_0 = 140.9 ± 2.0 kcal/mol

$S^\circ_{298.15}$ = [69.8 ± 0.5] cal/(mol K)

ΔHf°_0 = 19.0 ± 2.0 kcal/mol CLS$_2$

$\Delta Hf^\circ_{298.15}$ = 18.8 ± 2.0 kcal/mol

Electronic Levels and Quantum Weights | Vibrational Frequencies and Degeneracies

State	ε_i, cm^{-1}	g_i	ω, cm^{-1}
[$^2B_1$]	0	[2]	[500](1)
[$^2A_1$]	[23000]	[2]	[200](1)
[$^2A_1$]	[26000]	[2]	[550](1)
[$^2A_2$]	[30000]	[2]	

Point Group = [C_s] σ = [1]
Bond Distances: S-Cl = [2.00] Å
S-S = [1.90] Å
Product of Moments of Inertia:
$I_AI_BI_C$ = [4.8512×10^{-114}] g^3 cm^6

Heat of Formation

Perona et al. (1) have studied the infrared emission from vibrationally excited HCl and DCl formed in the reaction of H and D atoms on S_2Cl_2. From their observation that the highest HCl vibrational level occupied was v = 7, they obtained an upper limit estimate of the first bond dissociation energy for S_2Cl_2 of $D^\circ_0(S_2Cl{-}Cl) \leq 53$ kcal/mol. Combining this D°_0 value with ΔHf° data for gaseous Cl and S_2Cl_2 (2), we calculate that ΔHf° for $S_2Cl(g)$ is less than or equal to 20.8 kcal/mol. A recent independent analysis of these thermochemical data for S_2Cl_2/S_2Cl was made by Takacs (3) who reported $\Delta Hf^\circ_0(S_2Cl, g)$ = 17±2 kcal/mol based on slightly different auxiliary ΔHf datum for S_2Cl_2 (-7.7 kcal/mol) than what (-3.6 kcal/mol) was used here. In the same paper, Perona et al. (1) also used the infrared chemiluminescence technique to measure bond dissociation energies for Cl_2 and the first S-Cl bond in SCl_2. While this technique leads to results in accord with the known thermochemistry of Cl_2/Cl (2), it appears to give biased results in the case of SCl_2 (see SCl(g) table for discussion). Factors which can adversely influence the D° values determined from infrared chemiluminescence studies have been discussed by Perona et al. (1).

In a recent review of the thermochemistry of sulfur-containing species, Benson (4) has shown that in R_2S_2 compounds with R equal to H, alkyl, or aryl *the first R-S bond dissociation energy exceeds the second one by 9.5±1.0 kcal/mol. Assuming this* same trend holds for R=Cl, we obtain ΔHr°_0 = 9.5 kcal/mol for $S_2Cl_2(g) + S_2(g) = 2\ S_2Cl(g)$ which leads to $\Delta Hf^\circ_0(S_2Cl, g)$ = 18.3±1.0 kcal/mol by combining the value of ΔHr°_0 with JANAF ΔHf° values for S_2Cl_2 and S_2 (2).

We choose to adopt a ΔHf°_0 value of 19.0±2.0 kcal/mol which is a weighted average of the two results derived above. The values of ΔHf° at 298.15 K and of ΔHa° at 0 K are 18.8±2.0 kcal/mol and 140.9±2.0 kcal/mol, respectively. Using JANAF data (2), we find that the bond dissociation energies in the S_2Cl radical are $D^\circ_0(S_2{-}Cl)$ = 40.2 kcal/mol and $D^\circ_0(S{-}SCl)$ = 83.9 kcal/mol.

Heat Capacity and Entropy

S_2Cl has 19 valence electrons, and according to the Walsh correlation diagram (5), the radical should have a bent structure with a bond angle somewhat greater than that (102°, 2) found for the 20 valence electron molecule SCl_2. We adopt a Cl-S-S angle of 105° which is intermediate between the measured angles for SCl_2 and S_2Cl_2 (2). CNDO and INDO calculations (6) on S_2Cl as a function of bond angle show an energy minimum at 100°, supporting our adopted value. The S-Cl and S-S bond distances are estimated from experimentally measured structural data (2) for S_2Cl_2, SCl_2, and S_2. The principal moments of inertia are: $I_A = 3.3367 \times 10^{-38}$, $I_B = 2.8214 \times 10^{-38}$, and $I_C = 5.1533 \times 10^{-38}$ g cm^2.

Wight and Andrews (7) have observed an absorption band system at 21930-26178 cm^{-1} during mercury arc photolysis of Ar/S_2Cl_2 matrices and alkali metal S_2Cl_2 matrix reactions. They assigned this band system to S_2Cl and suggested that the S-Cl stretching frequency was ≥ 490 cm^{-1} based on the observed vibrational spacing in the absorption spectrum. We estimate ν_1 = 500 cm^{-1} based on the S-Cl stretching frequencies for S_2Cl_2 (466 and 461 cm^{-1}, 2), SCl_2 (528 cm^{-1}, 2), and SCl_2^+ (530±30 cm^{-1}, 8). The ν_2 bending and ν_3 S-S stretching frequencies are estimated by similar comparisons to that for ν_1. The value of ν_3 is chosen to lie between those (2, 9) observed for S_2Cl_2 (546 cm^{-1}) and S_3 (590 cm^{-1}).

An absorption band system has been observed at *22000-26000 cm^{-1} when gaseous S_2Cl_2 is flash photolyzed* (10, 11), *when* Ar/S_2Cl_2 matrices are mercury arc photolyzed during deposition (7), and when S_2Cl_2 is reacted with alkali metal atoms in argon matrices (7). Wight and Andrews (7), along with McGrath (10), have assigned this spectrum to the S_2Cl radical while Donovan et al. (11) believe that portions of the spectrum are due to SCl and S_3. In addition, Donovan et al. (11) observed during flash photolysis of S_2Cl_2 a number of transient bands in the region 30221-34200 cm^{-1} which may be due to S_2Cl. By analogy with the known electronic levels for the isoelectronic radical cations SCl_2^+ (8), OCl_2^+, and OF_2^+ (12), we predict the existence of three excited states for S_2Cl which should give rise to transitions from the ground state in the 20000-30000 cm^{-1} region. No attempt is made here to make definite assignments for the observed absorption spectra (7, 10, and 11) assigned to S_2Cl since this will require the results of higher resolution experiments. We prefer to predict the electronic configurations for the ground and excited states from the Walsh correlation diagram (5) and to estimate their relative term values based on the vertical ionization potentials (8, 12) observed in the photoelectron spectra of SCl_2, OCl_2, and OF_2. A detailed description of the factors considered in making these estimates can be found on the SF_2^+ gas table (2). The estimated electronic entropy contribution from the excited states amounts to only 0.02 cal/(mol K) at 4500 K.

Additional support for the existence of the S_2Cl radical is provided by the matrix photolysis work of Herring et al. (6) who reported observing its ESR spectrum at 4.2 K.

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CLS$_2$

SILICON MONOCHLORIDE (SiCl) ClSi

(IDEAL GAS) GFW=63.539

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.362	46.904	46.904	INFINITE
100	7.826	47.856	64.234	-1.638	47.216	44.780	-97.866
200	8.296	53.452	57.591	-0.828	47.382	42.265	-46.185
298	8.551	56.816	56.816	0.000	47.400	39.745	-29.134
300	8.555	56.869	56.816	0.016	47.399	39.698	-28.920
400	8.710	59.354	57.154	0.880	47.341	37.138	-20.291
500	8.803	61.308	57.796	1.756	47.247	34.598	-15.123
600	8.864	62.919	58.520	2.639	47.128	32.079	-11.685
700	8.907	64.289	59.248	3.528	46.992	29.581	-9.236
800	8.938	65.480	59.955	4.420	46.842	27.103	-7.404
900	8.964	66.534	60.628	5.315	46.680	24.647	-5.985
1000	8.984	67.480	61.267	6.213	46.506	22.207	-4.853
1100	9.002	68.337	61.871	7.112	46.322	19.786	-3.931
1200	9.018	69.121	62.443	8.013	46.128	17.382	-3.166
1300	9.033	69.843	62.985	8.916	45.925	14.994	-2.521
1400	9.047	70.513	63.499	9.820	45.712	12.623	-1.971
1500	9.059	71.138	63.988	10.725	45.489	10.268	-1.496
1600	9.071	71.723	64.453	11.632	45.257	7.927	-1.083
1700	9.083	72.275	64.897	12.539	33.022	5.708	-0.734
1800	9.094	72.793	65.321	13.448	32.825	4.107	-0.499
1900	9.105	73.285	65.728	14.358	32.629	2.517	-0.289
2000	9.116	73.752	66.117	15.269	32.433	0.938	-0.102
2100	9.127	74.197	66.492	16.182	32.238	-0.633	0.066
2200	9.137	74.622	66.852	17.095	32.042	-2.195	0.218
2300	9.148	75.028	67.198	18.009	31.847	-3.746	0.356
2400	9.158	75.418	67.533	18.924	31.651	-5.288	0.482
2500	9.169	75.792	67.856	19.841	31.456	-6.824	0.597
2600	9.179	76.152	68.168	20.758	31.261	-8.351	0.702
2700	9.189	76.498	68.470	21.676	31.065	-9.872	0.799
2800	9.200	76.833	68.763	22.596	30.869	-11.382	0.888
2900	9.211	77.156	69.047	23.516	30.673	-12.889	0.971
3000	9.222	77.468	69.322	24.438	30.477	-14.389	1.048
3100	9.233	77.771	69.590	25.361	30.280	-15.882	1.120
3200	9.245	78.064	69.850	26.285	30.083	-17.366	1.186
3300	9.257	78.349	70.103	27.210	29.885	-18.845	1.248
3400	9.270	78.625	70.350	28.136	29.688	-20.318	1.306
3500	9.283	78.894	70.590	29.064	29.490	-21.789	1.361
3600	9.296	79.156	70.825	29.993	-62.668	-20.993	1.274
3700	9.310	79.411	71.053	30.923	-62.767	-19.833	1.172
3800	9.325	79.659	71.276	31.855	-62.865	-18.672	1.074
3900	9.341	79.902	71.495	32.788	-62.964	-17.509	0.981
4000	9.357	80.138	71.708	33.723	-63.064	-16.341	0.893
4100	9.374	80.370	71.916	34.660	-63.162	-15.175	0.809
4200	9.392	80.596	72.120	35.598	-63.260	-14.004	0.729
4300	9.411	80.817	72.320	36.538	-63.357	-12.829	0.652
4400	9.430	81.034	72.515	37.480	-63.453	-11.652	0.579
4500	9.450	81.246	72.707	38.424	-63.548	-10.471	0.509
4600	9.472	81.454	72.895	39.370	-63.640	-9.292	0.441
4700	9.494	81.658	73.079	40.318	-63.732	-8.108	0.377
4800	9.517	81.858	73.260	41.269	-63.822	-6.926	0.315
4900	9.541	82.054	73.437	42.222	-63.909	-5.737	0.256
5000	9.566	82.247	73.612	43.177	-63.994	-4.553	0.199
5100	9.591	82.437	73.783	44.135	-64.077	-3.358	0.144
5200	9.618	82.623	73.951	45.095	-64.158	-2.168	0.091
5300	9.646	82.807	74.117	46.059	-64.235	-0.976	0.040
5400	9.674	82.987	74.279	47.024	-64.311	0.217	-0.009
5500	9.703	83.165	74.439	47.993	-64.383	1.412	-0.056
5600	9.734	83.340	74.596	48.965	-64.453	2.611	-0.102
5700	9.765	83.513	74.751	49.940	-64.520	3.810	-0.146
5800	9.797	83.683	74.904	50.918	-64.584	5.010	-0.189
5900	9.830	83.851	75.054	51.900	-64.646	6.206	-0.230
6000	9.863	84.016	75.202	52.884	-64.704	7.409	-0.270

Dec. 31, 1960; Sept. 30, 1967; Dec. 31, 1976

SILICON MONOCHLORIDE (SiCl) (IDEAL GAS) GFW = 63.539

D_0° = 88.3 ± 3.0 kcal/mol
$S^\circ_{298.15}$ = 56.816 ± 0.05 gibbs/mol
Symmetry Number = 1

ΔHf_0° = 46.9 ± 1.6 kcal/mol ClSi
$\Delta Hf^\circ_{298.15}$ = 47.4 ± 1.6 kcal/mol

Electronic Levels and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(3)	X $^2\Pi_{1/2}$	0	2	2.063	0.2539	0.00154	533.5	2.15
(3)	$^2\Pi_{3/2}$	207.2	2	2.063	0.2539	0.00154	533.5	2.15
(3)	A $^2\Sigma^+$	23010	2	2.352	0.1970	0.0007	295.2	0.72
(6,7)	B $^2\Sigma^+$	34107	2	1.984	0.2769	0.0020	703.8	3.9
(10)	B' $^2\Delta$	35618	4	2.035	0.2598	0.00240	509.1	5.6
(12,13)	C $^2\Pi$	41165	4	1.942	0.2865	0.0009	671.5	2.2
(15)	D $^2\Pi$	44943	4	[2.063]	[0.2539]	[0.00154]	656.8	3.8

Heat of Formation

The adopted value is based upon a third law analysis of effusion mass spectrometric data by Farber (1) who obtained ΔHr°_{298} = 27.1 kcal/mol for Si(g) + $SiCl_2$(g) = 2 SiCl(g). With auxiliary JANAF data (2) this yields ΔHf°_{298} = 47.4±1.6 kcal/mol. The error estimate is somewhat higher than that given by Farber and should more accurately reflect the uncertainties in relative cross-section values. A value of 88.3±3.0 kcal/mol is obtained for D_0° using auxiliary JANAF data (2). A linear Birge-Sponer extrapolation of the ground state vibrational data (3) yields D_0° = 93.8 kcal/mol in good agreement with the adopted value. Similar extrapolations for other electronic states yield higher values; Gaydon (4) obtained 104±12 kcal/mol from the B' $^2\Delta$ state. The value of D_0° may be compared to the average (per bond) heats of atomization of 94.7,96, and 101.9 kcal/mol for $SiCl_4$, $SiCl_3$, and $SiCl_2$, respectively (2).

Heat Capacity and Entropy

Vibrational and rotational constants and splitting for the ground state are taken from the analysis of the A-X system by Singhal and Verma (3). These are in excellent agreement with those of several other investigators (5-10, 12, 13, 15). Spectroscopic information for the A $^2\Sigma$ state is also taken from Singhal and Verma (3) and yields different molecular constants than an earlier study by Sanii and Verma (5). Molecular constants for the B $^2\Sigma$ state are taken from Ovcharenko (6) and Rai (7) and show good agreement with those of Ovcharenko (8) and Mishra (9). The molecular constants for the B' $^2\Delta$ state are taken from Verma (10) and are in good agreement with the less precise measurements by Ovcharenko (11). The vibrational properties of the C $^2\Pi$ state were taken from Jevons (12) while the rotational constants are from Pandey (13). The latter differ slightly from those of Ovcharenko (14). The spin splittings of 2.727 cm^{-1} (10) and 10-12 cm^{-1} (13, 14) for the B' and C states, respectively, have been ignored in our calculations. The vibrational constants for the D $^2\Pi$ state were taken from Oldershaw (15); since no rotational study is available we have used the ground state B_e and α_e as first approximations in our calculations. This introduces a nearly negligible error in the thermal functions. Oldershaw (15) has observed two additional sets of high energy levels but these are not included due to uncertainties in their states. It should be recognized that the $^4\Sigma^-$ state observed for SiF and SiI (2) has not been discovered for SiCl; by analogy with SiF and SiI it is expected to lie at 26,000±3,000 cm^{-1}. The stated uncertainty in the entropy should account for this level as well as the splittings mentioned above. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant (A = 207.2 cm^{-1}). This leads to slightly biased results at low temperatures (below 500K); the stated uncertainty in S°_{298} should account for this also. All molecular constant data has been corrected to reflect the natural isotopic abundances of Si and Cl.

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ClSi

DICHLOROSILANE (SiH_2CL_2) CL_2H_2SI

(IDEAL GAS) GFW=101.0078

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.199	-74.812	-74.812	INFINITE
100	9.188	56.044	79.685	-2.364	-75.496	-74.055	161.847
200	11.926	63.175	69.773	-1.320	-76.062	-72.404	79.119
298	14.860	68.504	68.504	0.000	-76.600	-70.491	51.671
300	14.908	68.596	68.504	0.028	-76.609	-70.453	51.325
400	17.094	73.203	69.117	1.634	-77.034	-68.333	37.336
500	18.649	77.193	70.343	3.425	-77.339	-66.120	28.901
600	19.823	80.702	71.783	5.351	-77.550	-63.856	23.259
700	20.751	83.830	73.284	7.382	-77.684	-61.561	19.220
800	21.502	86.651	74.782	9.496	-77.762	-59.254	16.187
900	22.116	89.220	76.245	11.678	-77.794	-56.935	13.826
1000	22.622	91.578	77.662	13.915	-77.793	-54.619	11.937
1100	23.041	93.754	79.028	16.199	-77.767	-52.303	10.392
1200	23.390	95.774	80.340	18.521	-77.724	-49.990	9.104
1300	23.681	97.658	81.600	20.875	-77.671	-47.682	8.016
1400	23.927	99.423	82.811	23.256	-77.613	-45.376	7.084
1500	24.135	101.081	83.974	25.659	-77.557	-43.074	6.276
1600	24.313	102.644	85.093	28.082	-77.505	-40.779	5.570
1700	24.465	104.123	86.169	30.521	-89.450	-38.376	4.934
1800	24.596	105.525	87.206	32.974	-89.355	-35.376	4.295
1900	24.710	106.858	88.205	35.440	-89.257	-32.379	3.724
2000	24.810	108.128	89.170	37.916	-89.161	-29.387	3.211
2100	24.897	109.341	90.102	40.401	-89.065	-26.402	2.748
2200	24.973	110.501	91.003	42.895	-88.971	-23.421	2.327
2300	25.041	111.612	91.875	45.396	-88.878	-20.442	1.942
2400	25.102	112.679	92.720	47.903	-88.789	-17.467	1.591
2500	25.156	113.705	93.539	50.416	-88.705	-14.500	1.268
2600	25.204	114.693	94.333	52.934	-88.622	-11.531	0.969
2700	25.247	115.645	95.105	55.456	-88.545	-8.570	0.694
2800	25.286	116.564	95.855	57.983	-88.472	-5.608	0.438
2900	25.322	117.452	96.585	60.513	-88.403	-2.648	0.200
3000	25.354	118.311	97.295	63.047	-88.339	0.304	-0.022
3100	25.383	119.142	97.986	65.584	-88.279	3.257	-0.230
3200	25.410	119.949	98.660	68.124	-88.225	6.211	-0.424
3300	25.434	120.731	99.317	70.666	-88.177	9.163	-0.607
3400	25.456	121.491	99.958	73.210	-88.133	12.111	-0.779
3500	25.477	122.229	100.584	75.757	-88.096	15.057	-0.940
3600	25.496	122.947	101.195	78.306	-180.024	20.263	-1.230
3700	25.513	123.646	101.792	80.856	-179.900	25.826	-1.525
3800	25.529	124.326	102.377	83.408	-179.779	31.383	-1.805
3900	25.544	124.989	102.948	85.962	-179.666	36.938	-2.070
4000	25.558	125.636	103.507	88.517	-179.559	42.492	-2.322
4100	25.571	126.268	104.055	91.074	-179.456	48.038	-2.561
4200	25.583	126.884	104.591	93.631	-179.360	53.585	-2.788
4300	25.594	127.486	105.116	96.190	-179.267	59.129	-3.005
4400	25.605	128.075	105.631	98.750	-179.180	64.674	-3.212
4500	25.615	128.650	106.137	101.311	-179.098	70.215	-3.410
4600	25.624	129.213	106.632	103.873	-179.018	75.757	-3.599
4700	25.633	129.764	107.118	106.436	-178.945	81.297	-3.780
4800	25.641	130.304	107.596	109.000	-178.874	86.829	-3.953
4900	25.648	130.833	108.065	111.564	-178.808	92.368	-4.120
5000	25.656	131.351	108.525	114.129	-178.745	97.895	-4.279
5100	25.662	131.859	108.978	116.695	-178.685	103.436	-4.433
5200	25.669	132.358	109.423	119.262	-178.628	108.965	-4.580
5300	25.675	132.847	109.860	121.829	-178.575	114.496	-4.721
5400	25.681	133.327	110.290	124.397	-178.526	120.020	-4.857
5500	25.686	133.798	110.713	126.965	-178.480	125.550	-4.989
5600	25.691	134.261	111.130	129.534	-178.437	131.076	-5.115
5700	25.696	134.716	111.539	132.103	-178.398	136.604	-5.238
5800	25.701	135.163	111.943	134.673	-178.362	142.132	-5.356
5900	25.705	135.602	112.340	137.244	-178.329	147.652	-5.469
6000	25.709	136.034	112.732	139.814	-178.300	153.177	-5.579

Dec. 31, 1960; Dec. 31, 1976

DICHLOROSILANE (SiH_2Cl_2) (IDEAL GAS) GFW = 101.0078

Point Group C_{2v}

$S^\circ_{298.15}$ = 68.50 ± 0.08 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = [-74.81 ± 3] kcal/mol CL_2H_2SI

$\Delta Hf^\circ_{298.15}$ = [-76.6 ± 3] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2224(1)	2237(1)
954(1)	602(1)
527(1)	876(1)
188(1)	590(1)
710(1)	

Bond Distances: Si-H = 1.480 Å Si-Cl = 2.033 Å σ = 2

Bond Angles: H-Si-H = 111.3° Cl-Si-Cl = 109.72°

Product of the Moments of Inertia: $I_AI_BI_C = 7.5293 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

ΔHf°_{298} is estimated from values for $SiCl_4$, $SiHCl_3$ and SiH_4 (1). Data for $SiHCl_3$ (1) suggest that ΔHf° shows minor deviations from linearity in the chlorosilanes. We assume that ΔHf° has a cubic variation with a constant third difference of -1.5 kcal/mol. ΔHf° values of the chloromethanes yield an almost constant third difference of about -2.5 kcal/mol (2, 3, 1). This approximation corresponds to Allen's bond additivity scheme involving near-neighbor interactions taken two and three at a time (2). Our adopted ΔHf° is 1.5 kcal/mol more negative than that estimated by linear interpolation between $SiCl_4$ and SiH_4.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Davis and Gerry (4) for three isotopic forms of dichlorosilane. Structural parameters are essentially substitutional (r_s) values. They are in reasonable agreement with an early electron diffraction study (5). The principal moments of inertia are $I_A = 5.9923 \times 10^{-39}$, $I_B = 33.0385 \times 10^{-39}$ and $I_C = 38.0313 \times 10^{-39}$ g cm^2.

Vibrational frequencies are those selected by Shimanouchi (6) from a gas-phase infrared study of SiH_2Cl_2, $SiDHCl_2$ and SiD_2Cl_2 done by Christensen and Nielsen (7). Assignments are based on band contours and isotopic rules and are supported by theoretical calculations (7, 4). Two frequencies, ν_4 = 188 and infrared inactive ν_5 = 710 cm^{-1}, are from liquid-phase Raman spectra (8) which also support the vibrational assignment. Christensen and Nielsen (7) found a weak infrared band at ~190 cm^{-1} but could not estimate a definite band contour.

We neglect excited states and assume the electronic ground state to be a singlet. A recent vacuum ultraviolet study of SiH_2Cl_2 (9) is not available to us. We assume that there is little shift in electronic levels between SiH_2Cl_2 and SiH_3Cl (1), since there is little shift in absorption spectra between CH_2Cl_2 and CH_3Cl (10). This implies that contributions from the excited states in SiH_2Cl_2 should be unimportant, just as we believe them to be in SiH_3Cl (1).

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CL_2H_2SI

NICKEL DICHLORIDE ($NiCl_2$) (CRYSTAL) GFW=129.606

CL_2NI

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-3.448	-72.990	-72.990	INFINITE
100	10.487	7.743	37.398	-2.966	-73.325	-69.406	151.685
200	15.509	16.922	24.984	-1.613	-73.150	-65.538	71.615
298	17.127	23.460	23.460	0.000	-72.880	-61.858	45.342
300	17.148	23.566	23.461	0.032	-72.874	-61.789	45.013
400	18.234	28.659	24.148	1.805	-72.584	-58.138	31.765
500	18.857	32.802	25.477	3.662	-72.289	-54.560	23.848
600	19.092	36.263	26.995	5.541	-72.042	-51.039	18.591
700	19.195	39.213	28.535	7.475	-71.800	-47.555	14.847
800	19.335	41.784	30.033	9.400	-71.499	-44.113	12.051
900	19.614	44.076	31.469	11.346	-71.191	-40.708	9.885
1000	20.094	46.165	32.835	13.330	-70.863	-37.339	8.160
1100	20.812	48.112	34.136	15.373	-70.496	-34.084	6.756
1200	21.794	49.962	35.379	17.501	-70.064	-30.705	5.592
1300	23.057	51.755	36.570	19.741	-69.560	-27.445	4.614
1400	24.611	53.519	37.717	22.122	-68.899	-24.231	3.783
1500	26.466	55.278	38.829	24.673	-68.111	-21.067	3.069
1600	28.626	57.053	39.913	27.425	-67.146	-17.960	2.453
1700	31.096	58.861	40.974	30.409	-65.975	-14.920	1.918
1800	33.880	60.716	42.019	33.655	-68.666	-11.786	1.431

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NICKEL DICHLORIDE ($NiCl_2$) (CRYSTAL) GFW = 129.606

$S^\circ_{298.15}$ = 23.46 ± 0.05 gibbs/mol
T_m = 1304 ± 4 K (P $\approx$ 2.5 atm)
T_s = [1246.15] K

ΔHf°_0 = -72.99 ± 0.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -72.88 ± 0.5 kcal/mol
ΔH°_m = 18.444 ± 0.2 kcal/mol
$\Delta H^\circ_{s_{298.15}}$ = 55.21 ± 0.3 kcal/mol

CL_2NI

Heat of Formation

The adopted value for ΔHf°_{298} of -72.88±0.5 kcal/mol is based on our third law analysis of equilibrium data for the reaction $NiCl_2(c) + H_2(g) \rightarrow Ni(c) + 2HCl(g)$ of Busey and Giauque (1). This value is selected from the studies shown below mainly because of the attention to purity of the sample, assurance of equilibrium, and correction for diffusion of hydrogen through pyrex by these authors. The results of Busey and Giauque (1) show excellent agreement between second and third law values with a consequent low drift. Our analysis of the other studies is given below and the large drifts for some of the studies indicate a lack of equilibrium which is attained very slowly in this system; this is certainly the case for Shchukarev et al. (2) and possibly also for (3, 4, 5). The emf results of Egan (6) and Gee and Shelton (7) are about 0.5 kcal/mol more negative than the adopted value and we increase the uncertainty in the event that these results prove to be more accurate.

Investigation	Reaction[a]	Method	No. of Points	Temp Range, K	ΔHr°_{298}, kcal/mol 2nd law	ΔHr°_{298}, kcal/mol 3rd law	drift gibbs/mol	$-\Delta Hf^\circ_{298}$[b] kcal/mol
Giauque and Busey (1)	A	static	15	630 - 738	28.86±0.05	28.75±0.02	-0.16±0.08	72.88±0.1
Sano (3)	A	static	5	661 - 792	29.96±0.38	29.26±0.13	-0.96±0.52	73.39±0.1
Egan (6)	B	emf	2	673, 723	-69.73	-73.32±0.36	-5.13	73.32±0.4
Shchukarev et al. (2)	A	circulation	7	573 - 823	26.52±0.13	28.90±0.58	3.35±0.19	73.03±0.6
Jellinek and Uloth (4)	A	dynamic	3	573 - 723	31.50±3.09	29.81±0.84	-2.64±4.80	73.94±0.8
Berger and Crut (5)	A	static	16	583 - 718	31.84±0.44	29.57±0.46	-3.52±0.67	73.70±0.5
Gee and Shelton (7)	C	emf	Equation	470 - 750	-0.97	-1.20±0.08	-0.39	73.50±0.3
Gee and Shelton (7)	D	emf	Equation	530 - 800	-7.35	-8.34±0.31	-1.51	73.36±0.3

[a] Reactions:
A) $NiCl_2(c) + H_2(g) \rightarrow Ni(c) + 2HCl(g)$
B) $Ni(c) + Cl_2(g) \rightarrow NiCl_2(c)$
C) $Co(c) + NiCl_2(g) \rightarrow CoCl_2(c) + Ni(c)$
D) $Fe(c) + NiCl_2(g) \rightarrow FeCl_2(c) + Ni(c)$

[b] Based on 3rd law analysis

Heat Capacity and Entropy

Heat capacity data below 300 K are based on the measurements of Kostryokova (8) (2-30 K) and Busey and Giauque (9) (14.14-336.36 K). The two sets of data are joined smoothly via a least squares procedure; Kostryokova's values (8) are higher than those of Busey and Giaugue (9) by 5.3% at 15 K and 0.3% at 30 K. The results of Busey and Giauque (9) indicate a sharp lambda peak at 52.35 K which is apparently associated with the cooperative ordering of the magnetic moments of the nickel ions. Cp° near the maximum is 6.74 gibbs/mol and the enthalpy associated with this transition is of the order of a few calories. The only other measurements in this temperature region are by Trapeznikowa et al. (10) (13-129 K) who report three peaks in Cp° at 49.55 K, 57-58 K, and 60-61 K. We put no weight on these results since the authors apparently suffered from an impure sample among other experimental problems (9); their results range from 4 to 13% higher than those of Busey and Giauque over the temperature range 40-130 K. Earlier results by Kostryokova (11) below 16 K are in good agreement with the adopted Cp° values. S°_{298} is obtained from integration of the adopted Cp's and is based on Cp°_2 = 0.0055.

Cp° data above 300 K are based on the high temperature enthalpy data of Coughlin (12) (376-1282 K). These data are corrected to IPTS 68 (13) and then joined smoothly with the low temperature Cp° data of Busey and Giauque (9) to yield the adopted Cp° values. Data above 1300 K are extrapolated. The high temperature enthalpy data of Krestovnikov and Karetinkov (14) range from 2 to 11% higher than those of Coughlin and are believed to be of lower accuracy.

Melting Data

See $NiCl_2(l)$ table.

Sublimation Data

T_s is calculated as the temperature at which $\Delta G^\circ_r = 0$ for $NiCl_2(c) \rightarrow NiCl_2(g)$ (15). See the heat of formation section of the $NiCl_2(g)$ table (15) for the derivation of the adopted heat of sublimation.

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CL_2NI

NICKEL DICHLORIDE ($NiCL_2$) CL_2NI
(LIQUID) GFW=129.606

T, K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.448	-55.922	-55.922	INFINITE
100	10.487	20.566	50.221	-2.966	-56.256	-53.620	117.185
200	15.509	29.745	37.807	-1.613	-56.081	-51.034	55.767
298	17.127	36.283	36.283	0.000	-55.812	-48.663	35.634
300	17.148	36.389	36.284	0.032	-55.806	-48.568	35.381
400	18.234	41.482	36.971	1.805	-55.516	-46.199	25.242
500	18.857	45.625	38.300	3.662	-55.220	-43.904	19.190
600	19.092	49.086	39.818	5.561	-54.974	-41.665	15.176
700	19.195	52.036	41.358	7.475	-54.732	-39.463	12.321
800	19.335	54.607	42.857	9.400	-54.430	-37.304	10.191
900	24.184	57.003	44.293	11.439	-54.030	-35.182	8.543
1000	24.184	59.551	45.693	13.857	-53.268	-33.129	7.240
1100	24.184	61.856	47.060	16.276	-52.525	-31.152	6.189
1200	24.184	63.960	48.382	18.694	-51.803	-29.241	5.325
1300	24.184	65.896	49.655	21.112	-51.101	-27.388	4.604
1400	24.184	67.688	50.880	23.531	-50.422	-25.590	3.995
1500	24.184	69.356	52.057	25.949	-49.767	-23.840	3.473
1600	24.184	70.917	53.187	28.368	-49.135	-22.132	3.023
1700	24.184	72.383	54.274	30.786	-48.530	-20.462	2.631
1800	24.184	73.766	55.319	33.204	-52.049	-18.657	2.265

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NICKEL DICHLORIDE ($NiCl_2$) (LIQUID) GFW = 129.606

$S^\circ_{298.15}$ = [36.283] gibbs/mol
Tm = 1304 ± 4 K(P $\overset{\sim}{=}$ 2.5 atm)
Ts = [1246.15] K

$\Delta Hf^\circ_{298.15}$ = [-55.812] kcal/mol
ΔHm° = 18.444 ± 0.2 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 55.21 ± 0.3 kcal/mol

CL_2NI

Heat of Formation

The heat of formation at 298.15 K is obtained from that of the crystal by addition of ΔHm° and the difference (H°_{1304} - H°_{298}) for the crystal and liquid (1).

Heat Capacity and Entropy

The adopted values of Cp° are obtained from our analysis of the high temperature enthalpy data of Coughlin (2) (1305 - 1337 K) after correction to IPTS 68 (3). The constant Cp° value obtained from these data is assumed to be valid above an assumed glass transition temperature at 880 K. The assumption of a constant Cp° over such a broad range based on data over a very short range leads to a rather large uncertainty in the thermal functions. Below the glass transition at 880 K, Cp° is assumed to be that of the crystal.

S°_{298} is obtained in a manner analogous to that for ΔHf°_{298}.

Melting Data

The temperature and heat of melting are obtained from our analysis of Coughlin's (2) measurements after correction to IPTS 68 (3). He observed pre-melting beginning at 1288 K and continuing to 1305 K where the enthalpy change again becomes regular. We adopt a melting point near the upper end of this range, Tm = 1304±4 K. The adopted enthalpy of melting is 18.444±0.2 kcal/mol at Tm.

Phase Data

$NiCl_2$(l) will not exist as a stable phase at 1 atm pressure according to calculations from our tables (1). We calculate sublimation at 1246.15 K in good agreement with the measured value of 1241±3 K at 730 torr (4). The adopted melting point of 1304±4 K is from Coughlin's work which was conducted at 2-3.5 atm in the presence of inert gas. These pressures are high enough to increase the sublimation point above the melting point and a relatively short liquid range will be observed. Information on the heat of sublimation is in the heat of formation section of the $NiCl_2$(g) table (1).

References

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CL_2NI

NICKEL DICHLORIDE ($NiCl_2$) Cl_2Ni

(IDEAL GAS) GFW=129.606

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.395	-17.727	-17.727	INFINITE
100	10.814	56.857	81.797	-2.494	-17.643	-18.636	40.728
200	12.727	64.979	71.535	-1.311	-17.638	-19.638	21.459
298	13.881	70.297	70.297	0.000	-17.670	-20.612	15.109
300	13.897	70.383	70.298	0.026	-17.670	-20.630	15.029
400	14.546	74.479	70.852	1.451	-17.728	-21.610	11.807
500	14.926	77.769	71.917	2.926	-17.815	-22.570	9.865
600	15.177	80.514	73.127	4.432	-17.961	-23.508	8.563
700	15.360	82.868	74.355	5.959	-18.106	-24.419	7.624
800	15.497	84.928	75.550	7.502	-18.187	-25.317	6.916
900	15.600	86.760	76.696	9.057	-18.270	-26.202	6.363
1000	15.676	88.408	77.786	10.621	-18.362	-27.080	5.918
1100	15.732	89.905	78.821	12.192	-18.467	-27.947	5.552
1200	15.773	91.275	79.802	13.767	-18.588	-28.804	5.246
1300	15.802	92.539	80.734	15.346	-18.725	-29.649	4.984
1400	15.822	93.711	81.620	16.928	-18.883	-30.484	4.759
1500	15.836	94.803	82.463	18.510	-19.064	-31.306	4.561
1600	15.846	95.825	83.266	20.095	-19.266	-32.116	4.387
1700	15.853	96.786	84.033	21.680	-19.494	-32.911	4.231
1800	15.857	97.692	84.767	23.265	-23.846	-33.523	4.070
1900	15.859	98.550	85.470	24.851	-24.102	-34.052	3.917
2000	15.860	99.363	86.145	26.437	-24.361	-34.569	3.778
2100	15.861	100.137	86.793	28.023	-24.620	-35.074	3.650
2200	15.862	100.875	87.416	29.609	-24.882	-35.566	3.533
2300	15.862	101.580	88.017	31.195	-25.145	-36.045	3.425
2400	15.863	102.255	88.596	32.781	-25.410	-36.513	3.325
2500	15.864	102.903	89.156	34.368	-25.677	-36.971	3.232
2600	15.865	103.525	89.696	35.954	-25.946	-37.416	3.145
2700	15.867	104.124	90.220	37.541	-26.217	-37.853	3.064
2800	15.870	104.701	90.727	39.128	-26.491	-38.278	2.988
2900	15.873	105.258	91.218	40.715	-26.767	-38.695	2.916
3000	15.877	105.796	91.695	42.302	-27.046	-39.103	2.849
3100	15.881	106.317	92.158	43.890	-27.327	-39.500	2.785
3200	15.885	106.821	92.609	45.479	-117.676	-38.731	2.645
3300	15.891	107.310	93.047	47.067	-117.568	-36.265	2.402
3400	15.896	107.784	93.473	48.657	-117.460	-33.802	2.173
3500	15.902	108.245	93.889	50.247	-117.356	-31.346	1.957
3600	15.908	108.693	94.294	51.837	-117.254	-28.888	1.754
3700	15.914	109.129	94.689	53.428	-117.154	-26.434	1.561
3800	15.920	109.554	95.075	55.020	-117.056	-23.985	1.379
3900	15.926	109.967	95.451	56.612	-116.962	-21.536	1.207
4000	15.932	110.371	95.819	58.205	-116.871	-19.090	1.043
4100	15.939	110.764	96.179	59.798	-116.782	-16.648	0.887
4200	15.945	111.148	96.531	61.393	-116.696	-14.207	0.739
4300	15.951	111.523	96.875	62.987	-116.614	-11.769	0.598
4400	15.956	111.890	97.212	64.583	-116.534	-9.328	0.463
4500	15.962	112.249	97.542	66.179	-116.459	-6.895	0.335
4600	15.967	112.600	97.866	67.775	-116.386	-4.461	0.212
4700	15.973	112.943	98.183	69.372	-116.318	-2.027	0.094
4800	15.977	113.279	98.494	70.970	-116.252	0.402	-0.018
4900	15.982	113.609	98.799	72.568	-116.192	2.834	-0.126
5000	15.986	113.932	99.099	74.166	-116.135	5.261	-0.230
5100	15.990	114.249	99.393	75.765	-116.082	7.691	-0.330
5200	15.994	114.559	99.681	77.364	-116.034	10.118	-0.425
5300	15.997	114.864	99.965	78.964	-115.992	12.541	-0.517
5400	16.000	115.163	100.244	80.564	-115.955	14.966	-0.606
5500	16.003	115.456	100.517	82.164	-115.924	17.392	-0.691
5600	16.005	115.745	100.787	83.764	-115.899	19.813	-0.773
5700	16.007	116.028	101.052	85.365	-115.881	22.234	-0.852
5800	16.009	116.306	101.312	86.966	-115.868	24.661	-0.929
5900	16.010	116.580	101.569	88.567	-115.864	27.081	-1.003
6000	16.011	116.849	101.821	90.168	-115.868	29.505	-1.075

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NICKEL DICHLORIDE ($NiCl_2$) (IDEAL GAS) GFW = 129.606

ΔHa_0° = 177.2 ± 2.0 kcal/mol
$S^\circ_{298.15}$ = 70.3 ± 2 gibbs/mol
Point Group $D_{\infty h}$

ΔHf_0° = −17.73 ± 0.6 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −17.67 ± 0.6 kcal/mol

Cl_2Ni

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i	State	ε_i, cm^{-1}	g_i
$^3\Pi_g$	0	6	$^1\Delta_g$	15466	2
$^3\Sigma_g^-$	[879]	3	$^1\Delta_g$	18236	2
$^3\Delta_g$	2454	6	$^3\Sigma_g^-$	21701	3
$^3\Phi_g$	5853	6	$^1\Pi_g$	[26740]	2
$^1\Sigma_g^+$	10601	1	$^1\Sigma_g^+$	[27234]	1
$^1\Pi_g$	11727	2	$^1\Gamma_g$	[28825]	2
$^3\Pi_g$	12984	6	$^1\Sigma_g^+$	[55433]	1
$^1\Phi_g$	14717	2			

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
360 (1)
87 (2)
523 (1)

Bond Distance: Ni-Cl = [2.09] Å σ = [2]
Bond Angle: Cl-Ni-Cl = 180°
Rotational Constant: B_0 = [0.054427] cm^{-1}

Heat of Formation

The adopted value of ΔHf°_{298} is calculated from ΔHs°_{298} = 55.21±0.3 kcal/mol by addition of $\Delta Hf^\circ_{298}(NiCl_2,c)$ (1). The adopted value is an average derived from our third law analysis of the sublimation data of Ratkovskii et al. (2), McCreary and Thorn (3), Schaefer et al. (4), and Hildenbrand (5). The data of Maier (6) are rejected because there is an apparent temperature dependent error at the high temperature end of his data.

Investigation	Method	Temp. Range K	No. of Points	ΔHr°_{298}, kcal/mol 2nd law	3rd law	drift gibbs/mol	ΔHf°_{298}(a) kcal/mol
Ratkovskii et al. (2)	Knudsen	973 - 1203	Equation	57.14	55.36±0.29	-1.6	-17.52±0.8
McCreary and Thorn (3)	Torsional Recoil	823 - 881	Equation	55.68	55.01±0.03	-0.80	-17.87±0.5
McCreary and Thorn (3)	Mass Effusion	823 - 881	Equation	54.85	55.08±0.01	0.27	-17.80±0.5
Schaefer et al. (4)	Transpiration	973 - 1056	10	55.25±1.50	55.62±0.23	0.36±1.47	-17.26±0.7
Maier (6)	Static (pure sample)	1047 - 1236	18	54.00±0.89	55.39±0.42	1.19±0.75	-17.49±0.7
Hildenbrand (5)	Torsion Effusion	706 - 771	19	55.14±0.34	54.99±0.08	-0.19±0.46	-17.89±0.5

(a) based on 3rd law analysis

Schoonmaker et al. (7) observed no dimers in their Knudsen-mass spectroscopic study while Schaefer and Binnewies (8) observed dimerization to the extent of 0.15% at 796 K by a similar technique. We have not corrected for this small dimerization effect. Of more importance may be the observation of significant quantities of $SiCl_4(g)$ and $Si_2Cl_6(g)$ by Schoonmaker et al. (7) indicating reaction between $NiCl_2(g)$ and the quartz liner in their experiment. Schaefer and Binnewies (8) make no mention of Si_xCl_y species even though their Knudsen cell contains a quartz crucible. Therefore we ignore this effect while recognizing the need for further work in the characterization of the vapor over $NiCl_2$.

Heat Capacity and Entropy

The adopted gas phase values of ν_2 = 87 cm^{-1} and ν_3 = 523 cm^{-1} are from the matrix isolation work of Thompson and Carlson (9), we have added 2 cm^{-1} to the observed values to account for the matrix effect. The symmetric stretching frequency, ν_1, has not been observed in the infrared spectrum and this is one of the major indications that the molecule is linear. The adopted value of ν_1 (360 cm^{-1}) is from the observed vibrational spacing of the fluorescence spectrum by Gruen et al (10) and is in good agreement with the value of 351 cm^{-1} calculated by Milligan et al. (11).

The rotational constant is calculated assuming the molecule is linear with the bond distance estimated to be 2.09 Å in accordance with Brewer et al. (12). Further support for a linear structure comes from the molecular beam work of Buchler et al. (13) which indicates a zero dipole moment for a number of transition metal difluorides including NiF_2.

The ground state of the linear $NiCl_2$ molecule is established as $^3\Pi_g$ from numerous studies on the Laporte-forbidden d-d transitions (14 - 16) as well as a study of the Laporte-allowed charge-transfer transitions (17). The very complex electronic spectra for both the gas phase and matrix isolated $NiCl_2$ have been studied by numerous investigators and interpreted using crystal field or ligand field theory. Our adopted values for the excited states are from Lever and Hollebone (14) who used an "orbital angular overlap" model to fit the spin-allowed and spin-forbidden d-d transition spectra. These assignments are in good agreement with those of DeKock and Gruen (16, 18) and Smith (15) but differ from those of Hougen et al. (19).

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Cl_2Ni

SULFUR DICHLORIDE (SCl_2) CL_2S
(LIQUID) GFW=102.966

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	21.750	43.900	43.900	0.000	-11.900	-6.817	4.997
300	21.750	44.035	43.900	0.040	-11.885	-6.785	4.943
329.935	21.750	46.103	44.008	0.691	-------- NORMAL BOILING ------		
400	21.750	50.292	44.754	2.215	-11.640	-5.183	2.832
500	21.750	55.145	46.365	4.390	-11.257	-3.617	1.581
600	21.750	59.111	48.168	6.565	-10.807	-2.129	0.776
700	21.750	62.463	49.977	8.740	-10.310	-0.722	0.225
800	21.750	65.368	51.724	10.915	-22.781	-0.587	0.160

June 30, 1978

SULFUR DICHLORIDE (SCl_2) (LIQUID) GFW = 102.966

$S^\circ_{298.15}$ = 43.9 ± 1.0 cal/(mol K)
Tb = 329.935 K

$\Delta Hf^\circ_{298.15}$ = -11.9 ± 0.5 kcal/mol
ΔHv° = 7.40 ± 1.3 kcal/mol CL_2S

Heat of Formation

Trautz and Hoffmann (1) have measured calorimetrically the enthalpy of solution of gaseous chlorine in liquid dichlorodisulfane at 289.5 K. They reported ΔH_{soln} = -9.8±0.4 kcal/mol for a final state consisting of SCl_2 dissolved in an excess of S_2Cl_2. Combining their measured ΔH_{soln} value with $\Delta Hf^\circ_{298}(S_2Cl_2, \ell)$ = -13.9±0.5 kcal/mol (2), we obtain the adopted result of $\Delta Hf^\circ_{298}(SCl_2, \ell)$ = -11.9±0.5 kcal/mol. In arriving at this value, no enthalpy corrections are applied for dissolution of the SCl_2 in the excess S_2Cl_2 and for the temperature difference since we expect both corrections to be small and they tend to cancel. Our adopted value agrees with the selected values of NBS (-12 kcal/mol, 3) and Mills (-11.8 kcal/mol, 4).

Heat Capacity and Entropy

The heat capacity of liquid SCl_2 is estimated as 21.75 cal/(mol K) using the value of 7.25 cal/(g-atm K) recommended by Kubaschewski et al. (5). This estimated value of Cp° corresponds to a specific heat of 0.21 cal/(g K) which agrees with the experimentally measured value for S_2Cl_2 of 0.22 cal/(g K) (2). We assume that Cp° is constant in the temperature range 298-800 K. The value of S°_{298} is selected as 43.9±1.0 cal/(mol K) which minimizes differences between the second and third law entropies of vaporization determined from vapor pressure data (6) on a pure stabilized sample of SCl_2. Further details on the results of these analyses can be found in the heat of formation section of the $SCl_2(g)$ table (2).

Heat of Vaporization

Tb is the temperature at which the free energy of vaporization becomes zero. The value of ΔHv° is calculated as the difference between the ΔHf° values for the gas and liquid at Tb. The experimental value of Tb determined from vapor pressure measurements is 332.7 K (6). The adopted values of Tb and ΔHv° correspond to an entropy of vaporization of 22.3 cal/(mol K) at Tb.

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CL_2S

SULFUR DICHLORIDE (SCl_2)

(IDEAL GAS) GFW=102.966

Cl_2S

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-2.974	-3.926	-3.926	INFINITE
100	9.074	55.772	77.228	-2.146	-3.958	-4.721	10.317
200	10.964	62.659	68.364	-1.141	-4.072	-5.443	5.948
298	12.164	67.285	67.285	0.000	-4.200	-6.089	4.463
300	12.180	67.360	67.285	0.023	-4.202	-6.100	4.444
329.935	12.416	68.530	67.346	0.391	------- NORMAL	BOILING ------	
400	12.821	70.962	67.772	1.276	-4.879	-6.691	3.656
500	13.173	73.864	68.710	2.577	-5.370	-7.089	3.099
600	13.382	76.286	69.776	3.906	-5.766	-7.394	2.693
700	13.515	78.360	70.858	5.251	-6.099	-7.638	2.385
800	13.604	80.170	71.911	6.607	-19.389	-9.037	2.469
900	13.666	81.777	72.920	7.971	-19.354	-7.743	1.880
1000	13.711	83.219	73.879	9.340	-19.323	-6.456	1.411
1100	13.745	84.527	74.788	10.713	-19.294	-5.170	1.027
1200	13.771	85.725	75.650	12.089	-19.269	-3.888	0.708
1300	13.791	86.828	76.468	13.467	-19.248	-2.607	0.438
1400	13.807	87.850	77.245	14.847	-19.230	-1.327	0.207
1500	13.821	88.803	77.984	16.228	-19.217	-0.049	0.007
1600	13.831	89.696	78.689	17.611	-19.208	1.228	-0.168
1700	13.840	90.534	79.361	18.995	-19.202	2.507	-0.322
1800	13.848	91.326	80.004	20.379	-19.202	3.782	-0.459
1900	13.854	92.075	80.620	21.764	-19.204	5.061	-0.582
2000	13.860	92.785	81.210	23.150	-19.211	6.338	-0.693
2100	13.864	93.462	81.778	24.536	-19.221	7.615	-0.792
2200	13.868	94.107	82.324	25.923	-19.236	8.893	-0.883
2300	13.872	94.723	82.850	27.310	-19.253	10.173	-0.967
2400	13.875	95.314	83.357	28.697	-19.275	11.453	-1.043
2500	13.878	95.880	83.846	30.085	-19.301	12.733	-1.113
2600	13.881	96.425	84.320	31.473	-19.329	14.016	-1.178
2700	13.883	96.949	84.778	32.861	-19.362	15.298	-1.238
2800	13.885	97.453	85.222	34.249	-19.399	16.584	-1.294
2900	13.887	97.941	85.652	35.638	-19.439	17.868	-1.347
3000	13.889	98.412	86.069	37.027	-19.483	19.154	-1.395
3100	13.891	98.867	86.475	38.416	-19.531	20.443	-1.441
3200	13.893	99.308	86.869	39.805	-19.583	21.733	-1.484
3300	13.896	99.736	87.252	41.194	-19.639	23.026	-1.525
3400	13.898	100.151	87.626	42.584	-19.697	24.321	-1.563
3500	13.901	100.553	87.989	43.974	-19.760	25.614	-1.599
3600	13.904	100.945	88.344	45.364	-19.826	26.913	-1.634
3700	13.907	101.326	88.690	46.755	-19.895	28.212	-1.666
3800	13.910	101.697	89.027	48.146	-19.967	29.512	-1.697
3900	13.914	102.058	89.357	49.537	-20.043	30.816	-1.727
4000	13.919	102.411	89.679	50.928	-20.123	32.121	-1.755
4100	13.923	102.754	89.993	52.320	-20.204	33.428	-1.782
4200	13.929	103.090	90.301	53.713	-20.288	34.736	-1.807
4300	13.935	103.418	90.602	55.106	-20.375	36.047	-1.832
4400	13.942	103.738	90.897	56.500	-20.464	37.363	-1.856
4500	13.949	104.052	91.186	57.895	-20.555	38.675	-1.878
4600	13.957	104.358	91.469	59.290	-20.647	39.994	-1.900
4700	13.965	104.659	91.747	60.686	-20.742	41.314	-1.921
4800	13.974	104.953	92.019	62.083	-20.839	42.633	-1.941
4900	13.984	105.241	92.286	63.481	-20.937	43.959	-1.961
5000	13.995	105.524	92.548	64.880	-21.035	45.283	-1.979
5200	14.019	106.073	93.057	67.681	-21.235	47.943	-2.015
5400	14.045	106.602	93.549	70.487	-21.440	50.604	-2.048
5600	14.074	107.114	94.025	73.299	-21.645	53.277	-2.079
5800	14.106	107.608	94.484	76.117	-21.852	55.958	-2.109
6000	14.140	108.087	94.930	78.942	-22.061	58.643	-2.136

June 30, 1978

SULFUR DICHLORIDE (SCl_2) (IDEAL GAS) GFW = 102.966

ΔHa_0° = 126.8 ± 0.9 kcal/mol

$S^\circ_{298.15}$ = 67.29 ± 0.03 cal/(mol K)

ΔHf_0° = -3.9 ± 0.8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -4.2 ± 0.8 kcal/mol

Cl_2S

Electronic Levels and Quantum Weights / **Vibrational Frequencies and Degeneracies**

State	ϵ_i, cm^{-1}	g_i	ω, cm^{-1}
$^1A_1$	0	1	528(1)
$^1A_2$	25810	1	205(1)
$^1B_2$	29762	1	525(1)

Point Group C_{2v} σ = 2

Bond Distance: S-Cl = 2.015 ± 0.001 Å

Bond Angle: Cl-S-Cl = 102.73 ± 0.05°

Product of the Moments of Inertia:
$I_AI_BI_C = 5.9228 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

Rosser and Whitt (1) have reported the results of a vapor pressure study of SCl_2. Measurements were conducted on a sample of SCl_2 stabilized with PCl_3 to suppress decomposition. Using JANAF free energy functions (2), we analyze their vapor pressure points (1) lying above 298 K by the second and third law methods. In the analysis we select $S^\circ_{298}(SCl_2, \ell)$ = 43.9 cal/(mol K) which minimizes the difference between the second and third law entropies of vaporization. Our results are ΔHv°(2nd law) = ΔHv°(3rd law) = 7.75 ± 0.02 kcal/mol which leads to the adopted heat of formation of $\Delta Hf^\circ_{298}(SCl_2, g)$ = -4.2±0.8 kcal/mol when combined with $\Delta Hf^\circ_{298}(SCl_2, \ell)$ = -11.9±0.5 kcal/mol (2). The adopted value of ΔHf° is rounded to the nearest 0.1 kcal/mol. The overall uncertainty is estimated as ±0.8 kcal/mol based on contributions from the uncertainty in ΔHf° of the liquid (±0.5 kcal/mol) and from the uncertainty in the entropy (±1.0 cal/(mol K)) of the liquid (2) which amounts to roughly 0.3 kcal/mol in ΔHf°.

Barton and Yost (3) have studied the dissociation of $S_2Cl_2(g)$ at various temperatures. Their measured dissociation data above 760 K have been reanalyzed by Yost and Russell (4) who have determined equilibrium constants for the reactions (a) $S_2(g) + Cl_2(g) = S_2Cl_2(g)$ and (b) $0.5S_2(g) + Cl_2(g) = SCl_2(g)$ by combining the dissociation pressures with molecular data and an estimated value for the ΔHf° of SCl_2. Second and third law analyses of the equilibrium data for reaction (b) give ΔHr°_{298}(2nd law) = ΔHr°_{298}(3rd law) = -20.69±0.01 kcal/mol which corresponds to $\Delta Hf^\circ_{298}(SCl_2, g)$ = -5.3 kcal/mol using the recent JANAF (2) value of ΔHf° for $S_2(g)$. This ΔHf° value for $SCl_2(g)$ is some 1.1 kcal/mol more negative than that obtained from an analysis of vapor pressure data described above. We find a similar discrepancy in the equilibrium data for reaction (a) where the derived ΔHf° value of $S_2Cl_2(g)$ is 3 kcal/mol more negative than that obtained from an analysis of vapor pressure data. (See $S_2Cl_2(g)$ table for details). We conclude that the equilibrium constants reported by Yost and Russell (4) are biased, and we give no weight to the ΔHf° values derived from their data.

Values of ΔHf° previously selected by Colwell (5) and Mills (6) have been based primarily on the equilibrium data of Yost and Russell (4). The value selected by NBS (7) is -4.7 kcal/mol. Our adopted results give a heat of atomization (ΔHa_0°) and mean S-Cl bond dissociation energy ($\bar{D}^\circ$) of 126.8±0.9 kcal/mol and 63.4 kcal/mol, respectively.

Heat Capacity and Entropy

Early electron diffraction studies (8, 9) and more recent microwave measurements (10, 11) have shown that the SCl_2 molecule has C_{2v} symmetry. We adopt structural parameters from the microwave work of Davis and Gerry (11). The bond length and angle refer to an average structure of $^{32}S^{35}Cl_2$ in the (000) vibrational state obtained from a quadratic potential function based solely on microwave data (11). This average structure is only slightly different from the effective structure determined by Murray et al. (10) but quite different from the molecular structure derived from electron diffraction measurements (8, 9) which are considered less accurate. The symmetrical stretch (ν_1) and bending (ν_2) frequencies are those observed by Frankiss and Harrison (12) in the Raman spectra of the vapor at 335 K. The asymmetrical stretching frequency (ν_3) was not detected in this recent Raman study (12) and still remains relatively uncertain (±10 cm^{-1}). We use ν_3 = 525 cm^{-1} based on the infrared measurements of Savoie and Tremblay (13), as suggested by Frankiss and Harrison (12). The electronic levels and configurations are taken from the CNDO/2 MO calculations and electronic absorption spectral measurements of Colton and Rabalais (14). The principal moments of inertia are: $I_A = 3.4979 \times 10^{-38}$, $I_B = 2.9176 \times 10^{-38}$, and $I_C = 5.8037 \times 10^{-39}$ g cm^2.

Our ideal gas thermal functions are essentially an extension of those previously published by Frankiss and Harrison (12) who also reviewed data published prior to their paper. All earlier functions require revision since they are based on liquid state vibrational frequencies and the molecular structure determined by electron diffraction.

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Cl_2S

SULFUR DICHLORIDE UNIPOSITIVE ION (SCL_2^+) CL_2S^+

(IDEAL GAS) GFW=102.96545

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0				−2.976	214.251		
100							
200							
298	12.156	68.645	68.645	0.000	215.460	211.679	−155.162
300	12.172	68.720	68.645	0.023	215.467	211.655	−154.188
400	12.814	72.320	69.132	1.275	215.286	210.352	−114.930
500	13.168	75.221	70.069	2.576	215.292	209.116	−91.403
600	13.378	77.642	71.135	3.904	215.392	207.874	−75.717
700	13.512	79.715	72.216	5.249	215.555	206.607	−64.505
800	13.601	81.525	73.269	6.605	202.762	204.117	−55.761
900	13.664	83.131	74.277	7.968	203.293	204.256	−49.600
1000	13.710	84.573	75.236	9.337	203.821	204.334	−44.657
1100	13.744	85.881	76.145	10.710	204.347	204.360	−40.602
1200	13.770	87.078	77.007	12.086	204.868	204.338	−37.214
1300	13.790	88.181	77.825	13.464	205.386	204.272	−34.341
1400	13.807	89.204	78.601	14.844	205.901	204.168	−31.872
1500	13.820	90.157	79.340	16.225	206.411	204.027	−29.726
1600	13.831	91.049	80.045	17.607	206.916	203.851	−27.844
1700	13.840	91.889	80.717	18.991	207.418	203.645	−26.180
1800	13.847	92.679	81.360	20.375	207.915	203.407	−24.697
1900	13.854	93.428	81.975	21.760	208.410	203.146	−23.367
2000	13.859	94.139	82.566	23.146	208.900	202.856	−22.167
2100	13.865	94.815	83.133	24.532	209.387	202.541	−21.078
2200	13.869	95.460	83.679	25.919	209.868	202.202	−20.087
2300	13.874	96.077	84.205	27.306	210.348	201.845	−19.179
2400	13.878	96.667	84.712	28.694	210.824	201.465	−18.346
2500	13.882	97.234	85.201	30.082	211.295	201.064	−17.577
2600	13.887	97.779	85.675	31.470	211.764	200.647	−16.866
2700	13.892	98.303	86.133	32.859	212.228	200.209	−16.206
2800	13.898	98.808	86.576	34.249	212.693	199.757	−15.592
2900	13.904	99.296	87.007	35.639	213.148	199.286	−15.018
3000	13.912	99.767	87.424	37.029	213.602	198.799	−14.482
3100	13.921	100.224	87.830	38.421	214.054	198.299	−13.980
3200	13.931	100.666	88.224	39.814	214.502	197.782	−13.508
3300	13.942	101.095	88.608	41.207	214.947	197.254	−13.063
3400	13.955	101.511	88.981	42.602	215.391	196.712	−12.644
3500	13.970	101.916	89.345	43.998	215.831	196.154	−12.248
3600	13.986	102.310	89.699	45.396	216.270	195.588	−11.874
3700	14.004	102.693	90.046	46.795	216.705	195.007	−11.518
3800	14.024	103.067	90.383	48.197	217.141	194.413	−11.181
3900	14.046	103.431	90.713	49.600	217.574	193.811	−10.861
4000	14.069	103.787	91.036	51.006	218.006	193.196	−10.556
4100	14.095	104.135	91.351	52.414	218.438	192.570	−10.265
4200	14.122	104.475	91.659	53.825	218.868	191.932	−9.987
4300	14.152	104.808	91.961	55.239	219.299	191.285	−9.722
4400	14.183	105.133	92.257	56.656	219.730	190.633	−9.469
4500	14.216	105.452	92.547	58.075	220.160	189.964	−9.226
4600	14.251	105.765	92.831	59.499	220.594	189.289	−8.993
4700	14.287	106.072	93.109	60.926	221.026	188.604	−8.770
4800	14.325	106.373	93.382	62.356	221.459	187.908	−8.556
4900	14.364	106.669	93.650	63.791	221.895	187.207	−8.350
5000	14.404	106.960	93.914	65.229	222.333	186.493	−8.151
5100	14.446	107.245	94.172	66.671	222.772	185.774	−7.961
5200	14.489	107.526	94.426	68.118	223.214	185.045	−7.777
5300	14.533	107.803	94.676	69.569	223.658	184.305	−7.600
5400	14.578	108.075	94.922	71.025	224.104	183.557	−7.429
5500	14.623	108.342	95.163	72.485	224.554	182.805	−7.264
5600	14.669	108.606	95.401	73.949	225.004	182.039	−7.104
5700	14.716	108.866	95.635	75.419	225.459	181.266	−6.950
5800	14.763	109.123	95.865	76.893	225.917	180.491	−6.801
5900	14.811	109.376	96.092	78.371	226.376	179.701	−6.656
6000	14.859	109.625	96.316	79.855	226.839	178.908	−6.517

June 30, 1978

SULFUR DICHLORIDE UNIPOSITIVE ION (SCl_2^+) (IDEAL GAS) GFW = 102.96545

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [68.6 ± 1.0] cal/(mol K)

ΔHf°_0 = 214.3 ± 1.3 kcal/mol
$\Delta Hf^\circ_{298.15}$ = [215.460] kcal/mol

CL_2S^+

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2B_1$	0	2
$^2A_1$	20325	2
$^2A_1$	[21000]	2
$^2A_2$	22422	2
$^2A_2$	34198	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
530±30(1)
[200](1)
[530](1)

Bond Distance: S-Cl = [2.00] Å σ = 2
Bond Angle: Cl-S-Cl = [105]°
Product of Moments of Inertia: $I_AI_BI_C$ = [5.6494×10^{-114}] g^3 cm^6

Heat of Formation

ΔHf°_0 is calculated from the selected value of the ionization potential (IP = 9.46±0.02 eV) by addition of the JANAF ΔHf°_0 value for SCl_2 (1). The selected value of IP is calculated as the adiabatic IP from the first band system observed in the HeI photoelectron spectrum of SCl_2 by Solouki et al. (2). The adiabatic IP is 0.21 eV less than the vertical value determined by photoelectron spectroscopy (2) and 0.24-0.74 eV less than the vertical IP's measured by electron impact (3, 4).

ΔHf°_{298} is obtained from the adopted ΔHf°_0 value by using JANAF enthalpies ($H^\circ_0-H^\circ_{298}$) (1) for S(α, c), Cl_2(g), and e^-(g). ΔHr°_{298} determined for the direct ionization $SCl_2 = SCl_2^+ + e^-$ from our tables differs from a room-temperature threshold energy due to inclusion of the enthalpies of all the species in this ionization process and to threshold effects discussed by Rosenstock et al. (5). ΔHf°_{298} should be changed by -1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

We perform bond energy calculations which show that the S-Cl primary bond dissociation energy for SCl_2^+ (66.6 kcal/mol) is quite similar to that for the neutral dichloride (69.7 kcal/mol), indicating that the removal of the electron during ionization should produce minimal structural changes. According to the Walsh diagram (6) for AB_2 molecules, the most loosely bound electron in SCl_2 occupies a $4b_1$ orbital which is S-Cl antibonding and Cl-Cl bonding. Thus, we would expect a slight increase in the bond angle and a decrease in the S-Cl bond distance upon removing this electron to form SCl_2^+. We estimate the Cl-S-Cl bond angle as 105° (102.7° for SCl_2) and the S-Cl bond distance as 2.00 Å (2.015 Å for SCl_2). Based on this estimated structure, the principal moments of inertia are calculated to be $I_A = 3.5075 \times 10^{-38}$, $I_B = 2.9641 \times 10^{-38}$, and $I_C = 5.4339 \times 10^{-39}$ g cm.

The photoelectron spectrum of SCl_2 has been measured by Solouki et al. (2) who reported observing a vibrational spacing of 530±30 cm^{-1} in the first band system. They assigned this progression to the S-Cl symmetric stretching frequency ν_1. By analogy with the observed vibrational frequencies for SCl_2 (1), the difference between ν_1 and ν_3 is expected to be small. We adopt $\nu_1 = \nu_3 = 530$ cm^{-1}, and we estimate the bending frequency to be 5 cm^{-1} lower than that for SCl_2 (205 cm^{-1}, 1).

The electronic configurations of the ground and excited states are predicted from Walsh's empirical diagram (6) which correlates well with the observed photoelectron spectra and calculated orbital energies for the related dihalide molecules SCl_2 (2), OCl_2, and OF_2 (7). We use relative term values for three of the four predicted states calculated from the vertical ionization energies reported by Solouki et al. (2). We include a second $^2A_1$ state at 21000 cm^{-1} based on the fact that this state has been observed in the PE spectrum of OCl_2 (7), lying 2258 cm^{-1} above the first $^2A_1$ state. Inclusion of this state is also supported by the results of orbital energy calculations (2) on SCl_2. The enthalpy between 0 K and 298.15 K is -2.9764 kcal/mol.

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1. JANAF Thermochemical Tables: SCl_2(g), 6-30-78; S(α, c), 9-30-77; e^-(g), 3-31-77; Cl_2(g), 9-30-65.
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CL_2S^+

DICHLORODISULFANE (S_2CL_2) CL_2S_2
(LIQUID) GFW=135.026

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	29.706	53.500	53.500	0.000	-13.900	-9.395	6.886
300	29.706	53.684	53.501	0.055	-13.880	-9.367	6.824
400	29.706	62.230	54.666	3.026	-13.939	-7.975	4.357
410.23	29.706	62.980	54.864	3.329	---------	NORMAL BOILING	-----
500	29.706	68.858	56.866	5.996	-13.700	-6.518	2.849
600	29.706	74.274	59.330	8.967	-13.310	-5.114	1.863
700	29.706	78.854	61.800	11.937	-12.818	-3.787	1.182
800	29.706	82.820	64.185	14.908	-38.253	-4.930	1.347
900	29.706	86.319	66.454	17.879	-37.050	-0.835	0.203
1000	29.706	89.449	68.600	20.849	-35.862	3.123	-0.683

March 31, 1978; June 30, 1978

DICHLORODISULFANE (S_2Cl_2) (LIQUID) GFW = 135.026

$S^\circ_{298.15}$ = 53.5 ± 1.0 cal/(mol K)
Tb = 410.23 ± 1 K

$\Delta Hf^\circ_{298.15}$ = -13.9 ± 0.5 kcal/mol
ΔHv° = 8.59 ± 1.5 kcal/mol

CL_2S_2

Heat of Formation

Fehér and Sträter (1) have measured calorimetrically the heats of chlorination of sulfur and liquid dichlorodisulfane at 283.15 K. Recalculation of their calorimetric data using 1975 atomic weights (2) and a ΔCp° of 10.80 gibbs/mol for the formation reaction $2\ S_{(rh)} + Cl_2(g) \rightarrow S_2Cl_2(\ell)$ leads to the adopted ΔHf° value of -13.9±0.5 kcal/mol.

Other calorimetric values for ΔHf° which were published prior to 1930 have been recently summarized by Mills (3). Two of these four values, which range from -14.3 to -17.6 kcal/mol, agree with the adopted ΔHf° value within the combined experimental error. Our selected value agrees with that from Mills (3) but is some 0.3 kcal/mol less negative than the value (-14.2 kcal/mol) recommended by NBS (4).

Heat Capacity and Entropy

Cp° has been measured calorimetrically as 29.706 cal/(mol K) by Trautz and Rick (5) at 295 K and by Ogier (6) as the mean Cp° value over the temperature range 285-343 K. We adopt this value and assume Cp° is constant from 298.15 K to 1000 K. The value of S°_{298} is selected as 53.5±1.0 cal/(mol K) which minimizes differences between the second and third law entropies of vaporization determined from two independent sets (7, 8) of vapor pressure data. Further details on the results of these analyses can be found in the heat of formation section of the S_2Cl_2 gas phase table (9).

Heat of Vaporization

Tb is the temperature at which the free energy of vaporization becomes zero. The value of ΔHv° is calculated as the difference between the ΔHf° values for the gas and liquid at Tb. Experimental values of Tb determined from vapor pressure measurements include 411 K (7) and 408.9 K (8). The adopted values of Tb and ΔHv° correspond to an entropy of vaporization of 21 cal/(mol K) at Tb.

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$S_2Cl_2(g)$ References

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CL_2S_2

DICHLORODISULFANE (S_2CL_2) CL_2S_2

(IDEAL GAS) GFW=135.026

T, K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.939	-3.637	-3.637	INFINITE
100	11.747	62.203	92.098	-2.989	-3.711	-4.818	10.530
200	15.405	71.567	79.653	-1.617	-3.851	-5.874	6.419
298	17.392	78.180	78.180	0.000	-4.000	-6.853	5.023
300	17.419	78.288	78.180	0.032	-4.003	-6.871	5.005
400	18.411	83.445	78.877	1.827	-5.238	-7.759	4.239
410.23	18.478	83.910	78.997	2.018	------- NORMAL BOILING ------		
500	18.965	87.617	80.221	3.698	-6.098	-8.296	3.626
600	19.316	91.107	81.752	5.613	-6.764	-8.668	3.157
700	19.560	94.104	83.308	7.557	-7.298	-8.942	2.792
800	19.739	96.728	84.825	9.522	-33.739	-11.542	3.153
900	19.871	99.061	86.279	11.503	-33.526	-8.778	2.131
1000	19.964	101.160	87.664	13.495	-33.316	-6.041	1.320
1100	20.024	103.065	88.979	15.495	-33.107	-3.323	0.660
1200	20.060	104.809	90.227	17.499	-32.905	-0.624	0.114
1300	20.074	106.416	91.411	19.506	-32.710	2.057	-0.346
1400	20.069	107.903	92.536	21.513	-32.523	4.725	-0.738
1500	20.053	109.287	93.608	23.520	-32.346	7.380	-1.075

March 31, 1978; June 30, 1978

DICHLORODISULFANE (S_2Cl_2) (IDEAL GAS) GFW = 135.026

ΔHa°_0 = 192.1 ± 1.0 kcal/mol
$S^\circ_{298.15}$ = 78.2 ± 0.1 cal/(mol K)
Ground State Quantum Weight = 1

ΔHf°_0 = -3.6 ± 1.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -4.0 ± 1.0 kcal/mol

CL_2S_2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
546 (1)	Internal Rotation
466 (1)	461 (1)
202 (1)	244 (1)

Point Group = C_2 σ (overall) = 2
Bond Distances: S-Cl = 2.057 ± 0.002 Å S-S = 1.931 ± 0.005 Å
Bond Angles: S-S-Cl = 108.2 ± 0.3° Dihedral angle = 84.8 ± 1.3°
Product of Moments of Inertia: $I_AI_BI_C = 6.3587 \times 10^{-113}\ g^3\ cm^6$
Reduced Moment of Inertia: $I_{red} = 5.487 \times 10^{-39}\ g\ cm^2$
Potential Function for Internal Rotation:
$V = 11.99 - 5.60(1-\cos 2\phi) - 0.70(1-\cos 3\phi)$ kcal/mol

Heat of Formation

Harvey and Schuette (1) and Trautz et al. (2) have used a static method to measure vapor pressures for liquid S_2Cl_2 at various temperatures below the normal boiling point. Barton and Yost (3) measured the extent of dissociation for gaseous S_2Cl_2 above 760 K. These dissociation data have been reanalyzed by Yost and Russell (4) who reported *equilibrium constants* for the reaction $S_2(g) + Cl_2(g) = S_2Cl_2(g)$. We analyze these data by the second and third law methods with the results presented below:

Investigator	Rxn	*No. of* Points	*Temp.* Range, K	ΔHr°_{298}, kcal/mol 2nd law	 3rd law	Drift cal/(mol K)	$-\Delta Hf^\circ_{298}$,[a] kcal/mol
Harvey and Schuette (1)	A	12[b]	304-411	9.46	9.89±0.07	1.1±0.2	4.01
Trautz and Acker (2)	A	Set 1 20[c]	374-410	10.0	9.93±0.01	-0.1±0.2	3.97
		Set 2 39[d]	329-374	10.15	9.95±0.02	-0.6±0.1	3.95
Trautz and Rick (2)	A	22	336-405	10.23	9.98±0.04	-0.8±0.1	3.92
Yost and Russell (4)	B	Equation	760-1100	-35.4	-38.1 ±0.9	-3.1±7	7.4

Rxn: (A) $S_2Cl_2(\ell) = S_2Cl_2(g)$; (B) $S_2(g) + Cl_2(g) = S_2Cl_2(g)$.

[a] Third law values with ΔHf°_{298} (S_2Cl_2, ℓ) = -13.9±0.5 kcal/mol.

[b] Points below 298 K not analyzed; 2 points rejected due to failure of a statistical test.

[c] Two points rejected due to failure of a statistical test. [d] Three points rejected.

We adopt $\Delta Hf^\circ_{298}(S_2Cl_2, g)$ = -4.0 kcal/mol which is the rounded mean value determined from the four third law heats of vaporization. We estimate the uncertainty in the ΔHf° value as ±1.0 kcal/mol which includes contributions from the uncertainties in the values of ΔHf°_{298} and S°_{298} for the liquid (5). ΔHf° at 0 K is -3.6 kcal/mol and the heat of atomization is 192.1±1.0 kcal/mol.

Bodewig and Plambeck (6) determined ΔGr = -12.4 kcal/mol for $2\ S(\ell) + 2\ Cl^- = S_2Cl_2(g) + 2\ e^-$ in fused LiCl-KCl eutectic at 693 K. This datum has been analyzed by Mills (7) who reported ΔHf°_{298} value of -5.8±2 kcal/mol. Our selected *ΔHf° value is some 0.4 kcal/mol less negative than that recommended by NBS (8) and is only 0.1 kcal/mol* less negative than the value adopted by Mills (7).

Heat Capacity and Entropy

The heat capacity and entropy values from 298.15 K to 1500 K are those calculated by Frankiss and Harrison (9) who used gas-phase infrared ($\nu_1 = 546\ cm^{-1}$, 10) and Raman (9) frequencies and the most recent structural data determined in an electron diffraction study by Beagley et al. (11). Contributions to the thermal functions for internal rotation were determined by integration of the potential function from $\phi = 0°$ to 2Π. Terms in the potential function were established from the torsional vibration ($\nu_4 = 92\ cm^{-1}$) and the dihedral angle (84.8°, 11) of the two rotamers. Thermal functions are calculated below 298.15 K by treating the torsion as a harmonic oscillator and including its contribution in the vibrational partition function. Justification for this treatment lies in the fact that values of the ratio V_o/RT become extremely large (>20) at these lower temperatures. We add Rℓn 2 to the calculated entropies below 298.15 K to account for the optical activity of the skew rotamer. The absorption spectra (12) reported for S_2Cl_2 vapor indicate no low-lying electronic states which would contribute to the thermal functions below 1500 K. The principal moments of inertia are: $I_A = 6.8822 \times 10^{-38}$, $I_B = 6.0660 \times 10^{-38}$, and $I_C = 1.5232 \times 10^{-38}\ g\ cm^2$.

Thermodynamic functions previously published for S_2Cl_2 have been reviewed by Frankiss and Harrison (9) who concluded that all previous calculations had treated incorrectly the internal rotation of the SCl top. *Noble and Mei* (14) *have* discussed the vibrational spectral data on S_2Cl_2 published prior to 1974.

CL_2S_2

References

See $S_2Cl_2(\ell)$ Table.

SILICON DICHLORIDE ($SiCl_2$) $\mathrm{CL_2SI}$
(IDEAL GAS) GFW=98.9915

T, K	C_p° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-2.993	-40.330	-40.330	INFINITE
100	9.117	55.609	77.240	-2.163	-40.260	-41.214	90.073
200	11.065	62.550	68.302	-1.150	-40.254	-42.176	46.087
298	12.248	67.214	67.214	0.000	-40.300	-43.111	31.601
300	12.264	67.290	67.214	0.023	-40.301	-43.128	31.418
400	12.881	70.912	67.704	1.283	-40.378	-44.060	24.073
500	13.216	73.826	68.646	2.590	-40.468	-44.969	19.656
600	13.414	76.254	69.718	3.922	-40.573	-45.860	16.704
700	13.539	78.332	70.803	5.270	-40.688	-46.732	14.590
800	13.623	80.146	71.860	6.628	-40.816	-47.588	13.000
900	13.681	81.754	72.872	7.994	-40.952	-48.425	11.759
1000	13.724	83.198	73.834	9.364	-41.100	-49.249	10.763
1100	13.756	84.507	74.745	10.738	-41.258	-50.056	9.945
1200	13.780	85.705	75.609	12.115	-41.426	-50.849	9.261
1300	13.799	86.809	76.429	13.494	-41.604	-51.627	8.679
1400	13.814	87.832	77.207	14.875	-41.792	-52.391	8.178
1500	13.826	88.786	77.948	16.257	-41.991	-53.140	7.742
1600	13.836	89.678	78.653	17.640	-42.201	-53.877	7.359
1700	13.845	90.518	79.327	19.024	-54.414	-54.493	7.005
1800	13.852	91.309	79.971	20.409	-54.590	-54.493	6.616
1900	13.858	92.058	80.587	21.794	-54.767	-54.482	6.267
2000	13.863	92.769	81.179	23.180	-54.946	-54.462	5.951
2100	13.867	93.446	81.747	24.567	-55.124	-54.434	5.665
2200	13.871	94.091	82.294	25.954	-55.305	-54.398	5.404
2300	13.875	94.708	82.820	27.341	-55.487	-54.352	5.165
2400	13.878	95.298	83.328	28.729	-55.670	-54.297	4.944
2500	13.882	95.865	83.818	30.117	-55.856	-54.238	4.741
2600	13.885	96.409	84.292	31.505	-56.043	-54.169	4.553
2700	13.889	96.933	84.750	32.894	-56.232	-54.094	4.379
2800	13.892	97.438	85.195	34.283	-56.424	-54.009	4.216
2900	13.897	97.926	85.625	35.672	-56.618	-53.921	4.064
3000	13.902	98.397	86.043	37.062	-56.814	-53.826	3.921
3100	13.907	98.853	86.449	38.453	-57.012	-53.724	3.787
3200	13.914	99.295	86.844	39.844	-57.213	-53.613	3.662
3300	13.921	99.723	87.227	41.236	-57.416	-53.496	3.543
3400	13.930	100.139	87.601	42.628	-57.621	-53.374	3.431
3500	13.940	100.543	87.965	44.022	-57.828	-53.249	3.325
3600	13.952	100.936	88.320	45.416	-149.998	-50.856	3.087
3700	13.965	101.318	88.666	46.812	-150.109	-48.100	2.841
3800	13.980	101.691	89.004	48.209	-150.221	-45.343	2.608
3900	13.996	102.054	89.334	49.608	-150.335	-42.582	2.386
4000	14.015	102.409	89.656	51.009	-150.450	-39.817	2.175
4100	14.036	102.755	89.972	52.411	-150.566	-37.053	1.975
4200	14.058	103.093	90.280	53.816	-150.681	-34.284	1.784
4300	14.083	103.424	90.582	55.223	-150.795	-31.511	1.602
4400	14.109	103.749	90.878	56.632	-150.910	-28.733	1.427
4500	14.138	104.066	91.167	58.045	-151.022	-25.953	1.260
4600	14.169	104.377	91.451	59.460	-151.132	-23.174	1.101
4700	14.202	104.682	91.729	60.879	-151.241	-20.389	0.948
4800	14.237	104.981	92.002	62.300	-151.348	-17.607	0.802
4900	14.274	105.275	92.270	63.726	-151.451	-14.816	0.661
5000	14.313	105.564	92.533	65.155	-151.551	-12.031	0.526
5100	14.354	105.848	92.791	66.589	-151.646	-9.234	0.396
5200	14.396	106.127	93.045	68.026	-151.739	-6.441	0.271
5300	14.441	106.402	93.295	69.468	-151.827	-3.648	0.150
5400	14.487	106.672	93.540	70.914	-151.912	-0.852	0.034
5500	14.534	106.938	93.781	72.365	-151.992	1.946	-0.077
5600	14.583	107.201	94.018	73.821	-152.067	4.747	-0.185
5700	14.634	107.459	94.252	75.282	-152.138	7.547	-0.289
5800	14.685	107.714	94.482	76.748	-152.204	10.352	-0.390
5900	14.738	107.966	94.708	78.219	-152.266	13.149	-0.487
6000	14.791	108.214	94.931	79.695	-152.323	15.955	-0.581

Dec. 31, 1960; Dec. 31, 1969; Dec. 31, 1970;
Dec. 31, 1976; Dec. 31, 1977

SILICON DICHLORIDE ($SiCl_2$) (IDEAL GAS) GFW = 98.9915

ΔHa_0° = 204.2 ± 1.0 kcal/mol
$S^\circ_{298.15}$ = [67.21 ± 0.2] gibbs/mol

ΔHf_0° = -40.3 ± 0.8 kcal/mol $\mathrm{CL_2SI}$
$\Delta Hf^\circ_{298.15}$ = -40.3 ± 0.8 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$^1A_1$]	0	[1]
[$^3B_1$]	[23000]	[3]
	[28300]	[1]
	[29950]	[1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
514.0(1)
202.2(1)
502.7(1)

Point Group: C_{2v} σ = 2
Bond Distance: Si-Cl = [2.03] Å
Bond Angle: Cl-Si-Cl = 105° ± 3°
Product of the Moments of Inertia: $I_AI_BI_C$ = [5.5517 x 10^{-114}] g^3 cm^6

Heat of Formation

The adopted $\Delta Hf^\circ_{298}(SiCl_2,g)$ = -40.3 kcal/mol is the mean value derived from four studies (2, 3, 7, 8). JANAF analyses of all the equilibrium data are summarized below. The ΔHf°_{298} values are calculated from the third law ΔHr°_{298} values using auxiliary JANAF data (1). Four sets of data (2, 3, 7, 8) yield average values of ΔHf° (from third law) which agree within ±0.4 kcal/mol and values of ΔSr° (second law) which are in reasonable agreement with the JANAF functions. Two of these equilibrium studies used flow techniques, one used mass spectrometry while the fourth used a static technique. The adopted ΔHf°_{298} value corresponds to ΔHa_0° = 204.2 kcal/mol and an average bond energy of 102.1 kcal/mol. This latter value compares with 94.7 kcal/mol for $SiCl_4(g)$, implying that the average bond energy in $SiCl_2(g)$ is 7% larger.

Two other flow studies (4, 5) yield large entropy errors, suggesting that there are temperature-dependent errors in Kp. The reported equilibrium constants are reasonable at the lower temperatures but deviate progressively at the higher temperatures. In contrast, the static study of Ishino (6) gave Kp values which differ by a factor of five from the adopted ones. These data yield a consistent entropy but ΔHr° (third law) is lower by 5 kcal/mol.

Source	Method	No. of pts.	range, K	Reaction	ΔHr°_{298}, kcal/mol 2nd law	ΔHr°_{298}, kcal/mol 3rd law	drift gibbs/mol	ΔHf°_{298} kcal/mol
Schäfer et al (2)	flow	Equation	1273-1473	A	80.56	77.93	-1.9	-40.2
Teichmann (3)	flow	Equation	1223-1573	A	80.83	78.06	-2.0	-40.2
Chechentsev (4)	flow	3	1473-1573	A	131.78	75.96	-37±6	-41.2
Antipin (5)	flow	5	1273-1673	A	113.99	75.00	-26±3	-41.7
Ishino et al. (6)	static	27	1448-1573	A	70.24	72.97	1.8±4	-42.7
Schafer (7)	static	Equation	1400-1593	A	79.78	78.38	-0.9	-40.0
Farber (8)	mass spec	10	1593-1792	B	-31.62	-30.95	0.4±2.0	-40.8

reaction A: $Si(c) + SiCl_4(g) = 2SiCl_2(g)$ reaction B: $Si(g) + SiCl_4(g) = 2SiCl_2(g)$

Heat Capacity and Entropy

Maass, Hauge, and Margrave (9) observed the infrared spectra of $SiCl_2$ in argon, neon, and nitrogen matrices. They observed and assigned all three fundamental frequencies. The bond angle was calculated to be 105±3° from the isotopic splitting. The bond length is assumed to be the same as in SiH_2Cl_2 (1). The earlier work of Milligan and Jacox (10) is consistent with these results. The principal moments of inertia are I_A = 5.101 x 10^{-39}, I_B = 30.54 x 10^{-39}, and I_C = 35.64 x 10^{-39} g cm^2.

The ground state is assumed to be $^1A_1$ as suggested by Hückel-molecular-orbital calculation (12). Singlet excited states (11, 13) are included near 28000 and 30000 cm^{-1}, but the values are placed in brackets to emphasize the uncertainty in the analysis. Also tentatively adopted is the suggestion by Hastie et al. (13) that the continuous spectrum near 23000 cm^{-1} is due to a triplet excited state.

References

1. JANAF Thermochemical Tables: $SiCl_4(g)$, 12-31-70; $SiH_2Cl_2(g)$, 12-31-76; Si(g), 3-31-67; Cl(g), 6-30-72.
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$\mathrm{CL_2SI}$

TRICHLOROSILANE ($SiHCl_3$)
(IDEAL GAS) GFW=135.4529

CL_3HSI

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.860	-117.388	-117.388	INFINITE
100	11.198	59.332	88.906	-2.957	-117.973	-115.823	253.130
200	15.109	68.338	76.516	-1.636	-118.323	-113.534	124.064
298	18.034	74.953	74.953	0.000	-118.600	-111.122	81.454
300	18.078	75.065	74.953	0.033	-118.605	-111.075	80.918
400	19.994	80.549	75.688	1.944	-118.793	-108.535	59.301
500	21.236	85.153	77.133	4.010	-118.900	-105.956	46.313
600	22.099	89.105	78.807	6.179	-118.952	-103.362	37.649
700	22.740	92.562	80.530	8.422	-118.962	-100.762	31.459
800	23.234	95.632	82.230	10.722	-118.944	-98.165	26.817
900	23.625	98.392	83.875	13.066	-118.904	-95.567	23.207
1000	23.939	100.898	85.454	15.445	-118.849	-92.979	20.320
1100	24.195	103.192	86.964	17.852	-118.785	-90.395	17.960
1200	24.406	105.307	88.405	20.282	-118.717	-87.817	15.994
1300	24.580	107.268	89.782	22.732	-118.647	-85.245	14.331
1400	24.726	109.095	91.097	25.197	-118.580	-82.678	12.907
1500	24.849	110.805	92.354	27.676	-118.518	-80.115	11.673
1600	24.953	112.412	93.558	30.166	-118.464	-77.557	10.594
1700	25.043	113.928	94.712	32.666	-130.409	-74.894	9.628
1800	25.119	115.361	95.820	35.175	-130.315	-71.632	8.697
1900	25.186	116.721	96.884	37.690	-130.221	-68.373	7.865
2000	25.243	118.015	97.909	40.211	-130.130	-65.120	7.116
2100	25.294	119.247	98.896	42.738	-130.037	-61.873	6.439
2200	25.338	120.425	99.848	45.270	-129.949	-58.630	5.824
2300	25.378	121.552	100.767	47.806	-129.861	-55.389	5.263
2400	25.413	122.633	101.656	50.345	-129.776	-52.151	4.749
2500	25.444	123.671	102.516	52.888	-129.697	-48.921	4.277
2600	25.472	124.670	103.349	55.434	-129.618	-45.690	3.841
2700	25.497	125.632	104.156	57.982	-129.546	-42.465	3.437
2800	25.519	126.559	104.940	60.533	-129.478	-39.238	3.063
2900	25.540	127.455	105.701	63.086	-129.413	-36.017	2.714
3000	25.558	128.321	106.441	65.641	-129.354	-32.801	2.390
3100	25.575	129.160	107.160	68.198	-129.300	-29.584	2.086
3200	25.590	129.972	107.860	70.756	-129.252	-26.366	1.801
3300	25.604	130.759	108.542	73.316	-129.209	-23.150	1.533
3400	25.617	131.524	109.207	75.877	-129.170	-19.936	1.281
3500	25.629	132.267	109.855	78.439	-129.139	-16.728	1.045
3600	25.640	132.989	110.488	81.003	-221.072	-11.256	0.683
3700	25.650	133.691	111.106	83.567	-220.952	-5.429	0.321
3800	25.659	134.376	111.709	86.133	-220.836	0.392	-0.023
3900	25.668	135.042	112.299	88.699	-220.727	6.213	-0.348
4000	25.676	135.692	112.876	91.266	-220.624	12.031	-0.657
4100	25.683	136.326	113.440	93.834	-220.525	17.842	-0.951
4200	25.690	136.945	113.992	96.403	-220.430	23.654	-1.231
4300	25.696	137.550	114.533	98.972	-220.339	29.464	-1.498
4400	25.702	138.141	115.063	101.542	-220.253	35.276	-1.752
4500	25.708	138.718	115.582	104.112	-220.171	41.082	-1.995
4600	25.713	139.283	116.091	106.684	-220.090	46.888	-2.228
4700	25.718	139.837	116.591	109.255	-220.015	52.693	-2.450
4800	25.723	140.378	117.081	111.827	-219.941	58.490	-2.663
4900	25.727	140.908	117.562	114.400	-219.871	64.295	-2.868
5000	25.732	141.428	118.034	116.973	-219.802	70.087	-3.064
5100	25.735	141.938	118.497	119.546	-219.734	75.893	-3.252
5200	25.739	142.438	118.953	122.120	-219.670	81.688	-3.433
5300	25.743	142.928	119.401	124.694	-219.607	87.481	-3.607
5400	25.746	143.409	119.841	127.268	-219.547	93.272	-3.775
5500	25.749	143.882	120.274	129.843	-219.489	99.066	-3.937
5600	25.752	144.346	120.699	132.418	-219.431	104.856	-4.092
5700	25.755	144.801	121.118	134.993	-219.377	110.645	-4.242
5800	25.757	145.249	121.530	137.569	-219.324	116.439	-4.388
5900	25.760	145.690	121.936	140.145	-219.274	122.221	-4.527
6000	25.762	146.123	122.336	142.721	-219.225	128.010	-4.663

Dec. 31, 1960; Dec. 31, 1976

TRICHLOROSILANE ($SiHCl_3$) (IDEAL GAS) GFW = 135.4529

Point Group C_{3v}
$S^\circ_{298.15}$ = 74.95 ± 0.1 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -117.39 ± 1 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -118.6 ± 1 kcal/mol

CL_3HSI

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2261(1)	811(2)
499(1)	600(2)
254(1)	176(2)

Bond Distances: *Si-H = 1.4555 Å* *Si-Cl = 2.0118 Å* *σ = 3*
Bond Angles: H-Si-Cl = 108.32° Cl-Si-Cl = 110.60°
Product of the Moments of Inertia: $I_AI_BI_C$ = 7.58925 x 10^{-113} g^3 cm^6

Heat of Formation

ΔHf°_{298} is calculated from that of $SiCl_4$(g) (1) using the difference Δ(ΔHf°) = 39.8 kcal/mol taken from the analysis of Hunt and Sirtl (2). The authors derived $\Delta Hf^\circ_{298}(SiHCl_3,g)$ = -116.9±0.7 kcal/mol from six previously reported equilibrium studies. These were at temperatures (773-1200 K) and compositions where the dominant equilibrium was $SiHCl_3+HCl = SiCl_4+H_2$. Selected data (2) were either close to or extrapolated to infinite residence time. Equilibria were reduced to ΔHf°_{298} using auxiliary data (2) which are similar to JANAF values (1), except for $\Delta Hf^\circ_{298}(SiCl_4,g)$. Since this is now 1.7 kcal/mol more negative, *we change ΔHf°($SiHCl_3$) accordingly. Our adopted value is 1.8 kcal/mol more negative than that estimated by linear* interpolation between $SiCl_4$(g) and SiH_4(g) (1).

We dismiss two calorimetric values due to probable bias. These include ΔHf°(ℓ) = -112 kcal/mol from oxygen-bomb calorimetry (3) and ΔHf°(g) = -117.4±1.7 kcal/mol from solution calorimetry (4) in dilute aqueous NaOH. Revised auxiliary data (1, 5) change these values to ΔHf°(g) = -115 (3) and -124 (4) kcal/mol. Wagman et al. (5) adopted -122.6 kcal/mol, presumably based on Wolf (4). The combustion result is suspect because the chemical reaction was determined only qualitatively and included corrosion reactions of the bomb (3). In our approximate revision of the solution result, we eliminate Na_2SiO_3(c) by taking the difference between the overall reactions (4) for $SiCl_4$(ℓ) and $SiHCl_3$(g). This yields the difference *Δ(ΔHf°) = ΔHf°($SiHCl_3$,g)-ΔHf°($SiCl_4$,g) = 34.6 compared to 39.8 kcal/mol* (2). The solution result is suspect due to the possibility that the two hydrolyses did not proceed to equivalent degrees. Solution results (4) for $SiCl_4$, $SiBr_4$(ℓ) and SiI_4(c) also have a negative bias compared to our adopted values (1).

Heat Capacity and Entropy

The molecular structure is based on microwave data of Mitzlaff et al. (6) for twelve isotopic forms of $SiHCl_3$ and $SiDCl_3$. Structural parameters are substitutional (r_s) values. They are in reasonable agreement with previous data (6) determined by various methods. The principal moments of inertia are $I_A = I_B$ = 34.325 x 10^{-39} and I_C = 64.415 x 10^{-39} g cm^2.

Vibrational frequencies are those selected by Shimanouchi (7) from gas-phase infrared spectra of Buerger and Ruoff (8). Assignments are based on band contours and isotopic splittings and are consistent with recent liquid-phase Raman spectra (9).

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from *excited states should be unimportant, as discussed on the tables for SiH_2Cl_2, SiH_3Cl and SiH_3Br* (1).

References

1. JANAF Thermochemical Tables: Cl_4Si(g) 12-31-70; Cl_2H_2Si(g), ClH_3Si(g), BrH_3Si(g), Br_4Si(ℓ) 12-31-76; I_4Si(c), H_4Si(g) 6-30-76; O_2Si(quartz) 6-30-67; ClH(g) 9-30-64; HNaO(c) 12-31-70; ClNa(c) 9-30-64.
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CL_3HSI

SILICON TRICHLORIDE ($SiCl_3$) CL3SI
(IDEAL GAS) GFW=134.4445

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.793	-93.033	-93.033	INFINITE
100	11.233	60.664	89.556	-2.889	-93.237	-92.439	202.024
200	14.867	69.664	77.513	-1.570	-93.288	-91.616	100.112
298	16.906	76.023	76.023	0.000	-93.300	-90.793	66.552
300	16.933	76.127	76.023	0.031	-93.300	-90.777	66.130
400	18.015	81.163	76.702	1.784	-93.299	-89.937	49.138
500	18.613	85.253	78.016	3.618	-93.289	-89.096	38.943
600	18.969	88.681	79.516	5.499	-93.280	-88.259	32.148
700	19.195	91.623	81.040	7.408	-93.273	-87.422	27.294
800	19.347	94.197	82.527	9.336	-93.274	-86.589	23.655
900	19.453	96.482	83.953	11.276	-93.281	-85.750	20.823
1000	19.530	98.536	85.311	13.225	-93.296	-84.915	18.558
1100	19.588	100.400	86.599	15.181	-93.321	-84.075	16.704
1200	19.633	102.107	87.821	17.142	-93.355	-83.234	15.159
1300	19.668	103.679	88.981	19.107	-93.398	-82.389	13.851
1400	19.695	105.138	90.084	21.076	-93.450	-81.540	12.729
1500	19.718	106.498	91.133	23.046	-93.514	-80.687	11.756
1600	19.736	107.771	92.134	25.019	-93.588	-79.829	10.904
1700	19.752	108.968	93.089	26.993	-105.665	-78.859	10.138
1800	19.764	110.097	94.003	28.969	-105.706	-77.282	9.383
1900	19.775	111.166	94.878	30.946	-105.747	-75.700	8.707
2000	19.785	112.181	95.718	32.924	-105.791	-74.117	8.099
2100	19.793	113.146	96.525	34.903	-105.835	-72.534	7.549
2200	19.800	114.067	97.302	36.883	-105.882	-70.948	7.048
2300	19.806	114.947	98.050	38.863	-105.930	-69.357	6.590
2400	19.811	115.790	98.772	40.844	-105.981	-67.765	6.171
2500	19.816	116.599	99.469	42.825	-106.036	-66.173	5.785
2600	19.820	117.376	100.143	44.807	-106.091	-64.577	5.428
2700	19.824	118.125	100.795	46.789	-106.151	-62.981	5.098
2800	19.827	118.846	101.427	48.772	-106.215	-61.377	4.791
2900	19.830	119.541	102.040	50.755	-106.282	-59.777	4.505
3000	19.833	120.214	102.634	52.738	-106.353	-58.174	4.238
3100	19.835	120.864	103.212	54.721	-106.428	-56.567	3.988
3200	19.838	121.494	103.773	56.705	-106.507	-54.956	3.753
3300	19.840	122.104	104.320	58.689	-106.591	-53.343	3.533
3400	19.842	122.697	104.852	60.673	-106.677	-51.726	3.325
3500	19.843	123.272	105.370	62.657	-106.769	-50.114	3.129
3600	19.845	123.831	105.875	64.642	-198.825	-46.233	2.807
3700	19.846	124.375	106.367	66.626	-198.826	-41.994	2.480
3800	19.848	124.904	106.848	68.611	-198.829	-37.758	2.172
3900	19.849	125.419	107.318	70.596	-198.838	-33.518	1.878
4000	19.850	125.922	107.777	72.581	-198.851	-29.278	1.600
4100	19.851	126.412	108.225	74.566	-198.866	-25.043	1.335
4200	19.852	126.891	108.664	76.551	-198.885	-20.805	1.083
4300	19.853	127.358	109.093	78.536	-198.905	-16.564	0.842
4400	19.854	127.814	109.514	80.521	-198.930	-12.319	0.612
4500	19.855	128.260	109.925	82.507	-198.956	-8.078	0.392
4600	19.855	128.697	110.329	84.492	-198.982	-3.836	0.182
4700	19.856	129.124	110.724	86.478	-199.012	0.409	-0.019
4800	19.857	129.542	111.112	88.464	-199.042	4.648	-0.212
4900	19.857	129.951	111.492	90.449	-199.074	8.897	-0.397
5000	19.658	130.352	111.865	92.435	-199.105	13.136	-0.574
5100	19.858	130.746	112.232	94.421	-199.137	17.388	-0.745
5200	19.859	131.131	112.591	96.407	-199.170	21.634	-0.909
5300	19.859	131.509	112.945	98.393	-199.204	25.877	-1.067
5400	19.860	131.881	113.292	100.379	-199.238	30.123	-1.219
5500	19.860	132.245	113.633	102.365	-199.273	34.372	-1.366
5600	19.861	132.603	113.969	104.351	-199.307	38.620	-1.507
5700	19.861	132.954	114.299	106.337	-199.343	42.867	-1.644
5800	19.861	133.300	114.623	108.323	-199.379	47.122	-1.776
5900	19.862	133.639	114.943	110.309	-199.415	51.365	-1.903
6000	19.862	133.973	115.257	112.295	-199.452	55.619	-2.026

Dec. 31, 1969; Dec. 31, 1977

SILICON TRICHLORIDE ($SiCl_3$) (IDEAL GAS) GFW = 134.4445

ΔHa_0° = 285.5 ± 4 kcal/mol
$S_{298.15}^\circ$ = [76.02 ± 1.0] gibbs/mol
Ground State Quantum Weight = [2]

ΔHf_0° = -93.0 ± 4 kcal/mol CL3SI
$\Delta Hf_{298.15}^\circ$ = -93.3 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
470(1)
[254](1)
582(2)
[176](2)

Point Group: C_{3v} σ = 3
Bond Distance: Si-Cl = [2.0118] Å
Bond Angle: Cl-Si-Cl = 110.9°
Product of the Moments of Inertia: $I_AI_BI_C$ = [73.6489 x 10^{-114}] g^3 cm^6

Heat of Formation

The adopted value for the heat of formation of $SiCl_3(g)$ is based on the mass spectrometric study of the silicon subchlorides by Farber and Srivastava (1). Our second and third law analysis of ten data points (1593-1792 K) for the equilibrium $SiCl_4(g) + SiCl_2(g) = 2SiCl_3(g)$ yield ΔHr_{298}° (second law) = 6.4±1.1 kcal/mol and ΔHr_{298}° (third law) = 12.0±0.5 kcal/mol with a drift of 3.3±0.6 gibbs/mol. Using the third law heat of reaction and auxiliary data (2), we calculate and adopt ΔHf_{298}° ($SiCl_3$,g) = -93.3±2 kcal/mol. This leads to ΔHa_0° = 285.5±2 kcal/mol or an average bond energy of 95.2 kcal/mol; a value which is within 0.5 kcal/mol of the average bond energy in $SiCl_4(g)$.

Many less definitive studies leading to the heat of formation of $SiCl_3(g)$ are reported in the literature. These studies yield values which are 5-10 kcal/mol less negative than our adopted value. These works include the relative reaction rates of $SiCl_3$ by Kerr et al. (3), decomposition studies of $SiCl_4$ by adiabatic compression by Vurzel et al. (4), interpretation of electron impact studies on several molecules by Steele et al. (5), examination of infrared emission of a reaction involving $SiCl_3(g)$ by Cadman et al. (6), silane kinetic studies by Walsh and Wells (7), and negative ion studies by Wang et al. (10) and Pabst et al. (11).

Heat Capacity and Entropy

Jacox and Milligan (8) studied the formation of $SiCl_3$ by photolysis of $HSiCl_3$ trapped in matrices of argon, nitrogen and CO. The two stretching fundamentals were assigned from the infrared spectra. Isotopic splittings were found to be consistent with an angle of 72±5° between the threefold axis and each of the Si-Cl bonds. This yields a bond angle of 110.9° which is similar to that of $HSiCl_3$. Non-planarity of $SiCl_3$ is consistent with the electron-spin-resonance studies of Roncin (9).

We adopt the results of Jacox (8) and estimate the bond length and two bending vibrations by analogy with $HSiCl_3$ (2). The ground state quantum weight is taken as two, but excited electronic levels are neglected. Jacox (8) observed unstructured absorptions corresponding to excitation energies of 30000-34500 cm^{-1} and 41000-46000 cm^{-1}. Principal moments of inertia are $I_A = I_B = 33.75 \times 10^{-39}$ and $I_C = 64.65 \times 10^{-39}$ g cm^2.

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CL3SI

COPPER (Cu) (REFERENCE STATE) GFW = 63.546

Cu

0 to 1358.0 K Crystal
1358.0 to 2844.6 K Liquid
2844.6 to 6000 K Ideal Monatomic Gas

See crystal, liquid, and monatomic gas tables for details.

Cu

COPPER (Cu)
(REFERENCE STATE) GFW=63.546

Cu

T, K	gibbs/mol			kcal/mol			
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	-1.197	0.000	0.000	0.000
100	3.826	2.398	12.766	-1.037	0.000	0.000	0.000
200	5.469	5.672	8.450	-0.556	0.000	0.000	0.000
298	5.842	7.926	7.926	0.000	0.000	0.000	0.000
300	5.847	7.963	7.927	0.011	0.000	0.000	0.000
400	6.051	9.676	8.159	0.607	0.000	0.000	0.000
500	6.193	11.043	8.603	1.220	0.000	0.000	0.000
600	6.329	12.185	9.108	1.846	0.000	0.000	0.000
700	6.452	13.169	9.619	2.485	0.000	0.000	0.000
800	6.570	14.039	10.118	3.136	0.000	0.000	0.000
900	6.703	14.820	10.598	3.800	0.000	0.000	0.000
1000	6.850	15.533	11.056	4.477	0.000	0.000	0.000
1100	7.045	16.195	11.494	5.171	0.000	0.000	0.000
1200	7.293	16.818	11.912	5.887	0.000	0.000	0.000
1300	7.682	17.416	12.312	6.635	0.000	0.000	0.000
1400	7.850	20.309	12.767	10.558	0.000	0.000	0.000
1500	7.850	20.850	13.288	11.343	0.000	0.000	0.000
1600	7.850	21.357	13.777	12.128	0.000	0.000	0.000
1700	7.850	21.833	14.237	12.913	0.000	0.000	0.000
1800	7.850	22.281	14.671	13.698	0.000	0.000	0.000
1900	7.850	22.706	15.083	14.483	0.000	0.000	0.000
2000	7.850	23.108	15.474	15.268	0.000	0.000	0.000
2100	7.850	23.491	15.847	16.053	0.000	0.000	0.000
2200	7.850	23.857	16.203	16.838	0.000	0.000	0.000
2300	7.850	24.206	16.543	17.623	0.000	0.000	0.000
2400	7.850	24.540	16.870	18.408	0.000	0.000	0.000
2500	7.850	24.860	17.183	19.193	0.000	0.000	0.000
2600	7.850	25.168	17.484	19.978	0.000	0.000	0.000
2700	7.850	25.464	17.774	20.763	0.000	0.000	0.000
2800	7.850	25.750	18.054	21.548	0.000	0.000	0.000
2900	5.892	51.236	18.806	94.046	0.000	0.000	0.000
3000	6.010	51.437	19.890	94.641	0.000	0.000	0.000
3100	6.131	51.636	20.911	95.248	0.000	0.000	0.000
3200	6.253	51.833	21.874	95.867	0.000	0.000	0.000
3300	6.375	52.027	22.785	96.498	0.000	0.000	0.000
3400	6.496	52.219	23.648	97.142	0.000	0.000	0.000
3500	6.616	52.409	24.467	97.798	0.000	0.000	0.000
3600	6.732	52.597	25.246	98.465	0.000	0.000	0.000
3700	6.845	52.783	25.988	99.144	0.000	0.000	0.000
3800	6.954	52.967	26.695	99.834	0.000	0.000	0.000
3900	7.059	53.149	27.371	100.535	0.000	0.000	0.000
4000	7.158	53.329	28.018	101.246	0.000	0.000	0.000
4100	7.252	53.507	28.637	101.966	0.000	0.000	0.000
4200	7.340	53.683	29.232	102.696	0.000	0.000	0.000
4300	7.422	53.857	29.802	103.434	0.000	0.000	0.000
4400	7.499	54.028	30.351	104.180	0.000	0.000	0.000
4500	7.570	54.198	30.879	104.934	0.000	0.000	0.000
4600	7.636	54.365	31.388	105.694	0.000	0.000	0.000
4700	7.696	54.530	31.878	106.461	0.000	0.000	0.000
4800	7.752	54.692	32.352	107.233	0.000	0.000	0.000
4900	7.804	54.853	32.810	108.011	0.000	0.000	0.000
5000	7.852	55.011	33.252	108.794	0.000	0.000	0.000
5100	7.896	55.167	33.680	109.581	0.000	0.000	0.000
5200	7.938	55.321	34.095	110.373	0.000	0.000	0.000
5300	7.977	55.472	34.497	111.169	0.000	0.000	0.000
5400	8.015	55.622	34.887	111.968	0.000	0.000	0.000
5500	8.052	55.769	35.265	112.772	0.000	0.000	0.000
5600	8.089	55.914	35.632	113.579	0.000	0.000	0.000
5700	8.125	56.058	35.990	114.389	0.000	0.000	0.000
5800	8.164	56.200	36.337	115.204	0.000	0.000	0.000
5900	8.203	56.339	36.675	116.022	0.000	0.000	0.000
6000	8.246	56.478	37.003	116.845	0.000	0.000	0.000

Dec. 31, 1965; June 30, 1977

COPPER (Cu) Cu

(CRYSTAL) GFW=63.546

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.197	0.000	0.000	0.000
100	3.826	2.398	12.766	-1.037	0.000	0.000	0.000
200	5.409	5.672	8.450	-0.556	0.000	0.000	0.000
298	5.842	7.926	7.926	0.000	0.000	0.000	0.000
300	5.847	7.963	7.927	0.011	0.000	0.000	0.000
400	6.051	9.676	8.159	0.607	0.000	0.000	0.000
500	6.193	11.043	8.603	1.220	0.000	0.000	0.000
600	6.328	12.185	9.108	1.846	0.000	0.000	0.000
700	6.452	13.169	9.619	2.485	0.000	0.000	0.000
800	6.571	14.039	10.118	3.136	0.000	0.000	0.000
900	6.703	14.820	10.598	3.800	0.000	0.000	0.000
1000	6.850	15.533	11.056	4.477	0.000	0.000	0.000
1100	7.045	16.195	11.494	5.171	0.000	0.000	0.000
1200	7.293	16.818	11.912	5.887	0.000	0.000	0.000
1300	7.682	17.416	12.312	6.635	0.000	0.000	0.000
1400	8.188	18.003	12.698	7.428	-3.130	0.097	-0.015
1500	8.706	18.586	13.071	8.272	-3.071	0.326	-0.047
1600	9.224	19.164	13.434	9.169	-2.959	0.549	-0.075
1700	9.742	19.739	13.788	10.117	-2.796	0.763	-0.098
1800	10.260	20.311	14.134	11.117	-2.581	0.967	-0.117
1900	10.778	20.879	14.474	12.169	-2.314	1.157	-0.133
2000	11.296	21.445	14.809	13.273	-1.995	1.331	-0.145

Dec. 31, 1965; June 30, 1977

COPPER (Cu) (CRYSTAL) GFW = 63.546

Cu

$S°_{298.15}$ = 7.926 ± 0.02 gibbs/mol
T_m = 1358.0 ± 0.2 K

$ΔHf°_0$ = 0 kcal/mol
$ΔHf°_{298.15}$ = 0 kcal/mol
ΔHm° = 3.140 ± 0.1 kcal/mol
$ΔHs°_{298.15}$ = 80.650 ± 0.5 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity and entropy of copper have been well established by the critical review of Furukawa et.al. (1). Their recommended smoothed values are adopted with minor corrections for a change in the gram formula weight from 63.54 to 63.546 (2) and for a change to the International Practical Temperature Scale of 1968 (3). These corrections increase the entropy at 298.15 K from 7.923 to 7.926 gibbs/mol and the enthalpy difference, $H_{298}-H_0$, from 1.1962 to 1.1967 kcal/mol. The values recommended by CODATA (4) are those of Furukawa (1).

From 300 K to the melting point, the heat capacity selected by Hultgren et al. (5) has been adopted, with correction for gram formula weight and temperature scale, and has been joined smoothly with the adopted low temperature data. The measurements of Chekhovskoi and Gerasina (6), as given by their equation (300-900 K), are in excellent agreement with the selection of Hultgren et al. (5). Also, while the data given by Brooks et al. (7) (313-1193 K) were 1 to 2% higher than Hultgren's selected values, the later measurements of Yeh and Brooks (8) on the same sample did not totally confirm the earlier results and measurements on a larger sample (370-870 K) are in good agreement with Hultgren et al. (5). The same evaluation used by Hultgren et al. (5) is used by two other tabulations (9, 10), although there are small differences in the tabulated values.

Melting Data

Righini et al. (11) reviewed the precise measurements of the freezing point of high-purity copper made since 1960. The mean value of five investigations is 1357.99±0.24 K (1968 International Practical Temperature Scale). N. N. Ergardt (12) found 1358.41 K and Righini et al. (11) measured 1357.98±0.1 K. We adopt 1358.0±0.2 K for the melting point. As a secondary fixed point, the 1968 International Practical Temperature Scale uses 1357.6 K (13).

The adopted value for ΔHm is based upon five measured values and an evaluation of $H°_{1358}-H°_{298}$ for the solid and the liquid.

Investigators	ΔHm, kcal/mol
Wust, Meuthen, and Durrer (14)	3.239
Oelsen, Schurmann, and Buchholz (15)	3.030
Shuermann and Kaune (16)	3.080
Dokken and Elliott (17)	3.290±0.275
Vollmer and Kohlhaus (18)	3.107±0.048

The average is 3.149 kcal/mol. Our least squares linear fit of the liquid enthalpy data of Wust, Meuthen, and Durrer (14) leads to ΔHm = 3.139 kcal/mol, and with this change, the average of the five measured values is 3.129 kcal/mol.

We adopt ΔHm = 3.140±0.1 kcal/mol in agreement with the range of measured values and with our evaluation of $(H_{1358}-H_{298})(c)$ = 7.088 kcal/mol and $(H_{1358}-H_{298})(\ell)$ = 10.228 kcal/mol.

Sublimation Data

See Cu(g) table for details.

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Cu

COPPER (Cu) Cu

(LIQUID) GFW=63.546

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	5.841	9.947	9.947	0.000	2.833	2.231	-1.635
300	5.847	9.983	9.947	0.011	2.833	2.227	-1.622
400	6.051	11.696	10.179	0.607	2.833	2.025	-1.106
500	6.193	13.064	10.624	1.220	2.833	1.823	-0.797
600	6.329	14.205	11.128	1.846	2.833	1.621	-0.591
700	6.452	15.190	11.639	2.485	2.833	1.419	-0.443
800	6.570	16.059	12.139	3.136	2.833	1.217	-0.333
900	7.850	16.840	12.618	3.800	2.833	1.015	-0.246
1000	7.850	17.667	13.083	4.585	2.941	0.807	-0.176
1100	7.850	18.415	13.534	5.370	3.032	0.589	-0.117
1200	7.850	19.098	13.970	6.155	3.101	0.364	-0.066
1300	7.850	19.727	14.389	6.940	3.138	0.134	-0.022
1400	7.850	20.309	14.791	7.725	0.000	0.000	0.000
1500	7.850	20.850	15.177	8.510	0.000	0.000	0.000
1600	7.850	21.357	15.548	9.295	0.000	0.000	0.000
1700	7.850	21.833	15.903	10.080	0.000	0.000	0.000
1800	7.850	22.281	16.245	10.865	0.000	0.000	0.000
1900	7.850	22.706	16.574	11.650	0.000	0.000	0.000
2000	7.850	23.108	16.891	12.435	0.000	0.000	0.000
2100	7.850	23.491	17.196	13.220	0.000	0.000	0.000
2200	7.850	23.857	17.491	14.005	0.000	0.000	0.000
2300	7.850	24.206	17.775	14.790	0.000	0.000	0.000
2400	7.850	24.540	18.050	15.575	0.000	0.000	0.000
2500	7.850	24.860	18.316	16.360	0.000	0.000	0.000
2600	7.850	25.168	18.574	17.145	0.000	0.000	0.000
2700	7.850	25.464	18.824	17.930	0.000	0.000	0.000
2800	7.850	25.750	19.066	18.715	0.000	0.000	0.000
2900	7.850	26.025	19.301	19.500	-71.713	1.397	-0.105
3000	7.850	26.291	19.530	20.285	-71.523	3.915	-0.285
3100	7.850	26.549	19.752	21.070	-71.345	6.427	-0.453
3200	7.850	26.798	19.968	21.855	-71.179	8.933	-0.610
3300	7.850	27.040	20.179	22.640	-71.025	11.434	-0.757
3400	7.850	27.274	20.384	23.425	-70.884	13.931	-0.895
3500	7.850	27.501	20.584	24.210	-70.755	16.423	-1.025
3600	7.850	27.723	20.780	24.995	-70.637	18.913	-1.148
3700	7.850	27.938	20.970	25.780	-70.531	21.398	-1.264
3800	7.850	28.147	21.156	26.565	-70.436	23.882	-1.373
3900	7.850	28.351	21.338	27.350	-70.352	26.362	-1.477
4000	7.850	28.550	21.516	28.135	-70.278	28.841	-1.576

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COPPER (Cu) (LIQUID) GFW = 63.546

Cu

$S°_{298.15}$ = 9.947 ± 0.1 gibbs/mol

Tm = 1358.0 ± 0.2 K

Tb = 2844.61 K

$\Delta Hf°_{298.15}$ = 2.833 ± 0.12 kcal/mol

ΔHm° = 3.140 ± 0.1 kcal/mol

ΔHv° = 71.823 ± 0.5 kcal/mol

Heat of Formation

The heat of formation at 298.15 is calculated from that of the crystal, defined as zero, by adding ΔHm° and the difference between $H°_{1358}-H°_{298}$ for the crystal and liquid. *The heat of formation between Tm and Tb is zero by definition.*

Heat Capacity and Entropy

Since the critical evaluation of Hultgren et al. (1) and the selection of 7.80 gibbs/mol for the heat capacity of liquid copper, there have been two experimental investigations. Chaudhuri et al. (2) measured $H_T°-H°_{298}$ (1386-1887 K) by levitation-heating aluminum-block drop calorimetry and determined Cp(ℓ) = 7.89±0.41 gibbs/mol. Stephens (3) found Cp(ℓ) = 8 gibbs/mol by levitation-heating liquid-argon calorimetry (1428 - 2007 K). The scatter in the new liquid argon calorimetry data is large and is considered only in that it tends to support a "chronological increase" in Cp(ℓ) of copper. The enthalpy differences, $(H_{1358}-H_{298})(\ell)$, derived from the measurements of Vollmer and Kohlhaus (4) and Chaudhuri et al. (2) are in good agreement at about 10.228 kcal/mol, which we adopt. The scatter of liquid enthalpy measurements easily accommodates a wide range of values for Cp(ℓ); we adopt 7.85 gibbs/mol, an average of the value selected by Hultgren et al. (1) and the later measurement of Chaudhuri et al. (2). This value is assumed constant from 900 to 4000 K. A glass transition is assumed at 900 K below which the heat capacity is that of the crystal.

The entropy was obtained in a manner similar to that used to obtain the heat of formation.

Melting Data

See Cu(c) table for details.

Vaporization Data

Tb = 2844.61 K is the calculated temperature at which the Gibbs energy difference is zero for the reaction Cu(ℓ) = Cu(g). ΔHv° is the difference in ΔHf° between gas and liquid at Tb.

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COPPER MONATOMIC (Cu)
(IDEAL GAS) GFW=63.546

T, K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	80.366	80.366	INFINITE
100	4.968	34.317	44.160	-0.984	80.703	77.511	-169.397
200	4.568	37.760	40.198	-0.488	80.718	74.301	-81.191
298	4.968	39.744	39.744	0.000	80.650	71.164	-52.164
300	4.968	35.774	39.744	0.009	80.648	71.105	-51.799
400	4.968	41.204	39.939	0.506	80.549	67.938	-37.119
500	4.968	42.312	40.307	1.003	80.433	64.798	-28.323
600	4.968	43.218	40.719	1.500	80.304	61.684	-22.468
700	4.968	43.984	41.132	1.996	80.161	58.591	-18.293
800	4.968	44.647	41.531	2.493	80.007	55.520	-15.167
900	4.968	45.232	41.910	2.990	79.840	52.469	-12.741
1000	4.968	45.756	42.269	3.487	79.660	49.437	-10.804
1100	4.969	46.229	42.608	3.984	79.463	46.425	-9.224
1200	4.970	46.662	42.928	4.480	79.243	43.431	-7.910
1300	4.972	47.059	43.231	4.978	78.993	40.456	-6.801
1400	4.977	47.428	43.517	5.475	75.567	37.600	-5.869
1500	4.985	47.772	43.790	5.973	75.280	34.898	-5.085
1600	4.597	48.094	44.049	6.472	74.994	32.215	-4.400
1700	5.016	48.397	44.296	6.973	74.710	29.550	-3.799
1800	5.041	48.685	44.532	7.475	74.427	26.901	-3.266
1900	5.074	48.958	44.757	7.981	74.148	24.269	-2.792
2000	5.116	49.219	44.974	8.491	73.873	21.651	-2.366
2100	5.168	49.470	45.182	9.005	73.602	19.046	-1.982
2200	5.229	49.712	45.383	9.524	73.336	16.455	-1.635
2300	5.300	49.946	45.576	10.051	73.078	13.875	-1.318
2400	5.379	50.173	45.763	10.585	72.827	11.306	-1.030
2500	5.468	50.394	45.944	11.127	72.584	8.748	-0.765
2600	5.564	50.611	46.119	11.679	72.351	6.199	-0.521
2700	5.668	50.823	46.289	12.240	72.127	3.659	-0.296
2800	5.778	51.031	46.455	12.812	71.914	1.127	-0.088
2900	5.892	51.236	46.616	13.396	0.000	0.000	0.000
3000	6.010	51.437	46.774	13.991	0.000	0.000	0.000
3100	6.131	51.636	46.927	14.598	0.000	0.000	0.000
3200	6.253	51.833	47.078	15.217	0.000	0.000	0.000
3300	6.375	52.027	47.225	15.849	0.000	0.000	0.000
3400	6.496	52.219	47.369	16.492	0.000	0.000	0.000
3500	6.616	52.409	47.510	17.148	0.000	0.000	0.000
3600	6.732	52.597	47.649	17.815	0.000	0.000	0.000
3700	6.845	52.783	47.785	18.494	0.000	0.000	0.000
3800	6.954	52.967	47.919	19.184	0.000	0.000	0.000
3900	7.059	53.149	48.051	19.885	0.000	0.000	0.000
4000	7.158	53.329	48.180	20.596	0.000	0.000	0.000
4100	7.252	53.507	48.308	21.316	0.000	0.000	0.000
4200	7.340	53.683	48.434	22.046	0.000	0.000	0.000
4300	7.422	53.857	48.558	22.784	0.000	0.000	0.000
4400	7.499	54.028	48.681	23.530	0.000	0.000	0.000
4500	7.570	54.198	48.801	24.284	0.000	0.000	0.000
4600	7.636	54.365	48.920	25.044	0.000	0.000	0.000
4700	7.696	54.530	49.038	25.811	0.000	0.000	0.000
4800	7.752	54.692	49.154	26.583	0.000	0.000	0.000
4900	7.804	54.853	49.269	27.361	0.000	0.000	0.000
5000	7.852	55.011	49.382	28.144	0.000	0.000	0.000
5100	7.896	55.167	49.494	28.931	0.000	0.000	0.000
5200	7.938	55.320	49.604	29.723	0.000	0.000	0.000
5300	7.577	55.472	49.714	30.519	0.000	0.000	0.000
5400	8.015	55.622	49.822	31.318	0.000	0.000	0.000
5500	8.052	55.769	49.929	32.122	0.000	0.000	0.000
5600	8.089	55.914	50.034	32.929	0.000	0.000	0.000
5700	8.125	56.058	50.139	33.739	0.000	0.000	0.000
5800	8.164	56.199	50.242	34.554	0.000	0.000	0.000
5900	8.203	56.339	50.344	35.372	0.000	0.000	0.000
6000	8.246	56.478	50.445	36.195	0.000	0.000	0.000

Dec. 31, 1965; June 30, 1977

COPPER (Cu) (IDEAL GAS) GFW = 63.546

Ground State Configuration $^2S_{1/2}$

$S^o_{298.15}$ = 39.744 ± 0.006 gibbs/mol

ΔHf^o_0 = 80.37 ± 0.5 kcal/mol

$\Delta Hf^o_{298.15}$ = 80.65 ± 0.5 kcal/mol

Electronic Levels and Quantum Weight

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.0	2	44406.3	6	54784.0	4	57948.7	4	60085.2	2
11202.6	6	44544.2	4	55027.7	2	57893.1	4	60594.5	4
13245.4	4	44915.6	2	55387.7	4	57895.1	6	60595.1	6
30535.3	2	43726.2	6	55391.3	6	57905.2	6	60595.0	4
30783.7	4	44963.2	8	55426.3	8	57908.7	8	60601.9	2
39018.7	6	45821.0	2	55429.8	6	58568.9	2	60956.9	4
40114.0	4	45879.3	4	56030.0	8	59249.5	4	60957.4	6
40943.7	2	46172.8	4	58119.3	6	59250.7	6	60958.0	4
40909.1	10	46598.4	6	56343.7	4	59275.3	4	60958.0	2
41153.4	8	49383.0	4	58364.7	2	59323.2	2	61215.6	4
41562.9	6	49383.6	2	56651.5	6	59647.9	2	61215.6	6
42302.5	4	49935.2	4	58690.9	4	60065.5	4		
43137.2	2	49942.1	6	56671.4	2	60066.3	6		
43514.0	8	52848.8	2	57419.3	2	60070.6	4		

Heat of Formation

The heat of sublimation has been determined from vapor pressure measurements by several investigators. Our second and third law analyses of twenty data sets are summarized in the following table:

Ref.	Range, K	Method	Points	ΔHs^o_{298}, kcal/mol 2nd Law	3rd Law	Drift Gibbs/Mol
1	1419-1463	Knudsen	7	63.4±11.7	81.83±0.77	12.9± 8.2
2	1768-2116	Boiling	6	66.8± 2.6	73.44±1.22	3.4± 1.3
3	1268-1320	Langmuir	7*	93.1± 3.6	81.25±0.49	-9.1± 2.8
3	1356-1466	Langmuir	5	79.3± 2.4	79.98±0.31	0.5± 1.7
4	1143-1292	Langmuir	5	81.4± 1.0	80.61±0.19	-0.6± 0.8
5	1242-1340	Knudsen	6	80.6± 0.2	81.40±0.05	0.6± 0.2
5	1370-1563	Knudsen	10*	83.1± 0.6	81.35±0.24	-1.2± 0.5
6	1605-1879	Transport	21*	79.8± 0.6	80.53±0.25	0.4± 0.4
7	1192-1360	Knudsen	13	80.3± 4.0	81.17±1.18	0.7± 3.1
8	987-1330	Knudsen	14	78.8± 2.4	82.14±1.73	2.8± 2.0
9	1429-1640	Knudsen	9	76.8± 1.0	80.30±0.41	2.3± 0.6
10	1367-1523	Langmuir	8	80.0± 1.6	80.21±0.32	0.1± 1.1
11	1475-1707	Knudsen	8	83.4± 1.3	81.05±0.42	-1.5± 0.8
12	1265-1356	Torsion Effusion	Equation	81.2	80.42	-0.6±
13	1307-1348	Atomic Absorption	3	101.7±29.2	80.11±1.16	-16.3±27.0
14	1066-1238	Atomic Absorption	9	75.7± 1.1	81.25±0.66	4.8± 1.0
15	1473-1673	Langmuir	5	77.0± 1.9	79.29±0.40	1.4± 1.2
16	1140-1348	Atomic Absorption	5	77.7± 2.6	79.52±0.61	1.5± 2.1
16	1375-1580	Atomic Absorption	5	79.0± 3.7	80.33±0.73	0.9± 2.5
17	1252-1323	Langmuir	4	77.9±11.8	80.86±0.78	2.3± 9.2

*One point rejected by statistical test.

The heat of sublimation calculated from the data of Baur and Brunner (2) is low and is discarded; three other data sets (1, 3 (1268-1320), 13) show large drift and poor agreement between second and third law heats. The average third law heat of sublimation at 298.15 K of the remaining 16 is 80.65 kcal/mol. Two other references list only single heats of vaporization (18, 19) which correct to ΔHs^o_{298} = 80.69±1.2 kcal/mol and 80.30±3.8 kcal/mol, respectively. We adopt ΔHs^o_{298} = 80.65±0.5 kcal/mol.

The heat of formation of the gas above Tb is defined as zero.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore (20). Many of the predicted levels are missing. A BETHE-FILL procedure (21) has been used for filling in the missing levels and cutting off the summation of the partition function, with b = 2 and Σg = 642 (480 more than observed) for the principal quantum number 4 (22). Tondello (23) has extended the energy levels up to n = 31 and obtained an ionization potential of 62 316.6±0.2 cm^{-1} which is only slightly lower than that adopted by Moore (20). Only the energy levels up through n = 11 (20) needed for the adopted BETHE-FILL procedure are listed above.

For copper monatomic ideal gas, it makes little difference up to about 4000 K which cut-off procedure (21) is used or whether or not missing levels are filled. At 6000 K, the difference in heat capacity calculated by the BETHE-FILL technique (21) and the TEMPER method (21) is 0.111 gibbs/mol; the free energy function difference is only 0.0006 gibbs/mol.

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COPPER UNIPOSITIVE ION (Cu^+) Cu^+
(IDEAL GAS) GFW=63.54545

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0				-1.481	258.538		
1CC							
20C							
298	4.968	38.366	38.366	0.000	260.303	249.740	-183.062
300	4.568	38.397	38.366	0.009	260.310	249.674	-181.885
400	4.968	39.826	38.561	0.506	260.708	246.069	-134.444
5C0	4.968	40.935	38.929	1.003	261.089	242.365	-105.936
600	4.968	41.841	39.341	1.500	261.457	238.586	-86.904
7CC	4.968	42.606	39.754	1.996	261.810	234.745	-73.290
800	4.968	43.270	40.153	2.493	262.153	230.855	-63.066
900	4.968	43.855	40.533	2.990	262.483	226.923	-55.104
1000	4.968	44.378	40.892	3.487	262.800	222.955	-48.726
11CC	4.968	44.852	41.230	3.984	263.100	218.956	-43.502
1200	4.968	45.284	41.550	4.480	263.376	214.930	-39.144
1300	4.968	45.682	41.853	4.977	263.622	210.882	-35.452
14C0	4.968	46.050	42.140	5.474	260.693	206.915	-32.300
15C0	4.968	46.393	42.412	5.971	260.902	203.067	-29.586
1600	4.568	46.713	42.671	6.468	261.111	199.204	-27.210
1700	4.968	47.014	42.918	6.964	261.318	195.328	-25.111
1800	4.968	47.298	43.153	7.461	261.527	191.440	-23.244
1900	4.568	47.567	43.379	7.958	261.736	187.541	-21.572
2000	4.969	47.822	43.594	8.455	261.945	183.631	-20.066
2100	4.969	48.064	43.802	8.952	262.154	179.710	-18.702
2200	4.971	48.296	44.001	9.449	262.362	175.779	-17.462
2300	4.973	48.517	44.192	9.946	262.571	171.839	-16.328
24C0	4.976	48.728	44.377	10.443	262.780	167.890	-15.288
2500	4.980	48.931	44.555	10.941	262.990	163.932	-14.331
2600	4.987	49.127	44.727	11.439	263.200	159.965	-13.446
27C0	4.996	49.315	44.894	11.939	263.411	155.99C	-12.626
2800	5.008	49.497	45.055	12.439	263.623	152.008	-11.865
29C0	5.024	49.673	45.211	12.940	192.123	149.415	-11.260
3000	5.044	49.844	45.363	13.444	192.529	147.936	-10.777
31C0	5.069	50.010	45.510	13.949	192.924	146.443	-10.324
3200	5.099	50.171	45.653	14.458	193.310	144.937	-9.899
3300	5.136	5C.328	45.792	14.969	193.687	143.420	-9.498
3400	5.180	50.482	45.928	15.485	194.056	141.891	-9.121
35C0	5.232	50.633	46.060	16.006	194.418	140.351	-8.764
36C0	5.291	50.782	46.189	16.532	194.774	138.802	-8.426
3700	5.359	50.927	46.315	17.064	195.123	137.242	-8.106
3800	5.436	51.071	46.439	17.604	195.470	135.673	-7.803
390C	5.521	51.214	46.559	18.151	195.813	134.095	-7.514
4000	5.617	51.355	46.677	18.708	196.156	132.508	-7.240
41C0	5.721	51.495	46.793	19.275	196.500	130.913	-6.978
42C0	5.835	51.634	46.907	19.853	196.844	129.308	-6.729
43CC	5.958	51.772	47.018	20.442	197.192	127.696	-6.490
440C	6.090	51.911	47.128	21.045	197.546	126.076	-6.262
4500	6.231	52.049	47.236	21.661	197.905	124.448	-6.044
4600	6.380	52.188	47.342	22.291	198.272	122.812	-5.835
47C0	6.537	52.327	47.447	22.937	198.647	121.166	-5.634
480C	6.702	52.466	47.550	23.599	199.034	119.514	-5.442
49C0	6.872	52.606	47.651	24.278	199.432	117.853	-5.256
500C	7.049	52.747	47.752	24.974	199.842	116.185	-5.078
5100	7.231	52.888	47.851	25.688	200.265	114.507	-4.907
5200	7.416	53.030	47.949	26.420	200.702	112.821	-4.742
53CC	7.605	53.173	48.047	27.171	201.156	111.127	-4.582
5400	7.797	53.317	48.143	27.941	201.622	109.425	-4.429
55CC	7.989	53.462	48.238	28.730	202.104	107.712	-4.280
5600	8.183	53.608	48.333	29.539	202.602	105.991	-4.136
57C0	8.375	53.754	48.427	30.367	203.117	104.262	-3.998
580C	8.567	53.902	48.520	31.214	203.646	102.523	-3.863
5900	8.756	54.050	48.612	32.080	204.191	100.776	-3.733
60C0	8.942	54.158	48.704	32.965	204.750	99.018	-3.607

Dec. 31, 1965; June 30, 1977

COPPER UNIPOSITIVE ION (Cu^+) (IDEAL GAS) GFW = 63.54545

Cu^+

Ground State Configuration $^1S_0$

$S^\circ_{298.15}$ = 38.366 ± 0.01 gibbs/mol

ΔHf°_0 = 258.538 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 260.303 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	1	69868.1	5	85388.8	5
21928.6	7	69704.8	9	88362.0	5
22847.0	5	71531.5	7	88605.2	3
23998.3	3	72724.0	5	88926.1	1
26264.5	5	70841.5	7	95565.7	9
66418.7	5	71493.9	5	107942.1	9
67916.6	3	73102.1	3	109275.9	7
68850.3	1	71920.1	7	110363.4	5
68730.8	9	73353.4	5	111124.0	3
68447.8	7	73595.9	3		

Heat of Formation

The ionization limit of Cu(g), 62316.6±0.2 cm^{-1} (178.172±0.0006 kcal/mol) reported by Tondello (1) is adopted as the heat at 0 K for the reaction $Cu(g) = Cu^+(g) + e^-(g)$. The heat of formation at 298.15 K, 260.303±0.5 kcal/mol, is derived from the heat of reaction using auxiliary JANAF data (2). The uncertainty in the heat of formation is due to the uncertainty in the heat of formation of Cu(g) (2).

Heat Capacity and Entropy

The ground state configuration and the electronic energy levels and quantum weights listed are taken from the compilation of Moore (3). Many predicted levels are missing but our calculations indicate that inclusion of higher observed energy levels (3) and any reasonable method of filling in the missing levels and cutting off the summation of the partition function (4) has no effect on the thermodynamic functions to 6000 K. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut-off procedures (4).

References

1. G. Tondello, J. Opt. Soc. Amer. 63, 346 (1973).
2. JANAF Thermochemical Tables: Cu(ref st), Cu(g), 6-31-77; e^-(ref st), 3-31-77.
3. C. E. Moore, U.S. Natl. Bur. Std., Circ. 467, Vol. II, 1952.
4. J. R. Downey, Jr., The Dow Chemical Company, Thermal Research, to be published, 1977.

COPPER MONOFLUORIDE (CuF) CuF

(CRYSTAL) GFW=82.544403

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	12.400	15.500	15.500	0.000	-67.000	-62.036	45.473
300	12.420	15.577	15.500	0.023	-66.995	-62.006	45.171
400	13.180	19.258	15.997	1.304	-66.694	-60.387	32.993
500	13.780	22.266	16.959	2.653	-66.360	-58.848	25.722
600	14.240	24.821	18.062	4.056	-65.999	-57.379	20.900
700	14.570	27.042	19.189	5.497	-65.621	-55.972	17.475
800	14.820	29.004	20.296	6.967	-65.233	-54.621	14.921
900	15.010	30.761	21.363	8.459	-64.840	-53.318	12.947
1000	15.140	32.350	22.383	9.966	-64.450	-52.058	11.377
1100	15.240	33.798	23.356	11.486	-64.067	-50.838	10.100
1200	15.310	35.127	24.282	13.013	-63.701	-49.651	9.043
1300	15.360	36.355	25.164	14.547	-63.363	-48.495	8.153
1400	15.387	37.494	26.005	16.084	-66.199	-47.265	7.378
1500	15.400	38.556	26.807	17.624	-65.896	-45.923	6.691
1600	15.400	39.550	27.572	19.164	-65.594	-44.602	6.092
1700	15.400	40.484	28.305	20.704	-65.293	-43.299	5.566
1800	15.400	41.364	29.006	22.244	-64.994	-42.014	5.101
1900	15.400	42.196	29.678	23.784	-64.695	-40.745	4.687
2000	15.400	42.986	30.324	25.324	-64.399	-39.493	4.315

June 30, 1966; Dec. 31, 1977

CuF

$S^\circ_{298.15}$ = [15.5 ± 0.5] gibbs/mol
Tm = Unknown

ΔHf°_0 = Unknown
$\Delta Hf^\circ_{298.15}$ = [-67 ± 10] kcal/mol
ΔHm° = Unknown
$\Delta Hs^\circ_{298.15}$ = [64] kcal/mol

Heat of Formation

The heat of formation is calculated by combining the adopted ΔHf°_{298}(CuF,g) = -3.0±4 kcal/mol with the estimated heat of sublimation of 64 kcal/mol. A comparison of heats of sublimation of LiF with LiCl, NaF with NaCl, and KF with KCl (1) along with a heat of sublimation of CuCl of 54.77 kcal/mol (1) indicates that ΔHs°_{298} (CuF,c) might be in the range of 58 to 71 kcal/mol. The tabulations of King et al. (2) lead to ΔHs°_{298} = 64 kcal/mol which we adopt. We derive ΔHf°_{298}(CuF,c) = -67±10 kcal/mol.

Heat Capacity and Entropy

We adopt the heat capacities estimated by King et al. (2) and S°_{298} = 15.5±0.5 gibbs/mol estimated by Kelley and King (3).

References

1. JANAF Thermochemical Tables: LiCl(c, g), 9-30-65; NaCl(c, g), 9-30-64; KCl(c, g), CuCl(c, g), 3-31-66; LiF(c, g), NaF(c, g), 12-31-68, KF(c, g), 6-30-69.
2. E. G. King, A. D. Mah, and L. B. Pankratz, "Thermodynamic Properties of Copper and Its Inorganic Compounds. INCRA Series on a Metallurgy of Copper, No. 2," INCRA, New York, 1973.
3. K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 1961.

CuG

COPPER MONOFLUORIDE (CuF) CuF

(IDEAL GAS) GFW=82.544403

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.171	-2.919	-2.919	INFINITE
100	6.980	46.078	60.832	-1.475	-2.731	-5.065	11.069
200	7.443	51.030	54.821	-0.758	-2.845	-7.363	8.045
298	7.978	54.108	54.108	0.000	-3.000	-9.547	6.998
300	7.986	54.157	54.108	0.015	-3.003	-9.588	6.985
400	8.334	56.506	54.426	0.832	-3.166	-11.758	6.424
500	8.547	58.391	55.036	1.677	-3.336	-13.887	6.070
600	8.682	59.962	55.730	2.539	-3.515	-15.980	5.821
700	8.775	61.308	56.433	3.412	-3.705	-18.043	5.633
800	8.841	62.484	57.117	4.293	-3.906	-20.078	5.485
900	8.892	63.528	57.773	5.180	-4.119	-22.087	5.363
1000	8.932	64.467	58.396	6.071	-4.345	-24.071	5.261
1100	8.965	65.320	58.987	6.966	-4.587	-26.032	5.172
1200	8.993	66.101	59.548	7.864	-4.851	-27.970	5.094
1300	9.018	66.822	60.080	8.764	-5.146	-29.885	5.024
1400	9.040	67.491	60.586	9.667	-8.616	-31.679	4.945
1500	9.060	68.116	61.067	10.572	-8.947	-33.314	4.854
1600	9.078	68.701	61.526	11.479	-9.278	-34.928	4.771
1700	9.096	69.252	61.965	12.388	-9.608	-36.521	4.695
1800	9.113	69.772	62.384	13.298	-9.939	-38.095	4.625
1900	9.130	70.265	62.786	14.211	-10.268	-39.649	4.561
2000	9.146	70.734	63.172	15.124	-10.598	-41.188	4.501
2100	9.163	71.181	63.543	16.040	-10.927	-42.709	4.445
2200	9.180	71.607	63.900	16.957	-11.255	-44.215	4.392
2300	9.198	72.016	64.244	17.876	-11.582	-45.706	4.343
2400	9.217	72.408	64.576	18.797	-11.908	-47.182	4.296
2500	9.238	72.784	64.897	19.719	-12.234	-48.645	4.253
2600	9.260	73.147	65.207	20.644	-12.558	-50.095	4.211
2700	9.285	73.497	65.508	21.571	-12.881	-51.533	4.171
2800	9.313	73.835	65.799	22.501	-13.202	-52.959	4.134
2900	9.343	74.163	66.082	23.434	-85.233	-52.975	3.992
3000	9.377	74.480	66.356	24.370	-85.360	-51.861	3.778
3100	9.414	74.788	66.624	25.310	-85.496	-50.742	3.577
3200	9.454	75.087	66.883	26.253	-85.641	-49.619	3.389
3300	9.498	75.379	67.136	27.200	-85.795	-48.490	3.211
3400	9.546	75.663	67.383	28.153	-85.957	-47.358	3.044
3500	9.597	75.941	67.624	29.110	-86.128	-46.220	2.886
3600	9.653	76.212	67.858	30.072	-86.305	-45.077	2.737
3700	9.712	76.477	68.088	31.040	-86.490	-43.929	2.595
3800	9.774	76.737	68.312	32.015	-86.679	-42.776	2.460
3900	9.841	76.992	68.531	32.996	-86.874	-41.619	2.332
4000	9.910	77.242	68.746	33.983	-87.074	-40.456	2.210
4100	9.983	77.487	68.956	34.978	-87.276	-39.288	2.094
4200	10.058	77.729	69.162	35.980	-87.481	-38.115	1.983
4300	10.136	77.966	69.364	36.989	-87.688	-36.937	1.877
4400	10.217	78.200	69.562	38.007	-87.895	-35.755	1.776
4500	10.299	78.431	69.757	39.033	-88.103	-34.568	1.679
4600	10.384	78.658	69.948	40.067	-88.310	-33.375	1.586
4700	10.469	78.882	70.136	41.109	-88.515	-32.179	1.496
4800	10.556	79.104	70.320	42.161	-88.718	-30.978	1.410
4900	10.644	79.322	70.502	43.221	-88.919	-29.773	1.328
5000	10.733	79.538	70.680	44.290	-89.117	-28.565	1.249
5100	10.822	79.752	70.856	45.367	-89.310	-27.351	1.172
5200	10.911	79.963	71.029	46.454	-89.501	-26.134	1.098
5300	10.999	80.171	71.200	47.550	-89.687	-24.914	1.027
5400	11.087	80.378	71.368	48.654	-89.869	-23.690	0.959
5500	11.175	80.582	71.533	49.767	-90.047	-22.463	0.893
5600	11.261	80.784	71.697	50.889	-90.221	-21.233	0.829
5700	11.346	80.984	71.858	52.019	-90.389	-19.999	0.767
5800	11.429	81.182	72.017	53.158	-90.555	-18.763	0.707
5900	11.511	81.378	72.174	54.305	-90.717	-17.523	0.649
6000	11.591	81.572	72.329	55.460	-90.876	-16.282	0.593

June 30, 1966; Dec. 31, 1977

COPPER MONOFLUORIDE (CuF) (IDEAL GAS) GFW = 82.544403

D_0° = 101.7 ± 5 kcal/mol

$S_{298.15}^\circ$ = 54.10 ± 0.05 gibbs/mol

ΔHf_0° = -2.9 ± 4 kcal/mol CuF

$\Delta Hf_{298.15}^\circ$ = -3.0 ± 4 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X(^1\Sigma)$	0	(1)
$A(^1\Pi)$	17546.8	(2)
$B(^1\Sigma)$	19738.5	(1)
$C(^1\Pi)$	20258.8	(2)

ω_e = 622.65 cm^{-1}

B_e = 0.3786 cm^{-1}

$\omega_e x_e$ = 3.950 cm^{-1}

α_e = 0.0032 cm^{-1}

σ = 1

r_e = 1.7449 Å

Heat of Formation

Hildenbrand (1) and Ehlert and Wang (2) have reported mass spectrometric measurements of equilibrium pressures of the reactions MgF(g) + Cu(g) = Mg(g) + CuF(g) and 1/2 CuF_2(c) + 1/2 Cu(c) = CuF(g), respectively. Our second and third law analyses follow.

Source	Reaction*	Temp., K	No. of Points	ΔHr_{298}°, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	ΔHf_{298}°** kcal/mol
(1)	A	1413-1590	12	11.52±2.84	7.08±0.68	-2.9±1.9	-4.15±3
(2)	B	936-948	3	75.97±3.90	62.34±0.19	-14.5±4.1	-2.06±21

*A MgF(g) + Cu(g) = Mg(g) + CuF(g).

B 1/2 CuF_2 + 1/2 Cu(c) = CuF(g).

** Derived from 3rd law value and JANAF auxiliary data (3).

We adopt the rounded average, ΔHf_{298}°(CuF,g) = -3.0±4 kcal/mol, which leads to D_{298}°(Cu-F) = 102.5±5 kcal/mol and D_0°(Cu-F) = 101.7±5 kcal/mol.

Another value extant in the literature is D_{298}° = 83.6±4.0 kcal/mol estimated from the heat of atomization of CuF_2, derived from sublimation studies, and the ratio D°(M-F)/ΔHa°(MF_2) = 0.46 (4). Hildenbrand (1) has discussed the valence-state concept which predicts that D°(M-F)>D°(MF-F); therefore the ratio D°(M-F)/[D(M-F) + D°(MF-F)] must be greater than 0.5. With ΔHa_{298}°(CuF_2) = 182.17 kcal/mol (3) and D_{298}°(Cu-F) = ~102.5 kcal/mol, the ratio based on JANAF values is 0.56. For ΔHa_{298}°(CuF_2) = 182.7 kcal/mol, D_{298}°(Cu-F) must be greater than 91.08 kcal/mol to agree with the valence-state concept.

Other calculations by Kent et al. (4) give D_{298}° values ranging from 84.4 to 94.5 kcal/mol. Gaydon (5) recommends D_0° = 81 kcal/mol from a linear Birge-Sponer extrapolation of spectroscopic data but suggests that it is probably higher. King et al. (6) used ΔHf_{298}° = 14 kcal/mol (D_{298}° = 84.7 kcal/mol) in their recent tabulation.

Heat Capacity and Entropy

The values of B_e, α_e, and r_e are from the microwave data of Hoeft et al. (7) adjusted for normal isotopic abundance; the electronic levels, ω_e, and $\omega_e x_e$ are taken from Rosen (8).

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(1) D. L. Hildenbrand, J. Chem. Phys. 48, 2457 (1968).

(2) T. C. Ehlert and J. S. Wang, J. Phys. Chem. 81, 2069 (1977).

(3) JANAF Thermochemical Tables: MgF(g), 6-30-76; Mg(g), 9-30-62; Cu(c),(g), 6-30-77; CuF_2(c),(g), 12-31-77.

(4) R. A. Kent, J. D. McDonald, and J. L. Margrave, J. Phys. Chem. 70, 874 (1966).

(5) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall Ltd., London, 1968.

(6) E. G. King, A. D. Mah, and L. B. Pankratz, "Thermodynamic Properties of Copper and its Inorganic Compounds. INCRA Series on the Metallurgy of Copper, No. 2," INCRA, New York, 1973.

(7) J. Hoeft, F. J. Lovas, E. Tiemann, and T. Toerring, Z. Naturforsch. A 25, 35 (1970).

(8) B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.

CuF

COPPER DIFLUORIDE (CuF_2)

(CRYSTAL) GFW=101.542806

CuF_2

T, K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.893	-128.387	-128.387	INFINITE
100	8.181	5.223	30.666	-2.544	-128.893	-125.106	273.416
200	13.320	12.704	19.880	-1.435	-128.965	-121.263	132.508
298	15.667	18.511	18.511	0.000	-128.800	-117.513	86.138
300	15.700	18.608	18.512	0.029	-128.796	-117.443	85.556
400	17.300	23.350	19.147	1.681	-128.509	-113.699	62.121
500	18.580	27.353	20.398	3.477	-128.130	-110.038	48.097
600	19.580	30.832	21.854	5.387	-127.676	-106.461	38.778
700	20.270	33.905	23.360	7.381	-127.169	-102.965	32.147
800	20.800	36.647	24.853	9.436	-126.627	-99.545	27.194
900	21.240	39.123	26.303	11.538	-126.060	-96.193	23.358
1000	21.600	41.381	27.700	13.681	-125.474	-92.906	20.304
1100	21.890	43.453	29.039	15.856	-124.879	-89.678	17.817
1200	22.120	45.368	30.321	18.057	-124.285	-86.504	15.754
1300	22.300	47.144	31.547	20.278	-123.707	-83.379	14.017
1400	22.430	48.804	32.722	22.515	-126.293	-80.200	12.520
1500	22.520	50.355	33.846	24.763	-125.733	-76.928	11.208
1600	22.570	51.810	34.924	27.018	-125.169	-73.693	10.066
1700	22.600	53.179	35.958	29.276	-124.604	-70.492	9.062
1800	22.600	54.471	36.951	31.536	-124.041	-67.326	8.174
1900	22.600	55.693	37.905	33.796	-123.479	-64.189	7.383
2000	22.600	56.852	38.824	36.056	-122.921	-61.084	6.675

June 30, 1966; Dec. 31, 1977

COPPER DIFLUORIDE (CuF_2) (CRYSTAL) GFW = 101.542806

CuF_2

$S^\circ_{298.15}$ = 18.51 ± 0.02 gibbs/mol

Tm = 1109 ± 10 K

ΔHf°_0 = -128.4 ± 2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -128.8 ± 2 kcal/mol

ΔHm° = 13.2 ± 5 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 65.0 ± 0.5 kcal/mol

Heat of Formation

Pervov et al. (1) have measured a heat of formation of -128.8±0.3 kcal/mol by direct fluorine combustion calorimetry. In view of the spread of values obtained from the equilibrium pressure and the emf data discussed below, we adopt ΔHf°_{298} (CuF_2, c) = -128.8±2 kcal/mol.

Jellinek and Rudat (2) and Domange (3) have measured equilibrium partial pressures for reactions of CuF_2(c) with hydrogen and with water, respectively. Koerber and De Vries (4) and Skelton and Patterson (5) have derived ΔGr° from emf studies. Our second and third law analyses are as follows, using auxiliary data from the JANAF Thermochemical Tables (6).

Source	Reaction*	Temp., K	No. of Points	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	ΔHf°_{298}** kcal/mol
(2)	A	423	1	--	22.6	--	-152.9
(3)	B	573-723	4	23.3±1.3	20.8±0.6	-3.9±2.0	-130.6±2
(4)	C	273-283	2	-1.9	-10.6±0.4	-31.4	-126.6±4
(5)	D	661-918	Eq	-132.1	-136.4	-5.5	-136.4

* A: $CuF_2(c) + H_2(g) = Cu(c) + 2HF(g)$

B: $CuF_2(c) + H_2O(g) = CuO(c) + 2HF(g)$

C: $Cu(c) + Hg_2F_2(c) = CuF_2(c) + 2Hg(\ell)$

D: $Cu(c) + F_2(g) = CuF_2(c)$

** Based on 3rd Law

The evaluation of King et al. (7), ΔHf°_{298} (CuF_2,c) = -130.2 kcal/mol, preceded the direct fluorination study of Pervov et al. (1) and is based mainly on the work of Domange (3) and Koerber and De Vries (4). We place greater reliance on the direct fluorination work (1).

Heat Capacity and Entropy

The heat capacity is based on smoothed values from the unpublished low temperature measurements of Boo and Stout (8) (10-300 K) and the differential scanning calorimetric measurements of heat capacity by Ehlert (9) (300-710 K). Our graphical joining and smoothing of the two data sets produces data which are 1 to 2% lower than Ehlert's measurements (9) in the 350-500 K range and are in agreement from 520-700 K; our extrapolation to 1000 K yields 21.60 gibbs/mol compared to 22.4 gibbs/mol by Ehlert (9).

Boo and Stout (8) show an anomaly in the heat capacity at 70.90 K. S°_{298} = 18.51 gibbs/mol is based on S°_{10} = 0.009 gibbs/mol given by Boo and Stout (8).

Melting Data

Ehlert and Wang (10) interpret their DTA measurements as indicating a solid state transition at 1065±10 K and a melting point at 1109±10 K. They believe the observed transitions at 1028 K and 1040 K are caused by Cu_2O-CuF_2 and $10CuO_2$-$20Cu$-$70CuF_2$ weight percent eutectics, respectively. Based on the latter, and ignoring the 1065 K solid state transition, they calculate a heat of fusion of 13.2±2 kcal/mol. We adopt Tm = 1109±10 K and ΔHm° = 13.2±5 kcal/mol and await confirmation of the solid state transition.

Sublimation Data

See CuF_2(g) table for details.

References

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CuF_2

COPPER DIFLUORIDE (CuF_2) CUF2

(LIQUID) GFW=101.542806

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	15.667	29.298	29.298	0.000	-116.600	-108.529	79.553
300	15.700	29.395	29.299	0.029	-116.596	-108.479	79.026
400	17.300	34.137	29.934	1.681	-116.309	-105.814	57.813
500	18.580	38.140	31.185	3.477	-115.930	-103.232	45.122
600	19.580	41.619	32.641	5.387	-115.476	-100.734	36.692
700	20.270	44.692	34.147	7.381	-114.969	-98.316	30.695
800	24.000	47.696	35.650	9.637	-114.226	-95.982	26.221
900	24.000	50.522	37.148	12.037	-113.361	-93.754	22.766
1000	24.000	53.051	38.614	14.437	-112.518	-91.621	20.023
1100	24.000	55.338	40.032	16.837	-111.698	-89.571	17.796
1200	24.000	57.427	41.396	19.237	-110.905	-87.594	15.953
1300	24.000	59.348	42.704	21.637	-110.148	-85.683	14.404
1400	24.000	61.126	43.957	24.037	-112.571	-83.731	13.071
1500	24.000	62.782	45.158	26.437	-111.859	-81.696	11.903
1600	24.000	64.331	46.308	28.837	-111.150	-79.708	10.887
1700	24.000	65.786	47.412	31.237	-110.443	-77.764	9.997
1800	24.000	67.158	48.471	33.637	-109.740	-75.862	9.211
1900	24.000	68.456	49.489	36.037	-109.038	-73.998	8.512
2000	24.000	69.687	50.468	38.437	-108.340	-72.173	7.887
2100	24.000	70.858	51.411	40.837	-107.643	-70.382	7.325
2200	24.000	71.974	52.321	43.237	-106.948	-68.623	6.817
2300	24.000	73.041	53.199	45.637	-106.256	-66.897	6.357
2400	24.000	74.062	54.047	48.037	-105.565	-65.201	5.937
2500	24.000	75.042	54.867	50.437	-104.876	-63.533	5.554

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COPPER DIFLUORIDE (CuF_2) (LIQUID) GFW = 101.542806

$S°_{298.15}$ = 29.298 kcal/mol
Tm = 1109 ± 10 K
Tb = 1948.9 K

$ΔHf°_{298.15}$ = -116.600 kcal/mol
ΔHm° = 13.2 ± 5 kcal/mol
ΔHv° = 19.391 kcal/mol

CUF2

Heat of Formation

The heat of formation at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H°_{1109}-H°_{298.15}$ for the crystal and the liquid.

Heat Capacity and Entropy

The heat capacity is estimated from an average heat capacity of 8 gibbs/(mol of atoms) for several difluorides and dichlorides. A glass transition is assumed at 740 K below which the heat capacity is that of the crystal.

The entropy is obtained in a manner analagous to that for the heat of formation.

Melting Data

See CuF_2(c) table for details.

Vaporization Data

Tb is the calculated temperature at which the gibbs energy difference is zero for the reaction $CuF_2(\ell) = CuF_2(g)$. ΔHv° is the difference in ΔHf° between gas and liquid at Tb.

CUF2

COPPER DIFLUORIDE (CuF_2) CuF_2

(IDEAL GAS) GFW=101.542806

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.881	-63.375	-63.375	INFINITE
100	9.108	52.761	73.226	-2.047	-63.396	-64.362	140.662
200	10.353	59.457	64.824	-1.073	-63.603	-65.252	71.303
298	11.469	63.809	63.809	0.000	-63.800	-66.018	48.392
300	11.487	63.880	63.809	0.021	-63.804	-66.032	48.104
400	12.258	67.298	64.270	1.211	-63.979	-66.748	36.469
500	12.743	70.090	65.163	2.463	-64.144	-67.421	29.469
600	13.052	72.443	66.186	3.754	-64.309	-68.061	24.791
700	13.257	74.471	67.228	5.070	-64.480	-68.672	21.440
800	13.398	76.251	68.247	6.403	-64.660	-69.260	18.921
900	13.499	77.835	69.226	7.749	-64.849	-69.823	16.955
1000	13.575	79.262	70.159	9.102	-65.053	-70.365	15.378
1100	13.633	80.558	71.046	10.463	-65.272	-70.886	14.084
1200	13.682	81.747	71.889	11.829	-65.513	-71.386	13.001
1300	13.725	82.843	72.690	13.199	-65.786	-71.865	12.081
1400	13.767	83.862	73.452	14.574	-69.234	-72.224	11.274
1500	13.809	84.813	74.178	15.952	-69.544	-72.426	10.552
1600	13.854	85.706	74.871	17.336	-69.851	-72.609	9.918
1700	13.903	86.547	75.534	18.723	-70.157	-72.771	9.355
1800	13.957	87.343	76.168	20.116	-70.461	-72.916	8.853
1900	14.016	88.100	76.776	21.515	-70.760	-73.044	8.402
2000	14.080	88.820	77.360	22.920	-71.057	-73.157	7.994
2100	14.148	89.509	77.923	24.331	-71.349	-73.255	7.624
2200	14.220	90.169	78.464	25.749	-71.636	-73.339	7.285
2300	14.296	90.802	78.987	27.175	-71.918	-73.410	6.975
2400	14.374	91.412	79.492	28.609	-72.193	-73.469	6.690
2500	14.454	92.001	79.981	30.050	-72.463	-73.516	6.427
2600	14.535	92.569	80.454	31.500	-72.726	-73.553	6.183
2700	14.617	93.119	80.913	32.957	-72.984	-73.580	5.956
2800	14.698	93.652	81.359	34.423	-73.235	-73.598	5.744
2900	14.779	94.170	81.791	35.897	-145.192	-72.209	5.442
3000	14.858	94.672	82.212	37.379	-145.241	-69.692	5.077
3100	14.936	95.161	82.622	38.868	-145.295	-67.172	4.736
3200	15.012	95.636	83.022	40.366	-145.355	-64.651	4.415
3300	15.085	96.099	83.411	41.871	-145.421	-62.127	4.114
3400	15.155	96.550	83.791	43.383	-145.495	-59.602	3.831
3500	15.222	96.991	84.162	44.902	-145.576	-57.076	3.564
3600	15.286	97.420	84.524	46.427	-145.663	-54.545	3.311
3700	15.347	97.840	84.878	47.959	-145.757	-52.013	3.072
3800	15.405	98.250	85.225	49.496	-145.858	-49.478	2.846
3900	15.459	98.651	85.564	51.040	-145.965	-46.940	2.630
4000	15.510	99.043	85.896	52.588	-146.080	-44.400	2.426
4100	15.558	99.427	86.221	54.142	-146.199	-41.856	2.231
4200	15.602	99.802	86.540	55.700	-146.326	-39.310	2.046
4300	15.643	100.170	86.853	57.262	-146.458	-36.760	1.868
4400	15.680	100.530	87.160	58.828	-146.596	-34.208	1.699
4500	15.714	100.882	87.461	60.398	-146.740	-31.653	1.537
4600	15.746	101.228	87.756	61.971	-146.888	-29.093	1.382
4700	15.774	101.567	88.046	63.547	-147.041	-26.531	1.234
4800	15.799	101.899	88.332	65.125	-147.200	-23.965	1.091
4900	15.821	102.225	88.612	66.706	-147.362	-21.396	0.954
5000	15.841	102.545	88.887	68.290	-147.529	-18.824	0.823
5100	15.858	102.859	89.158	69.875	-147.699	-16.247	0.696
5200	15.873	103.167	89.425	71.461	-147.876	-13.669	0.574
5300	15.885	103.470	89.687	73.049	-148.056	-11.086	0.457
5400	15.895	103.767	89.945	74.638	-148.239	-8.499	0.344
5500	15.903	104.058	90.199	76.228	-148.428	-5.910	0.235
5600	15.908	104.345	90.449	77.818	-148.622	-3.318	0.129
5700	15.912	104.627	90.695	79.410	-148.818	-0.721	0.028
5800	15.914	104.903	90.938	81.001	-149.021	1.879	-0.071
5900	15.915	105.175	91.177	82.592	-149.229	4.484	-0.166
6000	15.913	105.443	91.412	84.184	-149.443	7.090	-0.258

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COPPER DIFLUORIDE (CuF_2) (IDEAL GAS) GFW = 101.542806

CuF_2

ΔHa°_0 = 180.5 ± 4 kcal/mol
$S^\circ_{298.15}$ = [63.81 ± 0.5] gibbs/mol
Ground State Quantum Weight = [2]

ΔHf°_0 = -63.4 ± 3 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -63.8 ± 3 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$^2\Sigma^+g$]	0	[2]
[$^2\Pi g$]	[9000]	[4]
[$^2\Delta g$]	[18000]	[4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
625(1)
185±5(1)
782(1)

Point Group: C_{2v} σ = 2
Bond Distance: Cu-F = [1.72] Å
Bond Angle: F-Cu-F = 165 ± 8°
Product of the Moments of Inertia: $I_AI_BI_C$ = [67.7132 x 10^{-117}] g^3 cm^6

Heat of Formation

Sublimation pressures, $CuF_2(c) = CuF_2(g)$, have been measured by Kent et al. (1, 897-1026 K) and by Ehlert and Wang (2, 874-1005 K) by effusion cell-mass spectrometric techniques. Using JANAF data of 12-31-77 for $CuF_2(c)$, we derive the following by second and third law analysis:

			ΔHs°_{298}, kcal/mol			
Source	Temp., K	No. of Points	2nd Law	3rd Law	Drift gibbs/mol	ΔHf°_{298},(c) kcal/mol
(1)	897-1026	26[(a)]	63.20±0.50	62.74±0.17	-0.5±0.5	-66.1
(2) via CuF_2^+	874-1005	33[(b)]	65.82±0.72	64.992±0.33	-0.9±0.8	-63.8
(2) via CuF^+	874-1005	33[(b)]	65.92±0.67	65.085±0.30	-0.9±0.7	

(a) Two data points eliminated by a statistical test.
(b) One data point eliminated by a statistical test.
(c) Based on the third law values.

We adopt $\Delta Hf^\circ_{298}(CuF_2,g)$ = -63.8 ± 3 kcal/mol.

Heat Capacity and Entropy

The bond distance is taken from Brewer et al. (3). The bond distances for all of the transition metal difluorides from chromium through copper were estimated to be the same with the assessment that an error of 0.5 Å would lead to an error of less than 1 gibbs/mol in the entropy. The bond angle and vibrational frequencies are those derived by Hastie et al. (4) from infrared studies of matrix-isolated isotopic species. The electronic states and levels are assumed the same as those assigned to $CuCl_2$ (5). Principal moments of inertia are I_A = 18.5459 x 10^{-39}, I_B = 18.3469 x 10^{-39}, and I_C = 0.1990 x 10^{-39} g cm^2.

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CuF_2

COPPER MONOXIDE (CuO) CuO
(CRYSTAL) GFW=79.5454

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.695	-36.761	-36.761	INFINITE
100	3.943	2.335	17.729	-1.539	-37.112	-35.036	76.570
200	8.316	6.458	11.055	-0.920	-37.321	-32.856	35.903
298	10.097	10.180	10.180	0.000	-37.300	-30.667	22.479
300	10.125	10.243	10.180	0.019	-37.299	-30.626	22.310
400	11.187	13.318	10.592	1.090	-37.178	-28.417	15.526
500	11.774	15.882	11.401	2.240	-37.007	-26.246	11.472
600	12.174	18.066	12.335	3.439	-36.812	-24.111	8.782
700	12.486	19.967	13.292	4.672	-36.606	-22.011	6.872
800	12.751	21.652	14.234	5.934	-36.394	-19.941	5.447
900	12.988	23.167	15.144	7.221	-36.178	-17.897	4.346
1000	13.208	24.547	16.016	8.531	-35.959	-15.877	3.470
1100	13.416	25.816	16.850	9.863	-35.741	-13.880	2.758
1200	13.618	26.992	17.647	11.214	-35.529	-11.902	2.168
1300	13.814	28.090	18.408	12.586	-35.333	-9.941	1.671
1400	14.006	29.121	19.137	13.977	-38.297	-7.897	1.233
1500	14.196	30.093	19.835	15.387	-38.107	-5.732	0.835
1600	14.384	31.016	20.505	16.816	-37.902	-3.581	0.489
1700	14.569	31.893	21.150	18.264	-37.680	-1.442	0.185
1800	14.753	32.731	21.770	19.730	-37.443	0.683	-0.083
1900	14.937	33.534	22.368	21.214	-37.191	2.794	-0.321
2000	15.119	34.305	22.946	22.717	-36.922	4.892	-0.535

June 30, 1966; Dec. 31, 1977

COPPER MONOXIDE (CuO) (CRYSTAL) GFW = 79.5454

$\Delta Hf°_0$ = -36.8 ± 0.5 kcal/mol CuO
$S°_{298.15}$ = 10.18 ± 0.1 gibbs/mol
$\Delta Hf°_{298.15}$ = -37.3 ± 0.5 kcal/mol
T_d = 1397 K

Heat of Formation

The heat of formation of CuO(c) has been investigated calorimetrically (both oxidation and reduction reactions) and by extensive study of the $Cu_2O(c) + 1/2\ O_2(g) = 2\ CuO(c)$ equilibrium by pressure and by emf measurement. The more consistent data leading to the adopted value are summarized below.

					$\Delta Hr°_{298}$, kcal/mol		Drift	$\Delta Hf°_{298}$**
Source	Method	Reaction*	Temp. K	No. of Points	2nd law	3rd law	gibbs/mol	kcal/mol
(1)	Aq Calorim	A	291	--	31.15		--	-37.16
(2)	Calorimetric	A	295	--	30.27±0.2		--	-38.04
(3)	Calorimetric	See Text	298.15	--	--		--	-37.23±0.15
(4)	Calorimetric	A	297.9	(Coarse grain CuO)	--		--	-38.72±0.30
		A	298	(Fine powder CuO)	--		--	-36.50±0.2
		B	297.9	(Coarse grain CuO)	--		--	-38.59±0.35
(5)	Equil Press	B	1011-1156	5	-33.84±0.31	-37.73±0.43	-3.6±0.3	-37.73
(6)	emf	B	845-1270	Equation	-37.26	-37.38	-0.1±0.0	-37.38
(7)	Equil Press	C	1223-1322	7	-32.52±0.18	-33.65±0.06	-0.9±0.1	-37.23
(8)	Equil Press	C	1189-1358	20	-33.28±0.06	-33.68±0.04	-0.3±0.0	-37.24
(9)	Equil Press	C	1193-1293	6	-33.23±0.28	-33.68±0.04	-0.4±0.2	-37.24
(10)	Equil Press	C	1047-1342	11	-32.79±0.14	-33.69±0.17	-0.7±0.1	-37.25
(11)	Equil Press	C	1026-1072	3	-35.50±0.37	-33.62±0.07	1.4±0.3	-37.21
(12)	emf	C	973-1273	Equation	-33.57	-33.64	-0.6	-37.22
(13)	emf	C	892-1320	Equation	-33.53	-33.58	-0.6	-37.19
(14)	emf	C	1023-1294	Equation	-33.39	-33.58	0.2	-37.19
(15)	emf	C	870-1170	Equation	-34.37	-35.00	0.6	-37.90
(16)	Press	C	993-1021	4	-34.18±0.06	-34.12±0.0	-0.1±0.1	-37.46
(17)	Equil Press	C	800-950	Equation	-29.92	-34.30	10.0	-37.55
(18)	Equil Press	C	873-1073	Equation	-40.06	-35.26	4.9	-38.03

*A: $Cu(c) + H_2O(\ell) = CuO(c) + H_2(g)$
B: $Cu(c) + 1/2\ O_2(g) = CuO(c)$
C: $Cu_2O(c) + 1/2\ O_2(g) = 2\ CuO(c)$

**Based on third law where possible and $\Delta Hf°_{298}(Cu_2O,c)$ = -40.8 kcal/mol in Reaction C.

Thomsen's data (1) may be reduced to the heat of reduction of CuO(c) with H_2 by combining heats of reaction for CuO + H_2SO_4, Fe + H_2SO_4, and Fe + $CuSO_4$(aq). Wartenberg and Werth (2) and Nunez et al. (4) have measured the direct heat of reduction of CuO(c) by H_2; Mah et al. (3) and Nunez et al. (4) have measured the direct heat of oxidation of copper by O_2. Mah et al. (3) obtained a mixed Cu_2O and CuO product and used $\Delta Hr°_{298}$ = -33.63±0.05 kcal/mol for the equilibrium reaction $Cu_2O(c) + 1/2\ O_2(g) = 2\ CuO(c)$ to resolve their results into $\Delta Hf°_{298}$(CuO,c) and $\Delta Hf°_{298}(Cu_2O,c)$. From the measurement of the reduction of coarse and fine CuO(c), Nunez et al. (4) conclude that ΔHf° of the copper oxides is influenced by material history, state of subdivision, and non-stoichiometry.

Eliminating three studies (5, 17, and 18) from our third law analysis because of large drift and poor 2nd and 3rd law agreement, the average of the eleven remaining studies is -37.32 kcal/mol. We adopt $\Delta Hf°_{298}$ (CuO,c) = -37.3±0.5 kcal/mol.

Heat Capacity and Entropy

The adopted values are based on the low temperature heat capacities by Hu and Johnston (19) (15-297 K) and the high temperature enthalpies by Mah et al. (3) (410-1400 K). Changes are made where appropriate to adjust to the 1975 atomic weights (20) and the IPTS-68 temperature scale (21). A small anomaly in the heat capacity is observed in the 210-230 K region. Magnetic measurements of O'Keefe and Stone (22) and neutron diffraction studies of Brockhouse (23) suggest that this is a Néel point associated with antiferromagnetism.

The entropy is obtained from the adopted heat capacities based on a T^3 extrapolation to obtain $S°_{15}$ = 0.016 gibbs/mol.

Decomposition Data

Td = 1397 K is the calculated temperature at which the Gibbs energy difference is zero for the reaction $2\ CuO(c) = Cu_2O(c)+1/2\ O_2(g)$.

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CuO

COPPER MONOXIDE (CuO)
(IDEAL GAS) GFW=79.5454

CuO

	gibbs/mol			kcal/mol			
T, K	$C_p°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	0.000	0.000	INFINITE	-2.330	73.104	73.104	INFINITE
100	7.542	47.209	63.415	-1.621	73.307	70.896	-154.940
200	8.245	52.698	56.821	-0.825	73.274	68.490	-74.842
298	8.531	56.049	56.049	0.000	73.200	66.158	-48.494
300	8.535	56.102	56.049	0.016	73.198	66.114	-48.163
400	8.700	58.581	56.386	0.878	73.110	63.764	-34.839
500	8.802	60.535	57.027	1.754	73.007	61.441	-26.856
600	8.870	62.146	57.750	2.637	72.887	59.139	-21.541
700	8.920	63.517	58.478	3.527	72.749	56.859	-17.752
800	8.958	64.711	59.184	4.421	72.593	54.599	-14.916
900	8.988	65.767	59.858	5.318	72.419	52.359	-12.714
1000	9.014	66.716	60.497	6.219	72.229	50.141	-10.958
1100	9.037	67.576	61.102	7.121	72.018	47.943	-9.525
1200	9.057	68.363	61.675	8.026	71.782	45.764	-8.335
1300	9.076	69.089	62.218	8.933	71.513	43.606	-7.331
1400	9.094	69.762	62.733	9.841	68.067	41.568	-6.489
1500	9.111	70.390	63.223	10.751	67.757	39.687	-5.782
1600	9.127	70.979	63.689	11.663	67.445	37.825	-5.167
1700	9.143	71.533	64.135	12.577	67.133	35.984	-4.626
1800	9.159	72.056	64.560	13.492	66.819	34.160	-4.148
1900	9.175	72.551	64.968	14.409	66.504	32.354	-3.722
2000	9.191	73.022	65.359	15.327	66.187	30.565	-3.340
2100	9.208	73.471	65.735	16.247	65.870	28.792	-2.996
2200	9.225	73.900	66.096	17.169	65.552	27.034	-2.686
2300	9.244	74.311	66.444	18.092	65.232	25.290	-2.403
2400	9.264	74.704	66.780	19.017	64.912	23.560	-2.145
2500	9.285	75.083	67.105	19.945	64.591	21.844	-1.910
2600	9.309	75.446	67.419	20.875	64.271	20.140	-1.693
2700	9.335	75.799	67.723	21.807	63.950	18.449	-1.493
2800	9.363	76.139	68.017	22.742	63.629	16.770	-1.309
2900	9.394	76.468	68.303	23.679	-8.404	16.500	-1.243
3000	9.427	76.787	68.581	24.620	-8.534	17.360	-1.265
3100	9.464	77.097	68.850	25.565	-8.674	18.226	-1.285
3200	9.504	77.398	69.113	26.513	-8.824	19.096	-1.304
3300	9.548	77.691	69.368	27.466	-8.984	19.972	-1.323
3400	9.595	77.977	69.617	28.423	-9.154	20.851	-1.340
3500	9.646	78.256	69.860	29.385	-9.334	21.736	-1.357
3600	9.700	78.528	70.097	30.352	-9.521	22.627	-1.374
3700	9.757	78.795	70.329	31.325	-9.717	23.522	-1.389
3800	9.818	79.056	70.555	32.304	-9.919	24.423	-1.405
3900	9.882	79.312	70.776	33.289	-10.128	25.329	-1.419
4000	9.950	79.563	70.993	34.280	-10.341	26.241	-1.434
4100	10.021	79.809	71.205	35.279	-10.559	27.159	-1.448
4200	10.094	80.052	71.413	36.285	-10.780	28.081	-1.461
4300	10.170	80.290	71.616	37.298	-11.004	29.009	-1.474
4400	10.249	80.525	71.816	38.319	-11.229	29.942	-1.487
4500	10.330	80.756	72.012	39.348	-11.455	30.880	-1.500
4600	10.413	80.984	72.205	40.385	-11.682	31.824	-1.512
4700	10.497	81.209	72.394	41.430	-11.908	32.772	-1.524
4800	10.583	81.431	72.580	42.484	-12.132	33.725	-1.536
4900	10.670	81.650	72.763	43.547	-12.355	34.683	-1.547
5000	10.758	81.866	72.943	44.618	-12.576	35.644	-1.558
5100	10.847	82.080	73.120	45.699	-12.793	36.612	-1.569
5200	10.936	82.292	73.294	46.788	-13.008	37.583	-1.580
5300	11.025	82.501	73.466	47.886	-13.221	38.556	-1.590
5400	11.114	82.708	73.635	48.993	-13.429	39.536	-1.600
5500	11.203	82.913	73.802	50.109	-13.635	40.518	-1.610
5600	11.291	83.115	73.966	51.233	-13.837	41.504	-1.620
5700	11.378	83.316	74.129	52.367	-14.036	42.496	-1.629
5800	11.464	83.514	74.289	53.509	-14.233	43.488	-1.639
5900	11.548	83.711	74.447	54.659	-14.427	44.486	-1.648
6000	11.632	83.906	74.603	55.818	-14.620	45.486	-1.657

Sept. 30, 1966; June 30, 1970; Dec. 31, 1977

$D_0° = 66.3 \pm 10$ kcal/mol

$S°_{298.15} = 56.05 \pm 0.2$ gibbs/mol

$\Delta Hf_0° = 73.1 \pm 10$ kcal/mol

$\Delta Hf°_{298.15} = 73.2 \pm 10$ kcal/mol

CuO

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Pi_{3/2}$	0	2
$X^2\Pi_{1/2}$	277.0	2
$A'^2\Sigma^+$	15531.9	2
$A^2\Sigma^+$	16492.4	2
$C^2\Pi_i$	18811.4	4
$E^2\Delta_{5/2}$	21103.7	4
$F^2\Pi_i$	21222	4
$G^2\Sigma^-$	21594.0	2
$M^2\Pi_{3/2}$	23898	4

$\omega_e = 640.14$ cm^{-1} $\omega_e x_e = 4.43$ cm^{-1} $\sigma = 1$

$B_e = 0.44454$ cm^{-1} $\alpha_e = 0.0046$ cm^{-1} $r_e = 1.7246$ Å

Heat of Formation

The adopted $\Delta Hf°_{298} = 73.2 \pm 10$ kcal/mol comes from our third law analysis of the mass-spectrometric Knudsen cell measurements of the equilibrium reaction $CuO(g) + Ni(g) = Cu(g) + NiO(g)$ (1611 - 1828 K) by Smoes et al. (1). Auxiliary data (2, 3) are used in the analysis. Also considered in the evaluation are: the unpublished but quoted (4, and others) value of R. P. Burns, $D_0° = 62.7 \pm 3$ kcal/mol, the sublimation pressure measurement of Mask et al. (5), the linear Birge-Sponer extrapolation of the ground state to obtain $D_0°$, and the linear Birge-Sponer extrapolation corrected for the ionic character of CuO according to Hildenbrand (6).

Source	kcal/mol	
	$D_0°$	$\Delta Hf°_{298}$
Smoes et al. (1), Equilibrium	66.3	73.2
Burns (4), Mass spec.	62.7±3	76.8±3
Mack et al. (5), Transpiration (1273 K)	80.2	59.02
Linear Birge-Sponer	65.2	74.2
Modified Linear Birge-Sponer	61.0±12	78.5±12

Mack et al. (5) report measurements at 873, 1073, and 1173 K which lead to higher dissociation energies. Because of the scatter of the measurements and the suspect nature of the analytical measurement recognized by the authors, the $D_0°$ value of 80.2 kcal/mol is discounted.

Heat Capacity and Entropy

The molecular constants and electronic levels are taken from the work of Appelblad and Lagerqvist (7, 8, 9), Lefebvre et al. (10), and Lefebvre et al. (11). The spectrum of CuO is complex and there are almost certainly excited states missing among those already analyzed (9); in fact some doubt still exists that the $X^2\Pi_i$ state is really the ground state (9) although the absence of esr signals in the matrix isolation study of Thompson et al. (12) supports this assignment. Because of the uncertain and incomplete spectral analysis, we choose to calculate the thermodynamic functions with first-order anharmonic corrections assuming the ground-state vibrational-rotational constants for all states. Use of the actual constants for each state increases the entropy at 6000 K by 0.045 gibbs/mol.

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CuO

DICOPPER MONOXIDE (Cu_2O) Cu_2O

(CRYSTAL) GFW=143.0914

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.011	-40.380	-40.380	INFINITE
100	9.441	8.865	33.622	-2.496	-40.531	-38.848	84.945
200	12.815	16.526	23.381	-1.371	-40.717	-37.131	40.575
298	14.948	22.075	22.075	0.000	-40.800	-35.350	25.912
300	14.977	22.167	22.075	0.028	-40.801	-35.316	25.727
400	16.178	26.657	22.679	1.591	-40.784	-33.488	18.297
500	16.951	30.354	23.855	3.249	-40.718	-31.671	13.843
600	17.555	33.499	25.207	4.976	-40.621	-29.870	10.880
700	18.080	36.246	26.592	6.758	-40.506	-28.087	8.769
800	18.563	38.692	27.954	8.590	-40.374	-26.322	7.191
900	18.999	40.904	29.272	10.469	-40.231	-24.575	5.968
1000	19.418	42.927	30.538	12.389	-40.078	-22.843	4.992
1100	19.930	44.800	31.750	14.355	-39.920	-21.126	4.197
1200	20.581	46.561	32.912	16.380	-39.751	-19.426	3.538
1300	21.313	48.237	34.026	18.474	-39.581	-17.740	2.982
1400	22.106	49.845	35.099	20.644	-45.688	-15.871	2.477
1500	22.941	51.399	36.134	22.896	-45.441	-13.749	2.003
1600	23.812	52.907	37.136	25.234	-45.112	-11.647	1.591
1700	24.708	54.377	38.107	27.660	-44.697	-9.567	1.230
1800	25.624	55.815	39.051	30.176	-44.195	-7.514	0.912
1900	26.557	57.226	39.970	32.785	-43.603	-5.493	0.632
2000	27.502	58.612	40.868	35.488	-42.920	-3.504	0.383

June 30, 1966; Dec. 31, 1977

DICOPPER MONOXIDE (Cu_2O) (CRYSTAL) GFW = 143.0914

ΔHf°_0 = -40.4 ± 0.5 kcal/mol Cu_2O

$S^\circ_{298.15}$ = 22.07 ± 0.08 gibbs/mol
Tm = 1516.7 K

$\Delta Hf^\circ_{298.15}$ = -40.8 ± 0.5 kcal/mol
ΔHm° = 15.48 ± 0.15 kcal/mol

Heat of Formation

The heat of formation of $Cu_2O(c)$ has been investigated calorimetrically (both oxidation and reduction reactions) and the oxidation reaction 2 Cu(c) + 1/2 $O_2(g)$ = $Cu_2O(c)$ has been studied extensively by pressure and by emf measurement. The more consistent data leading to the adopted value are summarized below.

					ΔHr°_{298}, kcal/mol		Drift	ΔHr°_{298} **
Source	Method	Reaction*	Temp., K	Points	2nd Law	3rd Law	gibbs/mol	kcal/mol
(1)	Aq Calorim.	A	291	--	27.61		--	-40.70
(2)	Calorimetric	See Text	298.15	--	--		--	-40.83 ± 0.30
(3)	Calorimetric	A	297.90	--	26.93		--	-41.39 ± 0.32
(4)	Aq emf	A	273 - 318	5	27.47 ± 0.04	27.58±0.02	0.4±0.1	-40.74
(5)	Aq emf	A	298 - 318	7	29.97 ± 0.38	28.02±0.14	-6.4±1.3	-40.30
(6)	Aq emf	A	288 - 308	3	29.54 ± 0.73	28.25±0.10	-4.3±2.5	-40.06
(7)	Equil Press	B	1011 - 1156	5	-35.79 ± 0.86	-41.55±0.66	-5.3±0.8	-41.55
(8)	emf vs. Fe/FexO	B	1073 - 1323	4	-42.29 ± 0.59	-40.96±0.23	1.1±0.5	-40.96
(9)	Fused Salt emf	B	987	1		-41.72		-41.72
(10)	emf	B	1100 - 1200	2	-60.17	-39.77±2.03	14.3	-39.77
(11)	emf	B	973 - 1273	Eqn	-41.10	-40.75	0.31	-40.75
(12)	emf	B	892 - 1320	Eqn	-40.75	-40.77	-0.01	-40.77
(13)	Equil Press	B	1200 - 1420	Eqn	-33.37	-40.30	5.4	-40.30
(14)	Equil Press	B	1280 - 1450	Eqn	-36.82	-40.24	5.0	-40.24
(15)	emf	B	973 - 1373	Eqn	-41.83	-41.01	1.4	-41.01
(16)	emf	B	845 - 1270	Eqn	-40.83	-40.88	-0.1	-40.88
(17)	emf	B	976 - 1234	Eqn	-39.84	-40.59	-0.7	-40.59
(18)	emf	B	1073 - 1273	Eqn	-41.07	-39.12	1.7	-39.12
(19)	Equil Press	B	1013 - 1243	Eqn	-43.07	-43.86	1.4	-43.86
(20)	emf	B	973 - 1273	Eqn	-42.62	-41.23	1.2	-41.23
(21)	emf	B	1173 - 1356	Eqn	-40.71	-40.90	-0.2	-40.90

*A: 2 Cu(c) + $H_2O(\ell)$ = $Cu_2O(c)$ + $H_2(g)$ B: 2 Cu(c) + 0.5 $O_2(g)$ = $Cu_2O(c)$ **Based on thrid law values where possible

Thomsen (1) obtained ΔHf°_{298} values of -40180, -40.87, and -41.51 kcal/mol from aqueous calorimetry using three different paths. He favored the first path which is recalculated by combination of the heats of reaction of Cu_2O + H_2SO_4, Fe + H_2SO_4, and Fe + $CuSo_4$(aq) to yield the heat of reduction of Cu_2O with H_2. Nunez et al. (3) measured the direct heat of reduction of Cu_2O by H_2; they conclude that the heats of formation of the copper oxides are influenced by material history, state of subdivision, and non-stoichiometry. Mah et al. (2) measured the direct heat of oxidation of copper by O_2, buty they obtained a mix product of Cu_2O and CuO and used ΔHr°_{298} = -33.63±0.05 kcal/mol for the equilibrium reaction $Cu_2O(c)$ + 1/2 $O_2(g)$ = 2 CuO(c) to resolve their results into $\Delta Hf^\circ_{298}(Cu_2O,c)$ and ΔHf°_{298}(CuO,c). The overall average from our third law analyses is -40.82 kcal/mol; without the three outlier (10, 18, 19) the average is 40.81; the average of the six data sets with an absolute drift less than 1 is -40.77. We adopt $\Delta Hf^\circ_{298}(Cu_2O,c)$ = -40.8±0.5 kcal/mol.

Heat Capacity and Entropy

The heat capacities are smoothed values adopted from a consideration of the work of Gregor (2.8-21 K)(22), Hu and Johnston (15-300 K)(23), and Mah et al. (52-296 K, 406-1464 K)(2). The data of Mah et al. (2) are favored over that of Hu and Johnston (23) above 120 K. Adjustment is made to the IPTS-68 temperature scale (24).

The entropy is based on a T^3 extrapolation to obtain $S^\circ_{2.8}$ = 0.0015 gibbs/mol.

Melting Data

For details, see $Cu_2O(\ell)$.

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Cu_2O

DICOPPER MONOXIDE (Cu_2O) Cu_2O
(LIQUID) GFW=143.0914

T, K	C_p° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	14.948	31.061	31.060	0.000	-26.768	-23.996	17.590
300	14.977	31.153	31.061	0.028	-26.768	-23.979	17.469
400	16.178	35.642	31.665	1.591	-26.752	-23.050	12.594
500	16.951	39.340	32.841	3.249	-26.685	-22.132	9.674
600	17.555	42.485	34.193	4.976	-26.589	-21.229	7.733
700	18.080	45.231	35.577	6.758	-26.473	-20.345	6.352
800	18.543	47.678	36.940	8.590	-26.342	-19.478	5.321
900	18.999	49.890	38.258	10.469	-26.198	-18.630	4.524
1000	23.880	51.913	39.523	12.389	-26.045	-17.796	3.889
1100	23.880	54.189	40.755	14.777	-25.465	-16.999	3.377
1200	23.880	56.267	41.962	17.165	-24.933	-16.254	2.960
1300	23.880	58.178	43.137	19.553	-24.469	-15.551	2.614
1400	23.880	59.948	44.275	21.941	-30.359	-14.685	2.292
1500	23.880	61.595	45.376	24.329	-29.976	-13.578	1.978
1600	23.880	63.136	46.438	26.717	-29.596	-12.498	1.707
1700	23.880	64.584	47.463	29.105	-29.219	-11.461	1.471
1800	23.880	65.949	48.453	31.493	-28.845	-10.406	1.263
1900	23.880	67.240	49.408	33.881	-28.474	-9.392	1.080
2000	23.880	68.465	50.330	36.269	-28.106	-8.396	0.918

June 30, 1966; Dec. 31, 1977

DICOPPER MONOXIDE (Cu_2O) (LIQUID) GFW = 143.0914

$S^\circ_{298.15}$ = 31.060 gibbs/mol
Tm = 1516.7 K

$\Delta Hf^\circ_{298.15}$ = -26.768 kcal/mol
ΔHm° = 15.48 ± 0.15 kcal/mol

Cu_2O

Heat of Formation

The heat of formation at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H^\circ_{1516.7}-H^\circ_{298.15}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is taken from the enthalpy measurements of Mah et al. (1521-1600 K)(1) and is assumed constant at 23.88 gibbs/mol from 1000 to 2000 K. A glass transition is assumed at 1000 K below which the heat capacity is that of the crystal.

The entropy is obtained in a manner similar to that used to obtain the heat of formation.

Melting Data

The melting point, 1515 K, was determined by drop calorimetry by Mah et al. (1). Correcting to the IPTS-68 temperature scale (2), we adopt Tm = 1516.7 K.

ΔHm° = 15.48 ± 0.15 kcal/mol is based on our smoothing through the pre-melt region of the enthalpy measurements of Mah et al. (1).

References

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2. The International Practical Temperature Scale of 1968, Metrologia 5, 35(1969); T. B. Douglas, J. Res. Nat. Bur. Stand. 73A, 451 (1969).

Cu_2O

DEUTERIUM, MONATOMIC (D) D

(IDEAL GAS) GFW=2.014102

T, K	gibbs/mol			kcal/mol			
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	52.535	52.535	INFINITE
100	4.968	24.028	33.872	-0.984	52.703	51.647	-112.873
200	4.968	27.472	29.910	-0.488	52.847	50.536	-55.223
298	4.968	29.455	29.455	0.000	52.992	49.371	-36.190
300	4.968	29.486	29.455	0.009	52.995	49.349	-35.950
400	4.968	30.915	29.650	0.506	53.143	48.111	-26.286
500	4.968	32.024	30.018	1.003	53.290	46.836	-20.472
600	4.968	32.930	30.430	1.500	53.434	45.532	-16.585
700	4.968	33.695	30.343	1.996	53.575	44.204	-13.801
800	4.968	34.359	31.242	2.493	53.710	42.856	-11.707
900	4.968	34.944	31.622	2.990	53.839	41.491	-10.075
1000	4.968	35.467	31.980	3.487	53.961	40.112	-8.766
1100	4.968	35.941	32.319	3.984	54.076	38.722	-7.693
1200	4.968	36.373	32.639	4.480	54.185	37.322	-6.797
1300	4.968	36.771	32.942	4.977	54.287	35.912	-6.037
1400	4.968	37.139	33.229	5.474	54.383	34.495	-5.385
1500	4.968	37.482	33.501	5.971	54.474	33.071	-4.818
1600	4.968	37.802	33.760	6.468	54.559	31.641	-4.322
1700	4.968	38.103	34.007	6.964	54.640	30.207	-3.883
1800	4.968	38.387	34.242	7.461	54.717	28.767	-3.493
1900	4.968	38.656	34.468	7.958	54.789	27.323	-3.143
2000	4.968	38.911	34.683	8.455	54.858	25.876	-2.828
2100	4.968	39.153	34.891	8.952	54.922	24.425	-2.542
2200	4.968	39.384	35.090	9.448	54.985	22.971	-2.282
2300	4.968	39.605	35.281	9.945	55.044	21.515	-2.044
2400	4.968	39.817	35.466	10.442	55.100	20.056	-1.826
2500	4.968	40.019	35.644	10.939	55.154	18.595	-1.626
2600	4.968	40.214	35.816	11.436	55.204	17.131	-1.440
2700	4.968	40.402	35.982	11.932	55.253	15.666	-1.268
2800	4.968	40.582	36.143	12.429	55.300	14.199	-1.108
2900	4.968	40.757	36.299	12.926	55.343	12.730	-0.959
3000	4.968	40.925	36.451	13.423	55.385	11.260	-0.820
3100	4.968	41.088	36.598	13.920	55.425	9.789	-0.690
3200	4.968	41.246	36.741	14.416	55.463	8.316	-0.568
3300	4.968	41.399	36.879	14.913	55.499	6.842	-0.453
3400	4.968	41.547	37.015	15.410	55.532	5.367	-0.345
3500	4.968	41.691	37.146	15.907	55.564	3.891	-0.243
3600	4.968	41.831	37.274	16.404	55.594	2.415	-0.147
3700	4.968	41.967	37.399	16.900	55.622	0.937	-0.055
3800	4.968	42.100	37.521	17.397	55.649	-0.542	0.031
3900	4.968	42.229	37.640	17.894	55.673	-2.021	0.113
4000	4.968	42.354	37.757	18.391	55.695	-3.500	0.191
4100	4.968	42.477	37.870	18.888	55.716	-4.980	0.265
4200	4.968	42.597	37.981	19.384	55.735	-6.461	0.336
4300	4.968	42.714	38.090	19.881	55.752	-7.942	0.404
4400	4.968	42.828	38.196	20.378	55.768	-9.423	0.468
4500	4.968	42.940	38.301	20.875	55.781	-10.906	0.530
4600	4.968	43.049	38.403	21.372	55.793	-12.387	0.589
4700	4.968	43.156	38.503	21.868	55.804	-13.870	0.645
4800	4.968	43.260	38.601	22.365	55.812	-15.352	0.699
4900	4.968	43.363	38.697	22.862	55.820	-16.835	0.751
5000	4.968	43.463	38.791	23.359	55.826	-18.318	0.801
5100	4.968	43.561	38.884	23.855	55.830	-19.801	0.849
5200	4.968	43.658	38.975	24.352	55.834	-21.284	0.895
5300	4.968	43.752	39.064	24.849	55.835	-22.767	0.939
5400	4.968	43.845	39.152	25.346	55.836	-24.250	0.981
5500	4.968	43.936	39.238	25.843	55.836	-25.733	1.023
5600	4.968	44.026	39.322	26.339	55.835	-27.216	1.062
5700	4.968	44.114	39.406	26.836	55.833	-28.699	1.100
5800	4.968	44.200	39.488	27.333	55.830	-30.182	1.137
5900	4.968	44.285	39.568	27.830	55.826	-31.665	1.173
6000	4.968	44.369	39.648	28.327	55.823	-33.147	1.207

March 31, 1977

DEUTERIUM, MONATOMIC (D) (IDEAL GAS) GFW = 2.014102

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 29.455 ± 0.004 gibbs/mol

ΔHf°_0 = 52.535 ± 0.001 kcal/mol D

$\Delta Hf^\circ_{298.15}$ = 52.992 ± 0.001 kcal/mol

Electronic Level and Quantum Weight

State	ε_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2

Heat of Formation

The adopted value for ΔHf°_{298} (D,g) is derived using $D^\circ_0(D_2)$ = 36748.9±0.4 cm^{-1} (105.070±0.001 kcal/mol) from Herzberg (1) and auxiliary data for D_2(2).

An earlier value for the dissociation energy was reported by Herzberg and Monfils (3) as $D^\circ_0(D_2)$ = 36743.6±0.5 cm^{-1}. Two theoretical studies by Kolos and Wolniewicz (4) and Bunker (5) yielded a value of 36748.2 cm^{-1}. More recently, LeRoy and Barwell (6), using a relationship involving the near-dissociation behavior of the rotational constants and the long range intermolecular potential, calculated $D^\circ_0(D_2)$ = 36748.88(±0.3) cm^{-1}.

Heat Capacity and Entropy

The electronic levels for D(g) are given in the compilation by Moore (7). Our calculations indicate that the inclusion of levels up to n = 12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the first excited state lies at 82281 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state. The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and the fundamental constants. The gram formula weight is that recommended by IUPAC (8). Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (9).

References

1. G. Herzberg, J. Mol. Spectrosc. 33, 147 (1970).
2. JANAF Thermochemical Tables: D_2(g), 3-31-77.
3. G. Herzberg and A. Monfils, J. Mol. Spectrosc. 5, 482 (1960).
4. W. Kolos and L. Wolniewicz, J. Mol. Spectrosc. 54, 303 (1975).
5. P. R. Bunker, private communication to G. Herzberg, Phys. Rev. Letters 23, 1081 (1969).
6. R. J. LeRoy and M. G. Barwell, Can. J. Phys. 53, 1983 (1975).
7. C. E. Moore, NSRDS-NBS 3, Section 6 (1972).
8. IUPAC Commission on Atomic Weights, Pure Appl. Chem. 37, 589 (1974).
9. J. R. Downey, Dow Chemical Company, Thermal Research, to be published, 1977.

DEUTERIUM UNIPOSITIVE ION (D^+) D^+
(IDEAL GAS) GFW=2.013553

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-1.481	366.208		
100							
200							
298	4.968	28.077	28.077	0.000	368.146	363.449	-266.411
300	4.968	28.108	28.077	0.009	368.158	363.419	-264.747
400	4.968	29.537	28.272	0.506	368.802	361.743	-197.644
500	4.968	30.646	28.640	1.003	369.446	359.904	-157.312
600	4.968	31.551	29.052	1.500	370.087	357.935	-130.376
700	4.968	32.317	29.465	1.996	370.724	355.859	-111.103
800	4.968	32.980	29.864	2.493	371.357	353.692	-96.623
900	4.968	33.566	30.243	2.990	371.982	351.446	-85.342
1000	4.968	34.089	30.602	3.487	372.602	349.131	-76.302
1100	4.968	34.563	30.941	3.984	373.214	346.755	-68.893
1200	4.968	34.995	31.261	4.480	373.819	344.322	-62.709
1300	4.968	35.392	31.564	4.977	374.418	341.840	-57.468
1400	4.968	35.761	31.851	5.474	375.011	339.312	-52.968
1500	4.968	36.103	32.123	5.971	375.598	336.741	-49.062
1600	4.968	36.424	32.382	6.468	376.181	334.132	-45.640
1700	4.968	36.725	32.628	6.964	376.758	331.486	-42.615
1800	4.968	37.009	32.864	7.461	377.331	328.806	-39.922
1900	4.968	37.278	33.089	7.958	377.900	326.095	-37.509
2000	4.968	37.533	33.305	8.455	378.466	323.354	-35.334
2100	4.968	37.775	33.512	8.952	379.028	320.584	-33.363
2200	4.968	38.006	33.711	9.448	379.586	317.788	-31.569
2300	4.968	38.227	33.903	9.945	380.142	314.966	-29.928
2400	4.968	38.438	34.088	10.442	380.695	312.121	-28.422
2500	4.968	38.641	34.266	10.939	381.246	309.253	-27.035
2600	4.968	38.836	34.438	11.436	381.794	306.362	-25.752
2700	4.968	39.024	34.604	11.932	382.339	303.450	-24.562
2800	4.968	39.204	34.765	12.429	382.882	300.519	-23.456
2900	4.968	39.379	34.921	12.926	383.423	297.567	-22.425
3000	4.968	39.547	35.073	13.423	383.962	294.598	-21.461
3100	4.968	39.710	35.220	13.920	384.498	291.610	-20.558
3200	4.968	39.868	35.362	14.416	385.032	288.605	-19.711
3300	4.968	40.020	35.501	14.913	385.565	285.583	-18.913
3400	4.968	40.169	35.636	15.410	386.096	282.546	-18.162
3500	4.968	40.313	35.768	15.907	386.625	279.493	-17.452
3600	4.968	40.453	35.896	16.404	387.152	276.425	-16.781
3700	4.968	40.589	36.021	16.900	387.676	273.341	-16.145
3800	4.968	40.721	36.143	17.397	388.199	270.244	-15.542
3900	4.968	40.850	36.262	17.894	388.720	267.133	-14.970
4000	4.968	40.976	36.378	18.391	389.240	264.009	-14.425
4100	4.968	41.059	36.492	18.888	389.757	260.872	-13.906
4200	4.968	41.219	36.603	19.384	390.273	257.722	-13.411
4300	4.968	41.335	36.712	19.881	390.787	254.560	-12.938
4400	4.968	41.450	36.818	20.378	391.299	251.386	-12.486
4500	4.968	41.561	36.922	20.875	391.810	248.200	-12.054
4600	4.968	41.670	37.024	21.372	392.319	245.004	-11.640
4700	4.968	41.777	37.124	21.868	392.825	241.795	-11.243
4800	4.968	41.882	37.222	22.365	393.331	238.576	-10.863
4900	4.968	41.984	37.319	22.862	393.835	235.347	-10.497
5000	4.968	42.085	37.413	23.359	394.339	232.108	-10.145
5100	4.968	42.183	37.506	23.855	394.839	228.858	-9.807
5200	4.968	42.280	37.596	24.352	395.339	225.599	-9.482
5300	4.968	42.374	37.686	24.849	395.838	222.330	-9.168
5400	4.968	42.467	37.773	25.346	396.336	219.052	-8.865
5500	4.968	42.558	37.860	25.843	396.833	215.764	-8.574
5600	4.968	42.648	37.944	26.339	397.327	212.466	-8.292
5700	4.968	42.736	38.027	26.836	397.822	209.161	-8.020
5800	4.968	42.822	38.109	27.333	398.316	205.847	-7.756
5900	4.968	42.907	38.190	27.830	398.810	202.525	-7.502
6000	4.968	42.990	38.269	28.327	399.303	199.195	-7.256

March 31, 1977

DEUTERIUM UNIPOSITIVE ION (D^+) (IDEAL GAS) GFW = 2.013553

ΔHf°_0 = 366.208 ± 0.01 kcal/mol D^+

$S^\circ_{298.15}$ = 28.077 ± 0.005 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 368.146 ± 0.01 kcal/mol

Heat of Formation

The heat of formation is calculated from the equation $D(g) = D^+(g) + e^-(g)$ with auxiliary data (1), using an ionization potential of IP = 109708.608 cm^{-1} (313.6727 kcal/mol). This ionization potential, as reported by Moore (2) in units of cm^{-1}, is converted to units of kcal/mol using the current CODATA fundamental constants (3).

Heat Capacity and Entropy

The thermodynamic functions of the $D^+(g)$ species is calculated using the current CODATA fundamental constants (3) and assuming that $D^+(g)$ is an ideal monatomic gas. Since there is no electron associated with this species, there is only a translational contribution to the thermodynamic functions.

References

1. JANAF Thermochemical Tables: D(g) and $e^-(g)$, 3-31-77.
2. C. E. Moore, *NSRDS-NBS 3, Section 6 (1972).*
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D^+

DEUTERIUM UNINEGATIVE ION (D^-) D^-

(IDEAL GAS) GFW=2.014651

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	35.143		
100							
200							
298	4.968	28.079	28.079	0.000	34.119	32.395	-23.746
300	4.968	28.109	28.079	0.009	34.113	32.385	-23.592
400	4.968	29.539	28.274	0.506	33.763	31.861	-17.408
500	4.968	30.647	28.642	1.003	33.413	31.426	-13.736
600	4.968	31.553	29.054	1.500	33.060	31.062	-11.314
700	4.968	32.319	29.467	1.996	32.705	30.757	-9.603
800	4.968	32.982	29.866	2.493	32.344	30.504	-8.333
900	4.968	33.567	30.245	2.990	31.975	30.295	-7.357
1000	4.968	34.091	30.604	3.487	31.601	30.128	-6.584
1100	4.968	34.564	30.943	3.984	31.219	30.000	-5.960
1200	4.968	34.996	31.263	4.480	30.832	29.907	-5.447
1300	4.968	35.394	31.565	4.977	30.437	29.845	-5.017
1400	4.968	35.762	31.852	5.474	30.036	29.815	-4.654
1500	4.968	36.105	32.124	5.971	29.629	29.812	-4.344
1600	4.968	36.426	32.383	6.468	29.218	29.838	-4.076
1700	4.968	36.727	32.630	6.964	28.803	29.890	-3.843
1800	4.968	37.011	32.866	7.461	28.382	29.966	-3.638
1900	4.968	37.279	33.091	7.958	27.957	30.066	-3.458
2000	4.968	37.534	33.307	8.455	27.529	30.187	-3.299
2100	4.968	37.777	33.514	8.952	27.097	30.330	-3.156
2200	4.968	38.008	33.713	9.448	26.663	30.496	-3.029
2300	4.968	38.229	33.905	9.945	26.225	30.679	-2.915
2400	4.968	38.440	34.089	10.442	25.784	30.882	-2.812
2500	4.968	38.643	34.267	10.939	25.341	31.104	-2.719
2600	4.968	38.838	34.439	11.436	24.895	31.343	-2.635
2700	4.968	39.025	34.606	11.932	24.448	31.600	-2.558
2800	4.968	39.206	34.767	12.429	23.997	31.873	-2.488
2900	4.968	39.380	34.923	12.926	23.544	32.162	-2.424
3000	4.968	39.549	35.074	13.423	23.089	32.467	-2.365
3100	4.968	39.711	35.221	13.920	22.631	32.787	-2.311
3200	4.968	39.869	35.364	14.416	22.173	33.122	-2.262
3300	4.968	40.022	35.503	14.913	21.712	33.471	-2.217
3400	4.968	40.170	35.638	15.410	21.249	33.835	-2.175
3500	4.968	40.314	35.770	15.907	20.784	34.211	-2.136
3600	4.968	40.454	35.898	16.404	20.317	34.602	-2.101
3700	4.968	40.590	36.023	16.900	19.849	35.006	-2.068
3800	4.968	40.723	36.145	17.397	19.378	35.421	-2.037
3900	4.968	40.852	36.264	17.894	18.905	35.849	-2.009
4000	4.968	40.978	36.380	18.391	18.431	36.290	-1.983
4100	4.968	41.100	36.494	18.888	17.954	36.742	-1.958
4200	4.968	41.220	36.605	19.384	17.478	37.207	-1.936
4300	4.968	41.337	36.713	19.881	16.998	37.682	-1.915
4400	4.968	41.451	36.820	20.378	16.516	38.168	-1.896
4500	4.968	41.563	36.924	20.875	16.033	38.665	-1.878
4600	4.968	41.672	37.026	21.372	15.548	39.173	-1.861
4700	4.968	41.779	37.126	21.868	15.062	39.693	-1.846
4800	4.968	41.884	37.224	22.365	14.574	40.222	-1.831
4900	4.968	41.986	37.320	22.862	14.084	40.761	-1.818
5000	4.968	42.086	37.415	23.359	13.594	41.311	-1.806
5100	4.968	42.185	37.507	23.855	13.102	41.870	-1.794
5200	4.968	42.281	37.598	24.352	12.608	42.439	-1.784
5300	4.968	42.376	37.687	24.849	12.113	43.017	-1.774
5400	4.968	42.469	37.775	25.346	11.617	43.605	-1.765
5500	4.968	42.560	37.861	25.843	11.120	44.202	-1.756
5600	4.968	42.649	37.946	26.339	10.622	44.809	-1.749
5700	4.968	42.737	38.029	26.836	10.123	45.423	-1.742
5800	4.968	42.824	38.111	27.333	9.623	46.047	-1.735
5900	4.968	42.909	38.192	27.830	9.123	46.679	-1.729
6000	4.968	42.992	38.271	28.327	8.622	47.320	-1.724

March 31, 1977

DEUTERIUM UNINEGATIVE ION (D^-) (IDEAL GAS) GFW = 2.014651

Ground State Configuration $^1S_0$

$S^\circ_{298.15}$ = 28.079 ± 0.004 gibbs/mol

ΔHf°_0 = 35.143 ± 0.01 kcal/mol D^-

$\Delta Hf^\circ_{298.15}$ = 34.119 ± 0.01 kcal/mol

Electronic Level and Quantum Weight

State	ε_i, cm^{-1}	g_i
$^1S_0$	0.00	1

Heat of Formation

The heat of formation is calculated from an adopted electron affinity of D(g), assumed to be identical to that for H(g), of EA = 0.754209 eV (17.3923 kcal/mol). This value for H(g) was recommended by Hotop and Lineberger (1) and Rosenstock et al. (2).

Heat Capacity and Entropy

The ground state for D^-(g) is assumed to be $1s^2\ {}^1S_0$ in analogy with H^-(g). The thermodynamic functions are calculated using the recent CODATA fundamental constants (3) and assuming that D^-(g) is an ideal monatomic gas.

A comparison of the isoelectronic sequence – H^-(g), He(g), and Li^+(g) – would suggest that stable electronic states may exist at 0.8 EA(H) or roughly 6400 cm^{-1}. This would greatly affect the entropy. However, Pekeris (4) states that he was unable to find any bound states. In addition, Seman and Branscom (5) state that theoretical and semiempirical evidence suggests that atomic negative ions have very few if any excited states below the continuum. We assume that the same arguments apply for D^-(g) and that no stable excited states exist.

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D^-

DEUTERIUM FLUORIDE (DF) DF

(IDEAL GAS) GFW=21.0125

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-2.065	-65.836	-65.836	INFINITE
100	6.959	35.320	49.113	-1.379	-65.827	-65.978	144.192
200	6.961	40.144	43.561	-0.683	-65.834	-66.125	72.257
298	6.964	42.924	42.924	0.000	-65.850	-66.265	48.573
300	6.964	42.967	42.924	0.013	-65.851	-66.268	48.275
400	6.973	44.971	43.197	0.710	-65.887	-66.401	36.280
500	7.002	46.530	43.713	1.408	-65.941	-66.524	29.077
600	7.065	47.811	44.293	2.111	-66.005	-66.635	24.271
700	7.161	48.907	44.875	2.822	-66.074	-66.734	20.835
800	7.281	49.871	45.441	3.544	-66.145	-66.824	18.255
900	7.413	50.736	45.982	4.279	-66.214	-66.905	16.246
1000	7.549	51.524	46.497	5.027	-66.280	-66.978	14.638
1100	7.681	52.250	46.988	5.788	-66.343	-67.045	13.320
1200	7.806	52.924	47.455	6.563	-66.402	-67.106	12.221
1300	7.923	53.553	47.900	7.349	-66.458	-67.162	11.291
1400	8.029	54.144	48.325	8.147	-66.511	-67.214	10.493
1500	8.126	54.702	48.732	8.955	-66.561	-67.263	9.800
1600	8.215	55.229	49.121	9.772	-66.608	-67.308	9.194
1700	8.295	55.730	49.496	10.598	-66.652	-67.350	8.658
1800	8.367	56.206	49.855	11.431	-66.696	-67.390	8.182
1900	8.433	56.660	50.202	12.271	-66.737	-67.427	7.756
2000	8.493	57.094	50.535	13.117	-66.777	-67.463	7.372
2100	8.547	57.510	50.858	13.969	-66.816	-67.497	7.024
2200	8.597	57.909	51.169	14.827	-66.853	-67.528	6.708
2300	8.643	58.292	51.471	15.689	-66.890	-67.558	6.419
2400	8.685	58.660	51.763	16.555	-66.927	-67.586	6.154
2500	8.724	59.016	52.046	17.425	-66.962	-67.613	5.911
2600	8.760	59.359	52.320	18.300	-66.998	-67.638	5.685
2700	8.794	59.690	52.587	19.177	-67.033	-67.662	5.477
2800	8.825	60.010	52.847	20.058	-67.069	-67.685	5.283
2900	8.854	60.320	53.099	20.942	-67.104	-67.706	5.102
3000	8.882	60.621	53.345	21.829	-67.140	-67.727	4.934
3100	8.907	60.913	53.584	22.719	-67.176	-67.745	4.776
3200	8.932	61.196	53.818	23.611	-67.212	-67.763	4.628
3300	8.955	61.471	54.045	24.505	-67.249	-67.779	4.489
3400	8.977	61.739	54.268	25.401	-67.287	-67.795	4.358
3500	8.998	61.999	54.485	26.300	-67.325	-67.810	4.234
3600	9.018	62.253	54.697	27.201	-67.363	-67.823	4.117
3700	9.037	62.500	54.905	28.104	-67.403	-67.835	4.007
3800	9.055	62.742	55.108	29.008	-67.443	-67.846	3.902
3900	9.073	62.977	55.307	29.915	-67.484	-67.856	3.802
4000	9.090	63.207	55.501	30.823	-67.526	-67.865	3.708
4100	9.106	63.432	55.692	31.733	-67.569	-67.873	3.618
4200	9.122	63.651	55.879	32.644	-67.612	-67.880	3.532
4300	9.138	63.866	56.062	33.557	-67.657	-67.886	3.450
4400	9.153	64.076	56.242	34.472	-67.703	-67.891	3.372
4500	9.167	64.282	56.418	35.388	-67.750	-67.895	3.297
4600	9.181	64.484	56.591	36.305	-67.798	-67.897	3.226
4700	9.195	64.682	56.761	37.224	-67.846	-67.899	3.157
4800	9.208	64.875	56.929	38.144	-67.897	-67.900	3.092
4900	9.222	65.065	57.093	39.066	-67.947	-67.899	3.028
5000	9.235	65.252	57.254	39.989	-67.999	-67.898	2.968
5100	9.247	65.435	57.413	40.913	-68.051	-67.895	2.909
5200	9.259	65.614	57.569	41.838	-68.105	-67.891	2.853
5300	9.272	65.791	57.722	42.764	-68.160	-67.887	2.799
5400	9.284	65.964	57.873	43.692	-68.214	-67.881	2.747
5500	9.295	66.135	58.022	44.621	-68.270	-67.874	2.697
5600	9.307	66.302	58.168	45.551	-68.326	-67.867	2.649
5700	9.318	66.467	58.312	46.483	-68.383	-67.858	2.602
5800	9.330	66.629	58.454	47.415	-68.440	-67.848	2.557
5900	9.341	66.789	58.594	48.348	-68.497	-67.837	2.513
6000	9.352	66.946	58.732	49.283	-68.554	-67.826	2.471

July 31, 1972 (NBS); June 30, 1977

DEUTERIUM FLUORIDE (DF) (IDEAL GAS) GFW = 21.0125

DF

D_0° = 136.7 ± 0.6 kcal/mol
$S^\circ_{298.15}$ = 42.924 gibbs/mol
Symmetry Number = 1

ΔHf_0° = -65.84 ± 0.2 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -65.85 ± 0.2 kcal/mol

Electronic States and Molecular Constants

State	ε_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0	1	2998.19	45.76	11.000	0.2907	0.9187
$V^1\Sigma^+$	83755	1	839.4	8.90	2.121	0.00712	2.088

Heat of Formation

The heat of formation was calculated from ΔHf°_{298} of HF(g), -65.13±0.2 kcal/mol, given in JANAF Thermochemical Tables (1) the appropriate thermal functions (see tables for H_2, D_2, DF and HF (1), and the estimated zero point energies. The energies for H_2(g) and D_2(g) are those given by Herzberg and Monfils (2). The energies for HF(g) and DF(g) include the Dunham correction and were calculated from the data given by Mann et al. (3) and Spanbauer et al. (4).

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen (5). The National Bureau of Standards prepared this table (6) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (6), we recalculate the table in terms of 1973 fundamental constants (7), 1975 atomic weights (8), and current JANAF reference states for the elements.

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DEUTERIUM HYDRIDE (HD)

(IDEAL GAS) GFW=3.022002

DH

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.034	0.079	0.079	INFINITE
100	7.000	26.718	40.547	-1.383	0.043	-0.080	0.175
200	6.976	31.558	34.982	-0.685	0.066	-0.211	0.230
298	6.979	34.343	34.343	0.000	0.077	-0.350	0.256
300	6.979	34.387	34.344	0.013	0.077	-0.353	0.257
400	6.986	36.395	34.617	0.711	0.079	-0.496	0.271
500	6.999	37.956	35.135	1.410	0.078	-0.639	0.279
600	7.025	39.234	35.715	2.111	0.077	-0.783	0.285
700	7.073	40.320	36.297	2.816	0.075	-0.926	0.289
800	7.144	41.269	36.860	3.527	0.071	-1.069	0.292
900	7.234	42.115	37.398	4.246	0.066	-1.211	0.294
1000	7.339	42.883	37.909	4.974	0.061	-1.353	0.296
1100	7.453	43.588	38.393	5.714	0.056	-1.494	0.297
1200	7.570	44.241	38.854	6.465	0.052	-1.634	0.298
1300	7.687	44.852	39.292	7.228	0.047	-1.775	0.298
1400	7.801	45.426	39.710	8.002	0.042	-1.915	0.299
1500	7.911	45.968	40.109	8.788	0.038	-2.055	0.299
1600	8.016	46.482	40.491	9.584	0.035	-2.194	0.300
1700	8.115	46.971	40.858	10.391	0.032	-2.333	0.300
1800	8.208	47.437	41.211	11.207	0.029	-2.472	0.300
1900	8.295	47.883	41.550	12.032	0.027	-2.611	0.300
2000	8.377	48.311	41.878	12.866	0.025	-2.750	0.300
2100	8.454	48.721	42.194	13.708	0.023	-2.889	0.301
2200	8.527	49.116	42.500	14.557	0.022	-3.027	0.301
2300	8.595	49.497	42.796	15.413	0.020	-3.166	0.301
2400	8.660	49.864	43.083	16.276	0.020	-3.304	0.301
2500	8.722	50.219	43.361	17.145	0.019	-3.442	0.301
2600	8.780	50.562	43.631	18.020	0.018	-3.581	0.301
2700	8.836	50.895	43.894	18.901	0.018	-3.719	0.301
2800	8.890	51.217	44.150	19.787	0.018	-3.858	0.301
2900	8.942	51.530	44.399	20.679	0.017	-3.997	0.301
3000	8.993	51.834	44.642	21.576	0.018	-4.135	0.301
3100	9.041	52.130	44.879	22.477	0.018	-4.273	0.301
3200	9.089	52.417	45.110	23.384	0.018	-4.412	0.301
3300	9.135	52.698	45.336	24.295	0.019	-4.550	0.301
3400	9.181	52.971	45.556	25.211	0.019	-4.689	0.301
3500	9.226	53.238	45.772	26.131	0.020	-4.827	0.301
3600	9.270	53.498	45.983	27.056	0.021	-4.965	0.301
3700	9.314	53.753	46.189	27.985	0.022	-5.104	0.301
3800	9.358	54.002	46.392	28.919	0.023	-5.243	0.302
3900	9.401	54.246	46.590	29.857	0.024	-5.381	0.302
4000	9.444	54.484	46.784	30.799	0.026	-5.520	0.302
4100	9.486	54.718	46.975	31.746	0.028	-5.659	0.302
4200	9.528	54.947	47.162	32.696	0.030	-5.797	0.302
4300	9.570	55.172	47.346	33.651	0.032	-5.936	0.302
4400	9.611	55.392	47.526	34.610	0.035	-6.075	0.302
4500	9.652	55.609	47.703	35.573	0.038	-6.214	0.302
4600	9.692	55.821	47.878	36.541	0.041	-6.353	0.302
4700	9.731	56.030	48.049	37.512	0.044	-6.492	0.302
4800	9.770	56.235	48.217	38.487	0.048	-6.631	0.302
4900	9.807	56.437	48.383	39.466	0.053	-6.770	0.302
5000	9.844	56.636	48.546	40.448	0.058	-6.909	0.302
5100	9.879	56.831	48.707	41.434	0.062	-7.049	0.302
5200	9.912	57.023	48.865	42.424	0.068	-7.188	0.302
5300	9.945	57.212	49.020	43.417	0.074	-7.328	0.302
5400	9.976	57.398	49.174	44.413	0.080	-7.468	0.302
5500	10.005	57.582	49.325	45.412	0.087	-7.607	0.302
5600	10.032	57.762	49.474	46.414	0.094	-7.747	0.302
5700	10.057	57.940	49.621	47.418	0.102	-7.888	0.302
5800	10.080	58.115	49.766	48.425	0.110	-8.028	0.302
5900	10.101	58.288	49.909	49.434	0.119	-8.168	0.303
6000	10.119	58.458	50.050	50.445	0.128	-8.309	0.303

July 31, 1972 (NBS); June 30, 1977

DEUTERIUM HYDRIDE (HD, or $^1H^2H$) (IDEAL GAS) GFW = 3.022002

D H

D_0^o = 104.090 ± 0.001 kcal/mol

$S^o_{298.15}$ = 34.343 ± 0.008 gibbs/mol

Ground State Configuration $^1\Sigma^+$

ΔHf_0^o = 0.079 ± 0.002 kcal/mol

$\Delta Hf^o_{298.15}$ = 0.077 ± 0.003 kcal/mol

Symmetry Number = 1

Vibrational and Rotational Levels (cm^{-1})

Direct Summation of Electronic Ground State:

$$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_o + BZ - DZ^2 + H^2Z^3/(H+LZ),$$

where Z = J(J+1), Y = v+1/2, and we omit subscript v on G, F, B, D, H, and L

$$G = 3815.403Y - 93.61504Y^2 + 1.39630Y^3 - 0.118666Y^4 + 5.97675\times10^{-3}Y^5 - 2.08092\times10^{-4}Y^6$$

$$B = 45.66910 - 2.031845Y + 7.27360\times10^{-2}Y^2 - 1.82824\times10^{-2}Y^3 + 3.06318\times10^{-3}Y^4$$
$$-3.00453\times10^{-4}Y^5 + 1.47623\times10^{-5}Y^6 - 2.98871\times10^{-7}Y^7$$

$$D = 2.6527\times10^{-2} - 1.1534\times10^{-3}Y + 1.7075\times10^{-4}Y^2 - 2.1142\times10^{-5}Y^3 + 9.9570\times10^{-7}Y^4$$

$$H = 2.206\times10^{-5} - 2.648\times10^{-6}Y + 3.047\times10^{-7}Y^2 - 1.327\times10^{-8}Y^3$$

$$L = 2.122\times10^{-8} - 3.912\times10^{-9}Y + 3.298\times10^{-10}Y^2$$

$$v_{max} = 17, \quad J_{max} = 46 - 42\ v/v_{max}$$

Heat of Formation

ΔHf_0^o is derived from D_0^o = 36406.0±0.4 cm^{-1} (104.090±0.001 kcal/mol) based on absorption limits analyzed by Herzberg (1). He derived D_0^o values of 36406.6 and 36405.8 cm^{-1} from lower and upper absorption edges. Thorson (2), by theoretical treatment of absorption-edge doubling, concluded that the value from the upper edge is more accurate. We adopt a value closer to that from the upper edge and essentially the same as that selected by the National Bureau of Standards (3).

Heat Capacity and Entropy

These are calculated by direct summation (4) over vibrational-rotational energy levels of the electronic ground state. We performed the direct summation with an extended version of a program written by W. H. Evans and provided through cooperation of D. D. Wagman, both of the U.S. National Bureau of Standards. Contributions of excited states (T_o > 90000 cm^{-1}, 5) are negligible at 6000 K.

Vibrational-rotational levels are represented by the polynomials given above. G, B, and D are our fits of data from Dabrowski and Herzberg (5). Data from Durie and Herzberg (6), McKellar et al. (7), Brannon et al. (8), and Stoicheff (9) were also used where appropriate. Observed HD data extend to v_{max} = 17 for G and B, v = 16 for D, but only v = 1 for H. We estimate polynomials H and L by isotopic relations from those of H_2 (4) in order to provide a similar extrapolation to high J values. Our H polynomial differs from H_o and H_1 (8, 9) by less than the experimental uncertainty. Our combination of H and L should be consistent with our adopted approximation for the infinite series (F) of rotational levels. We assume that F has the form proposed by Khachkuruzov (10) and Woolley et al. (11). We assume a linear approximation (10) for the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated by comparison with H_2 and D_2 (4) so that J_{max} is *consistent with observation for HD (5) of a rovibrational level at J = 6, v = 16.*

Thermodynamic functions are calculated using 1973 fundamental constants (12), 1975 atomic weight of H, and 1973 isotopic mass of D (13). Results apply either to $^1H^2H$ or to HD containing H of natural abundance, even though the vibrational-rotational constants are for $^1H^2H$. Maximum difference between thermodynamic functions for $^1H^2H$ and HD is 0.0002 gibbs/mol in S°. Our calculations agree to within 0.002 gibbs/mol (or kcal/mol) with those of Woolley et al. (11) up to 2000 K. The more approximate Cp° values of NBS (3) differ by less than 0.04 gibbs/mol in the range 3000 to 6000 K. We omit the nuclear-spin contribution (R ln 6) to entropy and Gibbs-energy function.

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D H

DEUTERIUM HYDRIDE UNIPOSITIVE ION (HD^+) DH^+

(IDEAL GAS) GFW=3.021453

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0				-2.059	354.238		
100							
200							
298	7.011	37.152	37.152	0.000	357.742	354.991	-260.212
300	7.012	37.195	37.152	0.013	357.751	354.974	-258.595
400	7.109	39.224	37.428	0.718	358.257	353.973	-193.389
500	7.280	40.827	37.953	1.437	358.774	352.842	-154.225
600	7.494	42.173	38.547	2.176	359.307	351.606	-128.071
700	7.715	43.345	39.150	2.936	359.856	350.279	-109.360
800	7.926	44.389	39.741	3.719	360.421	348.872	-95.306
900	8.117	45.334	40.311	4.521	360.997	347.394	-84.358
1000	8.287	46.198	40.857	5.341	361.581	345.851	-75.585
1100	8.438	46.995	41.379	6.178	362.170	344.250	-68.395
1200	8.572	47.735	41.878	7.028	362.760	342.595	-62.394
1300	8.692	48.426	42.356	7.891	363.352	340.890	-57.308
1400	8.801	49.074	42.813	8.764	363.946	339.140	-52.941
1500	8.901	49.685	43.251	9.651	364.538	337.348	-49.151
1600	8.995	50.262	43.671	10.546	365.130	335.516	-45.829
1700	9.082	50.810	44.075	11.450	365.721	333.647	-42.893
1800	9.166	51.332	44.464	12.363	366.311	331.743	-40.279
1900	9.247	51.830	44.838	13.283	366.901	329.807	-37.936
2000	9.327	52.306	45.200	14.212	367.492	327.839	-35.824
2100	9.406	52.763	45.549	15.149	368.082	325.842	-33.910
2200	9.484	53.202	45.887	16.093	368.672	323.816	-32.168
2300	9.562	53.626	46.215	17.045	369.263	321.764	-30.574
2400	9.640	54.034	46.532	18.006	369.857	319.687	-29.111
2500	9.718	54.429	46.840	18.973	370.452	317.585	-27.763
2600	9.795	54.812	47.139	19.949	371.049	315.458	-26.516
2700	9.872	55.183	47.430	20.933	371.648	313.308	-25.360
2800	9.946	55.544	47.714	21.923	372.248	311.136	-24.285
2900	10.018	55.894	47.990	22.922	372.852	308.943	-23.282
3000	10.086	56.235	48.259	23.927	373.457	306.729	-22.345
3100	10.149	56.566	48.522	24.939	374.065	304.495	-21.467
3200	10.208	56.890	48.778	25.957	374.672	302.240	-20.642
3300	10.260	57.204	49.029	26.980	375.282	299.968	-19.866
3400	10.306	57.511	49.274	28.008	375.892	297.677	-19.134
3500	10.344	57.811	49.513	29.041	376.502	295.368	-18.443
3600	10.374	58.103	49.748	30.077	377.111	293.041	-17.790
3700	10.395	58.387	49.978	31.115	377.717	290.697	-17.170
3800	10.408	58.665	50.202	32.156	378.322	288.337	-16.583
3900	10.413	58.935	50.423	33.197	378.924	285.961	-16.025
4000	10.409	59.199	50.639	34.238	379.521	283.570	-15.493
4100	10.396	59.455	50.851	35.278	380.114	281.164	-14.987
4200	10.376	59.706	51.059	36.317	380.701	278.743	-14.504
4300	10.347	59.950	51.263	37.353	381.281	276.308	-14.043
4400	10.311	60.187	51.463	38.386	381.855	273.861	-13.603
4500	10.267	60.418	51.659	39.415	382.420	271.400	-13.181
4600	10.218	60.643	51.852	40.439	382.977	268.927	-12.777
4700	10.162	60.863	52.042	41.458	383.524	266.441	-12.389
4800	10.100	61.076	52.228	42.472	384.064	263.944	-12.018
4900	10.034	61.284	52.410	43.478	384.593	261.436	-11.660
5000	9.963	61.486	52.590	44.478	385.112	258.918	-11.317
5100	9.889	61.682	52.766	45.471	385.619	256.389	-10.987
5200	9.811	61.873	52.939	46.456	386.117	253.850	-10.669
5300	9.730	62.059	53.110	47.433	386.605	251.302	-10.363
5400	9.647	62.241	53.277	48.402	387.080	248.745	-10.067
5500	9.562	62.417	53.442	49.362	387.546	246.179	-9.782
5600	9.475	62.588	53.604	50.314	387.999	243.604	-9.507
5700	9.388	62.755	53.763	51.257	388.442	241.021	-9.241
5800	9.299	62.918	53.919	52.192	388.875	238.431	-8.984
5900	9.211	63.076	54.073	53.117	389.297	235.834	-8.736
6000	9.122	63.230	54.224	54.034	389.709	233.230	-8.495

Sept. 30, 1977

DEUTERIUM HYDRIDE UNIPOSITIVE ION (HD^+) (IDEAL GAS) GFW = 3.021453

D_0^o = 61.518 ± 0.005 kcal/mol ($HD^+ \rightarrow H^+ + D$)
$S^o_{298.15}$ = 37.152 ± 0.01 gibbs/mol

ΔHf_0^o = 356.238 ± 0.005 kcal/mol
$\Delta Hf^o_{298.15}$ = [357.742] kcal/mol

DH^+

Vibrational and Rotational Levels (cm^{-1})

Direct Summation using Energy-Level Equations for the $^2\Sigma_g^+$ Electronic Ground State:

$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_o + BZ - DZ^2 + H^2Z^3/(H+LZ)$,
where $Z = N(N+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L
$G = 2012.19\ Y - 50.5532\ Y^2 + 0.0604244\ Y^3 - 0.0163194\ Y^4$
$B = 22.4643 - 1.03566\ Y + 0.0180076\ Y^2 - 0.000633616\ Y^3$ $r_e = 1.057$ Å
$D = 1.12041\times10^{-2} - 4.24035\times10^{-4}\ Y + 1.26643\times10^{-5}\ Y^2$
$H = 7.26086\times10^{-6} - 2.19375\times10^{-7}\ Y$ and $L = 5.06679\times10^{-9}$
$v_{max} = 21$ and $N_{max} \approx 47 - 38v/v_{max}$
Electronic statistical weight = 2 and rotational statistical weights = 1(even and odd N)

Heat of Formation

ΔHf_0^o = 356.238±0.005 kcal/mol is obtained from that of HD(g) (1) using the ionization potential IP(HD) = 124568.5±1.2 cm^{-1} (356.159±0.004 kcal/mol). Takezawa and Tanaka (2) determined IP = 124569.5±0.6 cm^{-1} from Rydberg spectra of HD. Similar studies on H_2 by Herzberg and Jungen (3) revealed a bias of ∿1.0 cm^{-1} attributed to a pressure shift in the spectra. We assume an equal shift for HD, adjust IP by -1.0 cm^{-1} and increase the uncertainty due to this adjustment. ΔHf_0^o is converted to ΔHf^o_{298} by use of JANAF (1) enthalpies ($H_0^o - H^o_{298}$) for H_2, D_2, HD^+ and e^-(g). The difference in ΔHf^o_{298} between HD^+ and HD should not be *interpreted as a room-temperature ionization threshold due to inclusion of these enthalpies and to threshold effects noted by* Rosenstock et al. (4).

The adopted spectroscopic IP(HD) receives strong support from a value calculated indirectly from experimental values (1) of D_0^o(HD) and IP(H) combined with the theoretical value (5) of $D_0^o(HD^+)$; this indirect value differs by only 0.3 cm^{-1}. Furthermore, IP(HD) can be predicted (6) approximately from that of H_2 (or D_2) using differences in zero-point energies (1) of the diatomic molecules and their ions. Predicted values of IP(HD) deviate from the observed value by -16 cm^{-1} (based on H_2) and +16 cm^{-1} (based on D_2). Inclusion of an empirical adjustment for the difference IP(D) - IP(H) overcorrects the predictions, giving deviations of +14 cm^{-1} (based on H_2) and -14 cm^{-1} (based on D_2). The average of deviations derived from H_2 and D_2 is zero, suggesting that the slight discrepancies are due to the approximate nature of the prediction. An approximate photoionization result, reviewed by Rosenstock et al. (4), deviates from the spectroscopic result by ∿130 cm^{-1}.

Heat Capacity and Entropy

Thermodynamic functions for ortho-para "equilibrium" HD^+ are calculated by direct summation using the energy-level equations listed above. We use 1973 fundamental constants (7) in an extended version of a computer program written by W. H. Evans and provided by D. D. Wagman of the U. S. National Bureau of Standards. Excited electronic states are neglected because they do not contribute significantly. The electronic statistical weight is taken equal to the multiplicity since we neglect the very small rotational splitting (8).

Coefficients of the energy-level polynomials are calculated from the theoretical values of H_2^+ (1) using rho = 0.866117 in isotopic equations. These polynomials are confirmed by six rotation-vibration transitions ($v \leq 3$, $N \leq 2$) observed between 1642 and 1869 cm^{-1} by an infrared laser-resonance method (8). Our polynomials predict these transitions within 0.1 cm^{-1}. We give the polynomial coefficients, especially higher order ones, to many more digits than are justified by their accuracy. The equations are very approximate near N_{max} but, judging by H_2^+ (1), this should have little effect on the thermodynamic functions even at 6000 K. The approximate v_{max} is derived from the G polynomial.

The thermodynamic functions *include contributions from quasi-bound levels lying above* $D_0^o(HD^+ \rightarrow H^+ + D)$ = 21516 cm^{-1}. At 6000 K these levels contribute 0.39 gibbs/mol to Cp° and 0.048 gibbs/mol to the Gibbs-energy function. Their contribution is negligible below 3000 K. Limiting rotational quantum numbers N_{max} are estimated from H_2^+, H_2 and HD (1) by comparing energy increments and rotational quanta found above the respective values of D_0^o. The crudity of these estimates makes Cp° at 6000 K somewhat more uncertain than in the case of H_2^+ (1).

References

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DH^+

DEUTERIUM HYDRIDE UNINEGATIVE ION (HD^-)　　DH^-

(IDEAL GAS)　GFW=3.022551

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.069	57.730		
100							
200							
298	7.115	36.113	36.113	0.000	56.282	56.815	-41.646
300	7.119	36.157	36.113	0.013	56.273	56.818	-41.392
400	7.358	38.236	36.395	0.736	55.803	57.072	-31.182
500	7.645	39.908	36.936	1.486	55.357	57.441	-25.107
600	7.916	41.327	37.552	2.265	54.936	57.897	-21.089
700	8.150	42.565	38.182	3.068	54.536	58.424	-18.240
800	8.346	43.666	38.800	3.893	54.150	59.005	-16.119
900	8.509	44.659	39.396	4.736	53.772	59.634	-14.481
1000	8.645	45.563	39.969	5.594	53.400	60.305	-13.180
1100	8.761	46.393	40.515	6.465	53.029	61.014	-12.122
1200	8.860	47.159	41.037	7.346	52.658	61.757	-11.247
1300	8.946	47.872	41.536	8.236	52.283	62.530	-10.512
1400	9.023	48.538	42.013	9.135	51.906	63.332	-9.887
1500	9.091	49.163	42.469	10.041	51.525	64.161	-9.348
1600	9.154	49.751	42.906	10.953	51.141	65.016	-8.881
1700	9.211	50.308	43.325	11.871	50.754	65.896	-8.471
1800	9.264	50.836	43.728	12.795	50.361	66.798	-8.110
1900	9.314	51.338	44.115	13.724	49.966	67.722	-7.790
2000	9.362	51.817	44.488	14.658	49.567	68.666	-7.503
2100	9.407	52.275	44.848	15.596	49.165	69.631	-7.246
2200	9.450	52.714	45.196	16.539	48.761	70.616	-7.015
2300	9.491	53.135	45.532	17.486	48.354	71.618	-6.805
2400	9.531	53.539	45.857	18.437	47.945	72.638	-6.615
2500	9.570	53.929	46.172	19.392	47.533	73.676	-6.441
2600	9.608	54.305	46.478	20.351	47.119	74.729	-6.281
2700	9.645	54.669	46.775	21.314	46.705	75.800	-6.136
2800	9.682	55.020	47.063	22.280	46.287	76.885	-6.001
2900	9.717	55.361	47.343	23.250	45.868	77.985	-5.877
3000	9.752	55.691	47.616	24.224	45.448	79.099	-5.762
3100	9.787	56.011	47.882	25.201	45.027	80.228	-5.656
3200	9.821	56.322	48.140	26.181	44.605	81.370	-5.557
3300	9.855	56.625	48.393	27.165	44.181	82.526	-5.465
3400	9.888	56.920	48.639	28.152	43.756	83.694	-5.380
3500	9.921	57.207	48.880	29.143	43.330	84.875	-5.300
3600	9.954	57.487	49.115	30.136	42.903	86.068	-5.225
3700	9.987	57.760	49.345	31.133	42.475	87.273	-5.155
3800	10.019	58.027	49.570	32.134	42.046	88.490	-5.089
3900	10.051	58.287	49.790	33.137	41.616	89.717	-5.028
4000	10.083	58.542	50.006	34.144	41.185	90.955	-4.970
4100	10.115	58.792	50.217	35.154	40.753	92.205	-4.915
4200	10.147	59.036	50.424	36.167	40.323	93.467	-4.864
4300	10.178	59.275	50.627	37.183	39.889	94.736	-4.815
4400	10.210	59.509	50.827	38.203	39.455	96.017	-4.769
4500	10.241	59.739	51.022	39.225	39.020	97.306	-4.726
4600	10.272	59.964	51.214	40.251	38.585	98.606	-4.685
4700	10.303	60.186	51.403	41.280	38.150	99.917	-4.646
4800	10.334	60.403	51.588	42.312	37.714	101.236	-4.609
4900	10.365	60.616	51.770	43.347	37.277	102.563	-4.574
5000	10.396	60.826	51.949	44.385	36.841	103.900	-4.541
5100	10.427	61.032	52.125	45.426	36.404	105.246	-4.510
5200	10.458	61.235	52.298	46.470	35.968	106.600	-4.480
5300	10.488	61.434	52.469	47.518	35.531	107.962	-4.452
5400	10.519	61.631	52.637	48.568	35.094	109.333	-4.425
5500	10.550	61.824	52.802	49.621	34.659	110.712	-4.399
5600	10.580	62.014	52.965	50.678	34.225	112.099	-4.375
5700	10.611	62.202	53.125	51.737	33.790	113.493	-4.351
5800	10.641	62.387	53.283	52.800	33.357	114.895	-4.329
5900	10.671	62.569	53.439	53.866	32.925	116.304	-4.308
6000	10.702	62.749	53.593	54.934	32.495	117.721	-4.288

Sept. 30, 1977

DEUTERIUM HYDRIDE UNINEGATIVE ION (HD^-)　(IDEAL GAS)　GFW = 3.022551

D_0° = [29.0 ± 10] kcal/mol　　ΔHf_0° = [57.73 ± 10] kcal/mol　DH^-

$S_{298.15}^\circ$ [36.11 ± 0.1] gibbs/mol　　$\Delta Hf_{298.15}^\circ$ = [56.282] kcal/mol

Electronic Levels and Quantum Weight

State	ε_i, cm^{-1}	g_i
$X^2\Sigma_u^+$	0	2

ω_e = [1473]cm^{-1}　$\omega_e x_e$ = [26.3] cm^{-1}　σ = 2

B_e = [19.0] cm^{-1}　α_e = [0.259] cm^{-1}　r_e = [1.15] Å

Heat of Formation

The heat of formation at 0 K for $HD^-(g)$ is based on the electron affinity (EA) value from a Rydberg-Klein-Rees configuration-interaction calculation for H_2^- (1). This study by Sharpe (1) led to EA(H_2) = -2.5 eV. Assuming this value is valid for $HD^-(g)$ and using auxiliary data (2), we calculate ΔHf_0° = 57.73±10 kcal/mol and $D_0^\circ(HD^-)$ = 29.0±10 kcal/mol; the latter value is calculated for dissociation into ground state D(g) and $H^-(g)$ or $D^-(g)$ and H(g). The adopted EA (H_2) value is suggested to be the more reliable value of eight studies considered by Rosenstock et al. (3).

In terms of molecular orbitals, the ground state for $HD^-(g)$ is the $(1s\sigma_g)^2\ (2p\sigma_u)\ {}^2\Sigma_u^+$ state involving two bonding electrons and one antibonding electron. We would expect, however, the ground state to be $(1s\sigma_g)^2(1s\sigma_u)$. As stated by Massey (4), we should expect only a weakly-bound molecule as compared with HD(g) for which the ground state has no electron in an antibonding orbital. Our adopted calculated EA (HD) value is consitent with this viewpoint. Further discussion of the $HD^-(g)$ ion may be found in Massey (4).

ΔHf_0° is converted to ΔHf_{298}° by use of JANAF (2) enthalpies ($H_0^\circ - H_{298}^\circ$) for $D_2(g)$, $H_2(g)$, $DH^-(g)$, and $e^-(g)$. ΔHf_{298}° should not be interpreted as a room temperature electron affinity due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al (3).

Heat Capacity and Entropy

The vibrational constants for $H_2^-(g)$ are estimated to be the same as in the isoelectronic species He_2^+ (5). The vibrational constants for $HD^-(g)$ are calculated from those for $H_2^-(g)$ using isotopic relations. The internuclear distance is estimated to be ~8% *larger than that for* $He_2^+(g)$. *The same relationship appeared to exist for the* (N_2^-, NO, O_2^+) isoelectronic series. B_e is calculated from r_e whereas α_e is calculated assuming a Morse function for the ground state.

The ground and excited electronic states are discussed in detail by Massey (4). No excited state contributions are included in this calculation.

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MONODEUTERO-WATER (HDO) DHO

(IDEAL GAS) GFW=19.021

T, K	gibbs/mol			kcal/mol			
	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	0.000	0.000	INFINITE	-2.372	-57.943	-57.943	INFINITE
100	7.959	38.940	54.770	-1.583	-58.188	-57.464	125.585
200	7.974	44.459	48.394	-0.787	-58.415	-56.651	61.904
298	8.075	47.658	47.658	0.000	-58.645	-55.736	40.855
300	8.078	47.708	47.658	0.015	-58.650	-55.718	40.590
400	8.311	50.062	47.978	0.834	-58.882	-54.705	29.889
500	8.615	51.949	48.589	1.680	-59.101	-53.635	23.443
600	8.951	53.549	49.286	2.558	-59.302	-52.523	19.131
700	9.302	54.955	49.957	3.471	-59.486	-51.378	16.041
800	9.657	56.220	50.697	4.419	-59.651	-50.208	13.716
900	10.008	57.378	51.376	5.402	-59.799	-49.019	11.903
1000	10.345	58.450	52.030	6.420	-59.928	-47.814	10.450
1100	10.665	59.451	52.660	7.470	-60.041	-46.597	9.258
1200	10.964	60.392	53.266	8.552	-60.139	-45.370	8.263
1300	11.240	61.281	53.848	9.662	-60.225	-44.136	7.420
1400	11.493	62.123	54.409	10.799	-60.299	-42.896	6.696
1500	11.724	62.924	54.951	11.960	-60.363	-41.650	6.068
1600	11.935	63.688	55.473	13.143	-60.418	-40.401	5.518
1700	12.126	64.417	55.978	14.347	-60.465	-39.148	5.033
1800	12.300	65.115	56.466	15.568	-60.506	-37.893	4.601
1900	12.458	65.785	56.939	16.806	-60.543	-36.636	4.214
2000	12.603	66.427	57.398	18.059	-60.575	-35.377	3.866
2100	12.734	67.045	57.842	19.326	-60.604	-34.116	3.550
2200	12.855	67.641	58.274	20.606	-60.630	-32.854	3.264
2300	12.965	68.215	58.694	21.857	-60.654	-31.591	3.002
2400	13.066	68.768	59.102	23.198	-60.677	-30.327	2.762
2500	13.160	69.304	59.500	24.510	-60.698	-29.062	2.541
2600	13.246	69.822	59.887	25.830	-60.719	-27.796	2.336
2700	13.325	70.323	60.264	27.159	-60.739	-26.529	2.147
2800	13.399	70.809	60.632	28.495	-60.761	-25.262	1.972
2900	13.468	71.280	60.991	29.838	-60.782	-23.994	1.808
3000	13.532	71.738	61.342	31.188	-60.804	-22.725	1.655
3100	13.592	72.183	61.684	32.545	-60.827	-21.455	1.513
3200	13.648	72.615	62.019	33.907	-60.851	-20.185	1.379
3300	13.701	73.036	62.347	35.274	-60.875	-18.913	1.253
3400	13.750	73.446	62.667	36.647	-60.902	-17.642	1.134
3500	13.797	73.845	62.981	38.024	-60.930	-16.369	1.022
3600	13.841	74.234	63.288	39.406	-60.959	-15.095	0.916
3700	13.883	74.614	63.589	40.792	-60.991	-13.821	0.816
3800	13.922	74.985	63.884	42.182	-61.024	-12.546	0.722
3900	13.960	75.347	64.173	43.577	-61.059	-11.270	0.632
4000	13.996	75.701	64.457	44.974	-61.096	-9.992	0.546
4100	14.030	76.047	64.736	46.376	-61.135	-8.715	0.465
4200	14.062	76.385	65.009	47.780	-61.176	-7.434	0.387
4300	14.093	76.717	65.277	49.188	-61.220	-6.155	0.313
4400	14.123	77.041	65.541	50.599	-61.265	-4.873	0.242
4500	14.151	77.359	65.800	52.013	-61.314	-3.592	0.174
4600	14.178	77.670	66.055	53.429	-61.364	-2.309	0.110
4700	14.204	77.975	66.305	54.848	-61.418	-1.024	0.048
4800	14.230	78.274	66.552	56.270	-61.473	0.262	-0.012
4900	14.254	78.568	66.794	57.694	-61.531	1.548	-0.069
5000	14.278	78.856	67.032	59.121	-61.591	2.836	-0.124
5100	14.300	79.139	67.267	60.550	-61.654	4.125	-0.177
5200	14.322	79.417	67.498	61.981	-61.720	5.416	-0.228
5300	14.344	79.690	67.725	63.414	-61.788	6.707	-0.277
5400	14.364	79.959	67.949	64.849	-61.859	8.000	-0.324
5500	14.385	80.222	68.170	66.287	-61.931	9.295	-0.369
5600	14.405	80.482	68.388	67.726	-62.006	10.590	-0.413
5700	14.424	80.737	68.602	69.168	-62.084	11.887	-0.456
5800	14.443	80.988	68.813	70.611	-62.163	13.186	-0.497
5900	14.461	81.235	69.022	72.056	-62.245	14.486	-0.537
6000	14.479	81.478	69.227	73.503	-62.329	15.787	-0.575

July 31, 1972 (NBS); June 30, 1977

MONODEUTERO-WATER (HDO) (IDEAL GAS) GFW = 19.02140

DHO

Point Group C_h
$S°_{298.15}$ = 47.658 gibbs/mol
Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -57.943 ± 0.015 kcal/mol
$\Delta Hf°_{298.15}$ = -58.645 ± 0.015 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
2723.66(1)
1402.80(1)
3707.47(1)

Bond Distances: O-H = 0.9584 Å σ = 1
O-D = 0.9584 Å
Bond Angle: H-O-D = 104.45°
Product of the Moments of Inertia: $I_AI_BI_C = 15.827 \times 10^{-120}$ g^3 cm^6

Heat of Formation

Third and second law (where possible) analyses of the more recent determinations (1-5) of the experimental equilibrium constants, Keq, were made for the reactions: (A) $H_2O(g) + HD(g) = HDO(g) + H_2(g)$, and (B) $H_2O(g) + D_2O(g) = 2\ HDO(g)$. Spectroscopic values for the heats of reaction, $\Delta Hr°_{298}$, of (A) and (B) were based on the zero point energies of H_2O, D_2O, and HDO given by Hulston (6) and Wolfsberg (7) and H_2, HD given by Herzberg and Monfils (8). The earlier work on (A) cited by Kirshenbaum (9) is in poor agreement except for that of Herrick, Kirshenbaum, Brown and Herrick, Crist, Davis ($\Delta Hr°_{298}$ = 928±30, 921 cal/mol; respectively). $\Delta Hr°_{298}$ for the reaction (C) $H_2O(\ell) + D_2O(\ell) = 2\ HDO(\ell)$ has been determined to be -32±1 cal/mol (10-12) assuming ideal solutions (see (13)) and Keq(C) ∿3.8. (We calculate Keq(C) = 3.76±0.04 from Keq(B) = 3.76±0.02, $P°(H_2O)/P°(D_2O)$ = 1.151±0.006 (14) at 298 K, and $P°(H_2O)/P°(HDO)$ = 1.073±0.004 (15) at 298 K.) $\Delta Hr°_{298}$ of (B) was calculated from the difference in heats of vaporization at 298 K of $D_2O(\ell) - H_2O(\ell)$ = 331±8 cal (see D_2O table), and $HDO(\ell) - H_2O(\ell)$ = 183±20 cal (14). Values selected for $\Delta Hr°_{298}$ based on non-spectroscopic and spectroscopic work for (A) and (B), underlined in the table, were used to calculate values of $\Delta Hf°_{298}$ of $HDO(g) - H_2O(g)$ of -845±6, -852±10, -852±12, and -851±10 cal/mol, respectively (see D_2O and HD tables). An average value of -850±10 cal was added to $\Delta Hf°_{298}$ of $H_2O(g)$ to obtain $\Delta Hf°_{298}$ HDO(g).

Reaction	Source	Temperature, K	$\Delta Hr°_{298}$, cal/mol	Drift, gibbs/mol
A	Cerrai et al. (1)	324 - 1015	-915±20	0.04±0.10 (-864±30, 0.12±0.07)[a]
A	Suess (2)	353 - 473	-921± 6	0.05±0.05 (-955±29, 0.09±0.09)[a]
A	Hulston (6)	Spectroscopic	-928±10	
A	Wolfsberg (7)	Spectroscopic	-937±10	
B	Pyper, Newbury, and Barton (3)	273.15 297.95	56±11 63±11	(3.75±0.08)[b] (3.74±0.04)[b]
B	Friedman and Shiner (4)	273.15	58± 3	(3.74±0.02)[b]
		298.15	60± 3	(3.76±0.02)[b]
		358.15	62± 7	(3.80±0.04)[b]
B	Kresge, Chiang (5)	298.15	46± 5	(3.85±0.03)[b]
B	Reaction C, see text	298.15	57±22	
B	Hulston (6)	Spectroscopic	55±10	
B	Wolfsberg (7)	Spectroscopic	70±10	

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[a] Second law: $\Delta Hr°_{298}$, $S°_{298}$(obsv.-calc.); [b] Keq at temperature cited.

Heat Capacity and Entropy

The thermodynamic functions of this table are analogous to those in the *JANAF table for $H_2O(g)$ (dated March 31, 1961)*: both tables are taken from Friedman and Haar (16). Friedman and Haar (16) applied their non-rigid-rotor, anharmonic-oscillator treatment (with vibrational-rotational coupling terms and low-temperature rotational corrections) to the infrared-spectra analyses of Benedict et al. (17, 18). In the present table for HDO, the values of Cp° of Friedman and Haar (16) between 4000 and 5000 K were extrapolated linearly (except with a term in T^{-2}) from 5000 to 6000 K. $I_A = 1.211 \times 10^{-40}$, $I_B = 3.060 \times 10^{-40}$, $I_C = 4.271 \times 10^{-40}$ gm cm^2 from Friedman and Haar (16). The National Bureau of Standards prepared this table (19) by critical analysis of data existing in 1972.

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DHO

DEUTERO-IMIDOGEN (ND) DN
(IDEAL GAS) GFW=16.0208

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.067	89.693	89.693	INFINITE
100	6.959	37.118	50.915	-1.380	89.705	89.249	-195.050
200	6.962	41.943	45.361	-0.684	89.700	88.794	-97.029
298	6.969	44.724	44.724	0.000	89.700	88.350	-64.761
300	6.969	44.767	44.724	0.013	89.700	88.341	-64.356
400	7.003	46.776	44.998	0.711	89.701	87.888	-48.019
500	7.088	48.346	45.516	1.415	89.703	87.435	-38.217
600	7.221	49.650	46.099	2.130	89.709	86.981	-31.682
700	7.383	50.775	46.688	2.860	89.720	86.525	-27.014
800	7.554	51.772	47.263	3.607	89.734	86.068	-23.512
900	7.719	52.671	47.814	4.371	89.750	85.609	-20.788
1000	7.874	53.493	48.342	5.151	89.768	85.148	-18.609
1100	8.013	54.250	48.845	5.945	89.787	84.685	-16.825
1200	8.138	54.952	49.325	6.753	89.806	84.221	-15.338
1300	8.249	55.608	49.783	7.572	89.825	83.754	-14.080
1400	8.347	56.223	50.222	8.402	89.844	83.286	-13.001
1500	8.435	56.802	50.641	9.241	89.862	82.817	-12.066
1600	8.512	57.349	51.043	10.089	89.881	82.347	-11.248
1700	8.582	57.867	51.430	10.944	89.898	81.876	-10.526
1800	8.644	58.360	51.801	11.805	89.915	81.403	-9.884
1900	8.700	58.828	52.159	12.672	89.931	80.930	-9.309
2000	8.751	59.276	52.504	13.545	89.947	80.456	-8.792
2100	8.798	59.704	52.836	14.422	89.961	79.980	-8.324
2200	8.840	60.114	53.158	15.304	89.976	79.505	-7.898
2300	8.880	60.508	53.469	16.190	89.990	79.029	-7.509
2400	8.916	60.887	53.770	17.080	90.004	78.552	-7.153
2500	8.950	61.252	54.062	17.973	90.017	78.075	-6.825
2600	8.982	61.603	54.346	18.870	90.029	77.596	-6.522
2700	9.011	61.943	54.621	19.770	90.042	77.119	-6.242
2800	9.039	62.271	54.888	20.672	90.054	76.639	-5.982
2900	9.066	62.589	55.148	21.577	90.065	76.160	-5.740
3000	9.091	62.896	55.401	22.485	90.076	75.680	-5.513
3100	9.115	63.195	55.648	23.396	90.086	75.200	-5.302
3200	9.138	63.485	55.888	24.308	90.096	74.720	-5.103
3300	9.161	63.766	56.123	25.223	90.106	74.239	-4.917
3400	9.182	64.040	56.352	26.140	90.115	73.759	-4.741
3500	9.202	64.306	56.575	27.060	90.123	73.277	-4.576
3600	9.222	64.566	56.793	27.981	90.131	72.796	-4.419
3700	9.242	64.819	57.007	28.904	90.139	72.314	-4.271
3800	9.260	65.066	57.216	29.829	90.146	71.833	-4.131
3900	9.279	65.306	57.420	30.756	90.153	71.350	-3.998
4000	9.296	65.542	57.620	31.685	90.158	70.868	-3.872
4100	9.314	65.771	57.816	32.615	90.164	70.386	-3.752
4200	9.331	65.996	58.008	33.548	90.169	69.904	-3.637
4300	9.347	66.216	58.197	34.482	90.173	69.421	-3.528
4400	9.364	66.431	58.381	35.417	90.178	68.938	-3.424
4500	9.380	66.641	58.563	36.354	90.180	68.455	-3.325
4600	9.396	66.848	58.741	37.293	90.184	67.973	-3.229
4700	9.411	67.050	58.915	38.233	90.185	67.489	-3.138
4800	9.427	67.248	59.087	39.175	90.187	67.006	-3.051
4900	9.442	67.443	59.255	40.119	90.189	66.523	-2.967
5000	9.457	67.634	59.421	41.064	90.191	66.041	-2.887
5100	9.472	67.821	59.584	42.010	90.191	65.558	-2.809
5200	9.486	68.005	59.744	42.958	90.192	65.075	-2.735
5300	9.501	68.186	59.902	43.907	90.192	64.592	-2.663
5400	9.515	68.364	60.057	44.858	90.193	64.109	-2.595
5500	9.529	68.538	60.209	45.810	90.193	63.626	-2.528
5600	9.543	68.710	60.360	46.764	90.193	63.143	-2.464
5700	9.557	68.879	60.508	47.719	90.193	62.659	-2.402
5800	9.571	69.046	60.653	48.675	90.194	62.177	-2.343
5900	9.585	69.209	60.797	49.633	90.195	61.693	-2.285
6000	9.599	69.371	60.939	50.592	90.196	61.211	-2.230

July 31, 1972 (NBS); June 30, 1977

DEUTERO-IMIDOGEN (ND) (IDEAL GAS) GFW = 16.0208
DN

D_0° = 75.4 ± 5 kcal/mol
$S^\circ_{298.15}$ = 44.724 gibbs/mol
Symmetry Number = 1

ΔHf_0° = 89.7 ± 5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 89.7 ± 5 kcal/mol

Electronic States and Molecular Constants

State	ε_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^3\Sigma^-$	0	3	2422	50.6	8.8993	0.252	1.040

Heat of Formation

ΔHf°_{298} of ND(g) minus NH(g) was calculated from the JANAF thermal functions and the zero point energies of H_2(g), D_2(g) [given by Herzberg and Monfils (1)], NH(g), and ND(g) [given by Haar, et al. (2)]. ΔHf°_{298} of ND(g) was calculated from this *value and the JANAF selection for* ΔHf°_{298} *of NH(g)* (3).

Heat Capacity and Entropy

The molecular constants *which are given for NH in the JANAF Thermochemical Tables* (3) *were adjusted for the isotope* effect. The National Bureau of Standards prepared this table (4) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (4), we recalculate the table in terms of 1973 fundamental constants (5), 1975 atomic weights (6), and current JANAF reference states for the elements.

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DN

DEUTERO-HYDROXYL (OD) D O
(IDEAL GAS) GFW=18.013502

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.200	8.609	8.609	INFINITE
100	7.796	37.148	51.819	-1.467	8.667	8.368	-18.289
200	7.355	42.406	45.962	-0.711	8.722	8.046	-8.792
298	7.167	45.302	45.302	0.000	8.748	7.708	-5.650
300	7.165	45.346	45.302	0.013	8.748	7.701	-5.610
400	7.100	47.396	45.582	0.726	8.757	7.351	-4.016
500	7.108	48.980	46.109	1.436	8.751	7.000	-3.060
600	7.176	50.281	46.699	2.149	8.735	6.651	-2.422
700	7.288	51.396	47.292	2.872	8.713	6.305	-1.969
800	7.423	52.377	47.868	3.608	8.688	5.963	-1.629
900	7.566	53.260	48.419	4.357	8.662	5.623	-1.365
1000	7.708	54.064	48.943	5.121	8.638	5.287	-1.156
1100	7.843	54.806	49.443	5.899	8.615	4.953	-0.984
1200	7.967	55.493	49.919	6.689	8.593	4.622	-0.842
1300	8.081	56.136	50.373	7.492	8.573	4.291	-0.721
1400	8.183	56.738	50.806	8.305	8.553	3.963	-0.619
1500	8.275	57.306	51.221	9.128	8.535	3.635	-0.530
1600	8.357	57.843	51.618	9.960	8.517	3.309	-0.452
1700	8.432	58.352	51.999	10.799	8.500	2.985	-0.384
1800	8.499	58.836	52.366	11.646	8.482	2.661	-0.323
1900	8.559	59.297	52.718	12.499	8.463	2.338	-0.269
2000	8.614	59.737	53.058	13.357	8.444	2.016	-0.220
2100	8.664	60.159	53.387	14.221	8.424	1.695	-0.176
2200	8.710	60.563	53.704	15.090	8.403	1.375	-0.137
2300	8.752	60.951	54.010	15.963	8.380	1.056	-0.100
2400	8.791	61.324	54.307	16.840	8.356	0.738	-0.067
2500	8.827	61.684	54.595	17.721	8.331	0.421	-0.037
2600	8.860	62.031	54.875	18.606	8.304	0.105	-0.009
2700	8.891	62.366	55.146	19.493	8.276	-0.209	0.017
2800	8.920	62.690	55.410	20.384	8.245	-0.523	0.041
2900	8.948	63.003	55.666	21.277	8.213	-0.836	0.063
3000	8.974	63.307	55.916	22.173	8.178	-1.148	0.084
3100	8.998	63.602	56.159	23.072	8.143	-1.458	0.103
3200	9.021	63.888	56.396	23.973	8.105	-1.767	0.121
3300	9.043	64.166	56.627	24.876	8.066	-2.075	0.137
3400	9.065	64.436	56.853	25.782	8.024	-2.381	0.153
3500	9.085	64.699	57.073	26.689	7.981	-2.687	0.168
3600	9.104	64.955	57.289	27.599	7.937	-2.991	0.182
3700	9.123	65.205	57.499	28.510	7.890	-3.294	0.195
3800	9.141	65.448	57.705	29.423	7.841	-3.596	0.207
3900	9.159	65.686	57.907	30.338	7.791	-3.896	0.218
4000	9.176	65.918	58.104	31.255	7.739	-4.195	0.229
4100	9.192	66.145	58.298	32.173	7.686	-4.493	0.239
4200	9.208	66.367	58.487	33.093	7.631	-4.788	0.249
4300	9.224	66.583	58.673	34.015	7.574	-5.084	0.258
4400	9.240	66.796	58.855	34.938	7.516	-5.377	0.267
4500	9.255	67.004	59.034	35.863	7.456	-5.670	0.275
4600	9.270	67.207	59.209	36.789	7.394	-5.961	0.283
4700	9.284	67.407	59.382	37.717	7.331	-6.251	0.291
4800	9.299	67.602	59.551	38.646	7.266	-6.539	0.298
4900	9.313	67.794	59.717	39.577	7.200	-6.826	0.304
5000	9.327	67.982	59.881	40.509	7.132	-7.112	0.311
5100	9.342	68.167	60.041	41.442	7.062	-7.396	0.317
5200	9.356	68.349	60.199	42.377	6.991	-7.678	0.323
5300	9.370	68.527	60.355	43.313	6.918	-7.960	0.328
5400	9.384	68.702	60.508	44.251	6.843	-8.240	0.333
5500	9.398	68.875	60.658	45.190	6.767	-8.518	0.338
5600	9.412	69.044	60.807	46.130	6.690	-8.796	0.343
5700	9.426	69.211	60.953	47.072	6.611	-9.072	0.348
5800	9.440	69.375	61.096	48.016	6.530	-9.346	0.352
5900	9.454	69.536	61.238	48.960	6.448	-9.619	0.356
6000	9.468	69.695	61.378	49.906	6.364	-9.890	0.360

July 31, 1972 (NBS); June 30, 1977

DEUTERO-HYDROXYL (OD) (IDEAL GAS) GFW = 18.013502
D O

D°_0 = 102.860 ± 0.33 kcal/mol
$S^\circ_{298.15}$ = 45.307 gibbs/mol*

ΔHf°_0 = 8.659 ± 0.3 kcal/mol*
$\Delta Hf^\circ_{298.15}$ = 8.748 ± 0.29 kcal/mol

Electronic States and Molecular Constants

State	ε, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0 139.7	2 2	2720.9	44.2	10.02	0.29	0.970
$A^2\Sigma^+$	35474	2	2322.6	55.4	9.198	0.322	1.012
$B^2\Sigma^+$	68769	2	684.3	55.6	2.91	0.25	1.80

σ = 1

Heat of Formation

The heat of formation was calculated from the selected value for ΔHf°_{298} of OH(g), -0.27±0.3 kcal/mol (see OH table, 8) the appropriate thermal functions, and zero point energies of H_2(g), D_2(g), OH(g), and OD(g). The zero point energies of H_2(g) and D_2(g) were taken from Herzberg and Monfils (1). The zero point energies of OH and OD include the Dunham correction (see Herzberg and Monfils (1)). The molecular constants are those given by Rosen (2) with the exception of the spin-coupling constants taken from Herzberg (3).

*Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen (2). Comparison of the results with those from a more exact treatment given by Haar et al. (4) indicates errors in the table above 400 K are negligible. Below this, they may be appreciable. In particular, it is recommended that $H^\circ_0-H^\circ_{298}$, S°_{298}, and Cp°_{298} be taken as -2.151 kcal/mol, 45.307 gibbs/mol, and 7.156 gibbs/mol, respectively. These errors result from dealing with the ground state ($X^2\Pi_i$) as two different electronic states separated by 139.7 cm^{-1}.

The National Bureau of Standards prepared this table (5) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (5), we recalculate the table in terms of 1973 fundamental constants (6), 1975 atomic weights (7), and current JANAF reference states for the elements.

References

1. G. Herzberg and A. Monfils, J. Mol. Spectroscopy 5, 482 (1960).
2. B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950, pp 232, 561.
4. L. Haar, A. S. Friedman, and C. W. Beckett, U.S. Natl. Bur. Std., Monograph 20, 1961.
5. S. Abramowitz et al., U.S. Natl. Bur. Std., Rept. 10904, 239, July, 1972.
6. CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, December, 1973.
7. IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976); 37, 589 (1974).
8. JANAF Thermochemical Tables: OH(g), 6-30-77.

SULFUR MONODEUTERIDE (SD) DS
(IDEAL GAS) GFW=34.074102

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.221	32.956	32.956	INFINITE
100	7.214	39.776	55.033	-1.526	33.159	30.824	-67.365
200	7.815	45.008	48.844	-0.767	33.171	28.478	-31.118
298	7.772	48.130	48.130	0.000	33.100	26.186	-19.195
300	7.770	48.178	48.130	0.014	33.098	26.144	-19.045
400	7.669	50.397	48.433	0.786	32.421	23.866	-13.040
500	7.678	52.107	49.003	1.552	31.899	21.788	-9.524
600	7.770	53.514	49.641	2.324	31.462	19.809	-7.215
700	7.898	54.721	50.283	3.107	31.089	17.921	-5.595
800	8.034	55.785	50.905	3.904	17.699	14.794	-4.042
900	8.162	56.739	51.501	4.714	17.703	14.431	-3.504
1000	8.277	57.605	52.069	5.536	17.710	14.068	-3.074
1100	8.378	58.398	52.609	6.369	17.718	13.702	-2.722
1200	8.467	59.131	53.122	7.211	17.728	13.337	-2.429
1300	8.544	59.812	53.611	8.062	17.739	12.971	-2.181
1400	8.611	60.448	54.077	8.919	17.749	12.604	-1.968
1500	8.670	61.044	54.522	9.784	17.759	12.234	-1.783
1600	8.722	61.605	54.947	10.653	17.770	11.867	-1.621
1700	8.768	62.135	55.354	11.528	17.779	11.498	-1.478
1800	8.810	62.638	55.745	12.407	17.788	11.128	-1.351
1900	8.847	63.115	56.121	13.290	17.796	10.759	-1.238
2000	8.881	63.570	56.482	14.176	17.803	10.388	-1.135
2100	8.912	64.004	56.830	15.066	17.809	10.015	-1.042
2200	8.940	64.419	57.165	15.958	17.815	9.646	-0.958
2300	8.966	64.817	57.489	16.853	17.819	9.273	-0.881
2400	8.991	65.199	57.803	17.751	17.824	8.902	-0.811
2500	9.013	65.567	58.106	18.652	17.828	8.531	-0.746
2600	9.035	65.921	58.400	19.554	17.830	8.159	-0.686
2700	9.055	66.262	58.685	20.458	17.833	7.786	-0.630
2800	9.074	66.592	58.961	21.365	17.834	7.413	-0.579
2900	9.093	66.910	59.230	22.273	17.834	7.041	-0.531
3000	9.110	67.219	59.491	23.183	17.833	6.670	-0.486
3100	9.127	67.518	59.745	24.095	17.833	6.297	-0.444
3200	9.143	67.808	59.993	25.009	17.831	5.925	-0.405
3300	9.159	68.090	60.234	25.924	17.829	5.552	-0.368
3400	9.174	68.363	60.469	26.841	17.826	5.182	-0.333
3500	9.189	68.629	60.698	27.759	17.821	4.807	-0.300
3600	9.204	68.888	60.922	28.678	17.817	4.437	-0.269
3700	9.218	69.141	61.141	29.600	17.810	4.066	-0.240
3800	9.232	69.387	61.355	30.522	17.804	3.694	-0.212
3900	9.246	69.627	61.564	31.446	17.797	3.322	-0.186
4000	9.260	69.861	61.768	32.371	17.788	2.954	-0.161
4100	9.274	70.090	61.968	33.298	17.780	2.582	-0.138
4200	9.287	70.314	62.164	34.226	17.771	2.212	-0.115
4300	9.301	70.532	62.357	35.155	17.760	1.840	-0.094
4400	9.315	70.746	62.545	36.086	17.749	1.471	-0.073
4500	9.328	70.956	62.729	37.018	17.736	1.102	-0.054
4600	9.342	71.161	62.910	37.952	17.724	0.732	-0.035
4700	9.356	71.362	63.088	38.887	17.712	0.361	-0.017
4800	9.370	71.559	63.263	39.823	17.698	-0.009	0.000
4900	9.384	71.752	63.434	40.761	17.684	-0.374	0.017
5000	9.399	71.942	63.602	41.700	17.670	-0.745	0.033
5100	9.413	72.128	63.767	42.641	17.655	-1.112	0.048
5200	9.428	72.311	63.930	43.583	17.641	-1.479	0.062
5300	9.443	72.491	64.090	44.526	17.626	-1.848	0.076
5400	9.459	72.668	64.247	45.471	17.611	-2.213	0.090
5500	9.475	72.841	64.402	46.418	17.597	-2.581	0.103
5600	9.491	73.012	64.554	47.366	17.582	-2.947	0.115
5700	9.507	73.180	64.704	48.316	17.568	-3.315	0.127
5800	9.524	73.346	64.851	49.268	17.555	-3.680	0.139
5900	9.541	73.509	64.997	50.221	17.543	-4.049	0.150
6000	9.559	73.669	65.140	51.176	17.532	-4.411	0.161

July 31, 1972 (NBS); June 30, 1977

SULFUR MONODEUTERIDE (SD) (IDEAL GAS) GFW = 34.074102

DS

D°_0 = 85.279 ± 1.2 kcal/mol
$S^\circ_{298.15}$ = 48.138 gibbs/mol*

ΔHf°_0 = 33.006 ± 1.2 kcal/mol*
$\Delta Hf^\circ_{298.15}$ = 33.1 ± 1.2 kcal/mol

Electronic States and Molecular Constants

State	ε, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0 376.8	2 2	1930.4	23.44	4.949	0.101	1.345
$A^2\Sigma^+$	30769	2	1417	48.85	4.392	0.172	1.423
$B^2\Sigma$	59566	2	1917.7	29.3	4.532	0.105	1.405
$C^2\Delta$	63872	4	[1930.4]	[23.44]	[4.949]	[0.101]	
$D^2\Delta$	71205	4					
$E^2\Sigma$	71328	2					
$F^2\Delta$	76717	4					
$G^2\Delta$	79320	4					
$H^2\Delta$	80858	4					

σ = 1

Heat of Formation

The heat of formation was calculated from the appropriate thermal functions (see tables for HS, DS, H_2, D_2, 1), the selected value for ΔHf°_{298} of HS(g) (33.3±1.2 kcal/mol, see table for HS(g), 1), and the zero point energies of H_2(g) (2), D_2(g) (2), HS(g) (3), and DS(g) (3). The Dunham corrections were made in ref. (2) for H_2(g) and D_2(g). Spectroscopic constants tabulated in ref. (3) were used to calculate the zero point energies of HS and DS including Dunham corrections.

*Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen (3). From a comparison of this approximate calculation with more exact methods (see HS(g) table, 1) it is concluded that the errors are neglibible above 400 K. Below this, they may be appreciable. In particular, it is recommended that $H^\circ_0-H^\circ_{298}$, S°_{298}, and Cp°_{298} be taken as -2.171 kcal/mol, 48.138 gibbs/mol, and 7.760 gibbs/mol, respectively. These errors result from dealing with the ground state ($^2\Pi_i$) as two different electronic states separated by 376.8 cm^{-1}.

The National Bureau of Standards prepared this table (4) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (4), we recalculate the table in terms of 1973 fundamental constants (5), 1975 atomic weights (6), and current JANAF references states for the elements. Our calculated Cp values agree with the NBS table up to 4000 K; above 4000 K our values trend slightly higher and at 6000 K the difference from the original NBS table is 0.017 gibbs/mol.

References

1. JANAF Thermochemical Tables: HS(g), DS(g), 6-30-77; H_2(g), D_2(g), 3-31-77.
2. G. Herzberg and A. Monfils, J. Mol. Spectrosc. 5, 482 (1960).
3. B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970. For spin-coupling constants, see L. Haar, A. S. Friedman, and C. W. Beckett, U.S. Natl. Bur. Std. Monograph 20, May 29, 1961.
4. S. Abramowitz et al., U.S. Natl. Bur. Std., Rept. 10904, 239, July, 1972.
5. CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, December, 1973.
6. IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976); 37, 589 (1974).

DEUTERIUM, DIATOMIC (D_2) D_2

(REFERENCE STATE - IDEAL GAS) GFW=4.028204

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.048	0.000	0.000	0.000
100	7.246	26.931	40.837	-1.391	0.000	0.000	0.000
200	6.980	31.835	35.258	-0.685	0.000	0.000	0.000
298	6.978	34.620	34.620	0.000	0.000	0.000	0.000
300	6.978	34.663	34.620	0.013	0.000	0.000	0.000
400	6.989	36.672	34.894	0.711	0.000	0.000	0.000
500	7.019	38.234	35.412	1.411	0.000	0.000	0.000
600	7.079	39.519	35.992	2.116	0.000	0.000	0.000
700	7.172	40.616	36.576	2.828	0.000	0.000	0.000
800	7.290	41.582	37.143	3.551	0.000	0.000	0.000
900	7.423	42.448	37.685	4.287	0.000	0.000	0.000
1000	7.561	43.237	38.201	5.036	0.000	0.000	0.000
1100	7.698	43.964	38.692	5.799	0.000	0.000	0.000
1200	7.830	44.640	39.160	6.575	0.000	0.000	0.000
1300	7.954	45.272	39.606	7.365	0.000	0.000	0.000
1400	8.070	45.865	40.032	8.166	0.000	0.000	0.000
1500	8.177	46.426	40.440	8.979	0.000	0.000	0.000
1600	8.275	46.957	40.831	9.801	0.000	0.000	0.000
1700	8.366	47.461	41.206	10.633	0.000	0.000	0.000
1800	8.450	47.942	41.567	11.474	0.000	0.000	0.000
1900	8.527	48.401	41.915	12.323	0.000	0.000	0.000
2000	8.598	48.840	42.250	13.179	0.000	0.000	0.000
2100	8.664	49.261	42.574	14.043	0.000	0.000	0.000
2200	8.726	49.666	42.887	14.912	0.000	0.000	0.000
2300	8.784	50.055	43.191	15.788	0.000	0.000	0.000
2400	8.839	50.430	43.484	16.669	0.000	0.000	0.000
2500	8.891	50.792	43.769	17.555	0.000	0.000	0.000
2600	8.940	51.141	44.046	18.447	0.000	0.000	0.000
2700	8.988	51.480	44.315	19.343	0.000	0.000	0.000
2800	9.033	51.807	44.577	20.244	0.000	0.000	0.000
2900	9.077	52.125	44.832	21.150	0.000	0.000	0.000
3000	9.119	52.434	45.080	22.060	0.000	0.000	0.000
3100	9.160	52.733	45.322	22.974	0.000	0.000	0.000
3200	9.201	53.025	45.558	23.892	0.000	0.000	0.000
3300	9.240	53.308	45.789	24.814	0.000	0.000	0.000
3400	9.279	53.585	46.014	25.740	0.000	0.000	0.000
3500	9.318	53.854	46.234	26.670	0.000	0.000	0.000
3600	9.356	54.117	46.450	27.603	0.000	0.000	0.000
3700	9.393	54.374	46.661	28.541	0.000	0.000	0.000
3800	9.430	54.625	46.867	29.482	0.000	0.000	0.000
3900	9.467	54.871	47.069	30.427	0.000	0.000	0.000
4000	9.504	55.111	47.267	31.376	0.000	0.000	0.000
4100	9.540	55.346	47.461	32.328	0.000	0.000	0.000
4200	9.575	55.576	47.652	33.283	0.000	0.000	0.000
4300	9.610	55.802	47.839	34.243	0.000	0.000	0.000
4400	9.644	56.023	48.022	35.205	0.000	0.000	0.000
4500	9.678	56.240	48.202	36.172	0.000	0.000	0.000
4600	9.711	56.454	48.379	37.141	0.000	0.000	0.000
4700	9.743	56.663	48.553	38.114	0.000	0.000	0.000
4800	9.774	56.868	48.724	39.090	0.000	0.000	0.000
4900	9.804	57.070	48.893	40.069	0.000	0.000	0.000
5000	9.832	57.268	49.058	41.050	0.000	0.000	0.000
5100	9.859	57.463	49.221	42.035	0.000	0.000	0.000
5200	9.885	57.655	49.382	43.022	0.000	0.000	0.000
5300	9.909	57.844	49.539	44.012	0.000	0.000	0.000
5400	9.931	58.029	49.695	45.004	0.000	0.000	0.000
5500	9.951	58.211	49.848	45.998	0.000	0.000	0.000
5600	9.969	58.391	49.999	46.994	0.000	0.000	0.000
5700	9.986	58.567	50.148	47.992	0.000	0.000	0.000
5800	10.000	58.741	50.295	48.991	0.000	0.000	0.000
5900	10.012	58.912	50.439	49.992	0.000	0.000	0.000
6000	10.022	59.081	50.582	50.993	0.000	0.000	0.000

March 31, 1977

DEUTERIUM, DIATOMIC (D_2) (REFERENCE STATE - IDEAL GAS) GFW = 4.028204

0 to 6000 K Ideal Gas

D_2

D_0° = 105.070 ± 0.001 kcal/mol
$S^\circ_{298.15}$ = 34.620 ± 0.01 gibbs/mol
Ground State Configuration $^1\Sigma_g^+$

ΔHf_0° = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol
Symmetry Number = 2

Vibrational and Rotational Levels (cm^{-1})

Direct Summation of Electronic Ground State:

$$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_0 + BZ - DZ^2 + H^2Z^3/(H+LZ),$$

where $Z = J(J+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L

$$G = 3116.334Y - 62.50516Y^2 + 0.7797565Y^3 - 5.48262\text{x}10^{-2}Y^4 + 2.25748\text{x}10^{-3}Y^5 - 6.30154\text{x}10^{-5}Y^6$$

$$B = 30.45273 - 1.102045Y + 0.0295505Y^2 - 5.99912\text{x}10^{-3}Y^3 + 8.37740\text{x}10^{-4}Y^4 - 6.87040\text{x}10^{-5}Y^5 + 2.80134\text{x}10^{-6}Y^6 - 4.68952\text{x}10^{-8}Y^7$$

$$D = 0.011525 - 3.6876\text{x}10^{-4}Y + 4.1199\text{x}10^{-5}Y^2 - 4.4723\text{x}10^{-6}Y^3 + 1.7858\text{x}10^{-7}Y^4$$

$$H = 6.55\text{x}10^{-6} - 6.42\text{x}10^{-7}Y + 6.03\text{x}10^{-8}Y^2 - 2.15\text{x}10^{-9}Y^3$$

$$L = 4.20\text{x}10^{-9} - 6.32\text{x}10^{-10}Y + 4.35\text{x}10^{-11}Y^2$$

$v_{max} = 21$, $J_{max} = 54 - 52v/v_{max}$

Normalized statistical weights = 2/3 (even J) and 1/3 (odd J)

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

These are calculated by direct summation (1) over vibrational-rotational energy levels of the electronic ground state. We performed the direct summation with an extended version of a program written by W. H. Evans and provided through cooperation of D. D. Wagman, both of the U.S. National Bureau of Standards. Contributions of excited states (T_o > 90000 cm^{-1}) are negligible at 6000 K. Polynomials G, B, and D are our fits of data from Stoicheff (2) and Bredohl and Herzberg (3). Polynominals H and L are estimated by isotopic relations from those of H_2 (1) in order to provide a similar extrapolation to high J values. The adopted H polynomial is not more accurate than the relatively scattered data (2-4), but it should be more consistent with our adopted approximation for the infinite-series (F) equation for rotational levels. We assume that F has the form proposed by Khachkuruzov (5) and Woolley et al. (6). We use a linear approximation for the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated by comparison with H_2 (1). We omit the nuclear-spin contribution (R ln 9) to entropy and gibbs-energy function.

We adopt ortho-para "equilibrium" D_2 as the reference state at all temperatures. Values differ from "normal" D_2 only at 100 K (6, 7). Our values differ from those of NBS (7) by -0.003 (5000 K) and -0.016 (6000 K) gibbs/mol in S° and -0.015 (5000 K) and -0.093 (6000 K) kcal/mol in $H^\circ_T - H^\circ_{298}$. The largest differences are about the same magnitude as uncertainties arising from extrapolation of the rotational levels.

References

1. JANAF Thermochemical Tables: H_2(g), 3-31-77.
2. B. P. Stoicheff, Can. J. Phys. 35, 730 (1957).
3. H. Bredohl and G. Herzberg, Can. J. Phys. 51, 867 (1973).
4. P. J. Brannon, C. H. Church, and C. W. Peters, J. Mol. Spectrosc. 27, 44 (1968).
5. G. A. Khachkuruzov, Opt. Spectrosc. 30, 455 (1971).
6. H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Natl. Bur. Std. 41, 379 (1948).
7. S. Abramowitz et al., U. S. Natl. Bur. Std., Rept. 10904, 239, July, 1972.

D_2

DEUTERIUM, DIATOMIC UNIPOSITIVE ION (D_2^+) D_2^+

(IDEAL GAS) GFW=4.027655

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0				-2.068	356.666		
100							
200							
298	7.053	37.434	37.434	0.000	358.166	355.840	-260.834
300	7.055	37.478	37.434	0.013	358.175	355.825	-259.215
400	7.237	39.530	37.713	0.727	358.688	354.965	-193.941
500	7.488	41.172	38.246	1.463	359.221	353.974	-154.720
600	7.748	42.560	38.852	2.225	359.775	352.873	-128.532
700	7.987	43.773	39.470	3.012	360.346	351.677	-109.797
800	8.194	44.853	40.077	3.821	360.929	350.389	-95.723
900	8.372	45.829	40.662	4.650	361.519	349.047	-84.759
1000	8.524	46.719	41.224	5.495	362.112	347.630	-75.973
1100	8.655	47.538	41.761	6.354	362.705	346.153	-68.773
1200	8.770	48.296	42.275	7.225	363.296	344.622	-62.763
1300	8.873	49.002	42.765	8.107	363.885	343.042	-57.670
1400	8.965	49.663	43.235	8.999	364.473	341.417	-53.297
1500	9.050	50.284	43.684	9.900	365.058	339.749	-49.501
1600	9.130	50.871	44.115	10.809	365.642	338.044	-46.174
1700	9.206	51.427	44.529	11.726	366.223	336.300	-43.234
1800	9.279	51.955	44.927	12.650	366.803	334.523	-40.616
1900	9.351	52.459	45.310	13.582	367.383	332.714	-38.270
2000	9.422	52.940	45.680	14.521	367.963	330.875	-36.156
2100	9.493	53.402	46.037	15.466	368.541	329.006	-34.240
2200	9.564	53.845	46.382	16.419	369.121	327.109	-32.495
2300	9.636	54.272	46.715	17.379	369.702	325.186	-30.899
2400	9.708	54.683	47.039	18.346	370.285	323.239	-29.435
2500	9.781	55.081	47.353	19.321	370.871	321.268	-28.085
2600	9.853	55.466	47.657	20.303	371.458	319.272	-26.837
2700	9.924	55.839	47.954	21.291	372.046	317.253	-25.679
2800	9.994	56.201	48.242	22.287	372.638	315.213	-24.603
2900	10.061	56.553	48.522	23.290	373.232	313.151	-23.599
3000	10.124	56.895	48.796	24.299	373.828	311.069	-22.661
3100	10.183	57.228	49.062	25.315	374.427	308.968	-21.782
3200	10.237	57.553	49.323	26.336	375.026	306.846	-20.956
3300	10.285	57.868	49.577	27.362	375.627	304.706	-20.180
3400	10.326	58.176	49.825	28.393	376.229	302.548	-19.447
3500	10.360	58.476	50.068	29.427	376.830	300.372	-18.756
3600	10.385	58.768	50.306	30.464	377.431	298.180	-18.102
3700	10.403	59.053	50.538	31.504	378.029	295.969	-17.482
3800	10.412	59.330	50.766	32.545	378.626	293.744	-16.894
3900	10.413	59.601	50.989	33.586	379.219	291.502	-16.335
4000	10.405	59.865	51.208	34.627	379.808	289.246	-15.803
4100	10.389	60.121	51.422	35.667	380.393	286.975	-15.297
4200	10.365	60.371	51.632	36.704	380.971	284.689	-14.814
4300	10.333	60.615	51.838	37.739	381.543	282.389	-14.352
4400	10.293	60.852	52.040	38.771	382.110	280.078	-13.911
4500	10.247	61.083	52.239	39.798	382.667	277.752	-13.489
4600	10.195	61.307	52.433	40.820	383.217	275.415	-13.085
4700	10.137	61.526	52.625	41.837	383.757	273.064	-12.697
4800	10.073	61.739	52.812	42.847	384.288	270.704	-12.325
4900	10.005	61.946	52.997	43.851	384.810	268.332	-11.968
5000	9.932	62.147	53.178	44.848	385.323	265.950	-11.625
5100	9.856	62.343	53.355	45.837	385.823	263.557	-11.294
5200	9.776	62.534	53.530	46.819	386.315	261.155	-10.976
5300	9.694	62.719	53.702	47.792	386.795	258.744	-10.669
5400	9.610	62.900	53.870	48.758	387.264	256.324	-10.374
5500	9.524	63.075	54.036	49.715	387.726	253.885	-10.089
5600	9.437	63.246	54.199	50.663	388.174	251.456	-9.813
5700	9.349	63.412	54.359	51.602	388.612	249.011	-9.547
5800	9.260	63.574	54.517	52.532	389.040	246.559	-9.290
5900	9.171	63.732	54.672	53.454	389.458	244.089	-9.042
6000	9.082	63.885	54.824	54.367	389.867	241.633	-8.801

Sept. 30, 1977

DEUTERIUM, DIATOMIC UNIPOSITIVE ION (D_2^+) (IDEAL GAS) GFW = 4.027655

D_0° = 62.077 ± 0.005 kcal/mol ΔHf_0° = 356.666 ± 0.003 kcal/mol

$S^\circ_{298.15}$ = 37.434 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = [358.166] kcal/mol D_2^+

Vibrational and Rotational Levels (cm^{-1})

Direct Summation using Energy-Level Equations for the $^2\Sigma_g^+$ Electronic Ground State:

$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_o + BZ - DZ^2 + H^2Z^3/(H+LZ)$,

where $Z = N(N+1)$, $Y = v+1/2$, *and we omit subscript v on G, F, B, D, H, and L*

$G = 1643.29\ Y - 33.7163\ Y^2 + 0.329116\ Y^3 - 0.00725916\ Y^4$

$B = 14.9825 - 0.564098\ Y + 0.00801011\ Y^2 - 0.000230173\ Y^3$ $r_e = 1.057$ Å

$D = 4.98379\text{x}10^{-3} - 1.54039\text{x}10^{-4}\ Y + 3.75711\text{x}10^{-6}\ Y^2$

$H = 2.15408\text{x}10^{-6} - 5.31503\text{x}10^{-8}\ Y$ and $L = 1.00253\text{x}10^{-9}$

$v_{max} = 26$ and $N_{max} = 57 - 46v/v_{max}$

Electronic statistical weight = 2 and normalized rotational statistical weights = 2/3 (even N) or 1/3 (odd N)

Heat of Formation

ΔHf_0° = 356.666±0.003 kcal/mol is the ionization potential IP(D_2) = 124745.6±1.2 cm^{-1}. Takezawa and Tanaka (1) determined IP = 124746.6±0.6 cm^{-1} from Rydberg spectra of D_2. Similar studies on H_2 by Herzberg and Jungen (2) revealed a bias of ~1.0 cm^{-1} attributed to a pressure shift in the spectra. We assume an equal shift for D_2, adjust IP by -1.0 cm^{-1} and increase the uncertainty due to this adjustment. ΔHf_0° is converted to ΔHf°_{298} by use of JANAF (3) enthalpies ($H_0^\circ - H^\circ_{298}$) for D_2, D_2^+ and e^- (g). ΔHf°_{298} should not be interpreted as a room-temperature ionization threshold due to inclusion of these enthalpies and to threshold effects noted by Rosenstock et al. (4).

The adopted spectroscopic IP(D_2) receives strong support from a value calculated indirectly from experimental values (3) of $D_0^\circ(D_2)$ and IP(D) combined with the theoretical value (5) of $D_0^\circ(D_2^+)$; this indirect value differs by only 0.4 cm^{-1}. Rosenstock et al. (4) review several less accurate determinations of IP(D_2) and recommend a value calculated from IP(H_2) using differences in zero-point energies of the diatomic molecules and their ions. Repeating this calculation with JANAF values (3), we predict an IP(D_2) which differs from the observed value by -32 cm^{-1}. Inclusion of an empirical adjustment for IP(D) - IP(H) overcorrects the prediction, giving a deviation of +28 cm^{-1}. These slight discrepancies are due (3, see HD^+, g) to the approximate nature of the prediction. Villarejo's average photoionization result (6), IP(D_2) = 124757±180 cm^{-1}, deviates by +11 cm^{-1} from the spectroscopic value.

Heat Capacity and Entropy

Thermodynamic functions for ortho-para "equilibrium" D_2^+ are calculated by direct summation using the energy-level equations listed above. We use 1973 fundamental constants (7) in an extended version of a computer program written by W. H. Evans and provided by D. D. Wagman of the U. S. National Bureau of Standards. Excited electronic states are neglected because they do not contribute significantly. The electronic statistical weight is taken equal to the multiplicity since we neglect rotational splitting which should be very small (see HD^+ and H_2^+, 3).

Coefficients of the energy-level polynomials are calculated from the theoretical values of H_2^+ (3) using rho = 0.707330 in isotopic equations. Theoretical calculations (5) on D_2^+ provide confirmation of B_e, ω_e and $\omega_e x_e$; the latter two are confirmed by vibrational structure observed (6) in the photoionization threshold of D_2^+. We give the polynomial coefficients, especially higher order ones, to many more digits than are justified by their accuracy. The equations are very approximate near N_{max} but, judging by H_2^+ (3), this should have little effect on the thermodynamic functions even at 6000 K. The approximate v_{max} is derived from the G polynomial.

The thermodynamic functions include contributions from quasi-bound levels lying above D_0° = 21712 cm^{-1}. At 6000 K these levels contribute 0.33 gibbs/mol to Cp° and 0.041 gibbs/mol to the Gibbs-energy function. Their contribution is negligible below 3000 K. Limiting rotational quantum numbers N_{max} are estimated from H_2^+, H_2 and D_2 (3) by comparing energy increments and rotational quanta found above the respective values of D_0°. The crudity of these estimates makes Cp° at 6000 K somewhat more uncertain than in the the case of H_2^+ (3).

References

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D_2^+

DEUTERIUM, DIATOMIC UNINEGATIVE ION (D_2^-) D_2^-

(IDEAL GAS) GFW=4.028753

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0				-2.083	57.700		
100							
200							
298	7.245	37.799	37.799	0.000	56.254	56.793	-41.630
300	7.251	37.844	37.799	0.013	56.245	56.787	-41.376
400	7.587	39.975	38.087	0.755	55.792	57.050	-31.170
500	7.911	41.703	38.643	1.530	55.370	57.413	-25.095
600	8.180	43.171	39.278	2.335	54.973	57.859	-21.075
700	8.394	44.448	39.927	3.165	54.594	58.371	-18.224
800	8.564	45.581	40.565	4.013	54.222	58.936	-16.100
900	8.701	46.598	41.179	4.876	53.853	59.567	-14.460
1000	8.813	47.520	41.768	5.752	53.483	60.200	-13.156
1100	8.908	48.365	42.330	6.638	53.109	60.889	-12.097
1200	8.989	49.143	42.866	7.533	52.732	61.614	-11.221
1300	9.060	49.866	43.377	8.436	52.347	62.369	-10.485
1400	9.124	50.540	43.865	9.345	51.859	63.155	-9.859
1500	9.181	51.171	44.331	10.260	51.564	63.967	-9.320
1600	9.234	51.765	44.777	11.181	51.166	64.808	-8.852
1700	9.283	52.327	45.205	12.107	50.764	65.674	-8.443
1800	9.329	52.858	45.615	13.038	50.356	66.562	-8.082
1900	9.373	53.364	46.010	13.973	49.965	67.473	-7.761
2000	9.415	53.846	46.390	14.912	49.532	68.407	-7.475
2100	9.455	54.306	46.756	15.856	49.114	69.359	-7.218
2200	9.493	54.747	47.109	16.803	48.697	70.335	-6.987
2300	9.531	55.170	47.451	17.754	48.275	71.327	-6.778
2400	9.568	55.576	47.781	18.709	47.852	72.339	-6.587
2500	9.604	55.968	48.100	19.668	47.427	73.368	-6.414
2600	9.639	56.345	48.410	20.630	47.000	74.414	-6.255
2700	9.673	56.709	48.711	21.595	46.574	75.477	-6.109
2800	9.708	57.062	49.003	22.565	46.145	76.555	-5.975
2900	9.741	57.403	49.287	23.537	45.715	77.648	-5.852
3000	9.774	57.734	49.563	24.513	45.283	78.756	-5.737
3100	9.807	58.055	49.832	25.492	44.851	79.879	-5.631
3200	9.840	58.367	50.093	26.474	44.420	81.017	-5.533
3300	9.872	58.670	50.349	27.460	43.986	82.167	-5.442
3400	9.904	58.965	50.598	28.449	43.552	83.330	-5.356
3500	9.936	59.253	50.841	29.441	43.117	84.506	-5.277
3600	9.968	59.533	51.079	30.436	42.682	85.695	-5.202
3700	9.999	59.807	51.311	31.434	42.247	86.896	-5.133
3800	10.031	60.074	51.538	32.436	41.810	88.109	-5.067
3900	10.062	60.335	51.760	33.440	41.373	89.332	-5.006
4000	10.093	60.590	51.978	34.448	40.935	90.567	-4.948
4100	10.124	60.839	52.191	35.459	40.497	91.814	-4.894
4200	10.155	61.084	52.400	36.473	40.059	93.072	-4.843
4300	10.186	61.323	52.604	37.490	39.619	94.338	-4.795
4400	10.216	61.558	52.805	38.510	39.181	95.616	-4.749
4500	10.247	61.787	53.002	39.533	38.740	96.903	-4.706
4600	10.278	62.013	53.196	40.559	38.300	98.200	-4.666
4700	10.308	62.234	53.386	41.589	37.860	99.508	-4.627
4800	10.338	62.452	53.572	42.621	37.420	100.824	-4.591
4900	10.369	62.665	53.756	43.656	36.979	102.149	-4.556
5000	10.399	62.875	53.936	44.695	36.539	103.484	-4.523
5100	10.429	63.081	54.113	45.736	36.100	104.828	-4.492
5200	10.460	63.284	54.288	46.781	35.660	106.180	-4.463
5300	10.490	63.484	54.459	47.828	35.221	107.539	-4.434
5400	10.520	63.680	54.628	48.879	34.782	108.908	-4.408
5500	10.550	63.873	54.795	49.932	34.345	110.285	-4.382
5600	10.580	64.064	54.958	50.989	33.909	111.670	-4.358
5700	10.610	64.251	55.120	52.048	33.474	113.062	-4.335
5800	10.640	64.436	55.279	53.111	33.040	114.462	-4.313
5900	10.670	64.618	55.436	54.176	32.608	115.869	-4.292
6000	10.700	64.798	55.590	55.245	32.178	117.285	-4.272

Sept. 30, 1977

DEUTERIUM, DIATOMIC UNINEGATIVE ION (D_2^-) (IDEAL GAS) GFW = 4.028753

D_0° = [30.0 ± 10] kcal/mol
$S^\circ_{298.15}$ = [37.80 ± 0.1] gibbs mol

ΔHf_0° = [57.7 ± 10] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [56.254] kcal/mol D_2^-

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Sigma_u^+$	0	2

ω_e = [1202] cm^{-1}
B_e = [12.7] cm^{-1}
$\omega_e x_e$ = [17.5] cm^{-1}
α_e = [0.141] cm^{-1}
σ = 2
r_e = [1.15] Å

Heat of Formation

The heat of formation at 0 K for $D_2^-(g)$ is based on the electron affinity (EA) value derived from a Rydberg-Klein-Rees configuration interaction calculation for H_2^- (1). This study by Sharpe (1) led to EA(H_2) = -2.5 eV. Assuming the same value for D_2 and using auxiliary data (2), we calculate ΔHf_0° = 57.7±10 kcal/mol and $D_0^\circ(D_2^-)$ = 30.0±10 kcal/mol; the latter value assumes dissociation into ground state D(g) and $D^-(g)$. The adopted EA(H_2) value is suggested to be the more reliable value of eight studies considered by Rosenstock et al. (3).

In terms of molecular orbitals, the ground state for $D_2^-(g)$ is the $(1s\sigma_g)^2(2p\sigma_u)$ $^2\Sigma_u^+$ state involving two bonding electrons and one antibonding electron. As stated by Massey (4), we should expect only a weakly-bound molecule as compared with $D_2(g)$ for which the ground state has no electrons in an antibonding orbital. We would expect, however, the ground state to be $(1s\sigma_g)^2(1s\sigma_u)$. Our calculated EA($D_2$) value is consistent with this viewpoint. Further discussion of the $D_2^-(g)$ ion may be found in Massey (4).

ΔHf_0° is converted to ΔHf°_{298} by use of JANAF (2) enthalpies ($H_0 - H_{298}$) for $D_2(g)$, $D_2^-(g)$, and $e^-(g)$. ΔHf°_{298} should not be interpreted as a room temperature electron affinity due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (3).

Heat Capacity and Entropy

The vibrational constants for $H_2^-(g)$ are estimated to be the same as in the isoelectronic species He_2^+ (5). The vibrational constants for $D_2^-(g)$ are calculated from those of $H_2^-(g)$ using isotopic relations (2). The internuclear distance is estimated to be ~8% larger than that for $He_2^+(g)$. The same relationship appeared to exist for the (N_2^-, NO, O_2^+) isoelectronic series. B_e is calculated from r_e whereas α_e is calculated assuming a Morse function for the ground state.

The ground and excited electronic states are discussed in detail by Massey (4). No excited state contributions are included in this calculation.

References

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DIDEUTERO-AMIDOGEN (ND_2) D_2N
(IDEAL GAS) GFW=18.034904

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.385	44.999	44.999	INFINITE
100	7.949	40.057	55.957	-1.590	44.790	45.386	-99.191
200	7.992	45.573	49.543	-0.794	44.532	46.084	-50.358
298	8.227	48.801	48.801	0.000	44.300	46.895	-34.375
300	8.233	48.852	48.801	0.015	44.296	46.911	-34.174
400	8.619	51.271	49.128	0.857	44.091	47.815	-26.125
500	9.070	53.241	49.759	1.741	43.924	48.766	-21.315
600	9.549	54.937	50.484	2.672	43.793	49.747	-18.120
700	10.025	56.445	51.230	3.651	43.696	50.748	-15.844
800	10.472	57.814	51.969	4.676	43.627	51.761	-14.140
900	10.877	59.071	52.689	5.744	43.579	52.780	-12.817
1000	11.235	60.236	53.386	6.850	43.549	53.804	-11.759
1100	11.546	61.322	54.059	7.989	43.531	54.831	-10.894
1200	11.817	62.338	54.707	9.158	43.524	55.859	-10.173
1300	12.051	63.293	55.331	10.351	43.522	56.886	-9.563
1400	12.256	64.194	55.932	11.567	43.526	57.914	-9.041
1500	12.437	65.046	56.511	12.802	43.533	58.941	-8.588
1600	12.599	65.854	57.070	14.054	43.545	59.969	-8.191
1700	12.746	66.622	57.610	15.321	43.559	60.995	-7.841
1800	12.882	67.355	58.131	16.602	43.575	62.020	-7.530
1900	13.009	68.055	58.635	17.897	43.595	63.045	-7.252
2000	13.130	68.725	59.123	19.204	43.617	64.068	-7.001
2100	13.247	69.368	59.595	20.523	43.640	65.089	-6.774
2200	13.361	69.987	60.054	21.853	43.669	66.110	-6.567
2300	13.472	70.584	60.499	23.195	43.701	67.129	-6.379
2400	13.582	71.159	60.931	24.548	43.737	68.147	-6.206
2500	13.690	71.716	61.351	25.911	43.778	69.164	-6.046
2600	13.796	72.255	61.760	27.286	43.822	70.178	-5.899
2700	13.901	72.778	62.159	28.671	43.872	71.191	-5.762
2800	14.003	73.285	62.547	30.066	43.925	72.202	-5.636
2900	14.103	73.778	62.926	31.471	43.984	73.211	-5.517
3000	14.201	74.258	63.296	32.886	44.047	74.217	-5.407
3100	14.296	74.725	63.657	34.311	44.115	75.222	-5.303
3200	14.387	75.180	64.010	35.745	44.187	76.224	-5.206
3300	14.475	75.625	64.355	37.188	44.264	77.224	-5.114
3400	14.560	76.058	64.693	38.640	44.345	78.222	-5.028
3500	14.641	76.481	65.024	40.100	44.429	79.217	-4.946
3600	14.718	76.895	65.348	41.568	44.517	80.210	-4.869
3700	14.790	77.299	65.665	43.044	44.608	81.200	-4.796
3800	14.859	77.694	65.977	44.526	44.702	82.188	-4.727
3900	14.922	78.081	66.282	46.015	44.798	83.173	-4.661
4000	14.982	78.460	66.582	47.511	44.896	84.155	-4.598
4100	15.037	78.830	66.876	49.012	44.996	85.136	-4.538
4200	15.088	79.193	67.165	50.518	45.098	86.114	-4.481
4300	15.134	79.549	67.449	52.029	45.199	87.089	-4.426
4400	15.177	79.897	67.728	53.545	45.303	88.063	-4.374
4500	15.215	80.239	68.002	55.064	45.404	89.032	-4.324
4600	15.249	80.574	68.272	56.588	45.508	90.001	-4.276
4700	15.280	80.902	68.537	58.114	45.609	90.967	-4.230
4800	15.307	81.224	68.798	59.643	45.710	91.931	-4.186
4900	15.331	81.540	69.055	61.175	45.811	92.892	-4.143
5000	15.352	81.850	69.308	62.710	45.912	93.853	-4.102
5100	15.369	82.154	69.557	64.246	46.009	94.810	-4.063
5200	15.383	82.452	69.802	65.783	46.106	95.767	-4.025
5300	15.395	82.746	70.043	67.322	46.201	96.721	-3.988
5400	15.404	83.033	70.281	68.862	46.295	97.673	-3.953
5500	15.411	83.316	70.516	70.403	46.386	98.624	-3.919
5600	15.416	83.594	70.747	71.944	46.477	99.573	-3.886
5700	15.418	83.867	70.974	73.486	46.564	100.519	-3.854
5800	15.418	84.135	71.199	75.028	46.651	101.466	-3.823
5900	15.417	84.398	71.420	76.570	46.735	102.410	-3.793
6000	15.414	84.658	71.639	78.111	46.819	103.354	-3.765

July 31, 1972 (NBS); June 30, 1977

DIDEUTERO-AMIDOGEN (ND_2) (IDEAL GAS) GFW = 18.034904

Point Group C_{2v}
$S^\circ_{298.15}$ = 48.801 gibbs/mol

ΔHf°_0 = 45.0 ± 2 kcal/mol D_2N
$\Delta Hf^\circ_{298.15}$ = 44.3 ± 2 kcal/mol

Electronic Levels (Quantum Weights) and Vibrational Frequencies (Degeneracies)

State	ε, cm^{-1}	(g)	ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
$\tilde{X}^2B_1$	0	(2)	[2305] (1)	1110 (1)	[2367] (1)
$\tilde{A}^2A_1$(*)	10393	(2)	[2305] (1)	[500](1)	[2367] (1)

Bond Distance: N-D = 1.024 Å
σ = 2
Bond Angle: D-N-D = 103.4°
Product of the Moments of Inertia: $I_AI_BI_C = 58.53 \times 10^{-120}\ g^3\ cm^6$

Heat of Formation

ΔHf°_{298} of ND_2(g) was calculated from the JANAF selection (1) for ΔHf°_{298} of NH_2(g), the JANAF thermal functions (1), and the zero point energies of H_2(g), D_2(g), NH_2(g), and ND_2(g). The zero point energies of H_2(g) and D_2(g) were those given by Herzberg and Monfils (2). The zero point energies of NH_2(g) and ND_2(g) were estimated from vibrational frequencies given by Milligan and Jacox (3) who observed the infrared and visible spectrum of matrix-isolated NH_2 and ND_2.

Heat Capacity and Entropy

The bond distance and angle are from the electronic absorption spectrum of NH_2 as summarized by Herzberg (4). The vibrational frequencies for the ground state are from Milligan and Jacox (3); those for the excited state are estimated by comparison with NH_2 (1, 4).

The National Bureau of Standards prepared this table (5) by critical analysis of data existing in 1972. Using S°, Cp° and ΔHf° selected by NBS (5), we recalculate the table in terms of current JANAF reference states for the elements.

References

1. JANAF Thermochemical Tables: NH_2(g), 7-31-72(NBS)/6-30-77.
2. G. Herzberg and A. Monfils, J. Mol. Spectrosc. 5, 482 (1960).
3. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 43, 4487 (1965).
4. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
5. S. Abramowitz et al., U.S. Natl. Bur. Std., Rept. 10904, 239, July, 1972.

CIS-DIDEUTERO-DIIMIDE (N_2D_2) D_2N_2

(IDEAL GAS) GFW=32.041604

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.464	51.156	51.156	INFINITE
100	7.954	44.544	61.232	-1.669	50.601	52.657	-115.080
200	8.311	50.125	54.434	-0.862	50.006	54.946	-60.042
298	9.327	53.617	53.617	0.000	49.500	57.482	-42.135
300	9.350	53.675	53.617	0.017	49.491	57.532	-41.911
400	10.632	56.539	53.999	1.016	49.095	60.275	-32.932
500	11.867	59.046	54.763	2.142	48.818	63.105	-27.583
600	12.972	61.310	55.668	3.385	48.643	65.979	-24.033
700	13.930	63.383	56.624	4.731	48.550	68.878	-21.504
800	14.747	65.298	57.590	6.166	48.519	71.785	-19.610
900	15.438	67.076	58.547	7.677	48.535	74.692	-18.137
1000	16.018	68.734	59.483	9.250	48.584	77.596	-16.958
1100	16.505	70.284	60.396	10.877	48.660	80.493	-15.992
1200	16.914	71.738	61.281	12.549	48.756	83.384	-15.186
1300	17.260	73.106	62.138	14.258	48.864	86.265	-14.502
1400	17.553	74.396	62.968	15.999	48.983	89.138	-13.915
1500	17.802	75.616	63.771	17.767	49.109	92.001	-13.404
1600	18.015	76.772	64.548	19.558	49.242	94.857	-12.957
1700	18.199	77.869	65.299	21.369	49.378	97.704	-12.560
1800	18.358	78.914	66.027	23.197	49.517	100.542	-12.207
1900	18.496	79.910	66.732	25.040	49.658	103.373	-11.890
2000	18.616	80.862	67.415	26.895	49.799	106.197	-11.604
2100	18.722	81.773	68.077	28.762	49.940	109.012	-11.345
2200	18.816	82.646	68.719	30.639	50.083	111.822	-11.108
2300	18.899	83.485	69.343	32.525	50.225	114.625	-10.892
2400	18.973	84.291	69.949	34.419	50.367	117.423	-10.693
2500	19.038	85.066	70.539	36.320	50.508	120.214	-10.509
2600	19.097	85.814	71.112	38.226	50.645	122.999	-10.339
2700	19.150	86.536	71.670	40.139	50.784	125.780	-10.181
2800	19.198	87.233	72.213	42.056	50.919	128.554	-10.034
2900	19.242	87.908	72.743	43.978	51.053	131.325	-9.897
3000	19.281	88.561	73.259	45.904	51.185	134.090	-9.768
3100	19.317	89.194	73.763	47.834	51.315	136.852	-9.648
3200	19.350	89.807	74.255	49.768	51.443	139.608	-9.535
3300	19.380	90.403	74.735	51.704	51.569	142.362	-9.428
3400	19.407	90.982	75.205	53.644	51.693	145.112	-9.328
3500	19.432	91.545	75.664	55.586	51.813	147.857	-9.233
3600	19.456	92.093	76.112	57.530	51.931	150.600	-9.143
3700	19.477	92.626	76.552	59.477	52.047	153.340	-9.057
3800	19.497	93.146	76.981	61.425	52.159	156.076	-8.976
3900	19.515	93.653	77.402	63.376	52.269	158.809	-8.899
4000	19.533	94.147	77.815	65.328	52.375	161.539	-8.826
4100	19.549	94.630	78.219	67.282	52.479	164.267	-8.756
4200	19.563	95.101	78.616	69.238	52.581	166.993	-8.689
4300	19.577	95.561	79.004	71.195	52.678	169.715	-8.626
4400	19.590	96.012	79.386	73.154	52.775	172.437	-8.565
4500	19.602	96.452	79.760	75.113	52.865	175.154	-8.507
4600	19.614	96.883	80.128	77.074	52.955	177.871	-8.451
4700	19.624	97.305	80.489	79.036	53.040	180.585	-8.397
4800	19.634	97.718	80.843	80.999	53.123	183.298	-8.346
4900	19.644	98.123	81.192	82.963	53.203	186.009	-8.296
5000	19.653	98.520	81.534	84.928	53.282	188.719	-8.249
5100	19.661	98.909	81.871	86.893	53.355	191.427	-8.203
5200	19.669	99.291	82.203	88.860	53.428	194.134	-8.159
5300	19.676	99.666	82.529	90.827	53.497	196.839	-8.117
5400	19.683	100.034	82.849	92.795	53.564	199.543	-8.076
5500	19.690	100.395	83.165	94.764	53.629	202.245	-8.036
5600	19.696	100.750	83.476	96.733	53.692	204.947	-7.998
5700	19.703	101.098	83.782	98.703	53.752	207.647	-7.962
5800	19.708	101.441	84.084	100.673	53.811	210.347	-7.926
5900	19.714	101.778	84.381	102.645	53.868	213.045	-7.892
6000	19.719	102.109	84.673	104.616	53.924	215.744	-7.858

July 31, 1972 (NBS); June 30, 1977

CIS-DI-DEUTERO-DI-IMIDE (N_2D_2) (IDEAL GAS) GFW = 32.041604

D_2N_2

Point Group C_{2v}
$S°_{298.15}$ = 53.617 gibbs/mol
Ground State Quantum Weight = 1

$\Delta Hf°_0$ = 51.2 ± 0.5 kcal/mol
$\Delta Hf°_{298.15}$ = 49.5 ± 0.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[2300](1)	[2400](1)
[1490](1)	[1150](1)
[1058](1)	[750](1)

Bond Distance: N-N = [1.230] Å N-D = [1.014] Å σ = 2
Bond Angle: D-N-N = [100°]
Product of Moments of Inertia: $I_AI_BI_C$ = 3.8165 x 10^{-117} g^3 cm^6

Heat of Formation

$\Delta Hf°_{298}$ of $N_2D_2(g)$ was estimated from $\Delta Hf°_{298}$ of $N_2H_2(g)$, 50.9±5 kcal/mol, given in the JANAF Thermochemical Tables (1), the appropriate thermal functions (see tables for N_2D_2, H_2, D_2, and N_2H_2, 1) and the estimated zero point energies. The zero point energies for $H_2(g)$, $D_2(g)$ are those given by Herzberg and Monfils (2). The zero point energies for $N_2D_2(g)$ and $N_2H_2(g)$ are taken to be one half the sum of the vibrational frequencies given above and for $N_2H_2(g)$ (1).

Heat Capacity and Entropy

The bond distances and angle are assumed the same as were obtained from a quantum mechanical calculation for N_2H_2 by Wheland and Chen (3). The three principal moments of inertia are I_A = 0.6122, I_B = 2.2094, I_C = 2.8216 x 10^{-39} g cm^2. The infrared spectrum of $N_2H_2(g)$ has been observed using matrix isolation techniques by Rosengren and Pimentel (4); they also observed absorptions at 1481 and 1058 cm^{-1} attributed to trans-HNND and at 946 cm^{-1} attributed to trans-DNND. For cis-HNNH, they assigned ω_1 or ω_4 = 3074 cm^{-1} and ω_3 = 1279 cm^{-1}. Based on these observations and the vibrational frequencies adopted for $N_2H_2(g)$ (1), the vibrational frequencies for N_2D_2 are estimated.

The National Bureau of Standards prepared this table (5) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (5), we recalculate the table in terms of 1973 fundamental constants (6), 1975 atomic weights (7), and current JANAF reference states for the elements.

References

1. JANAF Thermochemical Tables: $N_2H_2(g)$, 12-31-65; H_2(ref st), D_2(ref st), 3-31-77; $N_2D_2(g)$, 6-30-77.
2. G. Herzberg and A. Monfils, J. Mol. Spectrosc. 5, 482 (1960).
3. G. W. Wheland and P. S. K. Chen, J. Chem. Phys. 24, 67 (1956).
4. K. Rosengren and G. Pimentel, J. Chem. Phys. 43, 507 (1965).
5. S. Abramowitz et al., U.S. Natl. Bur. Std., Rept. 10904, 239, July, 1972.
6. CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, December, 1973.
7. IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976); 37, 589 (1974).

D_2N_2

DIDEUTERO-WATER (D_2O)
(IDEAL GAS) GFW=20.027604

D_2O

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.380	-58.855	-58.855	INFINITE
100	7.956	38.635	54.534	-1.590	-59.069	-58.170	127.129
200	7.995	44.157	48.122	-0.793	-59.326	-57.169	62.471
298	8.187	47.378	47.378	0.000	-59.561	-56.059	41.092
300	8.193	47.429	47.378	0.015	-59.565	-56.038	40.823
400	8.517	49.828	47.703	0.850	-59.783	-54.828	29.956
500	8.887	51.768	48.328	1.720	-59.979	-53.566	23.413
600	9.282	53.423	49.042	2.628	-60.153	-52.267	19.038
700	9.691	54.884	49.775	3.577	-60.306	-50.940	15.904
800	10.098	56.205	50.497	4.566	-60.438	-49.593	13.548
900	10.490	57.417	51.200	5.596	-60.551	-48.231	11.712
1000	10.857	58.542	51.878	6.664	-60.646	-46.856	10.240
1100	11.192	59.593	52.532	7.766	-60.726	-45.473	9.035
1200	11.494	60.580	53.162	8.901	-60.792	-44.083	8.028
1300	11.765	61.510	53.769	10.064	-60.846	-42.689	7.177
1400	12.007	62.391	54.354	11.253	-60.891	-41.290	6.446
1500	12.222	63.227	54.918	12.464	-60.927	-39.889	5.812
1600	12.413	64.022	55.462	13.696	-60.956	-38.485	5.257
1700	12.584	64.780	55.988	14.946	-60.979	-37.080	4.767
1800	12.737	65.504	56.497	16.213	-60.997	-35.673	4.331
1900	12.874	66.196	56.989	17.493	-61.013	-34.266	3.941
2000	12.998	66.860	57.466	18.787	-61.024	-32.858	3.590
2100	13.109	67.497	57.929	20.092	-61.036	-31.450	3.273
2200	13.210	68.109	58.378	21.408	-61.044	-30.041	2.984
2300	13.302	68.698	58.814	22.734	-61.052	-28.632	2.721
2400	13.385	69.266	59.237	24.068	-61.059	-27.222	2.479
2500	13.462	69.814	59.649	25.411	-61.066	-25.811	2.256
2600	13.533	70.343	60.051	26.761	-61.073	-24.401	2.051
2700	13.598	70.855	60.441	28.117	-61.081	-22.990	1.861
2800	13.658	71.351	60.822	29.480	-61.089	-21.579	1.684
2900	13.714	71.831	61.194	30.849	-61.100	-20.168	1.520
3000	13.766	72.297	61.556	32.223	-61.111	-18.757	1.366
3100	13.815	72.749	61.910	33.602	-61.124	-17.345	1.223
3200	13.861	73.188	62.255	34.986	-61.137	-15.932	1.088
3300	13.903	73.616	62.593	36.374	-61.153	-14.519	0.962
3400	13.944	74.031	62.924	37.766	-61.170	-13.106	0.842
3500	13.982	74.436	63.247	39.163	-61.189	-11.692	0.730
3600	14.018	74.830	63.563	40.563	-61.210	-10.277	0.624
3700	14.052	75.215	63.873	41.966	-61.234	-8.863	0.523
3800	14.085	75.590	64.176	43.373	-61.259	-7.447	0.428
3900	14.116	75.956	64.474	44.783	-61.286	-6.030	0.338
4000	14.145	76.314	64.765	46.196	-61.316	-4.613	0.252
4100	14.173	76.664	65.051	47.612	-61.348	-3.195	0.170
4200	14.200	77.006	65.332	49.031	-61.382	-1.776	0.092
4300	14.226	77.340	65.607	50.452	-61.419	-0.357	0.018
4400	14.251	77.668	65.877	51.876	-61.457	1.064	-0.053
4500	14.275	77.988	66.143	53.302	-61.500	2.485	-0.121
4600	14.298	78.302	66.404	54.731	-61.544	3.907	-0.186
4700	14.320	78.610	66.660	56.162	-61.590	5.331	-0.248
4800	14.341	78.911	66.912	57.595	-61.639	6.755	-0.308
4900	14.362	79.207	67.160	59.030	-61.690	8.180	-0.365
5000	14.382	79.498	67.404	60.467	-61.744	9.607	-0.420
5100	14.401	79.783	67.644	61.906	-61.800	11.035	-0.473
5200	14.420	80.063	67.880	63.347	-61.859	12.464	-0.524
5300	14.438	80.337	68.113	64.790	-61.920	13.893	-0.573
5400	14.456	80.607	68.342	66.235	-61.983	15.324	-0.620
5500	14.473	80.873	68.567	67.681	-62.049	16.757	-0.666
5600	14.490	81.134	68.789	69.130	-62.117	18.189	-0.710
5700	14.507	81.390	69.008	70.579	-62.187	19.624	-0.752
5800	14.523	81.643	69.224	72.031	-62.259	21.060	-0.794
5900	14.539	81.891	69.436	73.484	-62.333	22.497	-0.833
6000	14.555	82.136	69.646	74.939	-62.409	23.937	-0.872

July 31, 1972 (NBS); June 30, 1977

DIDEUTERO-WATER (D_2O) (IDEAL GAS) GFW = 20.027604

Point Group C_{2v}
$S^\circ_{298.15}$ = 47.378 gibbs/mol
Ground State Quantum Weight = 1

ΔHf°_0 = -58.855 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -59.561 ± 0.016 kcal/mol

D_2O

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
2671.69(1)	1178.33(1)	2788.02(1)

Bond Distance: O-D = 0.958 Å
Bond Angle: D-O-D = 104.45°
Product of the Moments of Inertia: $I_A I_B I_C = 39.948 \times 10^{-120}\ g^3\ cm^6$

σ = 2

Heat of Formation

Rossini, Knowlton, and Johnson (1) measured the ratio of the heats of formation of $D_2O(\ell)/H_2O(\ell)$. Recalculation of their results using ΔHf°_{298} of $H_2O(\ell)$ = -68.315±0.010 kcal/mol (see $H_2O(g)$ table (15)), yields ΔHf°_{298} of $D_2O(\ell) - H_2O(\ell)$ = -2.1098± 0.01492 x $\Delta Hf^\circ_{298}[HDO(\ell)-H_2O(\ell)]$±.016 kcal/mol. Using a value of 32±30 cal/mol for the reaction $H_2O(\ell) + D_2O(\ell) = 2\ HDO(\ell)$ from (2) (some justification that the uncertainty may be smaller is given by Van Hook (3), see also HDO table (15)), one obtains $\Delta Hf^\circ_{298}[D_2O(\ell)-H_2O(\ell)]$ = -2.094±0.016 kcal/mol.

The difference between the heats of vaporization of $D_2O(\ell)$ and $H_2O(\ell)$ at 298 K were evaluated as follows. A. By direct calorimetry, Rossini, Knowlton, and Johnston (1) determined the ratio of the heats of vaporization of $H_2O(\ell)/D_2O(\ell)$ at 298 K and zero pressure to be 0.969503±0.00070. B. Bartholomé and Clusius (4) determined the heat of vaporization of $D_2O(\ell)$ by direct calorimetry at 0°C. Recalculation of their results, using the energy equivalent of a Bunsen ice calorimeter given by (5) (compression correction assumed zero) and neglecting gas imperfection corrections, yields 12.637±0.026 kcal/mol. The heat of vaporization of $D_2O(\ell)$ at 25°C was calculated using a heat of fusion of $D_2O(\ell)$ selected by (6) and (7), the condensed phase *heat capacity data of $D_2O(\ell)$ given by Long and Kemp (8)* and the gas phase *thermal functions of Friedman* and Haar (see next section). C. The difference in heats of vaporization of $D_2O(\ell)$ and $H_2O(\ell)$ was derived by differentiating the formula given by Jones (9) (see (10) for a comparison with other measurements) for the ratio of the vapor pressures of $H_2O(\ell)/D_2O(\ell)$ as a function of temperature and assuming negligible corrections for gas imperfection (see (11), however).

Source	Method	$\Delta Hv^\circ_{298}[D_2O(\ell)-H_2O(\ell)]$, kcal/mol
Knowlton, Johnston, Rossini	*Calorimetry*	0.331±0.008*
Bartholome and Clusius	Calorimetry	0.340±0.028*
Jones	Vapor Pressure	0.307±0.020

*Calculated from ΔHv°_{298} of $H_2O(\ell)$ = 10.520±0.002 kcal/mol (12).

Selecting 0.331±.008 kcal/mol for the difference in the heats of vaporization, one obtains -1.763±0.018 kcal/mol for ΔHf°_{298} of $D_2O(g)-H_2O(g)$. The "spectroscopic" value for this difference was calculated to be -1.768±0.015 kcal/mol based on the zero point energies given by Hulston (13) for $H_2O(g)$ and $D_2O(g)$, and by Herzberg and Monfils (14) for $H_2(g)$ and $D_2(g)$, and the appropriate thermal functions ($H_2O(g)$, H_2(ref. st.), D_2(ref. st.), $D_2O(g)$ (15)). To close the consistency check, the "spectroscopic" value of ΔHf°_{298} of $D_2O(g)$ minus HDO(g) is -0.916±0.0015 kcal/mol and the "nonspectroscopic" value for this difference (see HDO table, reaction A (15)) is (-1.763±0.0018) + (0.846±0.006) = -0.917±0.019 kcal/mol. The average value of -1.766±0.016 kcal/mol for ΔHf°_{298} of $D_2O(g) - H_2O(g)$ and ΔHf°_{298} of $H_2O(g)$ = -57.795±0.010 kcal/mol (12) are used to obtain ΔHf°_{298} of $D_2O(g)$ = -59.561±0.016 kcal/mol.

Heat Capacity and Entropy

The thermodynamic functions of this table are analogous to those in the JANAF table for $H_2O(g)$ (15); both tables are taken from Friedman and Haar (16). Friedman and Haar applied their non-rigid-rotor, anharmonic-oscillator treatment (with vibrational-rotational coupling terms and low-temperature rotational corrections) to the infrared-spectra analyses of Benedict et al. (17), and of Benedict et al. (18). In the present table for D_2O, the values of Cp° of Friedman and Haar between 4000 and 5000 K were extrapolated linearly (except with a term in T^{-2}) from 5000 to 6000 K.

The National Bureau of Standards prepared this table (19) by critical analysis of data existing in 1972. Using S°_{298} and Cp° values selected by NBS (19), we recalculate the table in terms of the current JANAF reference states for the elements (15).

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D_2O

DEUTERIUM SULFIDE (D_2S) D_2S

(IDEAL GAS) GFW=36.088204

T, K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.411	-5.020	-5.020	INFINITE
100	7.950	42.510	58.670	-1.616	-5.046	-6.307	13.785
200	8.110	48.050	52.130	-0.816	-5.345	-7.464	8.156
298	8.547	51.428	51.428	0.000	-5.710	-8.446	6.191
300	8.555	51.481	51.428	0.016	-5.717	-8.463	6.165
400	9.082	54.013	51.770	0.897	-6.633	-9.300	5.081
500	9.642	56.100	52.433	1.834	-7.334	-9.883	4.320
600	10.199	57.908	53.198	2.826	-7.904	-10.338	3.766
700	10.716	59.520	53.988	3.872	-8.370	-10.681	3.335
800	11.173	60.981	54.772	4.967	-21.823	-12.252	3.347
900	11.589	62.322	55.538	6.106	-21.858	-11.054	2.684
1000	11.909	63.560	56.279	7.281	-21.873	-9.852	2.153
1100	12.196	64.709	56.993	8.487	-21.873	-8.651	1.719
1200	12.440	65.781	57.682	9.719	-21.861	-7.448	1.356
1300	12.649	66.785	58.344	10.974	-21.841	-6.247	1.050
1400	12.828	67.729	58.981	12.248	-21.815	-5.048	0.788
1500	12.983	68.619	59.594	13.538	-21.786	-3.854	0.562
1600	13.118	69.462	60.184	14.843	-21.751	-2.658	0.363
1700	13.236	70.261	60.754	16.161	-21.714	-1.465	0.188
1800	13.342	71.020	61.303	17.490	-21.676	-0.276	0.034
1900	13.434	71.744	61.834	18.829	-21.636	0.913	-0.105
2000	13.520	72.435	62.347	20.177	-21.595	2.098	-0.229
2100	13.595	73.097	62.843	21.533	-21.555	3.280	-0.341
2200	13.663	73.731	63.324	22.896	-21.513	4.464	-0.443
2300	13.726	74.340	63.789	24.265	-21.473	5.642	-0.536
2400	13.785	74.925	64.241	25.641	-21.431	6.821	-0.621
2500	13.839	75.489	64.680	27.022	-21.389	7.998	-0.699
2600	13.888	76.033	65.106	28.408	-21.349	9.172	-0.771
2700	13.934	76.558	65.521	29.800	-21.307	10.345	-0.837
2800	13.977	77.065	65.924	31.195	-21.268	11.515	-0.899
2900	14.017	77.556	66.317	32.595	-21.229	12.686	-0.956
3000	14.056	78.032	66.699	33.998	-21.192	13.856	-1.009
3100	14.093	78.494	67.072	35.406	-21.153	15.023	-1.059
3200	14.128	78.942	67.436	36.817	-21.117	16.189	-1.106
3300	14.160	79.377	67.792	38.231	-21.081	17.353	-1.149
3400	14.192	79.800	68.139	39.649	-21.046	18.519	-1.190
3500	14.223	80.212	68.478	41.070	-21.013	19.680	-1.229
3600	14.252	80.613	68.809	42.494	-20.979	20.843	-1.265
3700	14.280	81.004	69.134	43.920	-20.950	22.005	-1.300
3800	14.307	81.385	69.451	45.349	-20.920	23.165	-1.332
3900	14.334	81.757	69.762	46.782	-20.891	24.324	-1.363
4000	14.360	82.120	70.066	48.216	-20.865	25.486	-1.392
4100	14.385	82.475	70.365	49.654	-20.838	26.643	-1.420
4200	14.410	82.822	70.657	51.093	-20.814	27.802	-1.447
4300	14.434	83.161	70.944	52.535	-20.792	28.958	-1.472
4400	14.457	83.494	71.225	53.980	-20.770	30.115	-1.496
4500	14.481	83.819	71.502	55.427	-20.751	31.272	-1.519
4600	14.502	84.137	71.773	56.876	-20.732	32.427	-1.541
4700	14.524	84.449	72.039	58.327	-20.715	33.582	-1.562
4800	14.547	84.755	72.301	59.781	-20.699	34.736	-1.582
4900	14.568	85.056	72.558	61.237	-20.684	35.894	-1.601
5000	14.590	85.350	72.811	62.695	-20.670	37.046	-1.619
5100	14.609	85.639	73.060	64.155	-20.658	38.202	-1.637
5200	14.631	85.923	73.304	65.617	-20.646	39.356	-1.654
5300	14.651	86.202	73.545	67.081	-20.635	40.509	-1.670
5400	14.671	86.476	73.782	68.547	-20.625	41.664	-1.686
5500	14.691	86.745	74.015	70.015	-20.615	42.817	-1.701
5600	14.711	87.010	74.245	71.485	-20.606	43.971	-1.716
5700	14.731	87.271	74.471	72.957	-20.597	45.122	-1.730
5800	14.749	87.527	74.694	74.431	-20.587	46.276	-1.744
5900	14.770	87.779	74.914	75.907	-20.577	47.426	-1.757
6000	14.788	88.028	75.130	77.385	-20.566	48.583	-1.770

July 31, 1972 (NBS); June 30, 1977

DEUTERIUM SULFIDE (D_2S) (IDEAL GAS) GFW = 36.088204

D_2S

Point Group C_{2v}
$S^o_{298.15}$ = 51.428 gibbs/mol
Ground State Quantum Weight = 1

ΔHf^o_0 = -5.02 ± 0.2 kcal/mol
$\Delta Hf^o_{298.5}$ = -5.71 ± 0.2 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1896.38(1)
855.45(1)
1999 (1)

Bond Distance: S-D = 1.328 Å σ = 2
Bond Angle: D-S-D = 92.2°
Product of the Moments of Inertia: $I_AI_BI_C$ = 6.016 x 10^{-119} g^3 cm^6

Heat of Formation

ΔHf^o_{298} of $D_2S(g)$ was determined by Kapustinskii and Kankovskii (1) to be -5.692±0.06 kcal/mol (recalculated) from the reaction: (a+b) $D_2S(g)$ + (1.5a+0.5b) $O_2(g)$ = a $SO_2(g)$ + (a+b) $D_2O(g)$ + b S(rhombic). The difference of ΔHf^o_{298} of $D_2S(g)$ minus $H_2S(g)$ for their work was calculated using their results for ΔHf^o_{298} of $H_2S(g)$, -4.92±0.08 kcal/mol (recalculated), in the hope of eliminating possible systematic error due to uncertainty in the product formed.

The "spectroscopic" value of ΔHf^o_{298} of $D_2S(g)$ minus $H_2S(g)$ was calculated from the appropriate thermal functions (see H_2, D_2, H_2S, 5) and the zero point energies of $H_2S(g)$, $D_2S(g)$ (2, 3), $D_2(g)$ (4), and $H_2(g)$ (4).

The equilibrium data of Grafe et al. (5) for the exchange reaction $H_2(g) + D_2S(g) = D_2(g) + H_2S(g)$ were analyzed by third and second law methods.

Source	Hf^o_{298} of $D_2S(g) - H_2S(g)$ (kcal/mol)
Kapustinskii and Kankovskii (1)	-0.771±0.10
Spectroscopic (2, 3, 4)	-0.810±0.01
Grafe, Clusius, and Kruis (5) Third Law	-0.826±0.05
Second Law	-0.887±0.02

A weighted average of -0.81±0.02 kcal/mol was selected for ΔHf^o_{298} of $D_2S(g)$ minus $H_2S(g)$ and was added to the selected value of ΔHf^o_{298} of $H_2S(g)$ (6) to determine ΔHf^o_{298} of $D_2S(g)$.

Heat Capacity and Entropy

The thermodynamic functions were estimated from those in the present table for $H_2S(g)$ (6) by adding those for $D_2S(g)$ and subtracting those for $H_2S(g)$, where both the added and subtracted functions were generated using the rigid-rotor harmonic oscillator approximation. In this calculation the molecular constants for D_2S were taken from reference (2).

The National Bureau of Standards prepared this table (7) by critical analysis of data existing in 1972. Using S^o_{298} and C^o_p values selected by NBS (7), we recalculate the table in terms of the current JANAF reference states for the elements.

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TRIDEUTERO-AMMONIA (ND_3) D_3N
(IDEAL GAS) GFW=20.049006

	gibbs/mol			kcal/mol			
T, K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	0.000	0.000	INFINITE	-2.446	-12.338	-12.338	INFINITE
100	7.958	39.695	56.255	-1.656	-12.880	-10.901	23.825
200	8.258	45.267	49.517	-0.850	-13.481	-8.685	9.490
298	9.136	48.715	48.715	0.000	-14.000	-6.218	4.558
300	9.155	48.771	48.715	0.017	-14.009	-6.170	4.495
400	10.259	51.556	49.087	0.988	-14.434	-3.490	1.907
500	11.323	53.961	49.826	2.067	-14.756	-0.714	0.312
600	12.302	56.113	50.698	3.249	-14.988	2.117	-0.771
700	13.195	58.078	51.614	4.525	-15.144	4.981	-1.555
800	14.003	59.894	52.537	5.886	-15.239	7.863	-2.148
900	14.723	61.585	53.449	7.323	-15.285	10.754	-2.611
1000	15.358	63.170	54.343	8.827	-15.292	13.648	-2.983
1100	15.912	64.661	55.214	10.391	-15.266	16.541	-3.286
1200	16.394	66.066	56.060	12.007	-15.214	19.431	-3.539
1300	16.813	67.395	56.881	13.668	-15.144	22.315	-3.751
1400	17.177	68.655	57.678	15.368	-15.056	25.193	-3.933
1500	17.495	69.851	58.450	17.102	-14.956	28.064	-4.089
1600	17.773	70.989	59.198	18.866	-14.843	30.929	-4.225
1700	18.016	72.074	59.924	20.655	-14.723	33.787	-4.344
1800	18.231	73.110	60.628	22.468	-14.596	36.636	-4.448
1900	18.420	74.101	61.311	24.301	-14.463	39.479	-4.541
2000	18.587	75.050	61.975	26.151	-14.326	42.315	-4.624
2100	18.735	75.961	62.619	28.017	-14.187	45.142	-4.698
2200	18.867	76.835	63.245	29.897	-14.043	47.964	-4.765
2300	18.984	77.677	63.855	31.790	-13.898	50.779	-4.825
2400	19.089	78.487	64.448	33.694	-13.751	53.589	-4.880
2500	19.182	79.268	65.025	35.608	-13.603	56.392	-4.930
2600	19.264	80.022	65.587	37.530	-13.458	59.188	-4.975
2700	19.337	80.750	66.135	39.460	-13.311	61.981	-5.017
2800	19.403	81.455	66.670	41.397	-13.165	64.766	-5.055
2900	19.459	82.137	67.192	43.340	-13.022	67.547	-5.090
3000	19.511	82.797	67.701	45.289	-12.881	70.322	-5.123
3100	19.554	83.438	68.198	47.242	-12.741	73.093	-5.153
3200	19.592	84.059	68.684	49.199	-12.605	75.860	-5.181
3300	19.624	84.663	69.159	51.160	-12.471	78.622	-5.207
3400	19.652	85.249	69.624	53.124	-12.341	81.381	-5.231
3500	19.676	85.819	70.079	55.091	-12.216	84.135	-5.254
3600	19.696	86.373	70.524	57.059	-12.093	86.887	-5.275
3700	19.710	86.913	70.959	59.030	-11.976	89.635	-5.294
3800	19.720	87.439	71.386	61.001	-11.864	92.380	-5.313
3900	19.727	87.951	71.804	62.973	-11.757	95.121	-5.330
4000	19.730	88.451	72.214	64.946	-11.656	97.860	-5.347
4100	19.729	88.938	72.616	66.919	-11.560	100.597	-5.362
4200	19.726	89.413	73.010	68.892	-11.469	103.332	-5.377
4300	19.719	89.878	73.397	70.864	-11.387	106.063	-5.391
4400	19.710	90.331	73.777	72.836	-11.309	108.795	-5.404
4500	19.697	90.774	74.150	74.806	-11.240	111.522	-5.416
4600	19.682	91.206	74.516	76.775	-11.175	114.251	-5.428
4700	19.664	91.629	74.876	78.743	-11.119	116.976	-5.439
4800	19.643	92.043	75.229	80.708	-11.070	119.701	-5.450
4900	19.618	92.448	75.576	82.671	-11.028	122.424	-5.460
5000	19.590	92.844	75.918	84.632	-10.991	125.149	-5.470
5100	19.555	93.232	76.253	86.589	-10.965	127.871	-5.480
5200	19.546	93.611	76.584	88.544	-10.944	130.593	-5.489
5300	19.538	93.983	76.908	90.498	-10.929	133.314	-5.497
5400	19.530	94.349	77.228	92.451	-10.918	136.037	-5.506
5500	19.522	94.707	77.542	94.404	-10.912	138.758	-5.514
5600	19.515	95.059	77.852	96.356	-10.909	141.479	-5.521
5700	19.507	95.404	78.157	98.307	-10.911	144.199	-5.529
5800	19.501	95.743	78.457	100.257	-10.915	146.921	-5.536
5900	19.494	96.076	78.753	102.207	-10.924	149.642	-5.543
6000	19.488	96.404	79.045	104.156	-10.933	152.365	-5.550

July 31, 1972 (NBS); June 30, 1977

TRIDEUTERO-AMMONIA (ND_3) (IDEAL GAS) GFW = 20.049006

D_3N

Point Group C_{3v}
$S°_{298.15}$ = 48.715 gibbs/mol
Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -12.34 ± 0.1 kcal/mol
$\Delta Hf°_{298.15}$ = -14.00 ± 0.1 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
2495 (1)
793 (1)
2652 (2)
1225 (2)

Bond Length: N-D = 1.0124 Å
Bond Angle: 106.67°
Product of the Moments of Inertia: $I_AI_BI_C = 25.775 \times 10^{-119}\ g^3cm^6$

σ(external) = 3
σ(internal) = 2

Heat of Formation

A "spectroscopic" value for the difference in $\Delta Hf°_{298}$ of $ND_3(g)$ minus $NH_3(g)$ of -3.029±0.01 kcal/mol was calculated from the appropriate thermal functions (see H_2, D_2, NH_3 (6, 7)), zero point energies of $ND_3(g)$ and $NH_3(g)$ (1, 2), and the zero point energies of $H_2(g)$ and $D_2(g)$ given by Herzberg and Monfils (3).

Analysis of the equilibrium data of Schulz and Schaefer (4) for $K°_p$ (1 atm, 660-773 K) for $1/2N_2(g) + 3/2D_2(g) = ND_3(g)$ gave the following:

	$\Delta Hf°_{298}$(kcal/mol)	Drift (e.u.)	$\Delta S°_{298}$(obsv.-calc.)
Third Law	-13.80	-1.2	---
Second Law[a]	-13.0±0.38	--	+1.3±0.5 e.u.

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[a] Assuming $\Delta C°_p$ = 1.237 - 0.00608 (T-700) gibbs/mol

Using the results from the same authors' data for $NH_3(g)$ (6), one obtains a difference in $\Delta Hf°_{298}$ for $ND_3(g)$ minus $NH_3(g)$ of -2.93±0.14 kcal/mol (third law) and -2.22±0.4 kcal/mol (second law). The third law value agrees with the "spectroscopic" value within combined uncertainty intervals.

A value of -3.03±0.10 kcal/mol was added to the JANAF selection for $\Delta Hf°_{298}$ of $NH_3(g)$, -10.97±0.10 kcal/mol (5, 6), to obtain $\Delta Hf°_{298}$ of $ND_3(g)$.

Heat Capacity and Entropy

The thermodynamic functions were estimated from those in the present table for $NH_3(g)$ (6) by adding those for $ND_3(g)$ and subtracting those for $NH_3(g)$, *where both the added and subtracted functions were generated* using the *rigid-rotor harmonic-oscillator* approximation. In this calculation the molecular constants for ND_3 were taken from Duncan and Mills (1) and Benedict and Plyler (2).

The National Bureau of Standards prepared this table (7) by critical analysis of data existing in 1972. Using S°, $C°_p$ and ΔHf° selected by NBS (7), we recalculate the table in terms of current JANAF reference states for the elements.

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ELECTRON GAS (e^-) E^-

(REFERENCE STATE - IDEAL GAS) GFW=0.00054858

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				−1.481	0.000		
100							
200							
298	4.968	4.988	4.988	0.000	0.000	0.000	0.000
300	4.968	5.019	4.988	0.009	0.000	0.000	0.000
400	4.968	6.448	5.183	0.506	0.000	0.000	0.000
500	4.968	7.556	5.551	1.003	0.000	0.000	0.000
600	4.968	8.462	5.963	1.500	0.000	0.000	0.000
700	4.968	9.228	6.376	1.996	0.000	0.000	0.000
800	4.968	9.891	6.775	2.493	0.000	0.000	0.000
900	4.968	10.477	7.154	2.990	0.000	0.000	0.000
1000	4.968	11.000	7.513	3.487	0.000	0.000	0.000
1100	4.968	11.473	7.852	3.984	0.000	0.000	0.000
1200	4.968	11.906	8.172	4.480	0.000	0.000	0.000
1300	4.968	12.303	8.475	4.977	0.000	0.000	0.000
1400	4.968	12.672	8.762	5.474	0.000	0.000	0.000
1500	4.968	13.014	9.034	5.971	0.000	0.000	0.000
1600	4.968	13.335	9.293	6.468	0.000	0.000	0.000
1700	4.968	13.636	9.539	6.964	0.000	0.000	0.000
1800	4.968	13.920	9.775	7.461	0.000	0.000	0.000
1900	4.968	14.189	10.000	7.958	0.000	0.000	0.000
2000	4.968	14.443	10.216	8.455	0.000	0.000	0.000
2100	4.968	14.686	10.423	8.952	0.000	0.000	0.000
2200	4.968	14.917	10.622	9.448	0.000	0.000	0.000
2300	4.968	15.138	10.814	9.945	0.000	0.000	0.000
2400	4.968	15.349	10.998	10.442	0.000	0.000	0.000
2500	4.968	15.552	11.177	10.939	0.000	0.000	0.000
2600	4.968	15.747	11.349	11.436	0.000	0.000	0.000
2700	4.968	15.934	11.515	11.932	0.000	0.000	0.000
2800	4.968	16.115	11.676	12.429	0.000	0.000	0.000
2900	4.968	16.289	11.832	12.926	0.000	0.000	0.000
3000	4.968	16.458	11.984	13.423	0.000	0.000	0.000
3100	4.968	16.621	12.131	13.920	0.000	0.000	0.000
3200	4.968	16.778	12.273	14.416	0.000	0.000	0.000
3300	4.968	16.931	12.412	14.913	0.000	0.000	0.000
3400	4.968	17.080	12.547	15.410	0.000	0.000	0.000
3500	4.968	17.224	12.679	15.907	0.000	0.000	0.000
3600	4.968	17.364	12.807	16.404	0.000	0.000	0.000
3700	4.968	17.500	12.932	16.900	0.000	0.000	0.000
3800	4.968	17.632	13.054	17.397	0.000	0.000	0.000
3900	4.968	17.761	13.173	17.894	0.000	0.000	0.000
4000	4.968	17.967	13.289	18.391	0.000	0.000	0.000
4100	4.968	18.010	13.403	18.888	0.000	0.000	0.000
4200	4.968	18.129	13.514	19.384	0.000	0.000	0.000
4300	4.968	18.246	13.623	19.881	0.000	0.000	0.000
4400	4.968	18.361	13.729	20.378	0.000	0.000	0.000
4500	4.968	18.472	13.833	20.875	0.000	0.000	0.000
4600	4.968	18.581	13.935	21.372	0.000	0.000	0.000
4700	4.968	18.688	14.035	21.868	0.000	0.000	0.000
4800	4.968	18.793	14.133	22.365	0.000	0.000	0.000
4900	4.968	18.895	14.229	22.862	0.000	0.000	0.000
5000	4.968	18.996	14.324	23.359	0.000	0.000	0.000
5100	4.968	19.094	14.416	23.855	0.000	0.000	0.000
5200	4.968	19.190	14.507	24.352	0.000	0.000	0.000
5300	4.968	19.285	14.597	24.849	0.000	0.000	0.000
5400	4.968	19.378	14.684	25.346	0.000	0.000	0.000
5500	4.968	19.469	14.770	25.843	0.000	0.000	0.000
5600	4.968	19.559	14.855	26.339	0.000	0.000	0.000
5700	4.968	19.647	14.938	26.836	0.000	0.000	0.000
5800	4.968	19.733	15.020	27.333	0.000	0.000	0.000
5900	4.968	19.818	15.101	27.830	0.000	0.000	0.000
6000	4.968	19.901	15.180	28.327	0.000	0.000	0.000

March 31, 1965; March 31, 1977

ELECTRON GAS (e^-) (REFERENCE STATE - IDEAL GAS) GFW = 0.00054858

E^-

0 to 6000 K Ideal Gas

ΔHf°_0 = 0 kcal/mol

$S^\circ_{298.15}$ = 4.988 ± 0.003 (± 0.5) gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

As shown by Sommerfeld (1), the electron gas is a degenerate Fermi-Dirac gas and its properties will differ from the classical (Boltzmann) gas. These deviations will increase as the temperature decreases or as the density increases (2,3). Due to the low mass of the electron, these departures from classical behavior will persist to higher temperatures and lower densities than for atomic systems. Under standard conditions (1 atm pressure), Gordon (3) showed that the deviation of the Fermi-Dirac gas from the Boltzmann gas is negligible above 1250 K. Below this temperature the deviation between classical and quantum statistics will be significant; Mitchell (4) calculates S°_{298} = 5.43 gibbs/mol for the Fermi-Dirac gas compared to the classical value of 4.99 gibbs/mol.

Despite these known deviations we have chosen to present the classical (Boltzmann) values here since the primary purpose of this table is to serve as a reference state for the calculation of tables of thermodynamic properties for atomic and molecular ions. When ionization equilibria are considered, the density (or partial pressure) of the electron gas will be extremely low except at very high temperatures. At an electron partial pressure of 10^{-6} atm, the deviation between classical and quantum statistics will be significant only below 5 K (3). Deviations from classical statistics are encountered at about this same temperature in some atomic and molecular systems at 1 atm pressure; these are usually ignored since the deviations in the enthalpy and entropy are quite small. Therefore, although this ideal-gas table has the formalism of 1 atm as the standard reference state, it should not be applied to real systems where the electron partial pressure exceeds 10^{-6} atm. An equivalent statement is that the electron gas will behave as an ideal gas only at electron partial pressures less than about 10^{-6} atm, with deviations from ideal gas behavior at higher pressures as a result of the departure from classical statistics.

The thermodynamic functions are calculated here via Boltzmann (classical) statistics assuming the electron gas to be an *ideal monatomic gas with two equivalent spin states. The GFW is the electron rest mass as reported in the 1973 CODATA* fundamental constants (5). The first uncertainty in S°_{298} represents the uncertainty in the fundamental constants and electron rest mass (i.e., the uncertainty below 10^{-6} atm where classical statistics is valid) while the value given in parenthesis represents the uncertainty due to the use of classical rather than quantum statistics at 1 atm pressure. Values below 298.15 K are omitted from the table since the classical calculation (at 1 atm pressure) results in negative values of entropy below 109 K (4). The values of the thermodynamic functions agree with those published by Gurvich et al. (6) within the stated uncertainty.

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E^-

HYDROGEN FLUORIDE (HF) F H

(IDEAL GAS) GFW=20.006303

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.055	-65.129	-65.129	INFINITE
100	6.962	33.903	47.698	-1.380	-65.159	-65.312	142.738
200	6.962	38.728	42.145	-0.683	-65.135	-65.475	71.547
298	6.964	41.508	41.508	0.000	-65.140	-65.642	48.116
300	6.964	41.551	41.508	0.013	-65.141	-65.645	47.822
400	6.967	43.555	41.782	0.709	-65.176	-65.808	35.955
500	6.972	45.110	42.298	1.406	-65.230	-65.961	28.831
600	6.986	46.383	42.876	2.104	-65.297	-66.101	24.077
700	7.015	47.461	43.456	2.804	-65.372	-66.229	20.677
800	7.063	48.401	44.016	3.508	-65.453	-66.346	18.125
900	7.129	49.237	44.551	4.217	-65.534	-66.452	16.137
1000	7.211	49.992	45.058	4.934	-65.616	-66.550	14.544
1100	7.303	50.683	45.538	5.660	-65.697	-66.640	13.240
1200	7.402	51.323	45.994	6.395	-65.775	-66.722	12.152
1300	7.504	51.920	46.427	7.140	-65.850	-66.798	11.230
1400	7.606	52.479	46.839	7.896	-65.923	-66.868	10.438
1500	7.705	53.007	47.233	8.661	-65.992	-66.933	9.752
1600	7.800	53.508	47.610	9.437	-66.058	-66.994	9.151
1700	7.891	53.983	47.971	10.221	-66.121	-67.050	8.620
1800	7.977	54.437	48.318	11.015	-66.182	-67.103	8.147
1900	8.058	54.870	48.651	11.816	-66.240	-67.152	7.724
2000	8.133	55.286	48.973	12.626	-66.296	-67.199	7.343
2100	8.204	55.684	49.283	13.443	-66.350	-67.243	6.998
2200	8.270	56.067	49.583	14.267	-66.402	-67.284	6.684
2300	8.331	56.436	49.873	15.097	-66.453	-67.323	6.397
2400	8.389	56.792	50.153	15.933	-66.502	-67.360	6.134
2500	8.442	57.136	50.426	16.774	-66.550	-67.394	5.892
2600	8.493	57.468	50.690	17.621	-66.597	-67.427	5.668
2700	8.540	57.789	50.947	18.473	-66.644	-67.458	5.460
2800	8.584	58.101	51.197	19.329	-66.690	-67.488	5.268
2900	8.625	58.403	51.441	20.189	-66.735	-67.515	5.088
3000	8.664	58.696	51.678	21.054	-66.780	-67.541	4.920
3100	8.701	58.980	51.909	21.922	-66.824	-67.565	4.763
3200	8.736	59.257	52.134	22.794	-66.869	-67.589	4.616
3300	8.768	59.526	52.354	23.669	-66.914	-67.611	4.478
3400	8.800	59.789	52.569	24.548	-66.959	-67.631	4.347
3500	8.829	60.044	52.779	25.429	-67.004	-67.650	4.224
3600	8.857	60.293	52.984	26.313	-67.049	-67.668	4.108
3700	8.884	60.536	53.185	27.201	-67.095	-67.685	3.998
3800	8.910	60.774	53.381	28.090	-67.141	-67.700	3.894
3900	8.934	61.005	53.574	28.982	-67.188	-67.714	3.795
4000	8.958	61.232	53.763	29.877	-67.236	-67.727	3.700
4100	8.980	61.453	53.947	30.774	-67.284	-67.739	3.611
4200	9.002	61.670	54.129	31.673	-67.333	-67.749	3.525
4300	9.023	61.882	54.307	32.574	-67.383	-67.759	3.444
4400	9.043	62.090	54.481	33.478	-67.433	-67.767	3.366
4500	9.063	62.293	54.652	34.383	-67.485	-67.774	3.292
4600	9.082	62.493	54.821	35.290	-67.538	-67.780	3.220
4700	9.100	62.688	54.986	36.199	-67.591	-67.784	3.152
4800	9.118	62.880	55.149	37.110	-67.646	-67.788	3.086
4900	9.135	63.068	55.308	38.023	-67.701	-67.790	3.024
5000	9.152	63.253	55.465	38.937	-67.757	-67.792	2.963
5100	9.168	63.434	55.620	39.853	-67.814	-67.792	2.905
5200	9.184	63.612	55.772	40.771	-67.873	-67.791	2.849
5300	9.200	63.787	55.921	41.690	-67.931	-67.788	2.795
5400	9.215	63.960	56.069	42.611	-67.991	-67.785	2.743
5500	9.230	64.129	56.214	43.533	-68.051	-67.781	2.693
5600	9.244	64.295	56.356	44.457	-68.113	-67.775	2.645
5700	9.258	64.459	56.497	45.382	-68.175	-67.769	2.598
5800	9.272	64.620	56.636	46.308	-68.237	-67.761	2.553
5900	9.286	64.779	56.773	47.236	-68.299	-67.752	2.510
6000	9.300	64.935	56.907	48.166	-68.363	-67.743	2.468

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963;
Dec. 31, 1968; July 31, 1972 (NBS); June 30, 1977

HYDROGEN FLUORIDE (HF) (IDEAL GAS) GFW = 20.006303

F H

Symmetry Number = 1

$S^\circ_{298.15}$ = 41.508 ± 0.008 gibbs/mol

ΔHf°_0 = -65.13 ± 0.2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -65.14 ± 0.2 kcal/mol

Electronic States and Molecular Constants

State	T_o, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0	1	4138.73	90.05	20.9555	0.7958	0.9168
$V^1\Sigma^+$	83275	1	1158.46	17.718	4.0263	0.0173	2.091

Heat of Formation

The heat of formation was adopted from the 1968 JANAF Thermochemical Table (1). This value was obtained by simultaneous selection (2) of ΔHf°_{298} for HF(g), BF_3(g), NF_3(g), CF_4(g), NaF(c), and C_2F_4(polymer). Subsequent data have led CODATA (3) to recommend the more negative value of -65.32±0.17 kcal/mol for HF(g).

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen (4). These constants do not differ appreciably from those given in the 1968 JANAF Tables (1). The values of ΔHf°, ΔGf°, and log Kp are appreciably different because of the new thermal functions for the reference state F_2 (5).

The National Bureau of Standards prepared this table (6) from data existing in 1972. Using molecular constants and ΔHf° selected by NBS (6), we recalculate the table in terms of 1973 fundamental constants (7), 1975 atomic weights (8), and current JANAF reference states for the elements (5). A more complete analysis of electronic states and molecular constants is now available (9).

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PHOSPHORUS MONOFLUORIDE (PF)

FP

(IDEAL GAS) GFW=49.97216

	gibbs/mol			kcal/mol			
T, K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	0.000	0.000	INFINITE	-2.117	-8.546	-8.546	INFINITE
100	6.959	45.961	60.181	-1.422	-8.289	-10.701	23.387
200	7.135	50.817	54.420	-0.720	-8.255	-13.141	14.359
298	7.557	53.743	53.743	0.000	-8.345	-15.522	11.378
300	7.565	53.789	53.743	0.014	-8.347	-15.566	11.340
400	7.956	56.022	54.044	0.791	-8.488	-17.952	9.808
500	8.236	57.829	54.626	1.601	-8.650	-20.300	8.873
600	8.430	59.349	55.290	2.435	-8.832	-22.614	8.237
700	8.565	60.659	55.966	3.285	-9.039	-24.895	7.772
800	8.664	61.810	56.626	4.147	-29.691	-32.455	8.866
900	8.739	62.835	57.260	5.017	-29.693	-32.800	7.965
1000	8.799	63.759	57.864	5.894	-29.695	-33.145	7.244
1100	8.849	64.600	58.439	6.777	-29.696	-33.491	6.654
1200	8.895	65.372	58.985	7.664	-29.697	-33.836	6.162
1300	8.938	66.085	59.504	8.556	-29.697	-34.180	5.746
1400	8.980	66.749	59.998	9.452	-29.696	-34.525	5.390
1500	9.023	67.370	60.469	10.352	-29.694	-34.870	5.080
1600	9.066	67.954	60.919	11.256	-29.689	-35.216	4.810
1700	9.111	68.505	61.349	12.165	-29.682	-35.560	4.571
1800	9.156	69.027	61.761	13.078	-29.673	-35.907	4.360
1900	9.202	69.523	62.157	13.996	-29.661	-36.252	4.170
2000	9.249	69.996	62.537	14.919	-29.647	-36.602	4.000
2100	9.295	70.449	62.903	15.846	-29.628	-36.949	3.845
2200	9.342	70.882	63.256	16.778	-29.608	-37.297	3.705
2300	9.387	71.299	63.597	17.714	-29.584	-37.649	3.577
2400	9.432	71.699	63.926	18.655	-29.557	-38.001	3.460
2500	9.476	72.085	64.245	19.601	-29.525	-38.351	3.353
2600	9.518	72.457	64.553	20.551	-29.492	-38.706	3.253
2700	9.560	72.817	64.853	21.504	-29.457	-39.061	3.162
2800	9.599	73.166	65.144	22.462	-29.418	-39.417	3.077
2900	9.638	73.503	65.426	23.424	-29.375	-39.774	2.997
3000	9.675	73.831	65.701	24.390	-29.332	-40.134	2.924
3100	9.710	74.149	65.968	25.359	-29.284	-40.494	2.855
3200	9.744	74.457	66.229	26.332	-29.236	-40.858	2.790
3300	9.776	74.758	66.483	27.308	-29.184	-41.221	2.730
3400	9.807	75.050	66.730	28.287	-29.132	-41.587	2.673
3500	9.837	75.335	66.972	29.269	-29.077	-41.954	2.620
3600	9.866	75.612	67.208	30.254	-29.020	-42.324	2.569
3700	9.893	75.883	67.439	31.242	-28.962	-42.694	2.522
3800	9.920	76.147	67.665	32.233	-28.901	-43.064	2.477
3900	9.946	76.405	67.886	33.226	-28.840	-43.437	2.434
4000	9.972	76.657	68.102	34.222	-28.777	-43.815	2.394
4100	9.997	76.904	68.313	35.221	-28.712	-44.191	2.356
4200	10.022	77.145	68.521	36.222	-28.646	-44.567	2.319
4300	10.047	77.381	68.724	37.225	-28.579	-44.950	2.285
4400	10.072	77.612	68.923	38.231	-28.510	-45.328	2.251
4500	10.097	77.839	69.119	39.239	-28.441	-45.712	2.220
4600	10.122	78.061	69.311	40.250	-28.368	-46.100	2.190
4700	10.148	78.279	69.500	41.264	-28.295	-46.484	2.161
4800	10.174	78.493	69.685	42.280	-28.221	-46.872	2.134
4900	10.201	78.703	69.867	43.299	-28.144	-47.259	2.108
5000	10.229	78.910	70.045	44.320	-28.066	-47.650	2.083
5100	10.257	79.112	70.221	45.345	-27.987	-48.043	2.059
5200	10.287	79.312	70.394	46.372	-27.905	-48.439	2.036
5300	10.317	79.508	70.564	47.402	-27.822	-48.834	2.014
5400	10.349	79.701	70.732	48.435	-27.736	-49.232	1.993
5500	10.381	79.891	70.896	49.472	-27.648	-49.629	1.972
5600	10.415	80.079	71.059	50.511	-27.559	-50.031	1.953
5700	10.449	80.263	71.219	51.555	-27.467	-50.431	1.934
5800	10.485	80.445	71.376	52.601	-27.372	-50.837	1.916
5900	10.522	80.625	71.531	53.652	-27.274	-51.242	1.898
6000	10.561	80.802	71.684	54.706	-27.174	-51.648	1.881

Dec. 31, 1960; Sept. 30, 1962; June 30, 1977

PHOSPHORUS MONOFLUORIDE (PF) (IDEAL GAS) GFW = 49.97216

FP

D_0^o = 106.09 ± 4.6 kcal/mol
$S^o_{298.15}$ = 53.743 ± 0.01 gibbs/mol
Symmetry Number = 1

ΔHf_0^o = -8.546 ± 5.0 kcal/mol
$\Delta Hf^o_{298.15}$ = -8.345 ± 5.0 kcal/mol

Electronic and Molecular Constants

State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
$X^3\Sigma^-$	0	3	1.5896	0.5665	0.00456	846.75	4.489
$a^1\Delta$	7090.41	2	1.5849	0.5699	0.00467	858.79	4.438
$b^1\Sigma$	13353.91	1	1.5812	0.5725	0.0045	866.14	4.51
$B^3\Pi_0$	29338.69	2	1.752	0.4632	0.004	436	[1.5]
$B^3\Pi_1$	29481.80	2	1.752	0.4663	0.0038	436	[1.5]
$B^3\Pi_2$	29623.06	2	1.752	0.4693	0.0037	436	[1.5]
$d^1\Pi$	35812.29	2	1.721	0.4848	0.0062	413	[1.5]

Heat of Formation

There has been no report of a direct experimental determination of ΔHf°. Sufficient information is available, however, to allow a reasonable estimate of the P-F bond energy (D_0^o) to be made.

A linear Birge-Sponer extrapolation of the ground state vibrational constants leads to D"(LBX) = 4.90 eV. This value can be refined by taking into account the ionic character of the P-F bond. Using relationships developed by Hildenbrand (1), we adjust the value of D"(LBX) to obtain D_0'' = 4.25 eV. A similar treatment of spectroscopic data (5) for related molecules (AlF, SiF, and ClF) which have well-established bond energies indicates that the true D_0^o value could be higher than D_0'' by roughly 0.3 eV. Additional support for this is provided by the results of two molecular orbital studies (2, 3) which have led to estimates of D_0^o of 4.5 eV and 4.65±0.2 eV. The latter value, obtained from Hartree-Fock energies and estimated corrections for correlation effects, is believed to be reliable within the quoted uncertainty. A CNDO/2 MO study (4), employing energy partitioning concepts, has led to a much higher estimate of D_0^o equal to 5.17 eV.

We adopt D_0^o(PF) = 4.60±0.2 eV (106.08 kcal/mol) which gives ΔHf_0^o(PF) = -8.546±5.0 kcal/mol when combined with JANAF auxiliary data (5) for P and F. The adopted D_0^o value lies midway between the well-established bond energies (5) for SiF (130.3 kcal/mol) and SF (81.2 kcal/mol) and is near the mean bond energy ($\bar{D}$ = 109.1 kcal/mol) in PF_5 (5). ΔHf° at 298.15 K is -8.345 kcal/mol.

Heat Capacity and Entropy

The thermal functions are calculated from the partition function $Q = Q_t \Sigma_i g_i Q_r^i Q_v^i \exp(\varepsilon_i/kT)$ in which Q_r^i and Q_v^i contain first order corrections for anharmonicity. The electronic and molecular constants are taken from the compilation of Suchard (6). Values of $\omega_e x_e$ placed in brackets are estimates obtained from data on isoconfigurational states of SO ($A^3\Pi$, 6) and PF ($B^3\Pi$). Our entropies may contain significant errors, amounting to several tenths of a gibbs/mol, above 3500 K due to the omission of many unobserved electronic levels which have been predicted (7) to lie above the $b^1\Sigma$ state at 13353.91 cm^{-1}. In addition, Skolnik and Goodfriend (8) recently observed in emission a triple-headed band system near 5600 Å which was tentatively assigned to a $^3\Delta_{inv}$ - $^3\Pi_{inv}$ transition of PF. These inverted triplet levels are also omitted since we are unable to estimate their term values with respect to the $X^3\Sigma^-$ ground state.

Our calculations essentially update and extend those previously made on PF by O'Hare (9). The most significant difference is that our calculations are based on solid phosphorus (Red, V) as the reference state below 704 K rather than the ideal diatomic gas selected by O'Hare (9).

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FP

PHOSPHORUS MONOFLUORIDE UNIPOSITIVE ION (PF^+) FP^+
(IDEAL GAS) GFW=49.97161

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.254	217.823		
100							
200							
298	7.990	53.520	53.520	0.000	219.641	211.044	-154.697
300	7.992	53.569	53.520	0.015	219.649	210.990	-153.704
400	8.145	55.888	53.835	0.821	220.035	208.045	-113.669
500	8.310	57.723	54.435	1.644	220.382	205.006	-89.607
600	8.449	59.251	55.114	2.482	220.701	201.901	-73.541
700	8.559	60.562	55.801	3.333	220.990	198.743	-62.049
800	8.644	61.711	56.469	4.193	200.834	190.236	-51.969
900	8.711	62.733	57.110	5.061	201.327	188.883	-45.866
1000	8.763	63.654	57.719	5.935	201.819	187.473	-40.972
1100	8.806	64.491	58.297	6.814	202.311	186.014	-36.957
1200	8.841	65.259	58.846	7.696	202.800	184.510	-33.603
1300	8.870	65.968	59.367	8.581	203.291	182.967	-30.759
1400	8.895	66.626	59.862	9.470	203.782	181.386	-28.315
1500	8.916	67.240	60.333	10.360	204.272	179.770	-26.192
1600	8.935	67.816	60.783	11.253	204.761	178.119	-24.330
1700	8.952	68.359	61.213	12.147	205.250	176.440	-22.683
1800	8.967	68.871	61.624	13.043	205.739	174.731	-21.215
1900	8.980	69.356	62.019	13.940	206.227	172.996	-19.899
2000	8.993	69.817	62.397	14.839	206.715	171.232	-18.711
2100	9.005	70.256	62.761	15.739	207.203	169.447	-17.634
2200	9.016	70.675	63.111	16.640	207.689	167.638	-16.653
2300	9.026	71.076	63.449	17.542	208.175	165.805	-15.755
2400	9.036	71.460	63.775	18.445	208.661	163.952	-14.930
2500	9.045	71.829	64.090	19.349	209.148	162.082	-14.169
2600	9.054	72.184	64.394	20.254	209.633	160.188	-13.465
2700	9.063	72.526	64.689	21.160	210.117	158.276	-12.811
2800	9.071	72.856	64.975	22.067	210.602	156.348	-12.203
2900	9.079	73.174	65.252	22.974	211.087	154.402	-11.636
3000	9.087	73.482	65.521	23.883	211.570	152.440	-11.105
3100	9.095	73.780	65.783	24.792	212.054	150.462	-10.607
3200	9.102	74.069	66.038	25.702	212.536	148.465	-10.140
3300	9.110	74.350	66.285	26.612	213.019	146.456	-9.699
3400	9.117	74.622	66.526	27.524	213.501	144.432	-9.284
3500	9.124	74.886	66.761	28.436	213.983	142.394	-8.891
3600	9.131	75.143	66.991	29.348	214.464	140.340	-8.520
3700	9.138	75.393	67.214	30.262	214.944	138.274	-8.167
3800	9.145	75.637	67.433	31.176	215.425	136.197	-7.833
3900	9.152	75.875	67.646	32.091	215.905	134.107	-7.515
4000	9.159	76.107	67.855	33.007	216.385	132.001	-7.212
4100	9.166	76.333	68.059	33.923	216.864	129.886	-6.923
4200	9.173	76.554	68.259	34.840	217.342	127.761	-6.648
4300	9.180	76.770	68.454	35.757	217.820	125.619	-6.385
4400	9.187	76.981	68.645	36.676	218.299	123.473	-6.133
4500	9.194	77.187	68.833	37.595	218.776	121.312	-5.892
4600	9.201	77.390	69.017	38.515	219.254	119.138	-5.660
4700	9.209	77.588	69.197	39.435	219.731	116.957	-5.438
4800	9.216	77.782	69.374	40.356	220.206	114.766	-5.225
4900	9.223	77.972	69.547	41.278	220.684	112.567	-5.021
5000	9.231	78.158	69.718	42.201	221.159	110.355	-4.824
5100	9.239	78.341	69.885	43.124	221.634	108.133	-4.634
5200	9.247	78.520	70.049	44.049	222.110	105.901	-4.451
5300	9.255	78.697	70.211	44.974	222.585	103.663	-4.275
5400	9.263	78.870	70.370	45.900	223.060	101.414	-4.106
5500	9.272	79.040	70.526	46.826	223.535	99.159	-3.940
5600	9.281	79.207	70.679	47.754	224.009	96.891	-3.781
5700	9.290	79.371	70.830	48.683	224.483	94.619	-3.628
5800	9.299	79.533	70.979	49.612	224.958	92.335	-3.479
5900	9.308	79.692	71.125	50.542	225.433	90.065	-3.335
6000	9.318	79.848	71.269	51.474	225.907	87.747	-3.196

June 30, 1977

PHOSPHORUS MONOFLUORIDE UNIPOSITIVE ION (PF^+) (IDEAL GAS) GFW = 49.97161

FP^+

D_0° = 121.5 ± 10.0 kcal/mol
Symmetry Number = 1
$S^\circ_{298.15}$ = 53.52 ± 0.05 gibbs/mol

ΔHf_0° = 217.823 ± 9.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 219.641 ± 9.0 kcal/mol

Electronic and Molecular Constants

State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
$X^2\Pi_{1/2}$	0	2	1.5003	0.6360	0.0048	1053.25	5.047
$X^2\Pi_{3/2}$	323.95	2	1.5003	0.6360	0.0048	1053.25	5.047
$^2\Sigma$	35434.64	2	1.5998	0.5593	0.0079	619.0	4.615

Heat of Formation

Harland et al. (1) and Torgerson and Westmore (2) reported the appearance potential of PF^+ from PF_3 as 21.0±0.3 eV and 20.5±0.2 eV, respectively. We use the mean value of AP(PF^+/PF_3) = 20.75±0.3 eV (478.50 kcal/mol) in the expression ΔHr_0° = AP − E* for the process $PF_3(g) + e^- = PF^+(g) + 2F(g) + 2e^-$. With the assumption E* = 0, the value of ΔHr_0° gives $\Delta Hf_0^\circ(PF^+,g)$ = 217.823±9.0 kcal/mol with $\Delta Hf_0^\circ(PF_3,g)$ = −223.97±0.9 kcal/mol and $\Delta Hf_0^\circ(F,g)$ = 18.36±0.4 kcal/mol (3). We adopt this value. In the same paper, Harland et al. (1) also reported AP(PF^+/PF_2CN) = 19.1±0.2 eV which leads to $\Delta Hf_0^\circ(PF^+,g)$ = 233.56±21.3 kcal/mol, in reasonable accord with the adopted result.

ΔHf° at 298.15 K is 219.641±9.0 kcal/mol, and the adopted ionization potential (IP) is 9.82±0.61 eV. This IP compares favorably with values predicted from quantum-mechanical calculations. These have included (all in eV) 9.5±0.2 (4), 9.6 (5), and 10.35 (6). The latter value is based on IP(P) = 10.98 eV which is 0.5 eV higher than the current best value of 10.486 eV (7). Recalculation of the results of Companion and Hsia (6) gives IP(PF) = 9.85 eV.

The primary bond dissociation energy $D_0^\circ(PF^+)$ is calculated to be 121.5 kcal/mol which can be compared with 106.1 kcal/mol (3) in the neutral molecule. The stronger P-F bond in the ion is consistent with theoretical predictions (4-6) that the electron lost from PF occupies an antibonding orbital.

Heat Capacity and Entropy

The thermal functions are calculated from the partition function $Q = Q_t \Sigma_i g_i Q_r^i Q_v^i \exp(\varepsilon_i/kT)$ in which Q_r^i and Q_v^i contain first order corrections for anharmonicity. The electronic and molecular constants are taken from Douglas and Frackowiak (8) who observed one band system in the emission spectrum of PF^+ formed by passing a discharge through a mixture of PF_3 and He. We treat the ground state as two distinct electronic levels with a splitting of 323.95 cm^{-1}. This procedure gives functions which are slightly biased below 400 K. The uncertainty in the value of S°_{298} includes this error. By analogy with the isoelectronic molecules SiF and PO (3), other excited states are predicted to lie in the range 20000-30000 cm^{-1}. We prefer to omit these levels but, if they do exist, our entropies could be slightly low above 4500 K.

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PHOSPHORUS MONOFLUORIDE UNINEGATIVE ION (PF^-) FP^-
(IDEAL GAS) GFW=49.97271

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0				-2.274	-33.912		
100							
200							
298	8.314	53.802	53.802	0.000	-35.035	-40.742	29.865
300	8.318	53.854	53.802	0.015	-35.045	-40.777	29.706
400	8.509	56.275	54.131	0.857	-35.617	-42.603	23.277
500	8.640	58.188	54.758	1.715	-36.229	-44.280	19.355
600	8.732	59.772	55.465	2.584	-36.873	-45.832	16.694
700	8.798	61.124	56.180	3.461	-37.550	-47.271	14.758
800	8.847	62.302	56.873	4.343	-58.678	-53.923	14.731
900	8.885	63.346	57.535	5.230	-59.160	-53.299	12.942
1000	8.915	64.284	58.164	6.120	-59.646	-52.622	11.500
1100	8.940	65.135	58.759	7.013	-60.134	-51.897	10.311
1200	8.962	65.914	59.324	7.908	-60.624	-51.126	9.311
1300	8.980	66.632	59.859	8.805	-61.115	-50.314	8.458
1400	8.997	67.298	60.366	9.704	-61.608	-49.465	7.722
1500	9.012	67.919	60.849	10.604	-62.102	-48.580	7.078
1600	9.026	68.501	61.310	11.506	-62.597	-47.663	6.510
1700	9.038	69.049	61.749	12.409	-63.092	-46.713	6.005
1800	9.050	69.566	62.169	13.314	-63.589	-45.736	5.553
1900	9.062	70.055	62.571	14.219	-64.086	-44.730	5.145
2000	9.073	70.520	62.957	15.126	-64.584	-43.700	4.775
2100	9.083	70.963	63.328	16.034	-65.083	-42.643	4.438
2200	9.093	71.386	63.685	16.943	-65.581	-41.561	4.129
2300	9.103	71.790	64.028	17.853	-66.080	-40.460	3.845
2400	9.113	72.178	64.360	18.763	-66.581	-39.336	3.582
2500	9.122	72.550	64.680	19.675	-67.080	-38.189	3.338
2600	9.132	72.908	64.990	20.588	-67.581	-37.025	3.112
2700	9.141	73.253	65.290	21.502	-68.081	-35.839	2.901
2800	9.151	73.586	65.580	22.416	-68.583	-34.636	2.703
2900	9.160	73.907	65.862	23.332	-69.084	-33.414	2.518
3000	9.169	74.218	66.135	24.248	-69.586	-32.176	2.344
3100	9.179	74.518	66.401	25.166	-70.088	-30.920	2.180
3200	9.188	74.810	66.659	26.084	-70.590	-29.650	2.025
3300	9.198	75.093	66.910	27.003	-71.092	-28.361	1.878
3400	9.208	75.368	67.155	27.923	-71.596	-27.060	1.739
3500	9.218	75.635	67.393	28.845	-72.098	-25.743	1.607
3600	9.228	75.895	67.626	29.767	-72.601	-24.413	1.482
3700	9.239	76.148	67.853	30.690	-73.104	-23.066	1.362
3800	9.250	76.394	68.074	31.615	-73.606	-21.706	1.248
3900	9.261	76.634	68.291	32.540	-74.110	-20.332	1.139
4000	9.273	76.869	68.502	33.467	-74.613	-18.950	1.035
4100	9.285	77.098	68.709	34.395	-75.115	-17.552	0.936
4200	9.298	77.322	68.912	35.324	-75.618	-16.138	0.840
4300	9.311	77.541	69.110	36.255	-76.120	-14.720	0.748
4400	9.324	77.755	69.304	37.186	-76.623	-13.283	0.660
4500	9.338	77.965	69.494	38.119	-77.126	-11.839	0.575
4600	9.352	78.170	69.680	39.054	-77.627	-10.386	0.493
4700	9.367	78.372	69.863	39.990	-78.127	-8.916	0.415
4800	9.382	78.569	70.042	40.927	-78.629	-7.438	0.339
4900	9.398	78.763	70.218	41.866	-79.128	-5.948	0.265
5000	9.414	78.953	70.391	42.807	-79.629	-4.450	0.194
5100	9.430	79.139	70.561	43.749	-80.127	-2.942	0.126
5200	9.447	79.323	70.728	44.693	-80.626	-1.426	0.060
5300	9.465	79.503	70.892	45.639	-81.124	0.103	-0.004
5400	9.483	79.680	71.053	46.586	-81.621	1.639	-0.066
5500	9.501	79.854	71.211	47.535	-82.118	3.188	-0.127
5600	9.519	80.025	71.367	48.486	-82.613	4.743	-0.185
5700	9.538	80.194	71.520	49.439	-83.108	6.308	-0.242
5800	9.557	80.360	71.671	50.394	-83.602	7.879	-0.297
5900	9.577	80.523	71.820	51.351	-84.095	9.461	-0.350
6000	9.597	80.685	71.966	52.309	-84.588	11.051	-0.403

June 30, 1977

PHOSPHORUS MONOFLUORIDE UNINEGATIVE ION (PF^-) (IDEAL GAS) GFW = 49.97271

FP^-

D_0° = 53.1 ± 17.0 kcal/mol
Ground State Configuration $[^2\Pi_{3/2}]$
$S^\circ_{298.15}$ = [53.8 ± 0.5] gibbs/mol

ΔHf_0° = [-33.919 ± 16.5] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [-35.035 ± 16.5] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[2]
[350]	[2]
[25000]	[4]

ω_e = [840] cm^{-1} $\omega_e x_e$ = [4.6] cm^{-1} σ = 1

B_e = [0.56626] cm^{-1} α_e = [0.00424] cm^{-1} r_e = [1.59] Å

Heat of Formation

We calculate the heat of formation at 0 K as the difference between $\Delta Hf_0^\circ(PF,g)$ = -8.55±5.0 kcal/mol (1) and the selected value of 1.1±0.5 eV (25.366 kcal/mol) for the electron affinity (EA) of PF. The value of EA refers to the vertical electron detachment process $PF^-(g) = PF(g) + e^-$ and is taken from the molecular orbital study of O'Hare (2). This value was obtained from Hartree-Fock energies and estimated corrections for correlation effects. The estimated uncertainty in EA is 0.5 eV which should be adequate to cover the possibility that the adiabatic value is lower than the vertical EA. Other theoretical predictions of EA include 2.55 eV (3) and 1.4 eV (4).

ΔHf° at 298.15 K is -35.035 kcal/mol, and the primary bond dissociation energy (Products $P(g) + F^-(g)$) is 53.1 kcal/mol. The latter value can be compared with $D_0^\circ(PF)$ = 106.1 kcal/mol (1), indicating that the P-F bond is much weaker in the anion relative to the neutral molecule. This is consistent with MO predictions (2-4) which indicate that the electron captured by PF occupies an antibonding orbital located primarily on the phosphorus atom.

Our thermal functions indicate that PF^- is thermodynamically stable with respect to dissociation ($P + F^-$) below 2500 K. These predictions agree qualitatively with the results of MacNeil and Thynne (5) who observed PF^- in the negative ion mass spectrum of PF_3. Their reported appearance potential, $AP(PF^-/PF_3)$ = 11.4±0.1 eV, gives EA(PF) = -0.47 eV assuming that the dissociative electron capture process is $PF_3(g) + e^- = PF^-(g) + 2F(g)$. We believe this value is too low probably because of excess kinetic and/or excitation energies amounting to roughly 1.5 eV.

Heat Capacity and Entropy

The bond length and vibrational constants are assumed to lie between those for PF and SF (1). The value of B_e is obtained from r_e. We calculate α_e from the other constants assuming a Morse potential function. The moment of inertia is 4.9431×10^{-39} g cm^2.

The ground state electronic configuration ($^2\Pi_{3/2}$), ground state splitting (A = 350 cm^{-1}), and excited state ($^2\Pi$) at 25000 cm^{-1} are estimated by analogy with those for the isoelectronic molecule SF (1). The major source of error in our calculations below 500 K arises from the uncertainty in the ground state splitting. With A = 0 cm^{-1}, the value of S°_{298} increases by 0.5 gibbs/mol. At higher temperatures the differences in S become smaller, indicating that the uncertainty in the adopted entropies above 1000 K is less than 0.2 gibbs/mol.

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SULFUR MONOFLUORIDE UNINEGATIVE ION (SF^-) FS$^-$
(IDEAL GAS) GFW=51.05895

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-2.171	-43.178		
100							
200							
298	7.978	52.305	52.305	0.000	-44.596	-49.206	36.069
300	7.986	52.354	52.305	0.015	-44.607	-49.234	35.867
400	8.339	54.704	52.623	0.832	-45.771	-50.062	27.680
500	8.555	56.590	53.234	1.678	-46.764	-51.770	22.629
600	8.694	58.163	53.928	2.541	-47.671	-52.684	19.190
700	8.790	59.511	54.632	3.415	-48.518	-53.427	16.681
800	8.860	60.689	55.317	4.298	-62.390	-55.342	15.119
900	8.914	61.736	55.973	5.187	-62.874	-54.432	13.218
1000	8.957	62.678	56.597	6.081	-63.361	-53.467	11.685
1100	8.993	63.533	57.189	6.978	-63.849	-52.456	10.422
1200	9.024	64.317	57.751	7.879	-64.337	-51.397	9.361
1300	9.051	65.040	58.284	8.783	-64.827	-50.298	8.456
1400	9.076	65.712	58.791	9.689	-65.318	-49.162	7.675
1500	9.099	66.339	59.274	10.598	-65.810	-47.993	6.993
1600	9.120	66.927	59.734	11.509	-66.300	-46.787	6.391
1700	9.140	67.480	60.173	12.422	-66.792	-45.553	5.856
1800	9.160	68.003	60.594	13.337	-67.285	-44.290	5.378
1900	9.179	68.499	60.997	14.254	-67.777	-42.998	4.946
2000	9.197	68.970	61.384	15.173	-68.270	-41.681	4.555
2100	9.216	69.420	61.756	16.093	-68.762	-40.341	4.198
2200	9.235	69.849	62.114	17.016	-69.255	-38.975	3.872
2300	9.254	70.260	62.459	17.940	-69.748	-37.588	3.572
2400	9.274	70.654	62.793	18.867	-70.241	-36.179	3.295
2500	9.295	71.033	63.115	19.795	-70.733	-34.750	3.038
2600	9.318	71.398	63.426	20.726	-71.224	-33.300	2.799
2700	9.343	71.750	63.728	21.659	-71.714	-31.833	2.577
2800	9.370	72.090	64.021	22.594	-72.204	-30.349	2.369
2900	9.400	72.420	64.305	23.533	-72.493	-28.843	2.174
3000	9.433	72.739	64.581	24.474	-73.181	-27.326	1.991
3100	9.469	73.049	64.849	25.420	-73.663	-25.787	1.818
3200	9.508	73.350	65.110	26.368	-74.147	-24.235	1.655
3300	9.551	73.643	65.364	27.321	-74.627	-22.669	1.501
3400	9.598	73.929	65.612	28.279	-75.104	-21.085	1.355
3500	9.649	74.208	65.853	29.241	-75.578	-19.492	1.217
3600	9.705	74.481	66.089	30.209	-76.046	-17.881	1.086
3700	9.764	74.747	66.320	31.182	-76.513	-16.258	0.960
3800	9.828	75.008	66.545	32.162	-76.973	-14.624	0.841
3900	9.895	75.265	66.765	33.148	-77.430	-12.979	0.727
4000	9.967	75.516	66.981	34.141	-77.879	-11.316	0.618
4100	10.043	75.763	67.192	35.141	-78.323	-9.649	0.514
4200	10.122	76.006	67.399	36.150	-78.761	-7.968	0.415
4300	10.205	76.245	67.602	37.166	-79.192	-6.278	0.319
4400	10.291	76.481	67.801	38.191	-79.617	-4.578	0.227
4500	10.380	76.713	67.997	39.224	-80.033	-2.866	0.139
4600	10.471	76.942	68.188	40.267	-80.442	-1.148	0.055
4700	10.565	77.168	68.377	41.318	-80.843	0.579	-0.027
4800	10.661	77.392	68.563	42.380	-81.236	2.315	-0.105
4900	10.759	77.613	68.745	43.451	-81.621	4.063	-0.181
5000	10.859	77.831	68.925	44.532	-81.997	5.813	-0.256
5100	10.959	78.047	69.101	45.623	-82.365	7.573	-0.325
5200	11.060	78.261	69.275	46.724	-82.724	9.343	-0.393
5300	11.161	78.472	69.447	47.835	-83.074	11.116	-0.458
5400	11.263	78.682	69.616	48.956	-83.417	12.895	-0.522
5500	11.364	78.890	69.783	50.087	-83.748	14.683	-0.583
5600	11.465	79.095	69.947	51.229	-84.073	16.477	-0.643
5700	11.565	79.299	70.110	52.380	-84.389	18.274	-0.701
5800	11.663	79.501	70.270	53.542	-84.696	20.078	-0.757
5900	11.761	79.701	70.428	54.713	-84.994	21.882	-0.811
6000	11.856	79.900	70.584	55.894	-85.284	23.701	-0.863

Dec. 31, 1976

SULFUR MONOFLUORIDE UNINEGATIVE ION (SF^-) (IDEAL GAS) GFW = 51.05895

D°_0 = [48.9 ± 13.5] kcal/mol
$S^\circ_{298.15}$ = [52.3 ± 0.2] gibbs/mol

ΔHf°_0 = [-43.2 ± 13.0] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [-44.6 ± 13.0] kcal/mol

FS$^-$

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$X^1\Sigma^+$]	[0]	[1]
[$A\ ^3\Pi$]	[20000]	[6]

ω_e = [627] cm^{-1} $\omega_e x_e$ = [5.06] cm^{-1} σ = 1
B_e = [0.45620] cm^{-1} α_e = [0.0046] cm^{-1} r_e = [1.76] Å

Heat of Formation

The adopted value of ΔHf°_0 = -43.2±13.0 kcal/mol is calculated as the difference between the ΔHf°_0(SF,g) = 2.94±1.5 kcal/mol (1) and an estimate of the electron affinity (E.A.) for SF of 2.0±0.5 eV (46.121 kcal/mol). We estimate E.A. based on a consideration of trends in the electron affinities for other S-F species (1). These data follow a regular pattern among the even- and odd-electron molecules, with the odd-electron molecules having, as expected, the higher E.A.'s. Within each even- and odd-electron series, the E.A. values become progressively larger as the number of fluorine atoms in the ion is increased. Our ΔHf°_0 value corresponds to a fluoride-ion affinity I.A.(S) and bond dissociation energy ($SF^- = S + F^-$) of 48.9±13.5 kcal/mol. Correcting ΔHf°_0 to a temperature of 298.15 K, we obtain the value of -44.6 kcal/mol.

Several pieces of information are available which tend to provide support for our estimated E.A. value. Formation of SF^- involves the addition of an electron to an antibonding orbital of SF (2) which is located primarily on the sulfur atom. It is reasonable, therefore, to assume that E.A.(SF)≃E.A.(S) = 2.0772±0.005 eV (3). O'Hare (2) has pointed out that Koopmans' theorem (4) gives reliable estimates of electron affinities and ionization potentials provided that the parent molecule or ion have a closed-shell electronic configuration. Application of this theorem to SF^- which has the required closed-shell structure leads to E.A. = 1.7 eV (2). Other estimates of E.A. based on MO calculations have included (all in eV) 2.8 (5), 2.5±0.5 (6), and < 3.2 (2).

JANAF data (1) suggest that SF^- should be reasonably stable at moderate temperatures, with dissociative ionization becoming thermodynamically favorable above 2000 K. These predictions are supported qualitatively by the observations of Harland and Thynne (7, 8) who have identified SF^- in the negative ion mass spectra of SF_4, SF_6, and SF_5Cl. The temperature of the ion source was reported as around 325 K (8).

Heat Capacity and Entropy

The additional antibonding electron in SF^- should weaken the bonding in the ion relative to the parent molecule, as evidenced by a reduction (~32 kcal/mol) in the S-F bond strength for SF^- when compared with that for SF (1). In addition, MC calculations (9) on OF and OF^- show that the O-F bond length in OF increases by 0.159 Å upon forming the negative ion. We apply this difference to r_e(SF) = 1.5967 Å (1), and we obtain $r_e(SF^-)$ = 1.76 Å. The value of B_e is calculated from our estimate of r_e. We use Badger's rule (10) to estimate a value for ω_e. We write the equation in the form $\omega_e{}^2 = 3.159 \times 10^6/\mu(r_e-d_{ij})^3$, and we set d_{ij} equal to 0.8833 based on molecular data for CℓF (11). Barrow and Caunt (12) have shown that the product $x_e\mu^{1/2}$ is reasonably constant for a series of similar molecules. Using $x_e\mu^{1/2}$ = 0.0279 from CℓF (11), we calculate x_e = 0.008068 and $\omega_e x_e$ = 5.06 cm^{-1} for SF^-. The value of α_e is obtained from the other constants, assuming a Morse potential function (13). The moment of inertia is 6.1356×10^{-39} g cm^2.

The electronic states and levels are estimated by analogy with those for CℓF (11). The effect of the triplet level at 20000 cm^{-1} on our entropies is insignificant below 3000 K, but this level does contribute 0.15 gibbs/mol to S at 4500 K. We assign an uncertainty of ±0.2 gibbs/mol to the value of S°_{298} based on conservative estimates of the uncertainties in the vibrational and rotational data.

References

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FS$^-$

SILICON MONOFLUORIDE (SiF) FSI
(IDEAL GAS) GFW=47.0844

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.261	-5.237	-5.237	INFINITE
100	7.830	45.521	60.769	-1.525	-4.912	-7.338	16.037
200	7.616	50.870	54.643	-0.755	-4.773	-9.835	10.747
298	7.803	53.937	53.937	0.000	-4.800	-12.318	9.029
300	7.809	53.985	53.937	0.014	-4.802	-12.365	9.008
400	8.096	56.272	54.247	0.810	-4.898	-14.872	8.126
500	8.326	58.104	54.841	1.632	-5.024	-17.351	7.584
600	8.492	59.638	55.516	2.473	-5.167	-19.804	7.214
700	8.611	60.956	56.201	3.328	-5.322	-22.231	6.941
800	8.699	62.112	56.870	4.194	-5.489	-24.637	6.730
900	8.765	63.141	57.510	5.067	-5.666	-27.018	6.561
1000	8.817	64.067	58.120	5.947	-5.853	-29.381	6.421
1100	8.859	64.910	58.700	6.831	-6.050	-31.725	6.303
1200	8.893	65.682	59.250	7.718	-6.256	-34.050	6.201
1300	8.922	66.395	59.772	8.609	-6.472	-36.358	6.112
1400	8.946	67.057	60.269	9.502	-6.697	-38.648	6.033
1500	8.968	67.675	60.743	10.398	-6.931	-40.921	5.962
1600	8.988	68.254	61.194	11.296	-7.176	-43.180	5.898
1700	9.005	68.800	61.626	12.196	-19.423	-45.316	5.826
1800	9.021	69.315	62.039	13.097	-19.633	-46.834	5.686
1900	9.036	69.803	62.435	14.000	-19.842	-48.339	5.560
2000	9.050	70.267	62.815	14.906	-20.051	-49.832	5.445
2100	9.063	70.709	63.180	15.810	-20.261	-51.317	5.341
2200	9.076	71.131	63.532	16.717	-20.470	-52.792	5.244
2300	9.088	71.534	63.871	17.625	-20.680	-54.256	5.155
2400	9.099	71.921	64.199	18.534	-20.889	-55.710	5.073
2500	9.111	72.293	64.515	19.445	-21.099	-57.158	4.997
2600	9.122	72.651	64.821	20.356	-21.309	-58.596	4.925
2700	9.133	72.995	65.118	21.269	-21.519	-60.026	4.859
2800	9.143	73.327	65.405	22.183	-21.729	-61.448	4.796
2900	9.154	73.648	65.684	23.098	-21.939	-62.862	4.737
3000	9.165	73.959	65.954	24.014	-22.149	-64.272	4.682
3100	9.175	74.260	66.217	24.931	-22.359	-65.673	4.630
3200	9.186	74.551	66.473	25.849	-22.570	-67.064	4.580
3300	9.197	74.834	66.722	26.768	-22.780	-68.452	4.533
3400	9.209	75.109	66.965	27.688	-22.990	-69.833	4.489
3500	9.220	75.376	67.202	28.610	-23.201	-71.208	4.446
3600	9.232	75.636	67.432	29.532	-115.372	-70.318	4.269
3700	9.245	75.889	67.657	30.456	-115.483	-69.066	4.080
3800	9.258	76.136	67.877	31.381	-115.594	-67.809	3.900
3900	9.271	76.376	68.092	32.308	-115.706	-66.553	3.730
4000	9.285	76.611	68.302	33.236	-115.817	-65.289	3.567
4100	9.300	76.841	68.508	34.165	-115.929	-64.027	3.413
4200	9.315	77.065	68.709	35.096	-116.040	-62.760	3.266
4300	9.331	77.284	68.906	36.028	-116.150	-61.489	3.125
4400	9.348	77.499	69.098	36.962	-116.261	-60.217	2.991
4500	9.365	77.709	69.287	37.897	-116.370	-58.939	2.862
4600	9.383	77.915	69.473	38.835	-116.478	-57.663	2.740
4700	9.402	78.117	69.655	39.774	-116.586	-56.383	2.622
4800	9.422	78.315	69.833	40.715	-116.693	-55.101	2.509
4900	9.443	78.510	70.008	41.659	-116.798	-53.815	2.400
5000	9.465	78.701	70.180	42.604	-116.903	-52.532	2.296
5100	9.487	78.889	70.349	43.552	-117.006	-51.242	2.196
5200	9.511	79.073	70.515	44.501	-117.109	-49.950	2.099
5300	9.536	79.254	70.678	45.454	-117.208	-48.657	2.006
5400	9.561	79.433	70.839	46.409	-117.308	-47.366	1.917
5500	9.587	79.609	70.996	47.366	-117.406	-46.070	1.831
5600	9.615	79.782	71.152	48.326	-117.502	-44.769	1.747
5700	9.643	79.952	71.305	49.289	-117.597	-43.467	1.667
5800	9.673	80.120	71.455	50.255	-117.690	-42.167	1.589
5900	9.703	80.285	71.603	51.224	-117.781	-40.869	1.514
6000	9.734	80.449	71.750	52.195	-117.871	-39.564	1.441

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1963;
Dec. 31, 1969; Dec. 31, 1976

SILICON MONOFLUORIDE (SiF) (IDEAL GAS) GFW = 47.0844

D_0^o = 130 ± 4 kcal/mol
$S^o_{298.15}$ = 53.937 ± 0.04 gibbs/mol
Symmetry Number = 1

ΔHf_0^o = -5.2 ± 3 kcal/mol FSI
$\Delta Hf^o_{298.15}$ = -4.8 ± 3 kcal/mol

Electronic Levels and Molecular Constants

State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	a_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
X $^2\Pi_{1/2}$	0	2	1.6008	0.58138	0.00494	857.20	4.735
$^2\Pi_{3/2}$	161.93	2	1.6008	0.58138	0.00494	857.20	4.735
A $^2\Sigma^+$	22858.84	2	1.6049	0.57839	0.00941	718.5	10.167
a $^4\Sigma^-$	29805.06	4	1.604	0.5786	0.00502	863.16	5.730
B $^2\Sigma^+$	34561.5	2	1.5714	0.62707	0.00462	1011.2	4.825
C $^2\Delta$	39438.4	4	1.5714	0.60338	0.00539	829.41	7.01
C' $^2\Pi$	41964.9	4	-	0.6376	0.0039	1031.9	4.45
D' $^2\Pi$	46606.7	4	-	0.6329	0.0044	1032.9	5.28
D $^2\Sigma^+$	47418.6	2	1.54	0.625	0.005	1003.2	5.64

Heat of Formation

Ehlert and Margrave (1) have studied mass-spectrometrically the reaction $Si(g) + SiF_2(g) \rightarrow 2\ SiF(g)$ by monitoring the intensities of the Si^+, SiF_2^+ and SiF^+ ions in an equilibrium system containing CaF_2 and Si. The ionization cross-sections are assumed to cancel so that equilibrium constants can be obtained directly from the ion intensities. Eleven data points were reported in the 1395 to 1543 K range. We have analysed their data using present JANAF functions (2) and obtain ΔHr^o_{298} = 23.5±3 kcal/mol by the third law technique with a drift of -0.8±11 gibbs/mol; the second law value is 23.9±7 kcal/mol. Farber (6) also has determined equilibrium constants mass-spectrometrically for the $Si(g) + SiF_2(g) = 2\ SiF(g)$ reaction; ten data points over a 1590 to 1782 K range were obtained. Our analysis yields a third law ΔHr^o_{298} = 21.08±0.59 kcal/mol with a drift of -1.9±1.5 gibbs/mol; the second law value is 24.18±2.5 kcal/mol. The two groups of data are in good agreement. We adopt an average value and calculate ΔHf^o_{298}(SiF,g) = -4.8±3 kcal/mol.

D_0^o = 130±4 kcal/mol is calculated from the resulting ΔHf_0^o and auxiliary data (2). Johns and Barrow (3) recommended 125±10 kcal/mol from Birge-Sponer extrapolations of several states. Gaydon (4) preferred 115±12 kcal/mol from a Birge-Sponer extrapolation of the ground state.

Heat Capacity and Entropy

The molecular constants and electronic levels are those given by Suchard (5). Five higher levels are given but are not used since they do not significantly affect the calculations. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant (A=161.93 cm^{-1}). This approximation gives slightly biased results at lower temperatures. An error of ±0.04 gibbs/mol has been assigned to S^o_{298} to allow for this.

References

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FLUORINE, DIATOMIC (F_2) F_2

(REFERENCE STATE - IDEAL GAS) GFW=37.996806

T, K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.109	0.000	0.000	0.000
100	6.958	40.695	54.839	-1.414	0.000	0.000	0.000
200	7.095	45.542	49.114	-0.714	0.000	0.000	0.000
298	7.481	48.443	48.443	0.000	0.000	0.000	0.000
300	7.489	48.489	48.443	0.014	0.000	0.000	0.000
400	7.883	50.700	48.742	0.783	0.000	0.000	0.000
500	8.183	52.493	49.318	1.587	0.000	0.000	0.000
600	8.399	54.005	49.977	2.417	0.000	0.000	0.000
700	8.554	55.312	50.648	3.265	0.000	0.000	0.000
800	8.670	56.462	51.304	4.127	0.000	0.000	0.000
900	8.759	57.489	51.935	4.998	0.000	0.000	0.000
1000	8.829	58.415	52.538	5.878	0.000	0.000	0.000
1100	8.887	59.260	53.111	6.764	0.000	0.000	0.000
1200	8.935	60.035	53.656	7.655	0.000	0.000	0.000
1300	8.976	60.752	54.175	8.550	0.000	0.000	0.000
1400	9.012	61.418	54.669	9.450	0.000	0.000	0.000
1500	9.045	62.041	55.140	10.353	0.000	0.000	0.000
1600	9.074	62.626	55.589	11.259	0.000	0.000	0.000
1700	9.101	63.177	56.020	12.167	0.000	0.000	0.000
1800	9.126	63.698	56.432	13.079	0.000	0.000	0.000
1900	9.150	64.192	56.827	13.992	0.000	0.000	0.000
2000	9.172	64.662	57.207	14.909	0.000	0.000	0.000
2100	9.193	65.110	57.573	15.827	0.000	0.000	0.000
2200	9.214	65.538	57.926	16.747	0.000	0.000	0.000
2300	9.234	65.948	58.266	17.670	0.000	0.000	0.000
2400	9.253	66.341	58.594	18.594	0.000	0.000	0.000
2500	9.272	66.719	58.911	19.520	0.000	0.000	0.000
2600	9.290	67.083	59.219	20.448	0.000	0.000	0.000
2700	9.308	67.434	59.517	21.378	0.000	0.000	0.000
2800	9.326	67.773	59.805	22.310	0.000	0.000	0.000
2900	9.343	68.101	60.086	23.243	0.000	0.000	0.000
3000	9.361	68.418	60.358	24.179	0.000	0.000	0.000
3100	9.378	68.725	60.623	25.115	0.000	0.000	0.000
3200	9.394	69.023	60.881	26.054	0.000	0.000	0.000
3300	9.411	69.312	61.132	26.994	0.000	0.000	0.000
3400	9.427	69.594	61.377	27.936	0.000	0.000	0.000
3500	9.444	69.867	61.616	28.880	0.000	0.000	0.000
3600	9.460	70.133	61.849	29.825	0.000	0.000	0.000
3700	9.476	70.393	62.076	30.772	0.000	0.000	0.000
3800	9.492	70.646	62.298	31.720	0.000	0.000	0.000
3900	9.508	70.893	62.515	32.670	0.000	0.000	0.000
4000	9.524	71.133	62.728	33.622	0.000	0.000	0.000
4100	9.540	71.369	62.936	34.575	0.000	0.000	0.000
4200	9.556	71.599	63.139	35.530	0.000	0.000	0.000
4300	9.572	71.824	63.339	36.486	0.000	0.000	0.000
4400	9.587	72.044	63.534	37.444	0.000	0.000	0.000
4500	9.603	72.260	63.726	38.404	0.000	0.000	0.000
4600	9.619	72.471	63.913	39.365	0.000	0.000	0.000
4700	9.634	72.678	64.098	40.327	0.000	0.000	0.000
4800	9.650	72.881	64.279	41.292	0.000	0.000	0.000
4900	9.665	73.080	64.456	42.257	0.000	0.000	0.000
5000	9.681	73.276	64.631	43.225	0.000	0.000	0.000
5100	9.696	73.467	64.802	44.193	0.000	0.000	0.000
5200	9.711	73.656	64.970	45.164	0.000	0.000	0.000
5300	9.727	73.841	65.136	46.136	0.000	0.000	0.000
5400	9.742	74.023	65.299	47.109	0.000	0.000	0.000
5500	9.758	74.202	65.459	48.084	0.000	0.000	0.000
5600	9.773	74.378	65.617	49.061	0.000	0.000	0.000
5700	9.788	74.551	65.772	50.039	0.000	0.000	0.000
5800	9.803	74.721	65.925	51.018	0.000	0.000	0.000
5900	9.819	74.889	66.075	51.999	0.000	0.000	0.000
6000	9.834	75.054	66.224	52.982	0.000	0.000	0.000

Dec. 31, 1960; July 31, 1972 (NBS); June 30, 1977

FLUORINE, DIATOMIC (F_2) (REFERENCE STATE - IDEAL GAS) GFW = 37.996806

F_2

0 to 6000 K Ideal Gas

D_0° = 36.94 ± 0.14 kcal/mol (5)
$S^\circ_{298.15}$ = 48.443 ± 0.010 gibbs/mol
Ground State Configuration $^1\Sigma^+$

ΔHf_0° = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

ω_e = 917.85 cm^{-1} $\omega_e x_e$ = 11.95 cm^{-1} σ = 2
B_e = 0.8892 cm^{-1} α_e = 0.0131 cm^{-1} r_e = 1.40 Å

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The National Bureau of Standards prepared this table (1) by critical analysis of data existing in 1972. Using molecular constants selected by NBS (1) from the preliminary report of Di Lonardo and Douglas (2), we recalculate the table in terms of 1973 fundamental constants (3) and 1975 atomic weights (4). A more complete analysis of vibrational-rotational constants and D_0° is now available (5). Our values of S°_{298} and its uncertainty are the same as those selected by CODATA (6).

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HYDROGEN FLUORIDE DIMER (H_2F_2) F_2H_2
(IDEAL GAS) GFW=40.012606

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.683	-135.420	-135.420	INFINITE
100	8.287	46.924	65.744	-1.882	-136.031	-134.249	293.397
200	9.507	53.037	58.002	-0.993	-136.486	-132.282	144.549
298	10.725	57.060	57.060	0.000	-136.870	-130.135	95.390
300	10.748	57.127	57.060	0.020	-136.877	-130.093	94.772
400	11.879	60.378	57.496	1.153	-137.207	-127.780	69.815
500	12.795	63.131	58.355	2.388	-137.475	-125.391	54.808
600	13.512	65.530	59.355	3.705	-137.688	-122.954	44.785
700	14.090	67.658	60.392	5.086	-137.857	-120.484	37.616
800	14.579	69.572	61.422	6.520	-137.991	-117.993	32.234
900	15.012	71.315	62.426	8.000	-138.093	-115.487	28.044
1000	15.404	72.917	63.396	9.521	-138.170	-112.971	24.689
1100	15.763	74.402	64.329	11.080	-138.223	-110.448	21.944
1200	16.093	75.788	65.227	12.673	-138.257	-107.922	19.655
1300	16.396	77.088	66.090	14.298	-138.273	-105.392	17.718
1400	16.673	78.314	66.920	15.951	-138.276	-102.863	16.057
1500	16.926	79.473	67.718	17.631	-138.266	-100.334	14.619
1600	17.155	80.573	68.488	19.336	-138.244	-97.806	13.360
1700	17.364	81.619	69.230	21.062	-138.213	-95.279	12.249
1800	17.553	82.617	69.946	22.808	-138.176	-92.755	11.262
1900	17.724	83.571	70.638	24.572	-138.131	-90.232	10.379
2000	17.880	84.484	71.308	26.352	-138.083	-87.713	9.585
2100	18.021	85.360	71.956	28.147	-138.029	-85.195	8.866
2200	18.149	86.201	72.585	29.956	-137.972	-82.681	8.214
2300	18.265	87.010	73.194	31.777	-137.913	-80.170	7.618
2400	18.371	87.790	73.786	33.609	-137.851	-77.660	7.072
2500	18.468	88.542	74.362	35.451	-137.788	-75.153	6.570
2600	18.556	89.268	74.921	37.302	-137.725	-72.648	6.107
2700	18.636	89.970	75.465	39.161	-137.662	-70.146	5.678
2800	18.710	90.649	75.996	41.029	-137.599	-67.648	5.280
2900	18.778	91.307	76.512	42.903	-137.536	-65.150	4.910
3000	18.841	91.944	77.016	44.784	-137.474	-62.656	4.564
3100	18.898	92.563	77.508	46.671	-137.412	-60.161	4.241
3200	18.951	93.164	77.988	48.564	-137.353	-57.672	3.939
3300	19.000	93.748	78.456	50.461	-137.295	-55.182	3.654
3400	19.045	94.316	78.915	52.364	-137.239	-52.695	3.387
3500	19.087	94.868	79.363	54.270	-137.186	-50.209	3.135
3600	19.126	95.407	79.801	56.181	-137.134	-47.724	2.897
3700	19.162	95.931	80.230	58.095	-137.086	-45.242	2.672
3800	19.196	96.443	80.650	60.013	-137.040	-42.760	2.459
3900	19.227	96.942	81.061	61.934	-136.997	-40.279	2.257
4000	19.257	97.429	81.464	63.859	-136.957	-37.801	2.065
4100	19.284	97.905	81.859	65.786	-136.920	-35.322	1.883
4200	19.310	98.370	82.247	67.715	-136.887	-32.844	1.709
4300	19.334	98.824	82.627	69.648	-136.856	-30.367	1.543
4400	19.357	99.269	83.000	71.582	-136.830	-27.891	1.385
4500	19.378	99.704	83.367	73.519	-136.808	-25.417	1.234
4600	19.398	100.130	83.727	75.458	-136.788	-22.941	1.090
4700	19.417	100.548	84.080	77.399	-136.772	-20.466	0.952
4800	19.435	100.957	84.427	79.341	-136.761	-17.992	0.819
4900	19.451	101.358	84.769	81.285	-136.752	-15.517	0.692
5000	19.467	101.751	85.105	83.231	-136.748	-13.043	0.570
5100	19.482	102.137	85.435	85.179	-136.746	-10.568	0.453
5200	19.496	102.515	85.760	87.128	-136.749	-8.095	0.340
5300	19.510	102.886	86.079	89.078	-136.755	-5.620	0.232
5400	19.522	103.251	86.394	91.030	-136.764	-3.146	0.127
5500	19.534	103.610	86.704	92.982	-136.777	-0.671	0.027
5600	19.546	103.962	87.009	94.937	-136.792	1.804	-0.070
5700	19.557	104.308	87.309	96.892	-136.811	4.278	-0.164
5800	19.567	104.648	87.605	98.848	-136.832	6.754	-0.254
5900	19.577	104.983	87.897	100.805	-136.856	9.231	-0.342
6000	19.586	105.312	88.184	102.763	-136.884	11.705	-0.426

July 31, 1972 (NBS); June 30, 1977

HYDROGEN FLUORIDE DIMER (H_2F_2) (IDEAL GAS) GFW = 40.012606

F_2H_2

Point Group C_s
$S^\circ_{298.15}$ = 57.06 ± 2 gibbs/mol
Ground State Quantum Weight = 1

ΔHf°_0 = -135.4 ± 0.8 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -136.87 ± 0.8 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[4000](1)
[3400](1)
[1200](2)
[720](1)
[350](1)

Bond Distance: F-H = 0.92 Å H ... F = 1.87 Å $\sigma = 2$
Bond Angle: H ... F-H = 108° F-H ... F = 180°
Product of the Moments of Inertia: $I_AI_BI_C = 19.855 \times 10^{-117}\ g^3\ cm^6$

Heat of Formation

The enthalpy of 2 HF(g) → H_2F_2(g) was taken as the mean of the third law values which were obtained from the following equilibrium data. Briegleb and Strohmeier (1) measured the vapor density of associated HF(g) between 26 and 56°C and between 30 and 700 torr. Franck and Meyer (2) measured the heat capacity between -20 and 100°C and between 100 and 700 torr. Their second law values differed by 1.2 kcal/mol; and using the molecular constants discussed below gave respectively mean third law values which differed by 0.34 kcal/mol, a 0.14 kcal/mol temperature trend for Briegleb and Strohmeier, and a 0.02 kcal/mol temperature trend for Franck and Meyer. The ΔHf°_{298} of H_2F_2(g) was calculated using auxiliary JANAF data (3).

Heat Capacity and Entropy

The structure of the semi-rigid hydrogen bonded dimer is taken from Dyke et al. (4). Using bond distances and angles given by these authors we obtain $I_A = 1.2030 \times 10^{-40}$, $I_B = 1.2787 \times 10^{-38}$ and $I_C = 1.2907 \times 10^{-38}$ g cm^2. Dyke et al. (4) observed a doubling of the rotational energy levels of the dimer and attributed this to a tunneling motion involving breaking of the hydrogen bond, interchange of the two HF units, and formation of a new hydrogen bond. Thus there are two identical configurations for the dimer separated by a low energy barrier so that quantum mechanical tunneling occurs at a significant rate. Therefore the overall symmetry number is 2 even though the external symmetry number is 1.

Reliable experimental values of the vibrational frequencies of H_2F_2(g) are not available. The estimated frequencies are similar to those used for the higher polymers which were obtained from data on HF solid. The infrared absorption bands observed in the vapor (350 to 400 cm^{-1}, 700 to 800 cm^{-1}, and 1000-1200 cm^{-1} regions) are largely due to the higher polymers, such as the tetramer and hexamer. Calculated values (610, 443, and 144 cm^{-1}) were obtained from force constants given in a *paper on theory of molecular interactions of the HF polymers by Del Bene and Pople (5). The potential energy surface computed* for the dimer suggests very anharmonic low frequency motions for the external hydrogen (estimated at 600±200 cm^{-1}) and for the hydrogen bond stretching mode.

The National Bureau of Standards prepared this table (6) by critical analysis of data existing in 1972. Using our $I_AI_BI_C$ with other molecular constants and ΔHf° selected by NBS (6), we recalculate the table in terms of 1973 fundamental constants (7), 1975 atomic weights (8), and current JANAF reference states for the elements.

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7. CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, December, 1973.
8. IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

F_2H_2

PHOSPHORUS DIFLUORIDE (PF_2) F_2P
(IDEAL GAS) GFW=68.97056

T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-2.679	-112.231	-112.231	INFINITE
100	8.275	52.709	71.487	-1.878	-112.216	-113.268	247.543
200	9.485	58.804	63.762	-0.991	-112.347	-114.276	124.873
298	10.688	62.822	62.822	0.000	-112.523	-115.185	84.432
300	10.708	62.888	62.822	0.020	-112.526	-115.201	83.923
400	11.639	66.104	63.254	1.140	-112.708	-116.065	63.414
500	12.266	68.773	64.098	2.337	-112.886	-116.884	51.089
600	12.683	71.049	65.072	3.586	-113.068	-117.668	42.860
700	12.967	73.027	66.070	4.869	-113.266	-118.419	36.972
800	13.166	74.772	67.051	6.177	-133.903	-124.452	33.998
900	13.310	76.331	67.997	7.501	-133.886	-123.270	29.934
1000	13.416	77.739	68.902	8.837	-133.869	-122.092	26.683
1100	13.497	79.022	69.764	10.183	-133.850	-120.916	24.024
1200	13.560	80.199	70.586	11.536	-133.831	-119.742	21.808
1300	13.610	81.287	71.367	12.895	-133.811	-118.567	19.933
1400	13.650	82.297	72.112	14.258	-133.793	-117.395	18.326
1500	13.683	83.240	72.823	15.625	-133.775	-116.224	16.934
1600	13.709	84.124	73.502	16.994	-133.759	-115.056	15.716
1700	13.732	84.955	74.152	18.366	-133.743	-113.886	14.641
1800	13.751	85.741	74.774	19.740	-133.729	-112.719	13.686
1900	13.767	86.485	75.371	21.116	-133.715	-111.551	12.831
2000	13.781	87.191	75.944	22.494	-133.704	-110.387	12.062
2100	13.792	87.864	76.496	23.872	-133.694	-109.220	11.367
2200	13.803	88.506	77.027	25.252	-133.685	-108.054	10.734
2300	13.812	89.120	77.540	26.633	-133.678	-106.891	10.157
2400	13.820	89.708	78.035	28.014	-133.673	-105.727	9.628
2500	13.827	90.272	78.513	29.397	-133.667	-104.561	9.141
2600	13.833	90.814	78.976	30.780	-133.665	-103.398	8.691
2700	13.839	91.336	79.424	32.164	-133.664	-102.234	8.275
2800	13.845	91.840	79.858	33.548	-133.665	-101.069	7.889
2900	13.850	92.326	80.280	34.932	-133.667	-99.904	7.529
3000	13.855	92.795	80.689	36.318	-133.671	-98.741	7.193
3100	13.859	93.250	81.087	37.703	-133.676	-97.575	6.879
3200	13.864	93.690	81.474	39.090	-133.683	-96.412	6.585
3300	13.869	94.117	81.851	40.476	-133.691	-95.246	6.308
3400	13.874	94.531	82.218	41.863	-133.702	-94.081	6.047
3500	13.879	94.933	82.575	43.251	-133.713	-92.916	5.802
3600	13.884	95.324	82.924	44.639	-133.726	-91.752	5.570
3700	13.890	95.704	83.264	46.028	-133.740	-90.585	5.351
3800	13.896	96.075	83.597	47.417	-133.755	-89.417	5.143
3900	13.903	96.436	83.921	48.807	-133.772	-88.249	4.945
4000	13.911	96.788	84.239	50.198	-133.790	-87.085	4.758
4100	13.919	97.132	84.549	51.589	-133.809	-85.916	4.580
4200	13.928	97.467	84.852	52.981	-133.830	-84.745	4.410
4300	13.938	97.795	85.150	54.375	-133.850	-83.579	4.248
4400	13.949	98.116	85.441	55.769	-133.872	-82.407	4.093
4500	13.960	98.429	85.726	57.165	-133.895	-81.238	3.945
4600	13.973	98.736	86.005	58.561	-133.918	-80.070	3.804
4700	13.986	99.037	86.279	59.959	-133.941	-78.898	3.669
4800	14.001	99.331	86.548	61.358	-133.967	-77.726	3.539
4900	14.017	99.620	86.812	62.759	-133.990	-76.552	3.414
5000	14.033	99.904	87.071	64.162	-134.015	-75.380	3.295
5100	14.051	100.182	87.325	65.566	-134.040	-74.208	3.180
5200	14.070	100.455	87.575	66.972	-134.065	-73.037	3.070
5300	14.090	100.723	87.821	68.380	-134.090	-71.861	2.963
5400	14.111	100.986	88.062	69.790	-134.114	-70.688	2.861
5500	14.133	101.246	88.300	71.202	-134.138	-69.511	2.762
5600	14.155	101.500	88.533	72.617	-134.162	-68.337	2.667
5700	14.179	101.751	88.763	74.033	-134.186	-67.160	2.575
5800	14.204	101.998	88.989	75.453	-134.207	-65.986	2.486
5900	14.230	102.241	89.211	76.874	-134.229	-64.809	2.401
6000	14.256	102.480	89.431	78.299	-134.250	-63.632	2.318

June 30, 1962; June 30, 1977

PHOSPHORUS DIFLUORIDE (PF_2) (IDEAL GAS) GFW = 68.97056

F_2P

ΔHa_0° = [228.1 ± 6.0] kcal/mol
$S^\circ_{298.15}$ = [62.822 ± 0.2] gibbs/mol

ΔHf_0° = [-112.231 ± 5.0] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [-112.523 ± 5.0] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	2
[25000]	[2]
[28000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
831 (1)
[353](1)
852 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: P-F = [1.58] Å
Bond Angle: F-P-F = [99°]
Product of the Moments of Inertia: $I_AI_BI_C = [3.2842 \times 10^{-115}]\ g^3\ cm^6$

Heat of Formation

The adopted results at 0 K are ΔHf° = -112.2±5.0 kcal/mol, D°(PF-F) = 122.0±10.0 kcal/mol, and ΔHa° = 228.1±6.0 kcal/mol. We estimate ΔHf° such that the value gives $D_0^\circ(PF\text{-}F)/\Delta Ha_0^\circ = 0.535$. The value of this ratio is selected from those for SiF_2 (0.54±0.03) and SF_2(0.53±0.05) which are calculated from the most recent JANAF tables (1). Two previous estimates of ΔHf° are available for comparison. O'Hare (2) used the relationship $D^\circ(PF_2\text{-}F) = 1.1\ \bar{D}^\circ(PF_3)$ to obtain a ΔHf° of -115.7±5 kcal/mol. Corrected for the change in the phosphorus reference state (α-white to v-red), this estimate becomes -112.0 kcal/mol which agrees quite well with the results adopted here. An earlier JANAF table (3) gives $\Delta Hf^\circ(PF_2) = -104.7 \pm 15.0$ kcal/mol which was based on an estimated value for the D_0° of PF_3. We estimate that the uncertainty in the value of the ratio $D_0^\circ/\Delta Ha_0^\circ$ should not exceed ±0.06 which corresponds to an uncertainty in ΔHf° of ±5.0 kcal/mol.

The mean bond energy ($\bar{D}_0^\circ$) for PF_2 is 114.1 kcal/mol which lies midway between those (1) for PF_3 (119.4 kcal/mol) and PF_5(109.1 kcal/mol). At 298.15 K, we calculate ΔHf° as -112.5 kcal/mol.

Heat Capacity and Entropy

The results of electron spin resonance experiments (4, 5) and molecular orbital calculations (4, 6, and 7) are consistent with PF_2 having C_{2v} symmetry; however, no experimental determination of the structural parameters has been reported. Numerous values for the bond length and angle have been proposed based on energy-optimization (6, 7) and other estimation techniques (2, 4, 8, and 9). These estimates are widely scattered with the bond lengths ranging from 1.52-1.73 Å and the bond angles ranging from 98.6-112°. We prefer to use molecular parameters similar to those measured (10) for the related molecule PF_2H. The adopted values appear quite reasonable by comparison with structural data (1) for SiF_2 and SF_2. The principal moments of inertia are: $I_A = 1.2090 \times 10^{-38}$, $I_B = 9.1063 \times 10^{-39}$, and $I_C = 2.9832 \times 10^{-39}$ g cm^2.

The two stretching frequencies (ν_1 and ν_3) have been observed (11) in the infrared spectrum of PF_2 formed in an argon matrix by photolysis of PF_2H. The adopted values are rounded to the nearest cm^{-1}. The bending frequency (ν_2) is calculated from the force constant $f_\alpha/r^2 = 0.495$ mdyn/Å. We obtain the bending force constant from the ratio $f_r/(f_\alpha/r^2)$ equal to 9.59 which is the value calculated for SiF_2 (1).

The ground state is expected to be $^2B_1$, as shown by Wei et al. (4). We assume that the upper electronic levels and their correponding quantum weights are the same as those previously estimated for the isoelectronic SF_2^+ ion. The procedure used to estimate these levels is thoroughly discussed on the SF_2^+ table (1).

This table essentially updates the functions previously tabulated by O'Hare (2). The most significant difference is that our results are based on solid phosphorus (Red, V) as the reference state below 704 K rather than the ideal diatomic gas selected by O'Hare (2).

References

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F_2P

PHOSPHORUS DIFLUORIDE UNIPOSITIVE ION (PF_2^+) F_2P^+
(IDEAL GAS) GFW=68.97001

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.678	115.861		
100							
200							
298	10.668	61.484	61.484	0.000	117.049	113.299	-83.049
300	10.688	61.550	61.484	0.020	117.055	113.275	-82.520
400	11.616	64.760	61.915	1.138	117.368	111.969	-61.176
500	12.246	67.424	62.758	2.333	117.685	110.583	-48.335
600	12.666	69.697	63.730	3.580	117.998	109.132	-39.751
700	12.953	71.672	64.726	4.862	118.295	107.630	-33.603
800	13.155	73.416	65.706	6.168	98.153	100.776	-27.530
900	13.300	74.974	66.650	7.491	98.666	101.075	-24.544
1000	13.408	76.381	67.554	8.827	99.180	101.314	-22.142
1100	13.491	77.663	68.416	10.172	99.695	101.502	-20.166
1200	13.555	78.840	69.236	11.524	100.209	101.643	-18.511
1300	13.605	79.927	70.017	12.882	100.725	101.743	-17.104
1400	13.646	80.936	70.762	14.245	101.240	101.802	-15.892
1500	13.679	81.879	71.472	15.611	101.754	101.825	-14.836
1600	13.706	82.763	72.150	16.980	102.267	101.812	-13.907
1700	13.729	83.594	72.799	18.352	102.779	101.769	-13.083
1800	13.748	84.380	73.421	19.726	103.290	101.694	-12.347
1900	13.764	85.123	74.017	21.102	103.801	101.593	-11.686
2000	13.778	85.830	74.590	22.479	104.308	101.461	-11.087
2100	13.790	86.502	75.142	23.857	104.815	101.308	-10.543
2200	13.801	87.144	75.673	25.237	105.320	101.129	-10.046
2300	13.810	87.758	76.185	26.617	105.823	100.925	-9.590
2400	13.819	88.346	76.680	27.999	106.326	100.701	-9.170
2500	13.826	88.910	77.158	29.381	106.828	100.459	-8.782
2600	13.833	89.452	77.620	30.764	107.327	100.193	-8.422
2700	13.839	89.975	78.068	32.148	107.824	99.908	-8.087
2800	13.845	90.478	78.502	33.532	108.320	99.607	-7.775
2900	13.851	90.964	78.924	34.917	108.816	99.288	-7.482
3000	13.856	91.434	79.333	36.302	109.308	98.950	-7.208
3100	13.862	91.888	79.731	37.688	109.801	98.599	-6.951
3200	13.868	92.328	80.117	39.074	110.289	98.227	-6.708
3300	13.874	92.755	80.494	40.462	110.780	97.844	-6.480
3400	13.881	93.169	80.861	41.849	111.266	97.444	-6.264
3500	13.888	93.572	81.218	43.238	111.753	97.031	-6.059
3600	13.896	93.963	81.567	44.627	112.238	96.602	-5.864
3700	13.905	94.344	81.907	46.017	112.721	96.160	-5.680
3800	13.915	94.715	82.239	47.408	113.205	95.708	-5.504
3900	13.925	95.077	82.564	48.800	113.687	95.243	-5.337
4000	13.937	95.429	82.881	50.193	114.168	94.761	-5.177
4100	13.950	95.774	83.191	51.588	114.650	94.271	-5.025
4200	13.964	96.110	83.495	52.983	115.128	93.770	-4.879
4300	13.979	96.439	83.792	54.380	115.608	93.253	-4.740
4400	13.995	96.760	84.083	55.779	116.088	92.730	-4.606
4500	14.013	97.075	84.368	57.179	116.566	92.193	-4.477
4600	14.032	97.383	84.648	58.582	117.047	91.644	-4.354
4700	14.053	97.685	84.922	59.986	117.526	91.087	-4.235
4800	14.075	97.981	85.191	61.392	118.004	90.520	-4.121
4900	14.098	98.272	85.455	62.801	118.486	89.945	-4.012
5000	14.122	98.557	85.714	64.212	118.966	89.357	-3.906
5100	14.148	98.837	85.969	65.625	119.446	88.759	-3.804
5200	14.175	99.112	86.219	67.042	119.929	88.150	-3.705
5300	14.204	99.382	86.465	68.460	120.411	87.536	-3.610
5400	14.233	99.648	86.706	69.882	120.896	86.911	-3.517
5500	14.264	99.909	86.944	71.307	121.382	86.279	-3.428
5600	14.296	100.166	87.178	72.735	121.867	85.634	-3.342
5700	14.329	100.420	87.408	74.166	122.355	84.985	-3.258
5800	14.363	100.669	87.635	75.601	122.846	84.323	-3.177
5900	14.398	100.915	87.858	77.039	123.338	83.656	-3.099
6000	14.434	101.157	88.077	78.480	123.830	82.980	-3.022

June 30, 1977

ΔHa_0° = 241.9 ± 10.0 kcal/mol
$S_{298.15}^\circ$ = [61.5 ± 0.2] gibbs/mol

ΔHf_0° = 115.861 ± 8.0 kcal/mol
$\Delta Hf_{298.15}^\circ$ = 117.049 ± 8.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[1]
[25000]	[3]
[40000]	[1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[840](1)
[350](1)
[860](1)

Point Group: [C_{2v}] σ = [2]
Bond Distance: P-F = [1.59] Å
Bond Angle: F-P-F = [101]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [3.4118×10^{-115}] g^3 cm^6

Heat of Formation

A summary of the information available on the appearance potential (AP) of PF_2^+ from PF_3 is presented below. We analyze these electron-impact results using the expression ΔHr_0° = AP-E* by assuming that the dissociative ionization process is $PF_3(g) + e^- = PF_2^+(g) + F(g) + 2\ e^-$. Values of ΔHf° and the ionization potential (IP) are derived by setting E* in the above expression equal to zero. As a result, the values are listed in the table as inequalities to emphasize that they are limiting (upper) values.

Investigator	Method[a]	AP(PF_2^+/PF_3), eV	ΔHf_0°(PF_2^+,g), kcal/mol	IP(PF_2) eV
Harland et al. (1)	EI	15.4±0.2	<112.78	<9.76
Stafford (2)	EI	15.7±0.5	<119.70	<10.06
Torgerson and Westmore (3)	EI	15.5±0.2	<115.09	<9.86
Dean et al. (4)	EI	13.5	<68.97	<7.86

[a] EI = electron-impact

The results derived from the first three studies (1-3) are in excellent accord, and we adopt the mean values of ΔHf° = 115.861±8.0 kcal/mol and IP = 9.89 eV. Dean et al. (4) were unable to offer an explanation as to why their results were significantly lower than the other literature data. This study (4) indicates that IP(PF_2)<IP(PCl_2) (3) which we believe is very unlikely. Harland et al. (1) have reported the AP for PF_2^+ from PF_2CN as 13.4±0.2 eV, suggesting the possibility that the precursor responsible for the PF_2^+ ion in the measurements of Dean et al. (4) was PF_2CN rather than PF_3. A MO study (5) gave IP(PF_2) = 9.88 eV based on IP(P) = 10.98 eV. Recalculation of their results using a more recent value of IP(P) = 10.486 eV (6) gives IP(PF_2) = 9.39 eV. Our adopted value of IP (9.89 eV) is close to that for atomic phosphorus (10.49 eV). This is consistent with the results of electron spin resonance experiments (7, 8) and MO calculations (5, 7, 9, and 10) which show that the ionizing orbital is slightly antibonding and located primarily on the phosphorus atom.

The mean bond energy ($\bar{D}_0^\circ$) (products $P^+(g)+2F(g)$) is 120.9 kcal/mol which when compared with that for PF_2(114.1 kcal/mol, 11) suggests that the bonding is somewhat stronger in the positive ion. This predicted increase in bond strength upon ionization is also consistent with the antibonding nature of the ionizing orbital. ΔHf° at 298.15 K is calculated to be 117.049 kcal/mol.

Heat Capacity and Entropy

The molecular parameters and vibrational frequencies are assumed to lie between those for PF_2 and SiF_2 (11). The electronic levels and quantum weights are estimated by analogy with those for the isoelectronic molecule SiF_2 (11). The principal moments of inertia are: $I_A = 1.2395 \times 10^{-38}$, $I_B = 9.4970 \times 10^{-39}$, and $I_C = 2.8983 \times 10^{-39}$ g cm^2.

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9. D. Kilcast and C. Thomson, J. Chem. Soc., Faraday Trans. II, 68, 435 (1972).
10. A. Hudson and J. T. Wiffen, Chem. Phys. Lett. 29, 113 (1974).
11. JANAF Thermochemical Tables: PF_2(g), 8-30-77; SiF_2(g), 6-30-76.

PHOSPHORUS DIFLUORIDE UNINEGATIVE ION (PF_2^-) F_2P^- (IDEAL GAS). GFW=68.97111

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.681	-146.822		
100							
200							
298	10.711	61.485	61.485	0.000	-148.594	-149.370	109.490
300	10.732	61.551	61.485	0.020	-148.606	-149.375	108.818
400	11.664	64.775	61.918	1.143	-149.282	-149.529	81.698
500	12.288	67.449	62.765	2.342	-149.955	-149.513	65.351
600	12.701	69.729	63.740	3.593	-150.632	-149.363	54.405
700	12.982	71.709	64.740	4.878	-151.324	-149.096	46.549
800	13.178	73.456	65.723	6.187	-172.457	-154.040	42.081
900	13.320	75.017	66.670	7.512	-172.936	-151.708	36.839
1000	13.425	76.426	67.576	8.849	-173.415	-149.325	32.635
1100	13.504	77.709	68.440	10.196	-173.892	-146.894	29.185
1200	13.566	78.887	69.262	11.550	-174.368	-144.418	26.302
1300	13.615	79.975	70.045	12.909	-174.845	-141.901	23.855
1400	13.655	80.985	70.791	14.272	-175.324	-139.350	21.753
1500	13.687	81.929	71.502	15.640	-175.802	-136.763	19.926
1600	13.713	82.813	72.182	17.010	-176.282	-134.146	18.323
1700	13.735	83.645	72.832	18.382	-176.762	-131.496	16.905
1800	13.754	84.430	73.455	19.756	-177.245	-128.820	15.641
1900	13.769	85.174	74.052	21.133	-177.727	-126.116	14.506
2000	13.783	85.881	74.626	22.510	-178.214	-123.390	13.483
2100	13.795	86.554	75.178	23.889	-178.700	-120.635	12.554
2200	13.805	87.196	75.710	25.269	-179.187	-117.857	11.708
2300	13.814	87.810	76.223	26.650	-179.677	-115.060	10.933
2400	13.821	88.398	76.718	28.032	-180.168	-112.241	10.221
2500	13.828	88.962	77.196	29.414	-180.660	-109.399	9.563
2600	13.834	89.505	77.659	30.797	-181.155	-106.540	8.955
2700	13.840	90.027	78.108	32.181	-181.650	-103.660	8.391
2800	13.845	90.530	78.542	33.565	-182.148	-100.763	7.865
2900	13.849	91.016	78.964	34.950	-182.646	-97.846	7.374
3000	13.853	91.486	79.374	36.335	-183.148	-94.915	6.914
3100	13.857	91.940	79.772	37.721	-183.649	-91.964	6.483
3200	13.860	92.380	80.159	39.107	-184.153	-89.000	6.078
3300	13.863	92.806	80.536	40.493	-184.658	-86.017	5.697
3400	13.866	93.220	80.903	41.879	-185.167	-83.021	5.336
3500	13.868	93.622	81.261	43.266	-185.676	-80.010	4.996
3600	13.871	94.013	81.609	44.653	-186.187	-76.985	4.674
3700	13.873	94.393	81.950	46.040	-186.699	-73.944	4.368
3800	13.875	94.763	82.282	47.427	-187.213	-70.888	4.077
3900	13.876	95.124	82.607	48.815	-187.729	-67.819	3.800
4000	13.878	95.475	82.924	50.203	-188.247	-64.741	3.537
4100	13.880	95.818	83.234	51.590	-188.767	-61.646	3.286
4200	13.881	96.152	83.538	52.978	-189.288	-58.536	3.046
4300	13.882	96.479	83.835	54.367	-189.810	-55.420	2.817
4400	13.884	96.798	84.126	55.755	-190.335	-52.286	2.597
4500	13.885	97.110	84.411	57.143	-190.863	-49.144	2.387
4600	13.886	97.415	84.691	58.532	-191.390	-45.992	2.185
4700	13.887	97.714	84.965	59.921	-191.918	-42.822	1.991
4800	13.888	98.006	85.233	61.309	-192.452	-39.645	1.805
4900	13.889	98.292	85.497	62.698	-192.984	-36.454	1.626
5000	13.890	98.573	85.756	64.087	-193.520	-33.254	1.454
5100	13.890	98.848	86.010	65.476	-194.056	-30.044	1.287
5200	13.891	99.118	86.259	66.865	-194.595	-26.825	1.127
5300	13.892	99.382	86.504	68.254	-195.136	-23.593	0.973
5400	13.893	99.642	86.745	69.644	-195.677	-20.352	0.824
5500	13.893	99.897	86.982	71.033	-196.221	-17.098	0.679
5600	13.894	100.147	87.215	72.422	-196.767	-13.837	0.540
5700	13.894	100.393	87.444	73.812	-197.314	-10.565	0.405
5800	13.895	100.635	87.669	75.201	-197.863	-7.285	0.275
5900	13.895	100.872	87.891	76.591	-198.413	-3.995	0.148
6000	13.896	101.106	88.109	77.980	-198.967	-0.694	0.025

June 30, 1977

PHOSPHORUS DIFLUORIDE UNINEGATIVE ION (PF_2^-) (IDEAL GAS) GFW = 68.97111

F_2P^-

ΔHa_0° = [184.3 ± 17.5] kcal/mol
$S^\circ_{298.15}$ = [61.5 ± 0.2] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf_0° = [-146.822 ± 16.5] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [-148.594 ± 16.5] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[820](1)
[355](1)
[845](1)

Point Group [C_{2v}] σ = [2]
Bond Distance: P-F = [1.59] Å
Bond Angle: F-P-F = [98]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [3.4080×10^{-115}] g^3 cm^6

Heat of Formation

The PF_2^- anion has been observed in the negative ion mass spectra of PF_3 (1) and PF_2CN (2). Both studies included thermochemical calculations on plausible ion formation processes, showing that the measured appearance potentials contained large excess energy contributions. At present, definite values can not be assigned to these contributions; thus, their studies are of little value in defining ΔHf°.

Two estimates of the electron affinity (EA) of PF_2 have been reported (2, 3). Harland et al. (2) considered differences in bond energies for diatomic and triatomic species to obtain a value of EA(PF_2) = 1.4 eV. Rescaled CNDO calculations (3) have led to an EA = 1.71 eV. JANAF data (4) on the S-F system indicate that the EA values alternate between the even- and odd-electron molecules, with the odd-electron molecules having the higher EA values. Assuming the same trend is followed in the P-F system, we predict that EA(PF_2) > EA(PF) which is equal to 1.1±0.5 eV (4). We adopt an EA of 1.5±0.5 eV for the reaction PF_2^-(g) = PF_2(g) + e^- at 0 K which leads to ΔHf_0°(PF_2^-, g) = -146.822±16.5 kcal/mol with ΔHf_0°(PF_2, g) = -112.23±5.0 kcal/mol (4). The adopted value of EA is close to that for atomic phosphorus (0.77±0.05 eV, 5). This is in agreement with results of MO calculations (3, 6) and electron spin resonance experiments (6, 7) which show that the electron captured by PF_2 goes into an antibonding orbital which is located primarily on the phosphorus atom.

ΔHf° at 298.15 K and the fluoride-ion affinity (IA) are calculated to be -148.594 kcal/mol and 78.2 kcal/mol, respectively. The mean bond energy ($\bar{D}_0^\circ$) (products P(g)+F(g)+F^-(g)) is 92.2 kcal/mol which is 21.9 kcal/mol less than that for PF_2 (114.1 kcal/mol, 4). The predicted decrease in the bond strength for the anion is also consistent with the antibonding nature of the electron orbital.

Heat Capacity and Entropy

The molecular parameters and vibrational frequencies are assumed to lie between those for PF_2 and SF_2 (4). The ground state is assumed to be a singlet since PF_2^- has no unpaired electrons. Also, we neglect excited states since these probably lie at energies which would not contribute to the partition function (see the table for the isoelectronic species SF_2). The principal moments of inertia are: $I_A = 1.2168 \times 10^{-38}$, $I_B = 9.0851 \times 10^{-39}$, and $I_C = 3.0828 \times 10^{-39}$ g cm^2.

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SULFUR DIFLUORIDE UNIPOSITIVE ION (SF_2^+) F_2S^+

(IDEAL GAS) GFW=70.05625

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-2.685	166.872		
100							
200							
298	10.740	62.957	62.957	0.000	167.875	164.337	-120.462
300	10.761	63.023	62.957	0.020	167.880	164.315	-119.703
400	11.690	66.255	63.391	1.145	167.633	163.105	-89.116
500	12.309	68.934	64.239	2.347	167.587	161.978	-70.801
600	12.718	71.217	65.217	3.600	167.648	160.853	-58.591
700	12.995	73.200	66.219	4.887	167.780	159.734	-49.871
800	13.189	74.948	67.203	6.196	154.895	157.305	-42.974
900	13.329	76.510	68.152	7.523	155.405	157.576	-38.265
1000	13.432	77.920	69.059	8.861	155.914	157.790	-34.485
1100	13.511	79.204	69.924	10.208	156.423	157.952	-31.382
1200	13.572	80.383	70.747	11.562	156.932	158.069	-28.788
1300	13.620	81.471	71.531	12.922	157.441	158.145	-26.587
1400	13.658	82.482	72.277	14.286	157.948	158.179	-24.693
1500	13.690	83.425	72.989	15.654	158.454	158.178	-23.046
1600	13.716	84.309	73.670	17.024	158.957	158.143	-21.601
1700	13.738	85.142	74.320	18.397	159.460	158.077	-20.322
1800	13.756	85.927	74.943	19.771	159.959	157.979	-19.181
1900	13.771	86.672	75.541	21.148	160.459	157.858	-18.158
2000	13.785	87.378	76.116	22.526	160.956	157.709	-17.234
2100	13.796	88.051	76.668	23.905	161.449	157.531	-16.394
2200	13.806	88.693	77.200	25.285	161.941	157.334	-15.630
2300	13.815	89.307	77.713	26.666	162.431	157.114	-14.929
2400	13.823	89.895	78.209	28.048	162.919	156.873	-14.285
2500	13.830	90.460	78.687	29.430	163.404	156.611	-13.691
2600	13.836	91.002	79.151	30.814	163.887	156.329	-13.141
2700	13.842	91.525	79.599	32.198	164.369	156.030	-12.630
2800	13.847	92.028	80.034	33.582	164.848	155.710	-12.154
2900	13.852	92.514	80.456	34.967	165.325	155.378	-11.710
3000	13.856	92.984	80.866	36.352	165.798	155.025	-11.294
3100	13.861	93.438	81.264	37.738	166.271	154.658	-10.903
3200	13.866	93.878	81.652	39.124	166.740	154.276	-10.537
3300	13.870	94.305	82.029	40.511	167.209	153.878	-10.191
3400	13.875	94.719	82.396	41.899	167.676	153.470	-9.865
3500	13.880	95.121	82.754	43.286	168.138	153.044	-9.557
3600	13.885	95.512	83.103	44.675	168.601	152.608	-9.265
3700	13.891	95.893	83.443	46.063	169.059	152.157	-8.988
3800	13.897	96.263	83.776	47.453	169.518	151.695	-8.724
3900	13.904	96.625	84.101	48.843	169.973	151.216	-8.474
4000	13.912	96.977	84.418	50.234	170.427	150.734	-8.236
4100	13.920	97.320	84.729	51.625	170.879	150.234	-8.008
4200	13.929	97.656	85.033	53.018	171.330	149.726	-7.791
4300	13.939	97.984	85.330	54.411	171.780	149.207	-7.584
4400	13.949	98.304	85.621	55.805	172.226	148.677	-7.385
4500	13.961	98.618	85.907	57.201	172.672	148.135	-7.194
4600	13.974	98.925	86.186	58.598	173.118	147.584	-7.012
4700	13.987	99.226	86.460	59.996	173.562	147.025	-6.837
4800	14.002	99.520	86.729	61.395	174.005	146.456	-6.668
4900	14.017	99.809	86.993	62.796	174.447	145.882	-6.507
5000	14.034	100.092	87.253	64.199	174.887	145.289	-6.351
5100	14.052	100.370	87.507	65.603	175.327	144.692	-6.200
5200	14.070	100.643	87.757	67.009	175.767	144.091	-6.056
5300	14.090	100.912	88.003	68.417	176.207	143.478	-5.916
5400	14.111	101.175	88.244	69.827	176.645	142.853	-5.782
5500	14.133	101.434	88.482	71.239	177.083	142.225	-5.651
5600	14.156	101.689	88.715	72.654	177.521	141.589	-5.526
5700	14.180	101.940	88.945	74.070	177.958	140.942	-5.404
5800	14.204	102.187	89.171	75.490	178.398	140.290	-5.286
5900	14.230	102.430	89.394	76.911	178.836	139.624	-5.172
6000	14.257	102.669	89.613	78.336	179.274	138.959	-5.062

Dec. 31, 1976

SULFUR DIFLUORIDE UNIPOSITIVE ION (SF_2^+) (IDEAL GAS) GFW = 70.05625

Point Group [C_{2v}]

$S°_{298.15}$ = [62.96 ± 0.10] gibbs/mol

$\Delta Hf°_0$ = 166.9 ± 11.0 kcal/mol F_2S^+

$\Delta Hf°_{298.15}$ = 167.9 ± 11.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$^2B_1$]	[0]	[2]
[$^2A_1$]	[25000]	[2]
[$^2A_1$]	[28000]	[2]
[$^2A_2$]	[30000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[807](1)
[352](1)
[844](1)

Bond Distance: S-F = [1.59] Å

σ = [2]

Bond Angle: F-S-F = [100]°

Product of Moments of Inertia: $I_AI_BI_C$ = [3.4931 x 10^{-115}] g^3 cm^6

Heat of Formation

The adopted value of $\Delta Hf°_0$ = 166.9±11.0 kcal/mol is calculated as the sum of $\Delta Hf°_0(SF_2,g)$ = -70.42±4.0 kcal/mol (1) and the ionization potential IP(SF_2) = 10.29±0.3 eV (237.29 kcal/mol). The value of IP is the electron-impact appearance potential (AP) of SF_2^+ from SF_2 which was measured by Hildenbrand (2) in a mass spectral study of the products formed from the reaction of SF_6 with C at about 1500 K. We increase the uncertainty in IP to ±0.3 eV from the value (±0.1 eV) assigned by Hildenbrand (2) since recent photoelectron (PE) spectrometric studies on the related dihalides SCl_2 (3) and SiF_2 (4) show that their adiabatic ionization potentials lie 0.22 and 0.40 eV, respectively, below the corresponding vertical values. The adopted value of IP is bracketed by the accurately known adiabatic values for SCl_2(9.45±0.05 eV, 3) and SiF_2(10.78±0.05 eV, 4) and is close to the IP for atomic sulfur (10.36 eV, 5). MO calculations (6) predict IP (SF_2) = 9.6 eV.

Several fragmention appearance potentials for the ion-molecule systems SF_2^+/SF_6 (2, 7), SF_2^+/SF_4 (2), and SF_2^+/NSF_3 (8) have been reported and provide alternate paths leading to ΔHf° once the ion formation processes are assigned. We use plausible reactions for the formation of SF_2^+ to calculate ΔHf° values which cover the range 146-342 kcal/mol. The scatter in these values indicate that either the dissociative ionization processes have been incorrectly assigned, or perhaps more likely, the processes involve excess kinetic and/or excitation energies.

Our ΔHf° value at 298.15 K is 167.9 kcal/mol. In addition, we find that the primary bond dissociation energy $D°_0(SF^+-F)$ is 87.1 kcal/mol which when compared with JANAF $D°_0$ values (1) for SF_2(91.7 kcal/mol) and SF_2^-(68.7 kcal/mol) indicates that the trend is $D°_0(SF_2^+) \simeq D°_0(SF_2) > D°_0(SF_2^-)$. Similar trends in bond dissociation energies have been reported (9) for the ions and neutrals of phosphorus and nitrogen difluorides.

Heat Capacity and Entropy

According to the Walsh correlation diagram (10) for non-hydride AB_2 molecules, the most loosely bound pair of electrons in SF_2 is in a b_1'' orbital. The Walsh prediction is supported by the results of theoretical studies (3, 11, and 12) and assignments of the bands in the PE spectra (3, 12) for the isoelectronic molecules SCl_2, OF_2, and OCl_2. The b_1'' orbital is S-F antibonding and F-F bonding, but its binding energy (10) shows only a small positive angular dependence. We would expect then that removal of an electron from this orbital should be accompanied by a small increase in the bond angle. We adopt a bond angle of 100° which corresponds to roughly a 2° increase from that for SF_2 (1). The antibonding nature of the b_1'' orbital is also expected to produce upon ionization a decrease in the S-F bond length. However, a comparison of the S-F bond strengths in $SF_2^+(D°_0$ = 87.1 kcal/mol) and $SF_2(D°_0$ = 91.7 kcal/mol) would seem to indicate that any changes in molecular parameters are relatively small. We adopt $r_e(SF_2^+)$ = 1.59 Å which amounts to only a 0.002 Å reduction from that for SF_2 (1). Our estimated molecular parameters appear reasonable in comparison with those for SiF_2 (1). The individual moments of inertia are: $I_A = 1.2375 \times 10^{-38}$, $I_B = 9.3597 \times 10^{-39}$, and $I_C = 3.0157 \times 10^{-39}$ g cm^2.

We calculate the vibrational frequencies from the force constants f_r = 4.7 and f_α/r^2 = 0.49 mdyn/Å. The stretching force constant (f_r) is estimated from that for SiF_2 (1) and PF_2 (13). We obtain the bending force constant from the ratio $f_r/(f_\alpha/r^2)$ = 9.59 which is the value calculated for SiF_2 (1). The changes in our frequencies on going from SF_2 to SF_2^+ are insignificant, in agreement with the view that the bonding in the two molecules is very similar.

The electronic configurations of the ground and excited states are predicted from the Walsh correlation diagram (10). We also predict from this diagram that the two $^2A_1 \leftarrow {}^2B_1$ spacings will strongly depend on the bond angle. This is supported at least for the first spacing by PE studies (3, 12) on SCl_2, OCl_2, and OF_2. Based on the similarity in the bond angles for OF_2 (3) and SF_2 (1), we estimate the first $^2A_1 \leftarrow {}^2B_1$ spacing to be somewhat greater than that for OF_2^+ (23471 cm^{-1}, 12). The PE spectra for SCl_2 (3) and OF_2 (12) do not provide support for the existence of a second $^2A_1$ state. This state has been observed, however, in the PE spectrum of OCl_2 (12). These results show for OCl_2^+ that the second $^2A_1$ state lies 2258 cm^{-1} above the first $^2A_1$ state. We include a second $^2A_1$ state at 28000 cm^{-1} for SF_2^+ with a $^2A_1$ - $^2A_1$ spacing of 3000 cm^{-1}. We estimate a somewhat larger spacing for SF_2^+ based on the fact that the bond angle in SF_2^+ is predicted to be smaller than that for OCl_2^+. The relative term value for the upper most state ($^2A_2$) is estimated from that for OF_2^+ (12).

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F_2S^+

SULFUR DIFLUORIDE UNINEGATIVE ION (SF_2^-) F_2S^-

(IDEAL GAS) GFW=70.05735

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.898	-93.480		
100							
200							
298	11.989	63.894	63.894	0.000	-95.226	-96.069	70.420
300	12.007	63.968	63.894	0.022	-95.237	-96.074	69.990
400	12.707	67.529	64.375	1.262	-96.363	-96.243	52.585
500	13.094	70.410	65.303	2.553	-97.314	-96.103	42.007
600	13.325	72.819	66.360	3.875	-98.178	-95.779	34.887
700	13.471	74.885	67.434	5.216	-98.984	-95.289	29.751
800	13.570	76.691	68.481	6.568	-112.820	-95.977	26.220
900	13.639	78.293	69.484	7.929	-113.270	-93.845	22.789
1000	13.689	79.733	70.438	9.295	-113.727	-91.662	20.033
1100	13.726	81.039	71.343	10.666	-114.188	-89.435	17.769
1200	13.755	82.235	72.202	12.040	-114.651	-87.162	15.874
1300	13.778	83.337	73.016	13.417	-115.119	-84.851	14.265
1400	13.796	84.359	73.790	14.795	-115.592	-82.506	12.880
1500	13.810	85.311	74.527	16.176	-116.067	-80.127	11.675
1600	13.822	86.203	75.229	17.557	-116.545	-77.714	10.615
1700	13.832	87.041	75.900	18.940	-117.026	-75.272	9.677
1800	13.841	87.832	76.541	20.324	-117.511	-72.805	8.840
1900	13.848	88.580	77.155	21.708	-117.998	-70.306	8.087
2000	13.854	89.291	77.744	23.093	-118.488	-67.783	7.407
2100	13.859	89.967	78.310	24.479	-118.980	-65.238	6.789
2200	13.863	90.612	78.855	25.865	-119.476	-62.665	6.225
2300	13.867	91.228	79.379	27.252	-119.974	-60.072	5.708
2400	13.871	91.818	79.886	28.638	-120.476	-57.457	5.232
2500	13.874	92.385	80.374	30.026	-120.979	-54.822	4.792
2600	13.877	92.929	80.847	31.413	-121.485	-52.164	4.385
2700	13.879	93.453	81.304	32.801	-121.993	-49.488	4.006
2800	13.881	93.957	81.747	34.189	-122.504	-46.797	3.653
2900	13.883	94.444	82.176	35.577	-123.018	-44.081	3.322
3000	13.885	94.915	82.593	36.966	-123.535	-41.352	3.013
3100	13.887	95.370	82.998	38.354	-124.052	-38.604	2.722
3200	13.888	95.811	83.392	39.743	-124.574	-35.839	2.448
3300	13.889	96.239	83.774	41.132	-125.097	-33.059	2.189
3400	13.891	96.653	84.147	42.521	-125.623	-30.260	1.945
3500	13.892	97.056	84.510	43.910	-126.153	-27.449	1.714
3600	13.893	97.447	84.864	45.299	-126.682	-24.619	1.495
3700	13.894	97.828	85.209	46.688	-127.217	-21.777	1.286
3800	13.894	98.199	85.546	48.078	-127.752	-18.919	1.088
3900	13.895	98.560	85.876	49.467	-128.292	-16.052	0.900
4000	13.896	98.911	86.197	50.857	-128.831	-13.162	0.719
4100	13.897	99.254	86.511	52.247	-129.374	-10.266	0.547
4200	13.897	99.589	86.819	53.636	-129.921	-7.354	0.383
4300	13.898	99.916	87.120	55.026	-130.468	-4.429	0.225
4400	13.898	100.236	87.414	56.416	-131.020	-1.492	0.074
4500	13.899	100.548	87.702	57.806	-131.572	1.459	-0.071
4600	13.899	100.854	87.985	59.196	-132.127	4.420	-0.210
4700	13.900	101.153	88.262	60.586	-132.685	7.394	-0.344
4800	13.900	101.445	88.534	61.976	-133.245	10.381	-0.473
4900	13.901	101.732	88.800	63.366	-133.808	13.382	-0.597
5000	13.901	102.013	89.062	64.756	-134.373	16.389	-0.716
5100	13.901	102.288	89.318	66.146	-134.941	19.408	-0.832
5200	13.902	102.558	89.570	67.536	-135.511	22.445	-0.943
5300	13.902	102.823	89.818	68.926	-136.083	25.487	-1.051
5400	13.902	103.083	90.061	70.316	-136.659	28.538	-1.155
5500	13.903	103.338	90.300	71.707	-137.234	31.604	-1.256
5600	13.903	103.588	90.535	73.097	-137.815	34.681	-1.354
5700	13.903	103.834	90.766	74.487	-138.398	37.766	-1.448
5800	13.903	104.076	90.994	75.878	-138.981	40.862	-1.540
5900	13.904	104.314	91.217	77.268	-139.568	43.961	-1.628
6000	13.904	104.547	91.438	78.658	-140.157	47.082	-1.715

Dec. 31, 1976

SULFUR DIFLUORIDE UNINEGATIVE ION (SF_2^-) (IDEAL GAS) GFW = 70.05735

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [63.9 ± 0.2] gibbs/mol
Ground State Quantum Weight = [2]

ΔHf°_0 = [-93.5 ± 15.5] kcal/mol F_2S^-
$\Delta Hf^\circ_{298.15}$ = [-95.2 ± 15.5] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[479](1)
[286](1)
[594](1)

Bond Distance: S-F = [1.63] Å σ = [2]
Bond Angle: F-S-F = [130]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [2.8563 x 10^{-115}] g^3 cm^6

Heat of Formation

We calculate the adopted value of ΔHf°_0 = -93.5±15.5 kcal/mol as the difference between $\Delta Hf^\circ_0(SF_2,g)$ = -70.42±4.0 kcal/mol (1) and an estimate of the electron affinity of $EA(SF_2)$ = 1.0±0.5 eV (23.06 kcal/mol). The value of EA is estimated from a consideration of trends in the electron affinities for other S-F species (1). These data follow a regular pattern among the even- and odd-electron molecules, with the odd-electron molecules having, as expected, the higher electron affinities. Within each even- and odd-electron series, the EA values progressively increase as the number of fluorine atoms are increased in the ions. The only other estimate available to compare with our result is EA = 1.2±0.5 eV. This estimate was made by Hildenbrand (2) who used a method similar to ours. Our ΔHf° value corresponds to a fluoride-ion affinity for SF of IA = 36.4±17.0 kcal/mol, and ΔHf° at 298.15 K is -95.2 kcal/mol. In addition, we find that the primary bond dissociation energy $D^\circ_0(SF^- - F)$ is 68.7 kcal/mol which when compared with the values for SF_2(91.7 kcal/mol) and SF_2^+(87.1 kcal/mol) indicates that the trend is $D^\circ_0(SF_2^+) \simeq D^\circ_0(SF_2) > D^\circ_0(SF_2^-)$. Similar trends in bond dissociation energies have been reported (3) for the ions and neutrals of phosphorus and nitrogen difluorides.

JANAF data (1) predict that SF_2^- should be reasonably stable at moderate temperatures, with dissociative ionization ($SF + F^-$) becoming thermodynamically favorable above 1500 K. These predictions are qualitatively supported by the observations of Harland and Thynne (4, 5) who have observed SF_2^- in the negative ion mass spectra of SF_6, SF_4, and SF_5Cl. The temperature of the ion source was reported as around 325 K.

Heat Capacity and Entropy

According to the Walsh correlation diagram (6) for non-hydride AB_2 molecules, the most loosely bound electron in SF_2^- is in an $\tilde{a}_1'$ orbital whose binding energy falls markedly with an increase in bond angle. We predict then that electron capture by SF_2 should be accompanied by a large increase in bond angle. Based on the bond angle reported for the isoelectronic valence (21 electrons) molecule $C\ell F_2$(136±15°, 7), we estimate an angle for SF_2^- of 130° which represents a 32° increase from that for SF_2 (1). The addition of an antibonding electron to SF_2 should also produce an increase in the S-F bond length. We estimate $r_e(SF_2^-) = r_3(C\ell - F)$ = 1.63 Å (1) which corresponds to $r_e(SF_2^-) - r_e(SF_2)$ = 0.038 Å. The individual moments of inertia are: I_A = 1.5139 x 10^{-38}, I_B = 1.3769 x 10^{-38}, and I_C = 1.3702 x 10^{-39} g cm^2.

We calculate vibrational frequencies form the force constants f_r = 2.0 and f_α/r^2 = 0.27 mdyn/Å. These force constants are estimated from those for $C\ell F_2$ (f_r = 1.94 and f_α/r^2 = 0.26 mdyn/Å) which are obtained from the bond angle and vibrational frequencies reported by Mamantov et al. (7). Our frequencies on going from SF_2 to SF_2^- show a large decrease, in agreement with the view that the additional antibonding electron weakens the bonding in the radical anion relative to the neutral molecule.

The Walsh correlation diagram (6) predicts a ground stata electronic configuration of $^2A_1$ for a 21 valence electron molecule. In addition, the existence of two doublet excited states is highly probable. We omit these excited states since no spectroscopic information is available on these states for isoelectronic molecules which would allow us to estimate the relative term values. We speculate that these levels lie above 20000 cm^{-1}, and thus, their contributions to the thermal functions are probably small below 3000 K.

References

1. JANAF Thermochemical Tables: $SF_2(g)$, 6-30-76; $SF^-(g)$, $SF_3^-(g)$, $SF_4^-(g)$, $SF_5^-(g)$, and $SF_2^+(g)$, 12-31-16; $C\ell F(g)$, 9-30-65; $SF_6^-(g)$, 6-30-77.
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F_2S^-

SILICON DIFLUORIDE (SiF_2)

(IDEAL GAS) GFW=66.082306

F_2Si

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.678	-140.300	-140.300	INFINITE
100	8.298	51.186	69.946	-1.876	-140.257	-141.215	308.620
200	9.476	57.293	62.234	-0.988	-140.350	-142.143	155.324
298	10.638	61.298	61.298	0.000	-140.500	-142.991	104.814
300	10.658	61.363	61.298	0.020	-140.503	-143.007	104.179
400	11.581	64.564	61.728	1.134	-140.665	-143.817	78.577
500	12.214	67.221	62.568	2.326	-140.821	-144.586	63.198
600	12.640	69.488	63.537	3.570	-140.975	-145.326	52.934
700	12.932	71.459	64.531	4.850	-141.128	-146.038	45.595
800	13.137	73.200	65.508	6.154	-141.286	-146.730	40.084
900	13.285	74.757	66.451	7.475	-141.448	-147.399	35.793
1000	13.396	76.162	67.353	8.810	-141.617	-148.052	32.356
1100	13.480	77.443	68.213	10.154	-141.794	-148.688	29.541
1200	13.545	78.619	69.032	11.505	-141.979	-149.306	27.192
1300	13.597	79.705	69.811	12.862	-142.172	-149.909	25.202
1400	13.639	80.715	70.555	14.224	-142.375	-150.497	23.493
1500	13.673	81.657	71.264	15.590	-142.587	-151.069	22.010
1600	13.701	82.540	71.941	16.958	-142.810	-151.627	20.711
1700	13.724	83.372	72.589	18.330	-155.034	-152.065	19.549
1800	13.744	84.157	73.210	19.703	-155.223	-151.885	18.441
1900	13.760	84.900	73.806	21.078	-155.411	-151.695	17.449
2000	13.775	85.606	74.379	22.455	-155.601	-151.494	16.554
2100	13.787	86.279	74.929	23.833	-155.791	-151.284	15.744
2200	13.798	86.920	75.460	25.212	-155.982	-151.065	15.007
2300	13.808	87.534	75.972	26.593	-156.174	-150.838	14.333
2400	13.816	88.122	76.466	27.974	-156.367	-150.601	13.714
2500	13.823	88.686	76.943	29.356	-156.561	-150.357	13.144
2600	13.830	89.228	77.406	30.739	-156.756	-150.105	12.617
2700	13.836	89.750	77.853	32.122	-156.953	-149.846	12.129
2800	13.842	90.254	78.287	33.506	-157.151	-149.578	11.675
2900	13.847	90.739	78.708	34.890	-157.350	-149.304	11.252
3000	13.853	91.209	79.117	36.275	-157.551	-149.025	10.856
3100	13.858	91.663	79.514	37.661	-157.751	-148.736	10.486
3200	13.863	92.103	79.901	39.047	-157.954	-148.441	10.138
3300	13.868	92.530	80.277	40.433	-158.158	-148.140	9.811
3400	13.874	92.944	80.644	41.821	-158.362	-147.834	9.503
3500	13.880	93.346	81.001	43.208	-158.569	-147.523	9.212
3600	13.886	93.737	81.349	44.596	-250.737	-144.946	8.799
3700	13.893	94.118	81.689	45.985	-250.846	-142.007	8.388
3800	13.900	94.488	82.021	47.375	-250.955	-139.063	7.998
3900	13.908	94.850	82.346	48.765	-251.067	-136.118	7.628
4000	13.917	95.202	82.663	50.157	-251.179	-133.169	7.276
4100	13.927	95.546	82.973	51.549	-251.293	-130.219	6.941
4200	13.938	95.881	83.276	52.942	-251.407	-127.265	6.622
4300	13.950	96.210	83.573	54.337	-251.520	-124.307	6.318
4400	13.963	96.530	83.864	55.732	-251.636	-121.348	6.027
4500	13.977	96.844	84.149	57.129	-251.751	-118.382	5.749
4600	13.992	97.152	84.428	58.528	-251.865	-115.418	5.484
4700	14.009	97.453	84.702	59.928	-251.980	-112.450	5.229
4800	14.026	97.748	84.971	61.330	-252.095	-109.482	4.985
4900	14.045	98.037	85.235	62.733	-252.209	-106.508	4.750
5000	14.065	98.321	85.493	64.139	-252.323	-103.537	4.526
5100	14.086	98.600	85.748	65.546	-252.436	-100.555	4.309
5200	14.108	98.874	85.998	66.956	-252.549	-97.578	4.101
5300	14.132	99.143	86.243	68.368	-252.660	-94.596	3.901
5400	14.157	99.407	86.484	69.782	-252.771	-91.614	3.708
5500	14.183	99.667	86.722	71.199	-252.881	-88.630	3.522
5600	14.210	99.923	86.955	72.619	-252.990	-85.640	3.342
5700	14.238	100.175	87.185	74.041	-253.098	-82.649	3.169
5800	14.267	100.422	87.411	75.466	-253.205	-79.658	3.002
5900	14.297	100.667	87.634	76.894	-253.311	-76.668	2.840
6000	14.328	100.907	87.853	78.326	-253.415	-73.673	2.684

Dec. 31, 1960; Sept. 30, 1963; June 30, 1968
Dec. 31, 1968; June 30, 1976; Dec. 31, 1977

SILICON DIFLUORIDE (SiF_2) (IDEAL GAS) GFW = 66.082306

ΔHa_0° = 283.7 ± 5 kcal/mol

$S^\circ_{298.15}$ = 61.30 ± 0.10 gibbs/mol

ΔHf_0° = -140.3 ± 3 kcal/mol F_2Si

$\Delta Hf^\circ_{298.15}$ = -140.5 ± 3 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	26310	3
$^1B_1$	44109	1
$^1B_2$	62280	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
855 (1)
345 (1)
872 (1)

Point Group: C_{2v} σ = 2
Bond Distance: Si-F = 1.591 Å
Bond Angle: F-Si-F = 100° 59'
Product of the Moments of Inertia: $I_AI_BI_C = 3.20008 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

Margrave, Kannan, and Pease (1) have reported some approximate equilibrium constants for the reaction $Si(c) + SiF_4(g) = 2\ SiF_2(g)$. These were calculated from yields of polymerized products and a knowledge of the total system pressure given in U.S. Patent No. 2,840,588 (1958). The data are subjected to a third law analysis using the present JANAF functions (2) and yield ΔHr°_{298} = 92±11 kcal/mol, which gives $\Delta Hf^\circ_{298}(SiF_2, g)$ = -147±5 kcal/mol.

Ehlert and Margrave (3) and Farber (13) have determined equilibrium contants mass spectrometrically. A 2nd and 3rd law analysis of the data is shown below. We adopt $\Delta Hf^\circ_{298}(SiF_2,g)$ = -140.5±3 kcal/mol.

				ΔHr°_{298} kcal/mol		Drift	$\Delta Hf^\circ_{298}(g)$*
Source	Reaction	Range K	Points	2nd law	3rd law	gibbs/mol	kcal/mol
(3)	$CaF_2(c) + Si(g) = Ca(g) + SiF_2(g)$	1395-1543	12	80.2±14.1	88.0±3.0	4.6±9.7	-140.1
(3)	$CaF_2(g) + Si(g) = Ca(g) + SiF_2(g)$	1395-1543	12	-8.3±14.1	-18.0±3.0	-6.6±9.6	-140.7
(3)	$2CaF(g) + Si(g) = 2Ca(g) + SiF_2(g)$	1395-1543	12	-18.6± 7.5	-33.4±1.8	-10.0±5.1	-141.0
(13)	$SiF_4(g) + Si(g) = 2SiF_2(g)$	1590-1782	10	-2.0± 0.3	-3.2±0.3	0.7±0.8	-140.7

*$\Delta Hf^\circ_{298}(g)$ is calculated from the third law ΔHr°_{298} using auxiliary data (2).

Using JANAF values (2), we calculate ΔHa_0° = 283.7±5 kcal/mol for the process $SiF_2(g) = Si(g) + 2\ F(g)$. Within 2 kcal/mol the average bond energies in $SiF_2(g)$, $SiF_3(g)$, and $SiF_4(g)$ are the same.

Heat Capacity and Entropy

The electronic levels are adopted from the ultraviolet spectral work of Khanna, Besenbruch, and Margrave (4), Rao (5), and Gole et al. (6). The vibrational assignments of ν_1 = 855 cm^{-1} (symmetric stretch) and ν_3 = 872 cm^{-1} (asymmetric stretch) of Khanna et al. (7) are adopted. These assignments are supported by the argon matrix studies of Milligan and Jacox (8), the neon matrix and the argon matrix measurements of Hastie, Hauge, and Margrave (9), and the excited state microwave work of Shoji, Tanaka, and Hirota (10). The bending frequency assignment, ν_2 = 345 cm^{-1}, is adopted from the ultraviolet and microwave study of Rao and Curl (11). This assignment is also confirmed by Milligan and Jacox (8).

The gas phase geometry was established by Rao et al. (12) from microwave spectra. The principal moments of inertia are: $I_A = 2.747 \times 10^{-39}$, $I_B = 9.506 \times 10^{-39}$, and $I_C = 12.25 \times 10^{-39}\ g\ cm^2$.

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F_2Si

HYDROGEN FLUORIDE CYCLIC TRIMER (H_3F_3) F_3H_3
(IDEAL GAS) GFW=60.018909

T, K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.855	-207.765	-207.765	INFINITE
100	11.165	53.299	82.876	-2.958	-208.986	-204.605	447.157
200	15.087	62.299	70.483	-1.637	-209.681	-199.924	218.464
298	18.128	68.917	68.917	0.000	-210.110	-195.036	142.963
300	18.177	65.029	68.917	0.034	-210.117	-194.943	142.014
400	20.394	74.582	69.659	1.969	-210.376	-189.841	103.723
500	21.931	79.308	71.128	4.090	-210.510	-184.690	80.727
600	23.063	83.411	72.841	6.342	-210.553	-179.521	65.389
700	23.973	87.036	74.615	8.695	-210.525	-174.350	54.434
800	24.755	90.290	76.374	11.132	-210.439	-169.188	46.220
900	25.449	93.246	78.087	13.643	-210.301	-164.039	39.834
1000	26.071	95.960	79.741	16.220	-210.122	-158.909	34.729
1100	26.629	98.472	81.331	18.855	-209.904	-153.797	30.556
1200	27.128	100.810	82.858	21.543	-209.657	-148.707	27.083
1300	27.571	103.000	84.324	24.279	-209.383	-143.639	24.148
1400	27.966	105.058	85.732	27.056	-209.089	-138.593	21.635
1500	28.315	106.999	87.086	29.870	-208.780	-133.568	19.461
1600	28.625	108.837	88.388	32.718	-208.457	-128.565	17.561
1700	28.900	110.581	89.643	35.594	-208.123	-123.580	15.887
1800	29.144	112.239	90.852	38.497	-207.784	-118.618	14.402
1900	29.361	113.821	92.020	41.422	-207.437	-113.672	13.075
2000	29.555	115.332	93.148	44.368	-207.089	-108.748	11.883
2100	29.728	116.778	94.239	47.332	-206.737	-103.839	10.806
2200	29.883	118.165	95.295	50.313	-206.384	-98.947	9.829
2300	30.022	119.496	96.319	53.308	-206.032	-94.073	8.939
2400	30.147	120.777	97.311	56.317	-205.678	-89.211	8.124
2500	30.260	122.010	98.275	59.337	-205.326	-84.365	7.375
2600	30.363	123.199	99.211	62.369	-204.977	-79.533	6.685
2700	30.455	124.346	100.121	65.410	-204.630	-74.715	6.048
2800	30.540	125.456	101.006	68.459	-204.288	-69.911	5.457
2900	30.617	126.529	101.867	71.517	-203.946	-65.117	4.907
3000	30.687	127.568	102.707	74.582	-203.610	-60.336	4.395
3100	30.752	128.575	103.525	77.654	-203.275	-55.564	3.917
3200	30.811	129.552	104.323	80.733	-202.948	-50.806	3.470
3300	30.865	130.501	105.102	83.816	-202.623	-46.055	3.050
3400	30.915	131.423	105.863	86.906	-202.304	-41.317	2.656
3500	30.961	132.320	106.606	89.999	-201.990	-36.587	2.285
3600	31.004	133.193	107.333	93.098	-201.680	-31.865	1.934
3700	31.044	134.043	108.043	96.200	-201.376	-27.152	1.604
3800	31.081	134.871	108.738	99.306	-201.078	-22.447	1.291
3900	31.115	135.679	109.419	102.416	-200.785	-17.750	0.995
4000	31.147	136.467	110.085	105.529	-200.500	-13.062	0.714
4100	31.176	137.237	110.738	108.645	-200.219	-8.379	0.447
4200	31.204	137.988	111.378	111.764	-199.944	-3.702	0.193
4300	31.230	138.723	112.005	114.886	-199.675	0.967	-0.049
4400	31.254	139.441	112.621	118.010	-199.413	5.630	-0.280
4500	31.277	140.144	113.225	121.137	-199.158	10.285	-0.499
4600	31.299	140.832	113.817	124.266	-198.908	14.938	-0.710
4700	31.319	141.505	114.399	127.397	-198.665	19.584	-0.911
4800	31.338	142.164	114.971	130.529	-198.429	24.225	-1.103
4900	31.355	142.811	115.532	133.664	-198.196	28.862	-1.287
5000	31.372	143.444	116.084	136.801	-197.973	33.493	-1.464
5100	31.388	144.066	116.627	139.939	-197.754	38.121	-1.634
5200	31.403	144.676	117.160	143.078	-197.542	42.743	-1.796
5300	31.417	145.274	117.685	146.219	-197.335	47.363	-1.953
5400	31.431	145.861	118.202	149.362	-197.134	51.977	-2.104
5500	31.444	146.438	118.710	152.505	-196.938	56.589	-2.249
5600	31.456	147.005	119.210	155.650	-196.748	61.197	-2.388
5700	31.467	147.562	119.703	158.796	-196.563	65.801	-2.523
5800	31.478	148.109	120.188	161.944	-196.381	70.403	-2.653
5900	31.488	148.647	120.665	165.092	-196.204	75.002	-2.778
6000	31.498	149.176	121.136	168.241	-196.034	79.595	-2.899

July 31, 1972 (NBS); June 30, 1977

HYDROGEN FLUORIDE CYCLIC TRIMER (H_3F_3) (IDEAL GAS) GFW = 60.018909

F_3H_3

Point Group C_3
$S^\circ_{298.15}$ = [68.9 ± 3] gibbs/mol
Ground State Quantum Weight = 1

ΔHf°_0 = -207.8 ± 3 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -210.1 ± 3 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[202](3)
[962](3)
[552](3)
[3060](3)

Interatomic Distance: F-F = [2.5] Å σ = [3]
Product of the Moments of Inertia: $I_AI_BI_C$ = [2.238 x 10^{-114}]g^3 cm^6

Heat of Formation

The enthalpy of 3 HF(g) → H_3F_3(g) was taken as the mean of third law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier (1) measured the vapor density of HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer (2) measured C_p between -20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported second law values of ΔH and ΔS. At n = 3 their second law values differed by 2.7 kcal/mol, which was taken as an estimate of error, while the third law values differed by 0.20 kcal/mol. Using ΔHr°_{298} = -14.69 kcal/mol and auxiliary JANAF data (3) gives the heat of formation of H_3F_3(g).

Heat Capacity and Entropy

The molecular structure of H_3F_3 was assumed as planar with the F atoms forming the vertices of a regular triangle and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's (4) theoretical molecular-orbital studies on HF polymers. The length of side (F-F axis) was taken from Atoji and Lipscomb's (5) X-ray studies of solid HF (F-F = 2.49 Å) and agrees with 2.52 Å which Janzen and Bartell (6) determined for HF gaseous polymers by electron diffraction. Vibrational frequencies were taken from Kittelberger and Hornig's (7) work on crystalline HF. Huong and Couzi (8) and Smith (9) have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table (10) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (10), we recalculate the table in terms of 1973 fundamental constants (11), 1975 atomic weights (12), and current JANAF reference states for the elements.

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F_3H_3

NITROGEN TRIFLUORIDE (NF_3) F_3N

(IDEAL GAS) GFW=71.001909

T, K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0	0.000	0.000	INFINITE	-2.832	-30.203	-30.203	INFINITE
100	8.135	51.551	71.898	-2.035	-30.794	-27.937	61.054
200	10.224	57.735	63.387	-1.131	-31.288	-24.873	27.180
298	12.756	62.300	62.300	0.000	-31.570	-21.657	15.875
300	12.799	62.379	62.300	0.024	-31.574	-21.595	15.732
400	14.785	66.349	62.828	1.409	-31.691	-18.247	9.970
500	16.149	69.805	63.885	2.960	-31.697	-14.884	6.506
600	17.072	72.836	65.130	4.624	-31.635	-11.526	4.198
700	17.708	75.519	66.426	6.365	-31.529	-8.183	2.555
800	18.158	77.914	67.715	8.159	-31.399	-4.857	1.327
900	18.485	80.073	68.970	9.992	-31.252	-1.546	0.376
1000	18.728	82.034	70.180	11.853	-31.099	1.745	-0.381
1100	18.914	83.828	71.340	13.736	-30.939	5.021	-0.998
1200	19.059	85.480	72.451	15.635	-30.777	8.284	-1.509
1300	19.174	87.010	73.513	17.547	-30.613	11.533	-1.939
1400	19.266	88.435	74.528	19.469	-30.451	14.768	-2.305
1500	19.342	89.767	75.500	21.399	-30.290	17.992	-2.621
1600	19.404	91.017	76.431	23.337	-30.129	21.206	-2.897
1700	19.456	92.195	77.324	25.280	-29.970	24.410	-3.138
1800	19.500	93.308	78.182	27.228	-29.814	27.604	-3.351
1900	19.537	94.364	79.006	29.180	-29.658	30.791	-3.542
2000	19.569	95.366	79.799	31.135	-29.507	33.966	-3.712
2100	19.597	96.322	80.563	33.093	-29.357	37.137	-3.865
2200	19.621	97.234	81.300	35.054	-29.208	40.300	-4.003
2300	19.642	98.107	82.012	37.017	-29.064	43.456	-4.129
2400	19.660	98.943	82.700	38.983	-28.920	46.606	-4.244
2500	19.677	99.746	83.366	40.949	-28.779	49.750	-4.349
2600	19.691	100.518	84.011	42.918	-28.641	52.889	-4.446
2700	19.704	101.261	84.636	44.888	-28.505	56.022	-4.535
2800	19.716	101.978	85.243	46.859	-28.373	59.150	-4.617
2900	19.726	102.670	85.832	48.831	-28.241	62.274	-4.693
3000	19.736	103.339	86.405	50.804	-28.114	65.392	-4.764
3100	19.744	103.987	86.961	52.778	-27.987	68.508	-4.830
3200	19.752	104.614	87.503	54.753	-27.865	71.618	-4.891
3300	19.759	105.221	88.031	56.728	-27.743	74.726	-4.949
3400	19.766	105.811	88.545	58.705	-27.625	77.829	-5.003
3500	19.772	106.384	89.047	60.682	-27.510	80.928	-5.053
3600	19.777	106.942	89.536	62.659	-27.397	84.025	-5.101
3700	19.782	107.483	90.014	64.637	-27.286	87.119	-5.146
3800	19.787	108.011	90.481	66.615	-27.177	90.210	-5.188
3900	19.791	108.525	90.937	68.594	-27.071	93.297	-5.228
4000	19.795	109.026	91.383	70.574	-26.968	96.382	-5.266
4100	19.799	109.515	91.819	72.553	-26.867	99.465	-5.302
4200	19.802	109.992	92.246	74.533	-26.769	102.544	-5.336
4300	19.805	110.458	92.664	76.514	-26.672	105.623	-5.368
4400	19.808	110.914	93.074	78.494	-26.579	108.698	-5.399
4500	19.811	111.359	93.475	80.475	-26.489	111.770	-5.428
4600	19.814	111.794	93.869	82.457	-26.400	114.843	-5.456
4700	19.816	112.220	94.255	84.438	-26.313	117.912	-5.483
4800	19.818	112.638	94.633	86.420	-26.231	120.979	-5.508
4900	19.821	113.046	95.005	88.402	-26.149	124.046	-5.533
5000	19.823	113.447	95.370	90.384	-26.071	127.110	-5.556
5100	19.825	113.839	95.728	92.366	-25.995	130.174	-5.578
5200	19.826	114.224	96.080	94.349	-25.922	133.234	-5.600
5300	19.828	114.602	96.426	96.332	-25.851	136.295	-5.620
5400	19.830	114.973	96.766	98.315	-25.782	139.354	-5.640
5500	19.831	115.336	97.100	100.298	-25.717	142.411	-5.659
5600	19.833	115.694	97.429	102.281	-25.654	145.467	-5.677
5700	19.834	116.045	97.753	104.264	-25.594	148.522	-5.695
5800	19.835	116.390	98.071	106.248	-25.535	151.577	-5.711
5900	19.837	116.729	98.385	108.231	-25.480	154.630	-5.728
6000	19.838	117.062	98.693	110.215	-25.428	157.682	-5.743

Dec. 31, 1960; Mar. 31, 1961; Mar. 31, 1964;
June 30, 1969; July 31, 1972 (NBS); June 30, 1977

NITROGEN TRIFLUORIDE (NF_3) (IDEAL GAS) GFW = 71.001909

F_3N

Point Group C_{3v}

$S^\circ_{298.15}$ = 62.30 ± 0.05 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -30.20 ± 0.27 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -31.57 ± 0.27 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1032(1)
642(1)
906(2)
492(2)

Bond Distance: N-F = 1.371 Å

σ = 3

Bond Angle: F-N-F = 102°9'

Product of Moments of Inertia: $I_AI_BI_C = 8.855 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

The adopted enthalpy of formation is the mean of values calculated from the reaction processes listed below and weighted inversely as the squares of the standard deviations. Auxiliary enthalpies of formation were taken from NBS (1) or from simultaneous adjustment of several interconnecting pieces of data (2). Also given below are the references, individual and averaged measured values of enthalpies of reaction and their uncertainties, the value of enthalpy of formation calculated from each process and its uncertainty, and the weighted mean.

	Reaction	ΔHr°_{298} (selected) kcal/mol	$\Delta Hf^\circ_{298}(NF_3)$ kcal/mol
A	$NF_3(g) + 3/2\ H_2(g) = 3\ HF(aq,\ 50\ H_2O) + 1/2\ N_2(g)$ (3) -196.3±64; (4) -199.49±0.22; (5) we derive -196.23±0.77	-199.42±0.22	-30.92±1.72
B	$S(c,rh) + 2\ NF_3(g) = SF_6(g) + N_2(g)$ (6)	-228.26±0.2	-31.77±0.33
C	$NF_3(g) \rightarrow 1/2\ N_2(g) + 3/2\ F_2(g)$ (7)	31.44±0.3	-31.44±0.3
D	$8\ NF_3(g) + 3\ C_2N_2(g) = 6\ CF_4(g) + 7\ N_2(g)$ (8)	-1308.8 ±1.3	-31.4 ±4.4
E	$B(c) + NF_3(g) = BF_3(g) + 1/2\ N_2(g)$ (9)	-239.7 ±1.2	-31.7 ±1.6
F	$NF_3(g) + 4\ NH_3(g) = 3\ NH_4F(c) + N_2(g)$ (3)	-259.5 ±1.0	-29.0 ±3.0
	Weighted Mean		-31.57±0.27

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Schatz and Levin (10) and are in good agreement with those of Pace and Pierce (11), and Wilson and Polo (12). The adopted values are also in agreement with the Raman studies of Kotov and Tatevskii (13). The bond length and angle are from the microwave studies of Sheridan and Gordy (14), whose values are in substantial agreement with the electron diffraction results of Schomaker and Lu (15).

The principal moments of inertia are $I_A = I_B = 7.854 \times 10^{-39}$ g cm^2 and $I_C = 14.354 \times 10^{-39}$ g cm^2.

Pierce and Pace (16) have obtained the entropy of the gas at 144.15 K from solid heat capacity measurements and the heats of melting and vaporization. Their reported value of 54.50 gibbs/mol is in good agreement with our calculated value of 54.56 gibbs/mol.

The National Bureau of Standards prepared this table (17) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (17), we recalculate the table in terms of 1973 fundamental constants (18), 1975 atomic weights (19), and current JANAF reference states for the elements.

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19. IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

F_3N

SULFUR TRIFLUORIDE (SF_3) F_3S

(IDEAL GAS) GFW=89.0552

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.250	-119.261	-119.261	INFINITE
100	8.971	55.568	79.915	-2.435	-119.652	-118.808	259.651
200	12.484	62.869	69.673	-1.361	-120.021	-117.808	128.732
298	15.052	68.371	68.371	0.000	-120.227	-116.672	85.521
300	15.090	68.464	68.371	0.028	-120.230	-116.650	84.978
400	16.674	73.042	68.984	1.623	-120.888	-115.415	63.059
500	17.630	76.874	70.190	3.342	-121.313	-113.996	49.827
600	18.230	80.145	71.583	5.137	-121.619	-112.502	40.978
700	18.625	82.987	73.014	6.981	-121.847	-110.940	34.636
800	18.896	85.493	74.420	8.858	-135.088	-110.638	30.224
900	19.089	87.730	75.777	10.758	-134.933	-107.589	26.126
1000	19.230	89.749	77.075	12.674	-134.778	-104.560	22.851
1100	19.337	91.587	78.312	14.603	-134.621	-101.547	20.175
1200	19.420	93.273	79.489	16.541	-134.464	-98.546	17.947
1300	19.485	94.830	80.610	18.486	-134.306	-95.558	16.064
1400	19.537	96.276	81.678	20.437	-134.152	-92.584	14.453
1500	19.579	97.626	82.697	22.393	-133.998	-89.622	13.058
1600	19.614	98.890	83.670	24.353	-133.846	-86.667	11.838
1700	19.643	100.080	84.601	26.316	-133.694	-83.722	10.763
1800	19.667	101.204	85.492	28.281	-133.546	-80.788	9.809
1900	19.688	102.268	86.347	30.249	-133.398	-77.859	8.956
2000	19.706	103.278	87.169	32.219	-133.255	-74.942	8.189
2100	19.721	104.240	87.959	34.190	-133.113	-72.030	7.496
2200	19.734	105.158	88.720	36.163	-132.972	-69.123	6.867
2300	19.746	106.035	89.454	38.137	-132.835	-66.225	6.293
2400	19.756	106.876	90.162	40.112	-132.699	-63.331	5.767
2500	19.765	107.682	90.847	42.088	-132.565	-60.443	5.284
2600	19.773	108.458	91.510	44.065	-132.434	-57.561	4.838
2700	19.781	109.204	92.151	46.043	-132.305	-54.684	4.426
2800	19.787	109.924	92.773	48.021	-132.180	-51.814	4.044
2900	19.794	110.618	93.377	50.000	-132.055	-48.944	3.688
3000	19.799	111.289	93.963	51.980	-131.936	-46.080	3.357
3100	19.805	111.939	94.532	53.960	-131.815	-43.219	3.047
3200	19.810	112.567	95.086	55.941	-131.699	-40.364	2.757
3300	19.815	113.177	95.625	57.922	-131.584	-37.512	2.484
3400	19.820	113.769	96.150	59.904	-131.472	-34.661	2.228
3500	19.824	114.343	96.662	61.886	-131.364	-31.819	1.987
3600	19.829	114.902	97.160	63.868	-131.256	-28.975	1.759
3700	19.834	115.445	97.647	65.852	-131.152	-26.135	1.544
3800	19.839	115.974	98.123	67.835	-131.049	-23.298	1.340
3900	19.844	116.490	98.587	69.819	-130.949	-20.464	1.147
4000	19.850	116.992	99.041	71.804	-130.851	-17.630	0.963
4100	19.856	117.482	99.485	73.789	-130.754	-14.802	0.789
4200	19.862	117.961	99.919	75.775	-130.661	-11.975	0.623
4300	19.868	118.428	100.344	77.762	-130.568	-9.150	0.465
4400	19.875	118.885	100.760	79.749	-130.479	-6.328	0.314
4500	19.882	119.332	101.168	81.737	-130.392	-3.507	0.170
4600	19.889	119.769	101.568	83.725	-130.306	-0.689	0.033
4700	19.897	120.197	101.959	85.714	-130.221	2.128	-0.099
4800	19.905	120.616	102.344	87.705	-130.140	4.941	-0.225
4900	19.913	121.026	102.721	89.695	-130.059	7.759	-0.346
5000	19.922	121.428	103.091	91.687	-129.982	10.567	-0.462
5100	19.931	121.823	103.454	93.680	-129.905	13.380	-0.573
5200	19.941	122.210	103.811	95.673	-129.831	16.188	-0.680
5300	19.951	122.590	104.162	97.668	-129.757	18.995	-0.783
5400	19.961	122.963	104.507	99.664	-129.685	21.803	-0.882
5500	19.972	123.330	104.846	101.660	-129.615	24.606	-0.978
5600	19.983	123.690	105.179	103.658	-129.547	27.411	-1.070
5700	19.994	124.043	105.507	105.657	-129.480	30.211	-1.158
5800	20.006	124.391	105.830	107.657	-129.414	33.013	-1.244
5900	20.018	124.733	106.147	109.658	-129.349	35.811	-1.327
6000	20.030	125.070	106.460	111.661	-129.287	38.613	-1.406

June 30, 1976; June 30, 1977

SULFUR TRIFLUORIDE (SF_3) (IDEAL GAS) GFW = 89.0552

F_3S

ΔHa°_0 = 240.1 ± 10.0 kcal/mol

$S^\circ_{298.15}$ = [68.4 ± 1.0] gibbs/mol

ΔHf°_0 = -119.261 ± 8.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -120.227 ± 8.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[2]
[25000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[850](1)	[725](1)
[550](1)	[450](1)
[300](1)	[350](1)

Point Group: C_{2v}

σ = 2

Bond Distances: S-F* = [1.545] Å S-F** = [1.646] Å

Bond Angles: F*-S-F** = [89°] F**-S-F** = [178°]

(* - equatorial ** - axial)

Product of Moments of Inertia: $I_AI_BI_C$ = [2.2718 x 10^{-114}] g^3 cm^6

Heat of Formation

Our ΔHf°_0 of -119.261±8.0 kcal/mol is calculated from the primary bond dissociation energy for SF_4 of $D^\circ_0(SF_3-F)$ = 80.0±3.0 kcal/mol with JANAF (1) ΔHf° data for F(g) and SF_4(g). The value of D°_0 is taken to be equal to one-fourth the heat of atomization of SF_4 (1). We calculate the heat of atomization (ΔHa°_0) and mean bond dissociation energy ($\bar{D}^\circ_0$) for SF_3 to be 240.1 kcal/mol and 80.0 kcal/mol, respectively. ΔHf° is -120.227 kcal/mol at 298.15 K.

Several pieces of information are available which are relatively imprecise but do support our assumption that $D^\circ_0(SF_3-F) = \Delta Ha^\circ_0(SF_4)/4$. Bott (2) has reported the results of shock-tube experiments on the dissociation of SF_4 over the temperature range 1650-1950 K. Rate constants based on spectroscopic measurements were correlated with the Rice-Ramsperger-Kassel (RRK) theory. This study strongly suggests that $D^\circ_0(SF_3-F)$ = 79.0±3.0 kcal/mol.

Electron-impact threshold measurements for SF_3^+ from SF_4 have been reported by Hildenbrand (3) and Glemser et al. (4). The measured appearance potentials (AP) are in good agreement and indicate $AP(SF_3^+/SF_4)$ = 12.67±0.1 eV. Combining this value with an upper limit for the ionization potential of SF_3(IP≤9.25 eV, 5), we obtain a lower limit for $D^\circ_0(SF_3-F)$ of 78.9 kcal/mol.

Two upper limit values for $D^\circ_0(SF_3-F)$ can be obtained from threshold measurements by Harland and Thynne (6) on dissociative attachment in SF_6 and SF_4. We combine their $AP(F^-/SF_4)$ = 0.20±0.05 eV with the electron affinity of F(EA = 3.399 eV, 1) to obtain $D^\circ_0(SF_3-F) \leq$ 83.0 kcal/mol. In addition, their appearance potentials (6) for the formation of F^- from SF_6 by two distinct processes are combined directly to give $D^\circ_0(SF_3-F) \leq$ 80.7 kcal/mol.

The AP of SF_3^+ from SF_6 has been measured by electron-impact (3, 7) and photoelectron spectroscopy (8). These three threshold values are in agreement with $AP(SF_3^+/SF_6)$ = 19.97±0.1 eV. Assuming the ionization process to be $SF_6(g) + e^- = SF_3^+(g) + 3F(g) + 2e^-$, we combine the mean AP value with $IP(SF_3) \leq$ 9.25 eV (5) to obtain $\Delta Hf^\circ_0(SF_3,g) \leq$ -96.3 kcal/mol. This result conflicts with all of the other available information; thus, we are led to conclude that the formation of SF_3^+ from SF_6 probably involves significant kinetic and/or excitation energies.

Heat Capacity and Entropy

We assume a molecular structure in which the four atoms form a slightly distorted T-shaped molecule having bond angles similar to those for ClF_3 (1). We eliminate a nonplanar pyramid (C_{3v} symmetry) as a plausible structure since recent ESR studies (9) show that the radical has only two equivalent fluorine nuclei. The equatorial and axial S-F bond lengths are assumed to be equal to those for SF_4 (1). The principal moments of inertia are: $I_A = 2.2894 \times 10^{-38}$, $I_B = 1.7087 \times 10^{-38}$, and $I_C = 5.8072 \times 10^{-39}$ g cm^2.

The vibrational representation for the adopted structure is $3A_1 + 2B_1 + B_2$. We estimate the six fundamentals according to symmetry species by analogy with the frequencies and assignments for ClF_3 and SF_4 (1, 10). Since several of the assignments for SF_4 (11) are uncertain, more weight is given to the results for ClF_3. Bott (2) detected IR radiation in emission at 11.0-12.6 μ in SF_4/Ar mixtures which were shock-heated to temperatures above 2050 K. He attributed this radiation to SF_3, indicating that at least one fundamental lies in the region 794-909 cm^{-1}. We assume that the unpaired electron will form all doublet states, and we include an excited level at 25000 cm^{-1} by analogy with that which has been observed for SF_4^+ (8).

Wilkins (12) has previously reported thermal functions for SF_3 which cover an extended temperature range (0-6000 K). These functions are based on a pyramidal structure and vibrational frequencies obtained from estimated force constants. Since this structure now appears to be incorrect, our functions are believed to be more reliable.

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F_3S

SULFUR TRIFLUORIDE UNIPOSITIVE ION (SF_3^+) F_3S^+
(IDEAL GAS) GFW=89.05465

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.966	93.841		
100							
200							
298	13.437	64.259	64.259	0.000	94.070	97.366	-71.371
300	13.478	64.342	64.259	0.025	94.073	97.386	-70.945
400	15.314	68.487	64.812	1.470	93.761	98.481	-53.807
500	16.554	72.047	65.912	3.068	93.707	99.668	-43.565
600	17.385	75.144	67.198	4.767	93.799	100.855	-36.736
700	17.954	77.869	68.532	6.536	93.987	102.040	-31.858
800	18.355	80.294	69.853	8.353	81.177	101.905	-27.839
900	18.645	82.473	71.136	10.203	81.772	104.461	-25.367
1000	18.862	84.450	72.370	12.079	82.377	106.950	-23.374
1100	19.027	86.256	73.552	13.974	82.988	109.376	-21.731
1200	19.155	87.917	74.681	15.883	83.603	111.749	-20.352
1300	19.256	89.454	75.759	17.804	84.222	114.071	-19.177
1400	19.338	90.884	76.789	19.734	84.841	116.344	-18.162
1500	19.404	92.221	77.773	21.671	85.461	118.572	-17.276
1600	19.459	93.475	78.716	23.614	86.079	120.759	-16.495
1700	19.505	94.656	79.619	25.563	86.699	122.908	-15.801
1800	19.544	95.772	80.486	27.515	87.315	125.018	-15.179
1900	19.577	96.830	81.318	29.471	87.932	127.098	-14.620
2000	19.605	97.835	82.119	31.430	88.547	129.145	-14.112
2100	19.630	98.792	82.891	33.392	89.158	131.156	-13.650
2200	19.651	99.705	83.634	35.356	89.767	133.143	-13.226
2300	19.670	100.579	84.352	37.322	90.375	135.101	-12.838
2400	19.686	101.417	85.046	39.290	90.980	137.033	-12.479
2500	19.701	102.221	85.717	41.260	91.582	138.940	-12.146
2600	19.714	102.994	86.367	43.230	92.180	140.822	-11.837
2700	19.727	103.738	86.996	45.202	92.777	142.682	-11.549
2800	19.738	104.456	87.607	47.176	93.372	144.517	-11.280
2900	19.748	105.148	88.200	49.150	93.963	146.336	-11.028
3000	19.758	105.818	88.776	51.125	94.550	148.129	-10.791
3100	19.768	106.466	89.337	53.102	95.137	149.905	-10.568
3200	19.777	107.094	89.882	55.079	95.718	151.663	-10.358
3300	19.786	107.703	90.413	57.057	96.299	153.401	-10.159
3400	19.795	108.293	90.930	59.036	96.876	155.125	-9.971
3500	19.804	108.867	91.434	61.016	97.449	156.831	-9.793
3600	19.813	109.425	91.926	62.997	98.022	158.520	-9.623
3700	19.823	109.968	92.406	64.979	98.590	160.193	-9.462
3800	19.832	110.497	92.876	66.961	99.156	161.852	-9.309
3900	19.842	111.012	93.334	68.945	99.719	163.489	-9.162
4000	19.852	111.515	93.782	70.930	100.279	165.122	-9.022
4100	19.863	112.005	94.221	72.916	100.838	166.733	-8.888
4200	19.874	112.484	94.650	74.902	101.393	168.335	-8.759
4300	19.885	112.952	95.070	76.890	101.948	169.925	-8.637
4400	19.897	113.409	95.482	78.879	102.497	171.498	-8.518
4500	19.909	113.856	95.885	80.870	103.045	173.058	-8.405
4600	19.922	114.294	96.281	82.861	103.592	174.607	-8.296
4700	19.935	114.723	96.668	84.854	104.136	176.146	-8.191
4800	19.948	115.142	97.049	86.848	104.678	177.673	-8.090
4900	19.962	115.554	97.422	88.844	105.218	179.193	-7.992
5000	19.976	115.957	97.789	90.841	105.754	180.692	-7.898
5100	19.990	116.353	98.149	92.839	106.289	182.182	-7.807
5200	20.005	116.741	98.503	94.839	106.823	183.672	-7.720
5300	20.020	117.123	98.851	96.840	107.355	185.145	-7.635
5400	20.035	117.497	99.193	98.843	107.883	186.603	-7.552
5500	20.051	117.865	99.529	100.847	108.411	188.058	-7.473
5600	20.067	118.226	99.859	102.853	108.935	189.504	-7.396
5700	20.082	118.581	100.185	104.860	109.458	190.937	-7.321
5800	20.098	118.931	100.505	106.869	109.981	192.363	-7.248
5900	20.115	119.275	100.820	108.880	110.501	193.771	-7.178
6000	20.131	119.613	101.131	110.892	111.018	195.182	-7.110

Dec. 31, 1976

SULFUR TRIFLUORIDE UNIPOSITIVE ION (SF_3^+) (IDEAL GAS) GFW = 89.05465

Point Group C_{3v}
$S^\circ_{298.15}$ = 64.26 ± 0.5 gibbs/mol

ΔHf°_0 = 93.8 ± 8.0 kcal/mol F_3S^+
$\Delta Hf^\circ_{298.15}$ = 94.1 ± 8.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	1
21777	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
938(1)	914(2)
530(1)	411(2)

Bond Distance: S-F = 1.497 ± 0.03 Å σ = 3
Bond Angle: F-S-F = 97.51 ± 0.5°
Product of Moments of Inertia: $I_AI_BI_C$ = 1.5584 x 10^{-114} g^3cm^6

Heat of Formation

Glemser et al. (1) determined an appearance potential (AP) for SF_3^+ of 12.70±0.03 eV from electron-impact measurements on SF_4. Their results (1) are confirmed by the subsequent measurements of Hildenbrand (2) who reported AP values of 12.63±0.1 eV (from SF_4) and 12.8 eV (from SF_4 formed as a reaction product in SF_6 + C). From these results we arrive at a ΔHr°_0 = 293.1± 2.3 kcal/mol (mean AP value) for the process $SF_4(g) + e^- = SF_3^+(g) + F(g) + 2e^-$. Assuming that the products are formed with no excess energies, we combine the value of ΔHr°_0 with JANAF heats of formation (3) for SF_4 and F to obtain the result, ΔHf°_0 (SF_3^+,g) = 93.84±8.0 kcal/mol which is adopted. Our ΔHf° value corresponds to an ionization potential (IP) of IP(SF_3) = 213.1 ±16.0 kcal/mol (9.24±0.7 eV). This value is consistent with the observations of Fehsenfeld (4) who found no charge transfer reaction between NO and SF_3^+, suggesting that IP(SF_3) < 9.25 eV. In addition, we predict that IP(SF_3) << IP(SF_2) due to a stabilization of the positive charge in the even-electron SF_3^+ cation by resonance structures such as $F_2S{=}F^+$. JANAF data (3) gives IP(SF_2) - IP(SF_3) = 1.05 eV which compares favorably with the 1-2 eV lowerings (5) observed in other di- and trifluoride molecules and radicals.

Paulett and Lustig (6) reported appearance potentials for SF_3^+ and SF_4^+ from SF_5NF_2. We combine their results to arrive at ΔHr°_0 = 2.31±4.6 kcal/mol for the process $SF_4^+(g) + NF_3(g) = SF_3^+(g) + NF_2(g) + F_2(g)$ which leads to ΔHf°(SF_3^+,g) =61.5 kcal/mol. This value is in poor agreement with the adopted result, suggesting that the fragmentation processes involving SF_5NF_2 probably include unknown excess energy terms. Other reported fragment-ion appearance potentials for SF_3^+ have been previously analyzed (see SF_3(g) and SF_4(g) tables) and were shown to be seriously in error.

ΔHf° is calculated to be 94.07 kcal/mol at 298.15 K. Using JANAF data (3), we find that the primary bond dissociation energy $D^\circ_0(SF_2^+{-}F)$ is 91.4 kcal/mol which when compared with D°_0 values for SF_3 (67.3 kcal/mol) and SF_3^- (106.4 kcal/mol) indicates that the trend is $D^\circ_0(SF_3^-) > D^\circ_0(SF_3^+) >> D^\circ_0(SF_3)$. The observed increased bond strengths in both ions relative to the SF_3 radical provide additional support to the view that the positive and negative charges are delocalized in the even-electron ions. Furthermore, available structural information (see below) shows that the bond length in SF_3^+ is the shortest S-F bond that has so far been reported. The heat of atomization (ΔHa°_0) and average bond dissociation energy ($\bar{D}^\circ_0$) are 265.9 kcal/mol and 88.6 kcal/mol, respectively.

Heat Capacity and Entropy

The molecular structure and vibrational frequencies are those measured by Gibler et al. (7) for the SF_3^+ ion in the solid $SF_4 \cdot BF_3$ adduct. We adopt average values of the bond lengths and angles reported by Gibler et al. (7) since spectroscopic evidence (8) indicates that in crystal adducts the SF_3^+ symmetry is lowered somewhat as a result of fluorine bridging with the anion. The adopted bond length is estimated to be within ±2.0% of the true gas-phase value, based on a comparison of structural data for gaseous and crystalline ClF_3 (9). The adopted bond angle (97.51°) is close to the gas-phase value (97.8±0.2°) found for the isoelectronic molecule PF_3 (3), suggesting that the gas-phase bond angle for SF_3^+ is probably within ±0.5° of the adopted solid-state value. Our frequencies show good agreement with those determined by Azeem et al. (8) in their infrared and Raman studies of solid adducts of SF_4 with several fluoride acceptors. Their results (8) indicate that the SF_3^+ frequencies are relatively independent of the anion and are not significantly different when measured in the liquid state. Thus, we believe that the error introduced in the SF_3^+ thermal functions by use of solid-state frequencies is probably small. The individual moments of inertia are: I_A = 1.5987 x 10^{-38}, I_B = 9.8733 x 10^{-39}, and I_C = 9.8733 x 10^{-39}g cm^2.

Delwiche (10) has reported an ionization efficiency curve for SF_3^+ which was obtained by retarded potential difference (RPD) measurements. This curve reveals the existence of an excited state, lying 21777 cm^{-1} above the ground state. We include this level and assume that the ground and excited states are both singlets since SF_3^+ has no unpaired electrons.

References

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F_3S^+

SULFUR TRIFLUORIDE UNINEGATIVE ION (SF_3^-) (IDEAL GAS) GFW=89.05575 F_3S^-

T, °K	$C_p°$	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0				-3.250	-183.114		
100							
200							
298	15.052	66.942	66.942	0.000	-185.563	-180.092	132.011
300	15.090	67.035	66.942	0.028	-185.575	-180.058	131.172
400	16.673	71.612	67.555	1.623	-186.731	-178.103	97.311
500	17.630	75.444	68.760	3.342	-187.658	-175.838	76.859
600	18.230	78.716	70.154	5.137	-188.464	-173.397	63.160
700	18.625	81.557	71.584	6.981	-189.193	-170.802	53.327
800	18.896	84.063	72.991	8.858	-202.937	-169.397	46.277
900	19.088	86.300	74.348	10.758	-203.286	-165.183	40.112
1000	19.230	88.319	75.645	12.674	-203.636	-160.931	35.171
1100	19.337	90.157	76.882	14.602	-203.985	-156.645	31.123
1200	19.420	91.844	78.060	16.540	-204.333	-152.324	27.742
1300	19.484	93.401	79.181	18.486	-204.684	-147.974	24.877
1400	19.536	94.847	80.249	20.437	-205.037	-143.599	22.417
1500	19.579	96.196	81.267	22.393	-205.393	-139.199	20.281
1600	19.614	97.461	82.240	24.352	-205.750	-134.774	18.409
1700	19.642	98.651	83.171	26.315	-206.110	-130.326	16.755
1800	19.667	99.774	84.063	28.281	-206.474	-125.861	15.282
1900	19.688	100.838	84.918	30.249	-206.839	-121.370	13.961
2000	19.705	101.848	85.739	32.218	-207.208	-116.862	12.770
2100	19.721	102.810	86.529	34.190	-207.580	-112.338	11.691
2200	19.734	103.728	87.290	36.162	-207.956	-107.792	10.708
2300	19.745	104.605	88.024	38.136	-208.334	-103.231	9.809
2400	19.756	105.446	88.733	40.111	-208.716	-98.653	8.984
2500	19.765	106.253	89.418	42.087	-209.102	-94.060	8.223
2600	19.773	107.028	90.080	44.064	-209.489	-89.449	7.519
2700	19.780	107.774	90.722	46.042	-209.880	-84.825	6.866
2800	19.786	108.494	91.344	48.020	-210.274	-80.189	6.259
2900	19.792	109.188	91.947	49.999	-210.672	-75.533	5.692
3000	19.797	109.859	92.533	51.979	-211.075	-70.870	5.163
3100	19.802	110.508	93.102	53.958	-211.478	-66.188	4.666
3200	19.806	111.137	93.656	55.939	-211.887	-61.495	4.200
3300	19.810	111.747	94.195	57.920	-212.297	-56.791	3.761
3400	19.814	112.338	94.720	59.901	-212.712	-52.070	3.347
3500	19.817	112.913	95.232	61.882	-213.131	-47.339	2.956
3600	19.820	113.471	95.731	63.864	-213.550	-42.594	2.586
3700	19.823	114.014	96.218	65.846	-213.976	-37.839	2.235
3800	19.825	114.543	96.693	67.829	-214.403	-33.072	1.902
3900	19.827	115.058	97.157	69.811	-214.836	-28.300	1.586
4000	19.830	115.560	97.611	71.794	-215.269	-23.505	1.284
4100	19.832	116.049	98.055	73.777	-215.708	-18.709	0.997
4200	19.834	116.527	98.489	75.761	-216.150	-13.898	0.723
4300	19.835	116.994	98.914	77.744	-216.593	-9.076	0.461
4400	19.837	117.450	99.330	79.728	-217.044	-4.246	0.211
4500	19.838	117.896	99.738	81.711	-217.495	0.596	-0.029
4600	19.840	118.332	100.137	83.695	-217.949	5.446	-0.259
4700	19.841	118.758	100.529	85.679	-218.408	10.307	-0.479
4800	19.842	119.176	100.913	87.664	-218.869	15.179	-0.691
4900	19.844	119.585	101.290	89.648	-219.335	20.064	-0.895
5000	19.845	119.986	101.660	91.632	-219.804	24.951	-1.091
5100	19.846	120.379	102.023	93.617	-220.276	29.847	-1.279
5200	19.847	120.765	102.380	95.601	-220.752	34.763	-1.461
5300	19.848	121.143	102.730	97.586	-221.230	39.681	-1.636
5400	19.849	121.514	103.075	99.571	-221.713	44.603	-1.805
5500	19.849	121.878	103.413	101.556	-222.198	49.542	-1.969
5600	19.850	122.236	103.746	103.541	-222.688	54.490	-2.127
5700	19.851	122.587	104.074	105.526	-223.182	59.443	-2.279
5800	19.852	122.932	104.396	107.511	-223.676	64.406	-2.427
5900	19.852	123.272	104.713	109.496	-224.176	69.369	-2.570
6000	19.853	123.605	105.025	111.482	-224.678	74.355	-2.708

Dec. 31, 1976

SULFUR TRIFLUORIDE UNINEGATIVE ION (SF_3^-) (IDEAL GAS) GFW = 89.05575

Point Group [C_{2v}]
$S°_{298.15}$ = [66.9 ± 1.0] gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -183.1 ± 7.0 kcal/mol
$\Delta Hf°_{298.15}$ = -185.6 ± 7.0 kcal/mol
F_3S

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[850](1)	[300](1)	[450](1)
[550](1)	[725](1)	[350](1)

Bond Distances: S-F* = [1.545] Å S-F** = [1.646] Å σ = [2]
Bond Angles: F*-S-F** = [87°] F**-S-F** = [174°]
(* - equatorial ** - axial)
Product of Moments of Inertia: $I_AI_BI_C$ = [2.1580 x 10^{-114}] g^3 cm^6

Heat of Formation

Using time-of-flight measurements, Harland and Thynne (1, 2) have identified SF_3^- in the negative ion mass spectra of SF_4, SF_6, and SF_5Cl. Ionization efficiency curves obtained for a dissociative resonance capture process involving SF_4 were analyzed by a deconvolution procedure to give an appearance potential (AP) for SF_3^- of 0.70±0.05 eV. Harland and Thynne (1) suggested that the process responsible for ion formation was $SF_4(g) + e^- = SF_3^-(g) + F(g)$. Assuming that the products are formed with no excess energies, we assign the measured value of AP to $\Delta Hr°_0$ of the proposed ion-formation process, and we obtain the adopted value, $\Delta Hf°_0(SF_3^-,g)$ = -183.1±7.0 kcal/mol by combining $\Delta Hr°_0$ with JANAF heats of formation (3) for SF_4 and F. Using this ΔHf° value, we calculate an electron affinity (EA) of $EA(SF_3)$ = 2.77±0.65 eV and a fluoride-ion affinity (IA) of $IA(SF_2)$ = 52.7 kcal/mol. This value of EA is in excellent agreement with the result (EA = 2.71 eV) obtained by a magnetron technique (4), suggesting that the electron-impact data are reliable and that the interpretation is correct.

The electron-impact AP for SF_3^- from SF_5Cl has been reported (2) as 7.0±0.2 eV. Harland and Thynne (1, 2) have suggested two ion formation processes; namely, (A) $SF_5Cl(g) + e^- = SF_3^-(g) + F(g) + FCl(g)$ and (B) $SF_5Cl(g) + e^- = SF_3^-(g) + 2F(g) + Cl(g)$. We eliminate (A) as a plausible process since it leads to $EA(SF_3)$ = -2.1 eV. We are unable to reproduce the result (EA = 2.9±0.1 eV) obtained for process (A) by Harland and Thynne (1) and believe their calculations to be in error. Process (B) leads to $EA(SF_3)$ = 0.5 eV which suggests that $EA(SF_3) < EA(SF_4)$. We believe that this is very unlikely based on trends in the electron affinities for S-F species (3). We conclude that process (B) very likely involves excess energy terms, amounting to about 2.2 eV.

ΔHf° is calculated to be -185.6 kcal/mol at 298.15 K. In addition, we find that the primary bond dissociation energy $D°_0(SF_2^--F)$ is 108.0 kcal/mol which when compared with JANAF $D°_0$ values for SF_3^+(91.4 kcal/mol) and SF_3(67.3 kcal/mol) indicates that the trend is $D°_0(SF_3^-) > D°_0(SF_3^+) >> D°_0(SF_3)$. The observed increased bond strengths in both ions relative to the SF_3 radical suggest that the positive and negative charges are delocalized in the even-electron ions. Further evidence supporting this view is presented on the $SF_3^+(g)$ table (3). The heat of atomization ($\Delta Ha°_0$) and average bond dissociation energy ($\bar{D}°_0$) are 225.6 kcal/mol and 75.2 kcal/mol, respectively.

Heat Capacity and Entropy

SF_3^- has 28 valence electrons, and according to the Walsh correlation diagram (5), the ion should have a planar structure. We predict that this planar structure will have a slightly distorted T-shape (C_{2v} symmetry) by analogy with that for the isoelectronic molecule ClF_3(3). As pointed out by Frey et al. (6), the slightly distorted T-shaped structure of ClF_3 is closely related to the trigonal bipyramidal structure of SF_4. We estimate structural data for SF_3^- from that for SF_4 (3) by considering the effects of removing one of its equatorial fluorine atoms. We assume that this removal process would produce no change in the S-F bond lengths and only minor changes in the bond angles. The structural data obtained in this way appear reasonable in comparison with that for ClF_3 (3). The individual moments of inertia are: I_A = 2.2638 x 10^{-38}, I_B = 1.7046 x 10^{-38}, and I_C = 5.5923 x 10^{-39} g cm^2.

The vibrational representation for the adopted structure of SF_3^- is $3A_1 + 2B_1 + B_2$. We estimate the fundamentals according to symmetry species by analogy with the frequencies and assignments for ClF_3 and SF_4 (3, 6). Since several of the assignments for SF_4 (7) are uncertain, more weight is given to the results for ClF_3. We assume a singlet ground state (no unpaired electrons) and neglect excited states.

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F_3S^-

SILICON TRIFLUORIDE (SiF_3) F3SI

(IDEAL GAS) GFW=85.080709

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.202	-258.670	-258.670	INFINITE
100	9.250	54.845	78.628	-2.378	-258.952	-258.241	564.377
200	12.145	62.205	68.704	-1.300	-259.205	-257.425	281.298
298	14.251	67.464	67.464	0.000	-259.400	-256.508	188.023
300	14.285	67.553	67.465	0.026	-259.404	-256.491	186.851
400	15.856	71.891	68.045	1.538	-259.552	-255.496	139.594
500	16.932	75.552	69.190	3.181	-259.659	-254.467	111.226
600	17.660	78.708	70.520	4.913	-259.741	-253.422	92.308
700	18.162	81.470	71.891	6.706	-259.805	-252.363	78.790
800	18.518	83.920	73.244	8.541	-259.863	-251.298	68.650
900	18.776	86.117	74.555	10.406	-259.916	-250.222	60.761
1000	18.969	88.105	75.812	12.294	-259.972	-249.143	54.449
1100	19.116	89.921	77.013	14.198	-260.032	-248.057	49.284
1200	19.230	91.589	78.159	16.116	-260.096	-246.966	44.978
1300	19.321	93.132	79.252	18.043	-260.166	-245.868	41.334
1400	19.394	94.566	80.296	19.979	-260.245	-244.766	38.209
1500	19.453	95.907	81.292	21.922	-260.332	-243.657	35.500
1600	19.502	97.164	82.245	23.869	-260.428	-242.543	33.129
1700	19.543	98.347	83.158	25.822	-272.526	-241.315	31.023
1800	19.578	99.465	84.033	27.778	-272.588	-239.478	29.076
1900	19.608	100.525	84.873	29.737	-272.648	-237.636	27.334
2000	19.633	101.531	85.681	31.699	-272.711	-235.792	25.766
2100	19.655	102.490	86.459	33.664	-272.774	-233.944	24.347
2200	19.674	103.404	87.209	35.630	-272.837	-232.094	23.056
2300	19.690	104.279	87.932	37.598	-272.904	-230.242	21.878
2400	19.705	105.118	88.631	39.568	-272.970	-228.384	20.797
2500	19.718	105.922	89.306	41.539	-273.038	-226.525	19.803
2600	19.729	106.696	89.960	43.512	-273.107	-224.663	18.884
2700	19.740	107.441	90.594	45.485	-273.179	-222.799	18.034
2800	19.749	108.159	91.209	47.460	-273.252	-220.931	17.244
2900	19.757	108.852	91.805	49.435	-273.327	-219.060	16.509
3000	19.764	109.522	92.385	51.411	-273.405	-217.190	15.822
3100	19.771	110.170	92.948	53.388	-273.482	-215.314	15.179
3200	19.777	110.798	93.496	55.365	-273.563	-213.435	14.577
3300	19.783	111.406	94.030	57.343	-273.645	-211.554	14.010
3400	19.788	111.997	94.549	59.322	-273.729	-209.672	13.477
3500	19.793	112.571	95.056	61.301	-273.816	-207.789	12.975
3600	19.797	113.128	95.550	63.280	-365.865	-203.643	12.363
3700	19.801	113.671	96.033	65.260	-365.857	-199.137	11.762
3800	19.805	114.199	96.504	67.240	-365.850	-194.630	11.194
3900	19.808	114.713	96.964	69.221	-365.846	-190.126	10.654
4000	19.811	115.215	97.414	71.202	-365.845	-185.620	10.142
4100	19.814	115.704	97.854	73.183	-365.846	-181.116	9.654
4200	19.817	116.182	98.285	75.165	-365.849	-176.611	9.190
4300	19.820	116.648	98.707	77.147	-365.853	-172.104	8.747
4400	19.822	117.104	99.120	79.129	-365.861	-167.599	8.325
4500	19.824	117.549	99.524	81.111	-365.871	-163.090	7.921
4600	19.826	117.985	99.921	83.094	-365.882	-158.584	7.534
4700	19.828	118.411	100.310	85.076	-365.895	-154.077	7.164
4800	19.830	118.829	100.691	87.059	-365.912	-149.572	6.810
4900	19.832	119.238	101.066	89.042	-365.928	-145.063	6.470
5000	19.834	119.638	101.433	91.026	-365.949	-140.559	6.144
5100	19.836	120.031	101.794	93.009	-365.969	-136.046	5.830
5200	19.837	120.416	102.148	94.993	-365.994	-131.539	5.528
5300	19.839	120.794	102.497	96.977	-366.019	-127.030	5.238
5400	19.841	121.165	102.839	98.961	-366.047	-122.521	4.959
5500	19.842	121.529	103.175	100.945	-366.077	-118.013	4.689
5600	19.844	121.887	103.506	102.929	-366.110	-113.499	4.429
5700	19.846	122.238	103.832	104.914	-366.145	-108.987	4.179
5800	19.847	122.583	104.152	106.898	-366.182	-104.475	3.937
5900	19.849	122.922	104.468	108.883	-366.221	-99.965	3.703
6000	19.851	123.256	104.778	110.868	-366.264	-95.453	3.477

Sept. 30, 1963; Dec. 31, 1969; June 30, 1970
June 30, 1976; Dec. 31, 1977

SILICON TRIFLUORIDE (SiF_3) (IDEAL GAS) GFW = 85.080709

ΔHa°_0 = 420.4 ± 4 kcal/mol

$S^\circ_{298.15}$ = [67.46 ± 0.1] gibbs/mol

ΔHf°_0 = -258.7 ± 4 kcal/mol F3SI

$\Delta Hf^\circ_{298.15}$ = -259.4 ± 4 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$[X^2A_1]$	0	[2]
$[^2E]$	44120	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
832(1)
406(1)
954(2)
290(2)

Point Group: C_{3v} σ = 3

Bond Distance: Si-F = [1.5624] Å

Bond Angle: F-Si-F = 109.4712°

Product of the Moments of Inertia: $I_AI_BI_C = [25.3684 \times 10^{-115}]\ g^3\ cm^6$

Heat of Formation

The adopted $\Delta Hf^\circ_{298}(SiF_3, g) = -259.4\pm2$ kcal/mole is derived from the mass spectrometric equilibrium constants determined by Farber (9) for the reaction $SiF_4(g) + SiF_2(g) = 2\ SiF_3(g)$. Our second and third law analysis of the ten points in the 1590 to 1782 K range, using auxiliary data (1), gives $\Delta Hr^\circ_{298} = 7.47\pm0.19$ kcal/mol (second law) and $\Delta Hr^\circ_{298} = 7.61\pm0.04$ kcal/mol with a drift of 0.09±0.11 gibbs/mol (third law). The third law heat of reaction leads to the adopted heat of formation. The adopted value is consistent with the total pressure data above the silicon-magnesium fluoride system observed by Layne (2). The value of $\Delta Hf^\circ = -235\pm20$ kcal/mol, derived by McDonald et al. (3) from appearance and ionization potentials and by Wang, Margrave, and Franklin (4) from appearance potentials and translational energies, appears to be too positive. A later paper by Franklin (10) suggests that the assumption of the fraction of active vibrations as a constant may have caused a bias of 15 kcal/mol or more in the derived heat of formation.

$\Delta Hf^\circ_0 = -258.7$ kcal/mol corresponds to $\Delta Ha^\circ_0 = 420.4$ kcal/mol, using auxiliary data (1). The average bond energies in $SiF_2(g)$, $SiF_3(g)$, and $SiF_4(g)$ are all within ∿ 2 kcal/mol.

Heat Capacity and Entropy

The electronic levels are those tentatively assigned by Wang et al. (5) from emission spectral observations. The first excited state is designated as ^2E, rather than ^2B, as stated by So (11) based on ab initio Hartree-Fock calculations and group theory arguments. The vibrational frequencies are derived from matrix-isolation UV and IR spectra of Milligan et al. (6) They also determined the angle between the Si-F bonds and the three-fold axis to be 71±2° which is consistent with the adopted tetrahedral F-Si-F bond angle. Theoretical calculations (7,8,11) indicate that this angle should be somewhat less than the tetrahedral angle. Calculations based on a bond angle of 108° decrease S°_{298} by 0.029 gibbs/mol. As suggested by Milligan et al. (6), the Si-F bond length is assumed to be that in $SiHF_3$ (1). The C_{3v} structure is well established by ESR studies (12,13). The principal moments of inertia are $I_A = I_B = 11.1148 \times 10^{-39} g\ cm^2$ and $I_C = 20.5349 \times 10^{-39} g\ cm^2$.

References

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F3SI

HYDROGEN FLUORIDE CYCLIC TETRAMER (H_4F_4) F_4H_4
(IDEAL GAS) GFW=80.025212

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-5.389	-280.063	-280.063	INFINITE
100	16.024	61.249	103.185	-4.194	-281.692	-274.868	600.715
200	21.393	74.097	85.644	-2.309	-282.495	-267.692	292.516
298	25.474	83.437	83.437	0.000	-282.940	-260.321	190.818
300	25.540	83.595	83.438	0.047	-282.947	-260.182	189.540
400	28.504	91.375	84.478	2.759	-283.161	-252.554	137.987
500	30.559	97.969	86.534	5.718	-283.208	-244.894	107.042
600	32.070	103.680	88.926	8.852	-283.134	-237.237	86.412
700	33.285	108.718	91.401	12.122	-282.964	-229.600	71.683
800	34.328	113.232	93.852	15.504	-282.718	-221.994	60.645
900	35.254	117.330	96.237	18.984	-282.402	-214.420	52.068
1000	36.084	121.088	98.536	22.551	-282.031	-206.887	45.215
1100	36.829	124.563	100.747	26.198	-281.608	-199.393	39.615
1200	37.493	127.796	102.867	29.914	-281.146	-191.939	34.956
1300	38.085	130.821	104.903	33.694	-280.648	-184.524	31.021
1400	38.611	133.663	106.857	37.529	-280.125	-177.150	27.654
1500	39.077	136.343	108.734	41.414	-279.580	-169.814	24.742
1600	39.491	138.879	110.539	45.343	-279.017	-162.515	22.198
1700	39.857	141.284	112.278	49.311	-278.439	-155.249	19.958
1800	40.183	143.572	113.953	53.313	-277.855	-148.021	17.972
1900	40.472	145.752	115.570	57.346	-277.260	-140.822	16.198
2000	40.731	147.835	117.132	61.407	-276.663	-133.659	14.605
2100	40.961	149.828	118.641	65.491	-276.061	-126.522	13.167
2200	41.168	151.738	120.103	69.598	-275.458	-119.416	11.863
2300	41.353	153.572	121.518	73.724	-274.856	-112.337	10.674
2400	41.521	155.336	122.891	77.868	-274.252	-105.283	9.587
2500	41.671	157.034	124.223	82.028	-273.650	-98.254	8.589
2600	41.808	158.671	125.516	86.202	-273.052	-91.250	7.670
2700	41.932	160.251	126.774	90.389	-272.457	-84.268	6.821
2800	42.044	161.778	127.997	94.588	-271.868	-77.311	6.034
2900	42.147	163.255	129.187	98.797	-271.281	-70.372	5.303
3000	42.241	164.686	130.347	103.017	-270.699	-63.455	4.623
3100	42.327	166.072	131.477	107.245	-270.121	-56.553	3.987
3200	42.406	167.417	132.579	111.482	-269.552	-49.676	3.393
3300	42.478	168.723	133.655	115.726	-268.986	-42.812	2.835
3400	42.545	169.993	134.705	119.977	-268.429	-35.968	2.312
3500	42.607	171.227	135.731	124.235	-267.877	-29.139	1.819
3600	42.664	172.428	136.734	128.499	-267.331	-22.325	1.355
3700	42.716	173.597	137.714	132.768	-266.794	-15.527	0.917
3800	42.766	174.737	138.674	137.042	-266.264	-8.743	0.503
3900	42.811	175.849	139.613	141.321	-265.741	-1.972	0.111
4000	42.854	176.933	140.532	145.604	-265.228	4.782	-0.261
4100	42.893	177.992	141.433	149.891	-264.721	11.527	-0.614
4200	42.930	179.026	142.316	154.182	-264.222	18.260	-0.950
4300	42.965	180.037	143.181	158.477	-263.731	24.980	-1.270
4400	42.997	181.025	144.030	162.775	-263.249	31.689	-1.574
4500	43.028	181.991	144.863	167.077	-262.777	38.383	-1.864
4600	43.056	182.937	145.681	171.381	-262.311	45.073	-2.141
4700	43.083	183.864	146.483	175.688	-261.854	51.750	-2.406
4800	43.108	184.771	147.271	179.997	-261.407	58.417	-2.660
4900	43.132	185.660	148.046	184.309	-260.965	65.077	-2.903
5000	43.154	186.532	148.807	188.624	-260.534	71.725	-3.135
5100	43.176	167.386	149.555	192.940	-260.110	78.368	-3.358
5200	43.196	188.225	150.290	197.259	-259.695	84.999	-3.572
5300	43.215	189.048	151.014	201.579	-259.287	91.625	-3.778
5400	43.232	189.856	151.726	205.902	-258.886	98.242	-3.976
5500	43.249	190.649	152.426	210.226	-258.492	104.852	-4.166
5600	43.266	191.429	153.116	214.551	-258.107	111.455	-4.350
5700	43.281	192.195	153.795	218.879	-257.727	118.050	-4.526
5800	43.296	192.947	154.463	223.208	-257.352	124.640	-4.696
5900	43.309	193.688	155.122	227.538	-256.984	131.225	-4.861
6000	43.323	194.416	155.771	231.869	-256.625	137.798	-5.019

July 31, 1972 (NBS); June 30, 1977

HYDROGEN FLUORIDE CYCLIC TETRAMER (H_4F_4) (IDEAL GAS) GFW = 80.025212

F_4H_4

Point Group C_4

$S°_{298.15}$ = [83.4 ± 4] gibbs/mol

Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -280.1 ± 5 kcal/mol

$\Delta Hf°_{298.15}$ = -282.9 ± 5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[702](4)
[53](2)
[962](4)
[552](4)
[3060](4)

Interatomic Distance: F-F = [2.5] Å

σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.7903 x 10^{-113}] g^3 cm^6

Heat of Formation

The enthalpy of 4 HF(g) → H_4F_4(g) was taken as the mean of third law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier (1) measured the vapor density of associated HF between 20 and 60°C and between 50 and 550 torr. Franck and Meyer (2) measured C_p between -20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported second law values of ΔH and ΔS. At n = 4 their second law values differed by 4.2 kcal/mol, which was taken as an estimate of error, while the calculated third law values differed by 1.5 kcal/mol. Using $\Delta Hr°_{298}$ = -22.38 kcal/mol and auxiliary JANAF data (3) gives the heat of formation of H_4F_4(g).

Heat Capacity and Entropy

The molecular structure of H_4F_4 was assumed as planar with the F atoms forming the vertices of a square and with the H atoms also lying in the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's (4) theoretical molecular-orbital studies on HF polymers. The length of side (F-F axis) was taken from Atoji and Lipscomb's (5) X-ray studies of solid HF (F-F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell (6) determined for the gaseous polymers by electron diffraction. The low F-bending frequency (53 cm^{-1}) was taken from Boutin et al. (7). The other vibrational frequencies were taken from Kittelberger and Hornig's (8) work on crystalline HF. Huong and Couzi (9) and Smith (10) have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table (11) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (11), we recalculate the table in terms of 1973 fundamental constants (12), 1975 atomic weights (13), and current JANAF reference states for the elements.

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SULFUR TETRAFLUORIDE UNIPOSITIVE ION (SF_4^+) F_4S^+
(IDEAL GAS) GFW=108.05305

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-3.945	99.284		
100							
200							
298	19.215	74.464	74.464	0.000	99.437	106.912	-78.369
300	19.266	74.583	74.464	0.036	99.444	106.958	-77.919
400	21.425	80.447	75.249	2.079	99.345	109.422	-59.785
500	22.737	85.381	76.795	4.293	99.504	111.924	-48.922
600	23.564	89.605	78.587	6.611	99.798	114.383	-41.664
700	24.108	93.281	80.429	8.996	100.177	116.809	-36.469
800	24.482	96.526	82.242	11.427	87.548	117.886	-32.205
900	24.749	99.426	83.993	13.889	88.317	121.633	-29.537
1000	24.945	102.044	85.670	16.374	89.088	125.294	-27.383
1100	25.093	104.428	87.268	18.876	89.860	128.876	-25.605
1200	25.207	106.617	88.791	21.391	90.633	132.390	-24.111
1300	25.297	108.638	90.241	23.917	91.405	135.840	-22.837
1400	25.369	110.516	91.623	26.450	92.174	139.229	-21.735
1500	25.427	112.268	92.941	28.990	92.941	142.563	-20.771
1600	25.475	113.911	94.201	31.535	93.704	145.845	-19.921
1700	25.516	115.456	95.406	34.085	94.466	149.082	-19.166
1800	25.549	116.916	96.561	36.638	95.222	152.269	-18.488
1900	25.578	118.298	97.669	39.195	95.978	155.421	-17.877
2000	25.603	119.610	98.734	41.754	96.729	158.532	-17.324
2100	25.624	120.860	99.758	44.315	97.474	161.599	-16.818
2200	25.642	122.053	100.744	46.878	98.216	164.636	-16.355
2300	25.658	123.193	101.696	49.443	98.955	167.640	-15.929
2400	25.672	124.285	102.614	52.010	99.690	170.610	-15.536
2500	25.685	125.333	103.502	54.578	100.420	173.550	-15.172
2600	25.696	126.341	104.361	57.147	101.145	176.461	-14.833
2700	25.706	127.311	105.193	59.717	101.868	179.345	-14.517
2800	25.715	128.246	106.000	62.288	102.587	182.198	-14.221
2900	25.724	129.148	106.783	64.860	103.301	185.033	-13.944
3000	25.731	130.021	107.543	67.433	104.009	187.835	-13.684
3100	25.738	130.865	108.282	70.006	104.715	190.617	-13.438
3200	25.744	131.682	109.000	72.580	105.415	193.378	-13.207
3300	25.751	132.474	109.700	75.155	106.113	196.114	-12.988
3400	25.756	133.243	110.381	77.730	106.806	198.834	-12.781
3500	25.762	133.990	111.045	80.306	107.493	201.532	-12.584
3600	25.768	134.715	111.692	82.883	108.179	204.211	-12.397
3700	25.773	135.421	112.324	85.460	108.858	206.868	-12.219
3800	25.778	136.109	112.941	88.037	109.534	209.510	-12.050
3900	25.784	136.779	113.544	90.615	110.204	212.126	-11.887
4000	25.789	137.431	114.133	93.194	110.872	214.736	-11.733
4100	25.795	138.068	114.709	95.773	111.535	217.322	-11.584
4200	25.801	138.690	115.272	98.353	112.194	219.896	-11.442
4300	25.806	139.297	115.824	100.933	112.851	222.455	-11.306
4400	25.813	139.890	116.364	103.514	113.500	224.995	-11.176
4500	25.819	140.471	116.894	106.096	114.147	227.519	-11.050
4600	25.826	141.038	117.412	108.678	114.791	230.030	-10.929
4700	25.833	141.594	117.921	111.261	115.430	232.529	-10.813
4800	25.840	142.138	118.420	113.845	116.067	235.016	-10.701
4900	25.848	142.670	118.909	116.429	116.698	237.492	-10.593
5000	25.856	143.193	119.390	119.014	117.324	239.945	-10.488
5100	25.864	143.705	119.862	121.600	117.948	242.387	-10.387
5200	25.873	144.207	120.325	124.187	118.569	244.830	-10.290
5300	25.882	144.700	120.780	126.775	119.187	247.253	-10.196
5400	25.891	145.184	121.228	129.363	119.798	249.656	-10.104
5500	25.900	145.659	121.668	131.953	120.408	252.058	-10.016
5600	25.910	146.126	122.100	134.544	121.013	254.450	-9.930
5700	25.921	146.585	122.526	137.135	121.614	256.826	-9.847
5800	25.931	147.035	122.944	139.728	122.215	259.194	-9.767
5900	25.942	147.479	123.356	142.321	122.810	261.542	-9.688
6000	25.953	147.915	123.762	144.916	123.401	263.893	-9.612

Dec. 31, 1976

SULFUR TETRAFLUORIDE UNIPOSITIVE ION (SF_4^+) (IDEAL GAS) GFW = 108.05305

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [74.5 ± 2.0] gibbs/mol

ΔHf°_0 = 99.3 ± 12.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 99.4 ± 12.0 kcal/mol

F_4S^+

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
26213	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[850](1)	[200](1)	[500](1)
[500](1)	[450](1)	[800](1)
[300](1)	[700](1)	[200](1)

Bond Distances: S-F* = [1.62] Å S-F** = [1.73] Å

Bond Angles: F*-S-F* = [109°] F*-S-F** = [88.3°]

F**-S-F** = [174°] σ = [2]

(* - *equatorial* ** - *axial*)

Product of Moments of Inertia: $I_AI_BI_C$ = [9.3891 x 10^{-114}] g^3 cm^6

Heat of Formation

The electron-impact appearance potential (AP) of SF_4^+ from SF_4 has been reported as 12.28±0.03 eV (1), 12.08±0.1 eV (2), and 12.1±0.5 eV (2). Using the mean value (12.15 eV) of these three measured appearance potentials as ΔHr°_0 for the direct ionization process $SF_4(g) + e^- = SF_4^+(g) + 2e^-$, we obtain the adopted value $\Delta Hf^\circ_0(SF_4^+,g)$ = 99.3 kcal/mol, by combining ΔHr°_0 with $\Delta Hf^\circ_0(SF_4,g)$ = -180.9±5.0 kcal/mol (3). We estimate that the adiabatic AP (or ionization potential) could be as much as 0.3 eV lower than the measured vertical values (1, 2), suggesting uncertainties in ΔHr°_0 and ΔHf°_0 of ±7.0 kcal/mol and ±12.0 kcal/mol, respectively. Our predictions are based on the fact that photoelectron spectrometric studies (4) on the species ClF_3 show that the first adiabatic ionization potential (IP) is 0.23 eV lower than the vertical value and 0.35 eV lower than the results obtained by the electron-impact method. The similarity in the structures of SF_4 and ClF_3 has been noted (5), and we predict that the geometry changes produced by ionization should also be very similar for the two fluorides.

Additional information is available which tends to provide some support for our adopted value of $IP(SF_4)$ = 12.15±0.3 eV. Fehsenfeld (6) has observed a charge-transfer reaction between SF_4^+ and NO which sets the lower limit of IP at 9.25 eV. Binding energies (7) for SF_4 and SF_4^+, computed by CNDO/2 calculations and rescaled according to energy partitioning concepts, have been combined to give IP values of 11.1 eV and 10.6 eV. Three independent measurements (2, 8, and 9) of the fragment-ion AP for SF_4^+ from SF_6 are in agreement with the result AP = 18.61 eV. We combine this $AP(SF_4^+/SF_6)$ with our adopted IP value and obtain ΔHr°_0 = 149.0 kcal/mol for the process $SF_6(g) = SF_4(g) + 2F(g)$. This leads to a ΔHf° of -176.2 kcal/mol for SF_4 which compares favorably with JANAF data (3).

ΔHf° is calculated to be 99.4 kcal/mol at 298.15 K. Also, we find that the primary bond dissociation energy $D^\circ_0(SF_3^+\text{-}F)$ is 12.9 kcal/mol which when compared with D°_0 values (3) for SF_4 (80.0 kcal/mol) and SF_4^- (46.6 kcal/mol) indicates that the trend is $D^\circ_0(SF_4) >> D^\circ_0(SF_4^-) >> D^\circ_0(SF_4^+)$. The observed instability of the radical cation towards dissociation to SF_3^+ and F is consistent with ion abundances (9, 10) obtained for SF_4^+ and SF_3^+ in the mass spectra of SF_5Cl and SF_6. Values of the ratio $I(SF_3^+)/I(SF_4^+)$ lie in the range 3.1-7.0. (See the $SF_3^+(g)$ table for a discussion on its stability.) The heat of atomization (ΔHa°_0) and mean bond dissociation energy ($\bar{D}^\circ_0$) are 278.8 kcal/mol and 69.7 kcal/mol, respectively.

Heat Capacity and Entropy

Delwiche (8) has reported an ionization efficiency curve for SF_4^+ which was obtained from retarded potential difference (RPD) measurements on SF_6. This curve shows the existence of two excited states, lying 26213 cm^{-1} and 45167 cm^{-1} above the ground state. The level at 45167 cm^{-1} is not included here since it has a negligible effect on the thermal functions. We assume that the one unpaired electron forms two doublet states which are non-degenerate.

The ESR spectrum (11) of SF_4^+, recorded during the radiolysis of SF_6 with 2.8 MeV electrons, suggests that the four fluorine nuclei are equivalent. However, the assignment of this spectrum to SF_4^+ has been questioned by Morton and Preston (12) who presented evidence which indicates that the radical responsible is more likely to be SF_5. Their re-assignment (12) is substantiated by the results of SCF MO calculations (13) on SF_5. By analogy with the isoelectronic radical PF_4 (14, 15), we predict that the SF_4^+ structure is trigonal bipyramid with the unpaired electron occupying one of the equatorial positions. We use bond angles from PF_4 (14) and assume that the loss of an electron from SF_4 increases both the equatorial and axial bond lengths by 5%. Our view that the bonding in SF_4^+ is weaker than that in SF_4 follows the predictions (14) made for PF_4 and is further confirmed by the fact that the mean bond dissociation energy $\bar{D}^\circ_0$ in SF_4 (80.0 kcal/mol) is roughly 10 kcal/mol greater than in SF_4^+ (69.7 kcal/mol). The individual moments of inertia are: $I_A = 2.9805 \times 10^{-38}$, $I_B = 2.2107 \times 10^{-38}$, and $I_C = 1.4250 \times 10^{-38}$ g cm^2.

We estimate vibrational frequencies from those for SF_4 (3) by considering the effect of the structural changes brought about by ionization. Thus, on going from SF_4 to SF_4^+, we expect a decrease in all of the frequencies to reflect the weaker bonding in the cation.

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F_4S^+

SULFUR TETRAFLUORIDE UNINEGATIVE ION (SF_4^-) F_4S^-
(IDEAL GAS) GFW=108.05415

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-4.417	-209.772		
100							
200							
298	21.316	74.773	74.772	0.000	-212.109	-201.751	147.887
300	21.359	74.905	74.773	0.039	-212.117	-201.687	146.929
400	23.033	81.304	75.634	2.268	-213.024	-198.131	108.254
500	23.943	86.551	77.309	4.621	-213.720	-194.328	84.941
600	24.481	90.968	79.227	7.044	-214.315	-190.391	69.350
700	24.821	94.769	81.182	9.511	-214.846	-186.336	58.177
800	25.049	98.099	83.093	12.005	-228.406	-183.499	50.130
900	25.208	101.060	84.928	14.518	-228.580	-177.875	43.194
1000	25.324	103.722	86.676	17.045	-228.761	-172.232	37.641
1100	25.411	106.140	88.338	19.582	-228.948	-166.572	33.095
1200	25.477	108.354	89.915	22.127	-229.137	-160.890	29.302
1300	25.529	110.395	91.413	24.677	-229.335	-155.193	26.090
1400	25.570	112.288	92.837	27.232	-229.538	-149.484	23.335
1500	25.604	114.054	94.193	29.791	-229.746	-143.758	20.946
1600	25.632	115.707	95.487	32.353	-229.958	-138.018	18.852
1700	25.655	117.262	96.722	34.917	-230.176	-132.265	17.004
1800	25.675	118.729	97.905	37.484	-230.400	-126.503	15.360
1900	25.692	120.117	99.037	40.052	-230.627	-120.722	13.886
2000	25.708	121.436	100.125	42.622	-230.859	-114.930	12.559
2100	25.723	122.690	101.170	45.194	-231.095	-109.131	11.357
2200	25.736	123.887	102.175	47.767	-231.337	-103.316	10.264
2300	25.750	125.032	103.144	50.341	-231.583	-97.491	9.264
2400	25.763	126.128	104.079	52.916	-231.834	-91.657	8.346
2500	25.776	127.180	104.982	55.493	-232.089	-85.811	7.502
2600	25.790	128.191	105.856	58.072	-232.346	-79.954	6.721
2700	25.805	129.165	106.701	60.651	-232.608	-74.087	5.997
2800	25.820	130.103	107.520	63.233	-232.872	-68.215	5.324
2900	25.836	131.010	108.315	65.815	-233.142	-62.325	4.697
3000	25.852	131.886	109.086	68.400	-233.416	-56.435	4.111
3100	25.870	132.734	109.835	70.986	-233.689	-50.530	3.562
3200	25.888	133.555	110.563	73.574	-233.969	-44.617	3.047
3300	25.908	134.352	111.272	76.164	-234.250	-38.697	2.563
3400	25.928	135.126	111.963	78.755	-234.535	-32.764	2.106
3500	25.949	135.878	112.635	81.349	-234.824	-26.825	1.675
3600	25.970	136.609	113.291	83.945	-235.111	-20.875	1.267
3700	25.992	137.321	113.931	86.543	-235.405	-14.921	0.881
3800	26.014	138.014	114.556	89.144	-235.699	-8.956	0.515
3900	26.037	138.691	115.166	91.746	-235.999	-2.992	0.168
4000	26.061	139.350	115.762	94.351	-236.297	2.994	-0.164
4100	26.084	139.994	116.345	96.958	-236.600	8.976	-0.478
4200	26.108	140.623	116.916	99.568	-236.905	14.970	-0.779
4300	26.132	141.237	117.474	102.180	-237.210	20.973	-1.066
4400	26.155	141.838	118.021	104.794	-237.522	26.979	-1.340
4500	26.179	142.426	118.557	107.411	-237.832	32.993	-1.602
4600	26.202	143.002	119.082	110.030	-238.145	39.014	-1.854
4700	26.226	143.566	119.597	112.651	-238.462	45.042	-2.094
4800	26.249	144.118	120.102	115.275	-238.779	51.080	-2.326
4900	26.271	144.660	120.598	117.901	-239.100	57.125	-2.548
5000	26.294	145.191	121.085	120.529	-239.423	63.170	-2.761
5100	26.315	145.711	121.562	123.160	-239.748	69.220	-2.966
5200	26.337	146.223	122.032	125.792	-240.076	75.291	-3.164
5300	26.357	146.725	122.493	128.427	-240.405	81.359	-3.355
5400	26.378	147.217	122.946	131.064	-240.739	87.425	-3.538
5500	26.397	147.702	123.392	133.703	-241.072	93.509	-3.716
5600	26.416	148.177	123.830	136.343	-241.412	99.599	-3.887
5700	26.435	148.645	124.262	138.986	-241.753	105.691	-4.052
5800	26.453	149.105	124.686	141.630	-242.095	111.790	-4.212
5900	26.470	149.557	125.104	144.276	-242.441	117.885	-4.367
6000	26.486	150.002	125.515	146.924	-242.789	124.001	-4.517

Dec. 31, 1976

SULFUR TETRAFLUORIDE UNINEGATIVE ION (SF_4^-) (IDEAL GAS) GFW = 108.05415

Point Group [D_{4h}]
$S^\circ_{298.15}$ = [74.8 ± 2.0] gibbs/mol

ΔHf°_0 = -209.8 ± 8.0 kcal/mol F_4S^-
$\Delta Hf^\circ_{298.15}$ = -212.1 ± 8.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$^2A_1$]	0	[2]
[$^2B_1$]	[15000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[500](1)	[375](1)	[150](2)
[430](1)	[325](1)	
[300](1)	[595](2)	

Bond Distance: S-F = [1.63 ± 0.1] Å σ = [8]
Bond Angle: F-S-F = [90°]
Product of Moments of Inertia: $I_AI_BI_C$ = [9.4210 x 10^{-114}] g^3 cm^6

Heat of Formation

We adopt $\Delta Hf^\circ_0(SF_4^-,g)$ = -209.8±8.0 kcal/mol and an electron affinity (EA) of $EA(SF_4)$ = 1.25±0.56 eV. The value of ΔHf°_0 is obtained from the electron-impact appearance potential (AP) for SF_4^- from SF_6, reported by Harland and Thynne (1) as AP = 5.0± 0.1 eV. *This value has been verified in an independent study (9). We assume that the negative ion is formed by the process* $SF_6(g) + e^- = SF_4^-(g) + 2F(g)$ with no excess energies. We estimate the error in the electron-impact experiments to be ±0.3 eV (7.0 kcal/mol) which when combined with the uncertainties in the auxiliary data (2) gives an overall uncertainty in ΔHf°_0 of ±8.0 kcal/mol. Our adopted value of EA = 1.25 eV is supported by EA = 1.5 eV (3) and EA = 1.26 eV (10) which were predicted by theoretical calculations.

In the same paper, Harland and Thynne (1) also reported the $AP(SF_4^-/SF_5Cl)$ as 4.1±0.1 eV. This leads to $\Delta Hf^\circ_0(SF_4^-,g)$ = -199.9±5.0 kcal/mol and $EA(SF_4)$ = 0.82±0.4 eV. They (1) also reported appearance potentials for SF_3^- and SF_5^- from SF_5Cl which give EA values that are several tenths of an electron volt below JANAF data (2). Thus, we are led to conclude that dissociative ionization of SF_5Cl probably involves excess energies and that the derived electron affinities are lower limit values.

Our adopted results give ΔHf°_{298} = -212.1 kcal/mol and a fluoride-ion affinity (IA) of $IA(SF_3)$ = 30.5 kcal/mol. Also, we find that the primary bond dissociation energy $D^\circ_0(SF_3^--F)$ is 46.6 kcal/mol which when compared with D°_0 values (2) for SF_4 (80.0 kcal/mol) and SF_4^+ (12.9 kcal/mol) indicates that the trend is $D^\circ_0(SF_4) >> D^\circ_0(SF_4^-) >> D^\circ_0(SF_4^+)$. These thermochemical predictions of the SF_4^- stability are consistent with an autodetachment lifetime of 16.3 μsec, as measured by Harland and Thynne (4) using time-of-flight techniques. The heat of atomization (ΔHa°_0) for the products $S(g) + F^-(g) + 3F(g)$ and mean bond dissociation energy are 270.5 kcal/mol and 67.6 kcal/mol, respectively.

Heat Capacity and Entropy

We assume a square-planar configuration (D_{4h} symmetry) similar to that found for the isoelectronic radical ClF_4 (5-7). We estimate the bond length to be slightly greater (0.03 Å) than the mean (1.60 Å) of the equatorial and axial S-F bonds in SF_4 (2). *An upper limit value of 1.70 Å can be established from results of MO calculations on ClF_4 (7). The individual moments of* inertia are: $I_A = 3.3526 \times 10^{-38}$ and $I_B = I_C = 1.6763 \times 10^{-38}$ g cm^2.

The square-planar structure follows the vibrational representation $A_1 + A_2 + 2B_1 + B_2 + 2E$. We estimate the seven fundamentals by comparison with the observed frequencies for the approximately square-planar SF_4 part of SF_5^- (2). Comparison of the experimentally measured frequencies for the related species ClF_5 (2) and ClF_4^- (8) suggests that this procedure should give reliable estimates.

The electronic states and levels are based on those for ClF_4 which were predicted by Ungemach and Schaefer (7) from MO calculations. An independent MO study of ClF_4 by Gregory (6) indicates that the upper level is an $^2A_2$ state. This, however, would not alter our functions since both configurations have the same degeneracy.

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F_4S^-

HYDROGEN FLUORIDE CYCLIC PENTAMER (H_5F_5) F_5H_5
(IDEAL GAS) GFW=100.031515

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-6.924	-352.642	-352.642	INFINITE
100	20.883	68.837	123.130	-5.429	-354.677	-345.375	754.806
200	27.699	85.532	100.441	-2.982	-355.589	-335.668	366.795
298	32.820	97.594	97.594	0.000	-356.050	-325.778	238.799
300	32.903	97.797	97.594	0.061	-356.057	-325.592	237.190
400	36.615	107.804	98.934	3.548	-356.227	-315.402	172.325
500	39.186	116.267	101.576	7.346	-356.187	-305.197	133.400
600	41.077	123.586	104.648	11.363	-355.995	-295.016	107.458
700	42.597	130.036	107.823	15.549	-355.684	-284.875	88.941
800	43.902	135.811	110.967	19.875	-355.277	-274.789	75.068
900	45.060	141.050	114.023	24.324	-354.783	-264.755	64.290
1000	46.098	145.852	116.969	28.883	-354.219	-254.783	55.682
1100	47.028	150.290	119.799	33.540	-353.592	-244.868	48.650
1200	47.859	154.419	122.514	38.286	-352.914	-235.014	42.801
1300	48.600	158.279	125.118	43.109	-352.193	-225.217	37.862
1400	49.257	161.905	127.618	48.003	-351.440	-215.478	33.637
1500	49.840	165.324	130.019	52.958	-350.659	-205.795	29.984
1600	50.356	168.558	132.327	57.968	-349.857	-196.163	26.794
1700	50.815	171.624	134.549	63.027	-349.035	-186.580	23.986
1800	51.222	174.541	136.691	68.130	-348.205	-177.050	21.497
1900	51.584	177.320	138.757	73.270	-347.362	-167.562	19.274
2000	51.906	179.974	140.752	78.445	-346.517	-158.123	17.279
2100	52.195	182.514	142.680	83.650	-345.665	-148.722	15.478
2200	52.453	184.948	144.547	88.883	-344.812	-139.365	13.844
2300	52.685	187.285	146.354	94.140	-343.960	-130.047	12.357
2400	52.894	189.532	148.107	99.419	-343.106	-120.763	10.997
2500	53.083	191.695	149.807	104.718	-342.254	-111.515	9.748
2600	53.253	193.780	151.459	110.035	-341.407	-102.301	8.599
2700	53.408	195.793	153.064	115.368	-340.564	-93.121	7.537
2800	53.549	197.738	154.625	120.716	-339.729	-83.974	6.554
2900	53.677	199.619	156.144	126.078	-338.895	-74.853	5.641
3000	53.794	201.441	157.624	131.451	-338.069	-65.764	4.791
3100	53.902	203.206	159.066	136.836	-337.246	-56.697	3.997
3200	54.000	204.919	160.472	142.231	-336.436	-47.663	3.255
3300	54.091	206.582	161.844	147.636	-335.629	-38.649	2.560
3400	54.175	208.198	163.184	153.049	-334.833	-29.663	1.907
3500	54.252	209.770	164.493	158.471	-334.044	-20.700	1.293
3600	54.323	211.299	165.772	163.900	-333.263	-11.757	0.714
3700	54.389	212.789	167.022	169.335	-332.492	-2.837	0.168
3800	54.450	214.240	168.246	174.777	-331.730	6.062	-0.349
3900	54.507	215.655	169.443	180.225	-330.977	14.942	-0.837
4000	54.560	217.036	170.616	185.679	-330.236	23.800	-1.300
4100	54.610	218.384	171.765	191.137	-329.503	32.643	-1.740
4200	54.656	219.700	172.890	196.600	-328.780	41.468	-2.158
4300	54.699	220.987	173.994	202.068	-328.067	50.275	-2.555
4400	54.740	222.245	175.076	207.540	-327.365	59.066	-2.934
4500	54.778	223.475	176.138	213.016	-326.676	67.836	-3.295
4600	54.814	224.680	177.181	218.496	-325.994	76.599	-3.639
4700	54.847	225.859	178.204	223.979	-325.324	85.343	-3.968
4800	54.879	227.014	179.209	229.465	-324.665	94.074	-4.283
4900	54.908	228.146	180.196	234.954	-324.013	102.792	-4.585
5000	54.937	229.255	181.166	240.447	-323.376	111.494	-4.873
5100	54.963	230.343	182.120	245.942	-322.746	120.187	-5.150
5200	54.988	231.411	183.057	251.439	-322.128	128.864	-5.416
5300	55.012	232.459	183.979	256.939	-321.518	137.533	-5.671
5400	55.034	233.487	184.887	262.442	-320.918	146.188	-5.916
5500	55.055	234.497	185.780	267.946	-320.326	154.833	-6.152
5600	55.076	235.489	186.658	273.453	-319.745	163.468	-6.380
5700	55.095	236.464	187.524	278.961	-319.171	172.090	-6.598
5800	55.113	237.423	188.376	284.472	-318.603	180.705	-6.809
5900	55.130	238.365	189.215	289.984	-318.044	189.311	-7.012
6000	55.147	239.292	190.042	295.498	-317.495	197.901	-7.208

July 31, 1972 (NBS); June 30, 1977

HYDROGEN FLUORIDE CYCLIC PENTAMER (H_5F_5) (IDEAL GAS) GFW = 100.031515

F_5H_5

Point Group C_5
$S^{\circ}_{298.15}$ = [97.6 ± 5] gibbs/mol
Ground State Quantum Weight = 1

ΔHf°_{0} = -352.6 ± 6 kcal/mol
$\Delta Hf^{\circ}_{298.15}$ = -356.0 ± 6 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[202](5)
[53](4)
[962](5)
[552](5)
[3060](5)

Interatomic Distance: F-F = [2.5] Å   σ = [5]
Product of the Moments of Inertia: $I_AI_BI_C$ = [1.0598×10^{-112}] $g^3\ cm^6$

Heat of Formation

The enthalpy of 5 HF(g) → H_5F_5(g) was taken as the mean of the third law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier (1) measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer (2) measured C_p between -20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported second law values of ΔH and ΔS. At n = 5 their second law values differed by 5.2 kcal/mol, which was taken as an estimate of error, while the calculated third law values differed by 3.1 kcal/mol. Using ΔHr°_{298} = -30.35 kcal/mol and auxiliary JANAF data (3) gives the heat of formation of H_5F_5(g).

Heat Capacity and Entropy

The molecular structure of H_5F_5 was assumed as planar with the F atoms forming the vertices of a regular pentagon and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's (4) theoretical molecular-orbital studies on HF polymers. The length of side (F-F axis) was taken from Atoji and Lipscomb's (5) X-ray studies of solid HF (F-F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell (6) determined for HF gaseous polymers by electron diffraction. The low F-bending frequency (53 cm^{-1}) was taken from Boutin et al. (7). The other vibrational frequencies were taken from Kittelberger and Hornig's (8) work on crystalline HF. Huong and Couzi (9) and Smith (10) have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table (11) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (11), we recalculate the table in terms of 1973 fundamental constants (12), 1975 atomic weights (13), and current JANAF reference states for the elements.

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F_5H_5

SULFUR PENTAFLUORIDE (SF_5)
(IDEAL GAS) GFW=127.05202

F_5S

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.901	-214.699	-214.699	INFINITE
100	9.165	57.068	87.918	-3.085	-215.784	-211.018	461.173
200	15.856	65.363	74.609	-1.849	-216.691	-205.863	224.953
298	21.425	72.811	72.811	0.000	-217.124	-200.440	146.925
300	21.507	72.944	72.811	0.040	-217.129	-200.337	145.943
400	24.955	79.646	73.702	2.378	-217.814	-194.689	106.372
500	27.021	85.456	75.486	4.985	-218.155	-188.869	82.553
600	28.309	90.505	77.578	7.756	-218.315	-182.994	66.654
700	29.152	94.936	79.747	10.632	-218.359	-177.102	55.293
800	29.729	98.869	81.897	13.578	-231.329	-172.409	47.099
900	30.139	102.396	83.982	16.572	-230.951	-165.064	40.082
1000	30.440	105.587	85.985	19.602	-230.565	-157.765	34.479
1100	30.667	108.500	87.901	22.658	-230.171	-150.504	29.902
1200	30.842	111.176	89.731	25.734	-229.774	-143.279	26.094
1300	30.982	113.650	91.477	28.825	-229.375	-136.086	22.878
1400	31.095	115.951	93.144	31.929	-228.979	-128.926	20.126
1500	31.190	118.099	94.737	35.044	-228.584	-121.793	17.745
1600	31.271	120.115	96.261	38.167	-228.192	-114.687	15.665
1700	31.342	122.013	97.720	41.297	-227.800	-107.603	13.833
1800	31.406	123.806	99.120	44.435	-227.416	-100.546	12.208
1900	31.466	125.506	100.464	47.578	-227.030	-93.505	10.755
2000	31.522	127.121	101.757	50.728	-226.651	-86.490	9.451
2100	31.576	128.660	103.002	53.883	-226.272	-79.490	8.273
2200	31.628	130.130	104.202	57.043	-225.896	-72.509	7.203
2300	31.679	131.537	105.360	60.208	-225.523	-65.547	6.228
2400	31.730	132.887	106.479	63.379	-225.150	-58.598	5.336
2500	31.780	134.183	107.561	66.554	-224.780	-51.666	4.517
2600	31.829	135.430	108.609	69.735	-224.410	-44.749	3.761
2700	31.879	136.633	109.625	72.920	-224.043	-37.846	3.063
2800	31.927	137.793	110.611	76.110	-223.677	-30.957	2.416
2900	31.976	138.914	111.567	79.305	-223.310	-24.079	1.815
3000	32.024	139.999	112.497	82.505	-222.947	-17.218	1.254
3100	32.071	141.050	113.401	85.710	-222.580	-10.363	0.731
3200	32.118	142.069	114.281	88.920	-222.217	-3.525	0.241
3300	32.165	143.058	115.138	92.134	-221.853	3.304	-0.219
3400	32.211	144.019	115.974	95.353	-221.490	10.122	-0.651
3500	32.256	144.953	116.788	98.576	-221.129	16.927	-1.057
3600	32.300	145.862	117.583	101.804	-220.767	23.724	-1.440
3700	32.344	146.748	118.360	105.036	-220.406	30.510	-1.802
3800	32.387	147.611	119.118	108.272	-220.045	37.288	-2.145
3900	32.429	148.453	119.860	111.513	-219.685	44.055	-2.469
4000	32.470	149.274	120.585	114.758	-219.327	50.812	-2.776
4100	32.511	150.077	121.294	118.007	-218.968	57.562	-3.068
4200	32.551	150.861	121.989	121.260	-218.612	64.303	-3.346
4300	32.590	151.627	122.669	124.517	-218.256	71.035	-3.610
4400	32.628	152.377	123.336	127.778	-217.902	77.758	-3.862
4500	32.666	153.110	123.990	131.043	-217.550	84.472	-4.102
4600	32.703	153.829	124.630	134.311	-217.198	91.181	-4.332
4700	32.740	154.532	125.259	137.584	-216.847	97.882	-4.551
4800	32.775	155.222	125.876	140.859	-216.502	104.573	-4.761
4900	32.810	155.898	126.482	144.139	-216.154	111.260	-4.962
5000	32.844	156.561	127.077	147.421	-215.811	117.936	-5.155
5100	32.877	157.212	127.662	150.707	-215.467	124.611	-5.340
5200	32.910	157.851	128.236	153.997	-215.129	131.273	-5.517
5300	32.942	158.478	128.801	157.289	-214.792	137.933	-5.688
5400	32.973	159.094	129.356	160.585	-214.456	144.584	-5.852
5500	33.004	159.699	129.902	163.884	-214.123	151.231	-6.009
5600	33.034	160.294	130.440	167.186	-213.795	157.870	-6.161
5700	33.063	160.879	130.969	170.491	-213.467	164.504	-6.307
5800	33.091	161.455	131.489	173.798	-213.141	171.133	-6.448
5900	33.119	162.020	132.002	177.109	-212.819	177.757	-6.584
6000	33.146	162.577	132.507	180.422	-212.501	184.373	-6.716

June 30, 1976; Dec. 31, 1977

SULFUR PENTAFLUORIDE (SF_5) (IDEAL GAS) GFW = 127.05202

ΔHa_0° = 372.2 ± 5.6 kcal/mol
$S^\circ_{298.15}$ = [72.8 ± 2.0] gibbs/mol

ΔHf_0° = -214.7 ± 3.6 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -217.1 ± 3.6 kcal/mol

F_5S

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	[2]	[25000]	[2]
[10000]	[2]	[30000]	[2]
[20000]	[2]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[800](1)	[550](1)	812(2)
[600](1)	[400](1)	552(2)
[550](1)	[450](1)	[350](2)

Point Group : C_{4v} σ = 4
Bond Distances: S-F* = [1.56] Å S-F** = [1.51] Å
Bond Angles: F*-S-F* = 90° F**-S-F* = [90°] (* = equatorial ** = axial)
Product of Moments of Inertia: $I_AI_BI_C$ = [1.4157 x 10^{-113}] g^3 cm^6

Heat of Formation

ΔHf_0° is calculated from the bond dissociation process $SF_6(g) = SF_5(g) + F(g)$ with D_0° = 92.0±3.0 kcal/mol and JANAF auxiliary heats of formation (1). The information which was considered in arriving at the selected D_0° value is reviewed below. Another recent review (2) of the thermodynamics of SF_5 led to selected values of D_0° (SF_5-F) = 92.6±3.0 kcal/mol and ΔHf°_{298} = -218±3 kcal/mol which agree with the results adopted here.

The electron-impact appearance potential (AP) of F^- from SF_6 has been reported as approximately zero by Harland and Thynne (3) and Curran (4). In addition, Curran (4) measured the kinetic energy of the negative ion and found K.E. (Total) = 0.23±0.05 eV. Combining these results with the electron affinity (EA) of F of 3.399 eV (1), we obtain an upper limit value for D_0° of <3.2 eV (73.1 kcal/mol).

Modica (5) performed shock tube measurements on mixtures of SF_6/Ar, SF_5Cl/Ar, and SF_6/H_2 and analyzed the equilibrium data with a thermochemical equilibrium computer program. With ΔHf_0° (SF_4,g) = -172.2 kcal/mol, Modica (5) adjusted the value of ΔHf° for SF_5 to bring the calculated and experimental SF_4/HF concentrations into good agreement. These results suggest $\Delta Hf_0^\circ(SF_5,g)$= -241.7 kcal/mol, or $D_0^\circ(SF_5\text{-}F)$ = 65.2 kcal/mol. We are unable to reanalyze these shock tube equilibrium data but presumably the ΔHf° and D° values should be adjusted for the changes in ΔHf° of SF_4 (1).

Bott and Jacobs (6) used infrared and ultraviolet absorption techniques to study the thermal (1650-2050 K) dissociation of SF_6 in a shock tube. They interpreted their rate data in terms of the RRK theory and showed that the results were consistent with D°(SF_5-F) = 75.9±4.0 kcal/mol. Lyman (7) has reevaluated the SF_6 dissociation data in terms of the more complete RRKM unimolecular reaction rate theory and presented evidence which indicates that the D°(SF_5-F) is considerably higher than previously reported. His analysis of the rate data yielded a D_0° value of 92 kcal/mol which we adopt.

The heat of atomization (ΔHa_0°) and mean bond dissociation energy ($\bar{D}_0^\circ$) are calculated to be 372.2 kcal/mol and 74.4 kcal/mol, respectively. ΔHf_0° combined with that for SF_5^+ (1) gives an ionization potential (IP) of 11.14 eV which appears reasonable in comparison with IP values for the other sulfur fluorides (1).

Heat Capacity and Entropy

We assume that the five fluorine atoms form a tetragonal pyramid around the central sulfur atom based on evidence from an EPR study (8) which shows that four of the fluorine atoms are equivalent. This structure is further supported by recent SCF MO calculations (9) which predict that the F**-S-F* bond angle is near 90°. The geometry optimized bond lengths (9) appear to be about 0.2 Å too large in comparison with experimentally measured S-F bond lengths for other sulfur-fluorine species (1). We assume that the S-F* bond length is the same as that reported for SF_6 and S_2F_{10} (1). The axial bond length is taken to be slightly shorter than the equatorial bonds, in accordance with the pattern followed in the related molecules ClF_5 (1) and TeF_5^- (10). The principal moments of inertia are: I_A = 3.0708 x 10^{-38} and $I_B = I_C$ = 2.1471 x 10^{-38} g cm^2.

Smardzewski and Fox (11) reported the matrix infrared spectra of SF_5 formed during the vacuum ultraviolet photolysis of SF_6 and its derivatives, SF_5X (X=F, Cl, Br, SF_5), in argon matrices at 8 K. Values of ν_7 and ν_8 are taken from this recent study. The other seven fundamentals are estimated by analogy with those for SF_5^- (1) and ClF_5 (12). Double (ν_1 and ν_7) and triple (ν_3, ν_4, and ν_8) coincidences are predicted at about 800 cm^{-1} and 550 cm^{-1}, respectively, based on the infrared spectra of ClF_5 (12). The four upper electronic levels are estimated from those observed for SF_6^+ (13). We assume that the ground state and upper levels are all doublets.

Our thermal functions essentially update and extend those previously reported by O'Hare (14). Wilkins (15) has also calculated functions covering the temperature range 50 - 6000 K. He assumed that the structure of the radical was a trigonal bipyramid (D_{3h} symmetry). We cannot completely rule out this structure but consider it to be unlikely.

References

1. JANAF Thermochemical Tables: $SF_6(g)$, $SF_4(g)$, $SF_3(g)$, $SF_2(g)$, and SF(g), 6-30-76; F(g), 9-30-65; $F^-(g)$, 12-31-71; $S_2F_{10}(g)$, $SF_5^+(g)$, and $SF_5^-(g)$, 12-31-77; $ClF_5(g)$, 6-30-68.
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F_5S

SULFUR PENTAFLUORIDE UNIPOSITIVE ION (SF_5^+) F_5S^+

(IDEAL GAS) GFW=127.051466

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-3.907	42.201		
100							
200							
298	21.473	71.234	71.234	0.000	41.263	56.930	-41.730
300	21.555	71.367	71.234	0.040	41.267	57.027	-41.543
400	25.000	78.083	72.126	2.383	41.084	62.255	-34.014
500	27.057	83.901	73.913	4.994	41.243	67.529	-29.517
600	28.338	88.956	76.009	7.768	41.584	72.757	-26.501
700	29.176	93.392	78.182	10.647	42.038	77.917	-24.326
800	29.748	97.327	80.334	13.595	29.568	81.808	-22.349
900	30.155	100.856	82.421	16.591	30.445	88.289	-21.439
1000	30.453	104.049	84.427	19.622	31.329	94.667	-20.689
1100	30.678	106.963	86.345	22.679	32.221	100.958	-20.058
1200	30.854	109.640	88.176	25.756	33.116	107.167	-19.517
1300	30.993	112.115	89.924	28.849	34.013	113.303	-19.048
1400	31.108	114.416	91.592	31.954	34.907	119.368	-18.634
1500	31.205	116.566	93.186	35.070	35.800	125.369	-18.266
1600	31.289	118.583	94.711	38.195	36.691	131.311	-17.936
1700	31.365	120.482	96.172	41.327	37.581	137.199	-17.638
1800	31.434	122.277	97.573	44.467	38.465	143.031	-17.366
1900	31.499	123.978	98.918	47.614	39.351	148.819	-17.118
2000	31.561	125.595	100.212	50.767	40.230	154.556	-16.889
2100	31.621	127.136	101.457	53.926	41.110	160.252	-16.677
2200	31.680	128.609	102.658	57.091	41.987	165.904	-16.481
2300	31.737	130.018	103.818	60.262	42.863	171.516	-16.298
2400	31.794	131.370	104.938	63.438	43.738	177.092	-16.126
2500	31.851	132.669	106.021	66.621	44.613	182.630	-15.965
2600	31.906	133.920	107.070	69.808	45.486	188.135	-15.814
2700	31.961	135.125	108.087	73.002	46.358	193.604	-15.671
2800	32.016	136.288	109.074	76.201	47.230	199.041	-15.536
2900	32.069	137.413	110.031	79.405	48.103	204.448	-15.407
3000	32.122	138.501	110.962	82.615	48.972	209.822	-15.285
3100	32.174	139.555	111.868	85.829	49.846	215.173	-15.169
3200	32.225	140.577	112.749	89.049	50.715	220.490	-15.059
3300	32.275	141.569	113.607	92.274	51.587	225.783	-14.953
3400	32.323	142.534	114.444	95.504	52.458	231.049	-14.851
3500	32.370	143.471	115.260	98.739	53.328	236.288	-14.754
3600	32.416	144.384	116.057	101.978	54.199	241.503	-14.661
3700	32.461	145.273	116.834	105.222	55.067	246.693	-14.571
3800	32.504	146.139	117.594	108.470	55.937	251.862	-14.485
3900	32.546	146.984	118.337	111.723	56.806	257.007	-14.402
4000	32.586	147.808	119.063	114.980	57.673	262.128	-14.322
4100	32.625	148.613	119.774	118.240	58.540	267.230	-14.244
4200	32.663	149.400	120.470	121.505	59.404	272.309	-14.170
4300	32.699	150.169	121.152	124.773	60.268	277.368	-14.097
4400	32.734	150.921	121.820	128.044	61.129	282.407	-14.027
4500	32.767	151.657	122.475	131.319	61.988	287.425	-13.959
4600	32.799	152.378	123.117	134.598	62.847	292.427	-13.893
4700	32.830	153.083	123.747	137.879	63.704	297.408	-13.829
4800	32.860	153.775	124.366	141.164	64.555	302.370	-13.767
4900	32.888	154.453	124.973	144.451	65.408	307.317	-13.707
5000	32.915	155.117	125.569	147.741	66.255	312.244	-13.648
5100	32.941	155.770	126.155	151.034	67.102	317.158	-13.591
5200	32.965	156.409	126.731	154.329	67.942	322.050	-13.535
5300	32.989	157.038	127.297	157.627	68.782	326.931	-13.481
5400	33.011	157.654	127.853	160.927	69.619	331.793	-13.428
5500	33.032	158.260	128.400	164.229	70.452	336.641	-13.377
5600	33.053	158.856	128.939	167.533	71.279	341.472	-13.326
5700	33.072	159.441	129.469	170.840	72.105	346.290	-13.277
5800	33.091	160.016	129.991	174.148	72.929	351.094	-13.229
5900	33.108	160.582	130.504	177.458	73.747	355.885	-13.183
6000	33.125	161.139	131.010	180.769	74.560	360.658	-13.137

Dec. 31, 1976; Dec. 31, 1977

SULFUR PENTAFLUORIDE UNIPOSITIVE ION (SF_5^+) (IDEAL GAS)

GFW = 127.051466

ΔHf°_0 = 42.2 ± 5.0 kcal/mol F_5S^+

$\Delta Hf^\circ_{298.15}$ = [41.263] kcal/mol

Point Group [C_{4v}]

$S^\circ_{298.15}$ = [71.2 ± 2.0] gibbs/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	[1]	29036	[1]
9275	[1]	37101	[1]
17341	[1]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[800](1)	[550](1)	[800](2)
[600](1)	[400](1)	[550](2)
[550](1)	[450](1)	[350](2)

Bond Distances: S-F* = [1.50] Å

S-F** = [1.46] Å

Bond Angles: F**-S-F* = [90°]

F*-S-F* = [90°] (* - equatorial)

(** - axial)

Product of Moments of Inertia: $I_AI_BI_C$ = [1.1261 x 10^{-113}] g^3 cm^6 σ = [4]

Heat of Formation

The threshold energy for the formation of SF_5^+ from SF_6 has been measured by photoionization (1), electron-impact (2-5), and photoelectron spectroscopy (4, 6-8). Presented below is a summary of the reported appearance potentials (AP) along with results *arrived at from an analysis of the* data. Also included in the summary are results derived from an electron-impact study (9) on the formation of SF_5^+ from SF_5Cl. All auxiliary data are from the most recent JANAF tables (10) with the exception of the value for ΔHf°_0 of SF_5Cl. We use $\Delta Hf^\circ_0(SF_5Cl,g)$ = -247.48 kcal/mol (11).

REFERENCE	METHOD	AP[a], eV	ΔHf°_0, kcal/mol	IP, eV
(1)	Photoionization	<15.29	<45.88	<11.3
(2)	Electron-Impact	15.9±0.2	<59.94	<11.9
(3)	Electron-Impact	15.85±0.15	<58.79	<11.9
(4)	RPD	15.75±0.05	<56.48	<11.8
	Photoelectron Spectroscopy	15.30	46.11	11.31
(5)	Electron-Impact	15.50±0.1	<50.72	<11.5
(6)	Photoelectron Spectroscopy	15.35±0.2	47.26	11.36
(7)	Photoelectron Spectroscopy	15.15	42.65	11.16
(8)	Photoelectron Spectroscopy	14.72	32.73	10.73
(9)	Electron-Impact	13.2±0.2[b]	<28.33	<10.5

[a] $SF_6(g) + e^- = SF_5^+(g) + F(g) + 2e^-$ [b] $SF_5Cl(g) + e^- = SF_5^+(g) + Cl(g) + 2e^-$

No study has been made of the kinetic energies of the fragments produced by *photoionization or electron-impact of* SF_6 and SF_5Cl. As a result, the ionization potentials (IP) derived from these studies (1-5, 9) represent upper limits to the true value. SF_5^+ is produced in the photoionization of SF_6 by rapid dissociation of SF_6^+ whose ground state is expected to exhibit Jahn-Teller instability (1). As a result of this, an accurate determination of the threshold energy for the dissociation process is difficult. We choose to adopt a mean ΔHf°_0 value of 42.2±5.0 kcal/mol based on the results measured in four photoelectron spectroscopic studies (4, 6-8) of the SF_6/SF_5^+ dissociation. Our adopted heats of formation correspond to $IP(SF_5)$ = 11.14±0.37 eV which is in agreement with the limiting values of 9.25<IP<12.05 eV (13).

ΔHf° is calculated to be 41.263 kcal/mol at 298.15 K. Using JANAF data (10), we find that the primary bond dissociation energy $D^\circ_0(SF_4^+-F)$ is 75.4 kcal/mol. This value appears reasonable in comparison with D°_0 values for other even-electron positive and negative S-F species (10), providing some additional support for our adopted results. The heat of atomization (products $S^+(g)+5F(g)$) (ΔHa°_0) and mean bond dissociation energy ($\bar{D}^\circ_0$) are 354.2 kcal/mol and 70.8 kcal/mol, respectively.

Heat Capacity and Entropy

By analogy with SF_5 (14, 15) and SF_5^- (10), we adopt a tetragonal pyramidal structure (C_{4v} symmetry). The SF_4 part of this configuration is predicted to be planar as a result of a reduction in the repulsive forces (16) upon ionization. The four equatorial S-F bond lengths are assumed equal to that for SF_3^+ (10). The axial bond length is assumed to be slightly shorter than the equatorial bonds, in accordance with the pattern followed in the related molecules ClF_5 (10) and TeF_5^- (17). The individual moments of inertia are: I_A = 2.8393 x 10^{-38} and $I_B = I_C$ = 1.9915 x 10^{-38} g cm^2. We estimate vibrational frequencies from those for SF_5 (10), SF_5^- (10), and ClF_5 (18). Double (ν_1 and ν_7) and triple (ν_3, ν_4, and ν_8) coincidences are predicted at 800 cm^{-1} and 550 cm^{-1}, respectively, based on the infrared spectra of ClF_5 (18). The electronic levels are calculated *from the RPD measurements of Delwiche* (4). We do not include levels predicted to lie above 40,000 cm^{-1} since these have a negligible effect on the thermal functions. The existence of the first two excited states is verified by an independent RPD study (3).

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F_5S^+

SULFUR PENTAFLUORIDE UNINEGATIVE ION (SF_5^-) F_5S^-
(IDEAL GAS) GFW=127.052564

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-4.579	-300.000		
100							
200							
298	24.267	75.397	75.397	0.000	-303.228	-285.828	209.515
300	24.334	75.547	75.397	0.045	-303.237	-285.720	208.144
400	27.022	82.955	76.389	2.626	-304.175	-279.795	152.871
500	28.533	89.162	78.340	5.411	-304.837	-273.625	119.600
600	29.442	94.451	80.596	8.313	-305.362	-267.331	97.374
700	30.025	99.037	82.910	11.289	-305.803	-260.957	81.473
800	30.419	103.073	85.183	14.312	-319.191	-255.722	69.859
900	30.696	106.673	87.375	17.369	-319.248	-247.782	60.169
1000	30.898	109.918	89.469	20.449	-319.309	-239.840	52.416
1100	31.049	112.870	91.465	23.546	-319.371	-231.891	46.072
1200	31.166	115.577	93.363	26.657	-319.434	-223.934	40.783
1300	31.257	118.076	95.169	29.779	-319.502	-215.972	36.308
1400	31.330	120.395	96.889	32.908	-319.578	-208.007	32.471
1500	31.389	122.558	98.529	36.044	-319.658	-200.035	29.145
1600	31.437	124.586	100.095	39.186	-319.745	-192.058	26.234
1700	31.478	126.493	101.592	42.331	-319.834	-184.072	23.664
1800	31.512	128.293	103.026	45.481	-319.935	-176.086	21.379
1900	31.540	129.998	104.401	48.633	-320.037	-168.089	19.334
2000	31.565	131.616	105.722	51.789	-320.149	-160.091	17.494
2100	31.586	133.157	106.992	54.946	-320.264	-152.085	15.827
2200	31.605	134.626	108.215	58.106	-320.385	-144.073	14.312
2300	31.621	136.032	109.394	61.267	-320.513	-136.057	12.928
2400	31.635	137.378	110.532	64.430	-320.645	-128.033	11.659
2500	31.647	138.669	111.632	67.594	-320.783	-120.005	10.491
2600	31.658	139.911	112.696	70.759	-320.926	-111.971	9.412
2700	31.668	141.106	113.726	73.926	-321.073	-103.931	8.412
2800	31.677	142.258	114.724	77.093	-321.227	-95.887	7.484
2900	31.685	143.369	115.693	80.261	-321.384	-87.835	6.619
3000	31.692	144.444	116.634	83.430	-321.549	-79.782	5.812
3100	31.699	145.483	117.548	86.600	-321.715	-71.717	5.056
3200	31.705	146.490	118.436	89.770	-321.887	-63.651	4.347
3300	31.710	147.465	119.301	92.941	-322.063	-55.577	3.681
3400	31.715	148.412	120.144	96.112	-322.245	-47.500	3.053
3500	31.719	149.331	120.965	99.283	-322.433	-39.418	2.461
3600	31.724	150.225	121.765	102.456	-322.623	-31.328	1.902
3700	31.727	151.094	122.546	105.628	-322.818	-23.234	1.372
3800	31.731	151.940	123.308	108.801	-323.017	-15.134	0.870
3900	31.734	152.765	124.053	111.974	-323.222	-7.029	0.394
4000	31.737	153.568	124.781	115.148	-323.432	1.080	-0.059
4100	31.740	154.352	125.493	118.322	-323.646	9.196	-0.490
4200	31.743	155.117	126.189	121.496	-323.864	17.318	-0.901
4300	31.745	155.864	126.871	124.670	-324.088	25.444	-1.293
4400	31.747	156.594	127.538	127.845	-324.317	33.574	-1.668
4500	31.749	157.307	128.191	131.020	-324.552	41.709	-2.026
4600	31.751	158.005	128.832	134.195	-324.791	49.852	-2.368
4700	31.753	158.688	129.460	137.370	-325.032	58.001	-2.697
4800	31.755	159.356	130.076	140.545	-325.285	66.151	-3.012
4900	31.756	160.011	130.680	143.721	-325.538	74.310	-3.314
5000	31.758	160.653	131.273	146.897	-325.799	82.471	-3.605
5100	31.759	161.282	131.855	150.073	-326.061	90.642	-3.884
5200	31.761	161.898	132.427	153.249	-326.333	98.813	-4.153
5300	31.762	162.503	132.989	156.425	-326.609	106.992	-4.412
5400	31.763	163.097	133.541	159.601	-326.891	115.175	-4.661
5500	31.764	163.680	134.084	162.777	-327.177	123.366	-4.902
5600	31.765	164.252	134.617	165.954	-327.470	131.560	-5.134
5700	31.767	164.814	135.142	169.130	-327.767	139.759	-5.359
5800	31.767	165.367	135.659	172.307	-328.069	147.964	-5.575
5900	31.768	165.910	136.167	175.484	-328.378	156.176	-5.785
6000	31.769	166.444	136.667	178.661	-328.693	164.389	-5.988

Dec. 31, 1976; Dec. 31, 1977

SULFUR PENTAFLUORIDE UNINEGATIVE ION (SF_5^-) (IDEAL GAS) GFW = 127.052564

ΔHa_0° = 379.1 ± 10.0 kcal/mol
$S_{298.15}^\circ$ = [75.4 ± 0.5] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf_0° = -300.0 ± 8.0 kcal/mol F_5S^-
$\Delta Hf_{298.15}^\circ$ = [-303.228] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
796(1)	435(1)	595(2)
522(1)	269(1)	[435](2)
470(1)	342(1)	241(2)

Point Group C_{4v} σ = 4
Bond Distances: S-F* = [1.56] Å S-F** = [1.46] Å
Bond Angles: F**-S-F* = [85°] F*-S-F* = 90°
(* - equatorial ** - axial)
Product of Moments of Inertia: $I_AI_BI_C$ = [1.2559 x 10^{-113}] g^3 cm^6

Heat of Formation

The threshold energy for the dissociative electron attachment process $e^- + SF_6(g) = SF_5^-(g) + F(g)$ has been measured directly by means of mass spectrometry (1-4). In addition, mass spectrometric studies (5, 6) have been reported on various electron transfer reactions which provide independent estimates of the enthalpy for the above process. Presented below is a summary of the results derived from these measurements. Also included in the summary are results obtained from an electron-impact study (1) of the process $e^- + SF_5Cl(g) = SF_5^-(g) + Cl(g)$. We assume that the fragment-ions are formed in each process with no excess or kinetic energies. As a result, the derived electron affinities (EA) represent lower limits to the true value. Other reported values of EA(SF_5) include >1.465 eV (9), 3.2 eV (5), and 3.66±0.04 eV (10). The first two results are based on charge-transfer studies (5, 9) while the latter value represents a direct measurement of EA using the magnetron technique (10).

Reference	Reaction	Method	AP or ΔHr_0° kcal/mol	$\Delta Hf_0^\circ(SF_5^-,g)^a$ kcal/mol	$EA(SF_5)^a$ eV
(1)	A	Electron-impact	2.31	-304.41	>3.89
(2)	A	RPD	1.15	-305.56	>3.94
(3)	A	RPD	5.77	-300.95	>3.74
(4)	A	Electron-impact	~0	-306.72	>3.99
(5)	A	Electron transfer	11.53	-295.19	>3.49
(6)	A	Collisional ionization	11.45	-295.07	>3.49
(1)	B	Electron-impact	4.61	-271.45	>2.46

Reactions: (A) $e^- + SF_6(g) = SF_5^-(g) + F(g)$
(B) $e^- + SF_5Cl(g) = SF_5^-(g) + Cl(g)$

[a] Auxiliary ΔHf_0° Data (in kcal/mol): SF_6 (7), -288.36±0.2; F (7), 18.36±0.4; Cl (7), 28.587; SF_5Cl (8), -247.48; SF_5 (7), -214.7±3.6.

We reject the electron-impact results on the dissociative electron attachment process for SF_5Cl since Harland and Thynne (1) also reported results for SF_3^- and SF_4^- which lead to EA that are too low (7). The other results are reasonably consistent with the mean EA value of 3.7±0.2 eV. This value corresponds to ΔHf_0° (SF_5^-,g) = -300.0±8.0 kcal/mol which we adopt.

ΔHf° is -303.228 kcal/mol at 298.15 K and the fluoride-ion affinity (IA) is IA(SF_4) = 59.1 kcal/mol. Using JANAF data (7), we find that the heat of atomization (ΔHa_0°) to form the products $S(g) + F^-(g) + 4F(g)$, the primary bond dissociation energy $D_0^\circ(SF_4^- - F)$, and mean bond dissociation energy $\bar{D}_0^\circ$ are 379.1 kcal/mol, 108.6 kcal/mol, and 75.8 kcal/mol, respectively.

Heat Capacity and Entropy

The infrared and Raman spectra (11, 12) of the solid adduct $CsF\cdot SF_4$ are consistent with a slightly distorted tetragonal pyramidal structure for the SF_5^- anion. We adopt this configuration and assume that the length of the four equivalent bonds is the same as that in SF_6 (7). The axial bond length is taken to be slightly shorter (0.1 Å) than the equatorial bonds, in accordance with the pattern followed in the related molecules ClF_5 (7) and TeF_5^- (13). The value of the F**-S-F* bond angle is that estimated by Drullinger and Griffiths (11). The principal moments of inertia are: $I_A = 3.0475 \times 10^{-38}$ and $I_B = I_C = 2.0301 \times 10^{-38}$ g cm^2.

Smardzewski and Fox (14) reported the matrix infrared spectra of SF_5^- formed during the vacuum ultraviolet photolysis of SF_6 and S_2F_{10} *in argon matrices at 8 K. Values of* ν_1, ν_3, *and* ν_7 *are taken from this recent study.* The other six fundamentals are those measured by Christe et al. (12) for the SF_5^- anion observed in the Raman spectra of the solid adduct $CsF\cdot SF_4$. An independent set (11) of vibrational frequencies for the SF_5^- anion show good agreement with those adopted here except for ν_8. Drullinger and Griffiths (11) observed a weak band at 388 cm^{-1} in the infrared spectra of solid $Cs^+SF_5^-$ which they assigned to ν_8. This band does not appear in the spectrum reported by Christe et al. (12) who assumed a double coincidence between ν_4 and ν_8 as observed for the related molecule ClF_5 (12). We adopt this latter assignment.

Drullinger and Griffiths (11) have previously evaluated thermal functions for SF_5^- at selected temperatures in the range 200 - 2000 K. Using the bond lengths estimated by Drullinger and Griffiths and their vibrational frequencies, we calculate entropies which are about 0.8 gibbs/mol lower than those reported. The reason for this discrepancy is not apparent.

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F_5S^-

HYDROGEN FLUORIDE CYCLIC HEXAMER (H_6F_6) F_6H_6
(IDEAL GAS) GFW=120.037818

T, K	gibbs/mol Cp°	 S°	 $-(G^\circ-H^\circ_{298})/T$	kcal/mol $H^\circ-H^\circ_{298}$	 ΔHf°	 ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-8.459	-428.100	-428.100	INFINITE
100	25.742	76.124	142.776	-6.665	-430.542	-418.732	915.125
200	34.005	96.667	114.939	-3.654	-431.563	-406.463	444.156
298	40.166	111.451	111.451	0.000	-432.040	-394.026	288.825
300	40.265	111.700	111.452	0.074	-432.047	-393.791	286.873
400	44.726	123.934	113.089	4.338	-432.172	-381.009	208.171
500	47.813	134.266	116.318	8.974	-432.045	-368.230	160.951
600	50.084	143.193	120.070	13.874	-431.735	-355.494	129.487
700	51.909	151.055	123.946	18.976	-431.283	-342.821	107.032
800	53.475	158.091	127.782	24.247	-430.716	-330.224	90.212
900	54.865	164.471	131.510	29.665	-430.044	-317.699	77.147
1000	56.111	170.317	135.102	35.215	-429.288	-305.258	66.713
1100	57.228	175.719	138.552	40.883	-428.456	-292.894	58.192
1200	58.225	180.742	141.861	46.657	-427.563	-280.610	51.105
1300	59.114	185.438	145.034	52.524	-426.619	-268.401	45.122
1400	59.903	189.848	148.080	58.476	-425.635	-256.267	40.005
1500	60.602	194.005	151.004	64.502	-424.619	-244.206	35.580
1600	61.222	197.937	153.816	70.594	-423.576	-232.213	31.718
1700	61.772	201.665	156.521	76.744	-422.511	-220.282	28.319
1800	62.260	205.210	159.129	82.946	-421.436	-208.420	25.305
1900	62.695	208.588	161.644	89.194	-420.345	-196.612	22.615
2000	63.082	211.814	164.072	95.483	-419.252	-184.868	20.201
2100	63.428	214.900	166.420	101.809	-418.149	-173.174	18.022
2200	63.738	217.858	168.691	108.168	-417.046	-161.535	16.047
2300	64.017	220.698	170.891	114.556	-415.944	-149.947	14.248
2400	64.267	223.428	173.023	120.970	-414.840	-138.403	12.603
2500	64.494	226.056	175.092	127.409	-413.738	-126.906	11.094
2600	64.699	228.589	177.102	133.868	-412.643	-115.454	9.705
2700	64.884	231.035	179.054	140.348	-411.551	-104.044	8.422
2800	65.053	233.397	180.953	146.845	-410.469	-92.678	7.234
2900	65.207	235.683	182.801	153.358	-409.389	-81.346	6.130
3000	65.348	237.896	184.601	159.886	-408.318	-70.054	5.103
3100	65.477	240.041	186.355	166.427	-407.252	-58.791	4.145
3200	65.595	242.122	188.065	172.981	-406.200	-47.572	3.249
3300	65.704	244.142	189.734	179.546	-405.152	-36.378	2.409
3400	65.804	246.105	191.363	186.121	-404.118	-25.220	1.621
3500	65.897	248.014	192.955	192.706	-403.092	-14.092	0.880
3600	65.982	249.871	194.510	199.300	-402.075	-2.991	0.182
3700	66.062	251.680	196.031	205.903	-401.070	8.080	-0.477
3800	66.135	253.443	197.518	212.513	-400.076	19.125	-1.100
3900	66.204	255.162	198.975	219.130	-399.093	30.145	-1.689
4000	66.267	256.839	200.400	225.753	-398.125	41.136	-2.248
4100	66.327	258.476	201.797	232.383	-397.165	52.107	-2.777
4200	66.382	260.075	203.165	239.018	-396.218	63.054	-3.281
4300	66.434	261.637	204.507	245.659	-395.283	73.978	-3.760
4400	66.483	263.165	205.823	252.305	-394.361	84.881	-4.216
4500	66.528	264.660	207.114	258.956	-393.455	95.758	-4.651
4600	66.571	266.122	208.381	265.611	-392.557	106.622	-5.066
4700	66.611	267.555	209.625	272.270	-391.673	117.465	-5.462
4800	66.649	268.957	210.846	278.933	-390.803	128.288	-5.841
4900	66.685	270.332	212.046	285.600	-389.941	139.095	-6.204
5000	66.719	271.680	213.226	292.270	-389.097	149.881	-6.551
5100	66.750	273.001	214.385	298.943	-388.262	160.654	-6.884
5200	66.780	274.298	215.524	305.620	-387.441	171.407	-7.204
5300	66.809	275.570	216.645	312.299	-386.630	182.148	-7.511
5400	66.836	276.819	217.748	318.982	-385.830	192.872	-7.806
5500	66.861	278.046	218.833	325.666	-385.041	203.582	-8.089
5600	66.886	279.250	219.902	332.354	-384.263	214.278	-8.362
5700	66.909	280.435	220.953	339.044	-383.495	224.957	-8.625
5800	66.930	281.598	221.989	345.735	-382.735	235.627	-8.879
5900	66.951	282.743	223.009	352.430	-381.983	246.284	-9.123
6000	66.971	283.868	224.014	359.126	-381.245	256.922	-9.358

July 31, 1972 (NBS); June 30, 1977

HYDROGEN FLUORIDE CYCLIC HEXAMER (H_6F_6) (IDEAL GAS) GFW = 120.037818

F_6H_6

Point Group C_6
$S^\circ_{298.15}$ = [111.5 ± 6] gibbs/mol
Ground State Quantum Weight = 1

ΔHf°_0 = −428.1 ± 2 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −432.0 ± 2 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[202](6)
[53](6)
[962](6)
[552](6)
[3060](6)

Interatomic Distance: F-F = [2.5] Å   σ = [6]
Product of the Moments of Inertia: $I_AI_BI_C$ = [4.834 x 10^{-112}] g^3 cm^6

Heat of Formation

The enthalpy of 6 HF(g) → H_6F_6(g) was taken as the mean of third law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier (1) measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer (2) measured C_p between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported second law values of ΔH and ΔS. At n = 6 their second law values differed by 0.8 kcal/mol, which was taken as an estimate of error, while the calculated third law values differed by 0.6 kcal/mol. Using ΔHr°_{298} = −41.20 kcal/mol and auxiliary JANAF data (3) gives the heat of formation of H_6F_6(g).

Heat Capacity and Entropy

The molecular structure of H_6F_6 was assumed as planar with the F atoms forming the vertices of a regular hexagon and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's (4) theoretical molecular-orbital studies on HF polymers. The length of side (F-F axis) was taken from Atoji and Lipscomb's (5) X-ray studies of solid HF (F-F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell (6) determined for HF gaseous polymers by electron diffraction. The low F-bending frequency (53 cm^{-1}) was taken from Boutin et al. (7). The other vibrational frequencies were taken from Kittelberger and Hornig's (8) work on crystalline HF. Huong and Couzi (9) and Smith (10) have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table (11) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (11), we recalculate the table in terms of 1973 fundamental constants (12), 1975 atomic weights (13), and current JANAF reference states for the elements.

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SULFUR HEXAFLUORIDE UNINEGATIVE ION (SF_6^-) F_6S^-
(IDEAL GAS) GFW=146.0501

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				−4.180	−316.035		
100							
200							
298	23.897	72.358	72.358	0.000	−320.716	−295.197	216.383
300	23.999	72.506	72.359	0.044	−320.733	−295.039	214.933
400	28.392	80.062	73.359	2.681	−321.999	−286.335	156.444
500	31.123	86.715	75.379	5.668	−322.859	−277.315	121.213
600	32.867	92.555	77.766	8.873	−323.498	−268.144	97.670
700	34.026	97.714	80.254	12.222	−323.989	−258.854	80.817
800	34.828	102.313	82.729	15.667	−337.452	−250.790	68.512
900	35.401	106.450	85.139	19.180	−337.487	−239.952	58.268
1000	35.824	110.203	87.461	22.742	−337.503	−229.116	50.072
1100	36.144	113.633	89.686	26.341	−337.502	−218.279	43.367
1200	36.392	116.789	91.815	29.969	−337.487	−207.439	37.779
1300	36.587	119.710	93.850	33.618	−337.465	−196.600	33.051
1400	36.744	122.427	95.795	37.285	−337.442	−185.767	28.999
1500	36.871	124.967	97.656	40.966	−337.415	−174.936	25.488
1600	36.976	127.350	99.438	44.658	−337.386	−164.104	22.415
1700	37.063	129.594	101.147	48.360	−337.353	−153.272	19.704
1800	37.137	131.715	102.787	52.070	−337.326	−142.447	17.295
1900	37.199	133.724	104.363	55.787	−337.295	−131.618	15.139
2000	37.253	135.634	105.879	59.510	−337.271	−120.798	13.200
2100	37.299	137.453	107.339	63.238	−337.246	−109.975	11.445
2200	37.339	139.189	108.748	66.969	−337.223	−99.150	9.849
2300	37.374	140.849	110.108	70.705	−337.206	−88.331	8.393
2400	37.405	142.441	111.422	74.444	−337.189	−77.510	7.058
2500	37.433	143.968	112.694	78.186	−337.175	−66.689	5.830
2600	37.457	145.437	113.925	81.931	−337.165	−55.870	4.696
2700	37.478	146.851	115.118	85.677	−337.159	−45.051	3.647
2800	37.498	148.214	116.276	89.426	−337.158	−34.235	2.672
2900	37.515	149.530	117.400	93.177	−337.158	−23.414	1.765
3000	37.531	150.802	118.493	96.929	−337.167	−12.597	0.918
3100	37.545	152.033	119.555	100.683	−337.173	−1.775	0.125
3200	37.558	153.225	120.588	104.438	−337.188	9.043	−0.618
3300	37.570	154.381	121.595	108.195	−337.204	19.863	−1.315
3400	37.581	155.503	122.576	111.952	−337.227	30.685	−1.972
3500	37.591	156.593	123.532	115.711	−337.255	41.502	−2.591
3600	37.600	157.652	124.465	119.470	−337.285	52.326	−3.177
3700	37.608	158.682	125.376	123.231	−337.320	63.150	−3.730
3800	37.616	159.685	126.266	126.992	−337.358	73.974	−4.254
3900	37.623	160.662	127.136	130.754	−337.402	84.798	−4.752
4000	37.629	161.615	127.986	134.516	−337.452	95.626	−5.225
4100	37.635	162.544	128.817	138.280	−337.503	106.453	−5.674
4200	37.641	163.451	129.631	142.043	−337.561	117.283	−6.103
4300	37.646	164.337	130.428	145.808	−337.621	128.113	−6.511
4400	37.651	165.202	131.209	149.573	−337.688	138.944	−6.901
4500	37.656	166.049	131.973	153.338	−337.761	149.777	−7.274
4600	37.660	166.876	132.723	157.104	−337.836	160.611	−7.631
4700	37.664	167.686	133.458	160.870	−337.913	171.450	−7.972
4800	37.668	168.479	134.180	164.637	−338.000	182.284	−8.300
4900	37.672	169.256	134.888	168.404	−338.087	193.130	−8.614
5000	37.675	170.017	135.583	172.171	−338.184	203.967	−8.915
5100	37.678	170.763	136.265	175.939	−338.279	214.816	−9.205
5200	37.681	171.495	136.936	179.707	−338.384	225.660	−9.484
5300	37.684	172.213	137.595	183.475	−338.492	236.507	−9.752
5400	37.687	172.917	138.242	187.243	−338.604	247.359	−10.011
5500	37.689	173.609	138.879	191.012	−338.721	258.211	−10.260
5600	37.692	174.288	139.505	194.781	−338.844	269.066	−10.501
5700	37.694	174.955	140.121	198.551	−338.970	279.921	−10.733
5800	37.696	175.610	140.728	202.320	−339.100	290.781	−10.957
5900	37.698	176.255	141.324	206.090	−339.235	301.641	−11.173
6000	37.700	176.888	141.912	209.860	−339.377	312.506	−11.383

June 30, 1977

SULFUR HEXAFLUORIDE UNINEGATIVE ION (SF_6^-) (IDEAL GAS) GFW = 146.0501

F_6S^-

Point Group O_h
$S^\circ_{298.15}$ = [72.4 ± 0.5] gibbs/mol
Ground State Quantum Weight = 2

ΔHf°_0 = −316.0 ± 7.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −320.7 ± 7.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[700](1)	[925](3)	[500](3)
[625](2)	594 (3)	[325](3)

Bond Distance: S-F = [1.72] Å σ = 24
Bond Angle: F-S-F = 90°
Product of Moments of Inertia: $I_AI_BI_C$ = [5.1981 x 10^{-113}] g^3cm^6

Heat of Formation

We calculate the heat of formation at 0 K as the difference between $\Delta Hf^\circ_0(SF_6,g)$ = −288.36±0.2 kcal/mol (1) and the selected value of the electron affinity (EA) equal to 1.2±0.3 eV (27.67 kcal/mol). There have been numerous values proposed for $EA(SF_6)$. Franklin and Harland (2) have recently reviewed several of the published values; other values of EA not included in the review are tabulated below. The only direct measurement of EA = 1.49 eV by the magnetron technique (3) is suspect since mass spectral studies (4) have shown that SF_5^- rather than SF_6^- is the predominant ion formed under conditions used in the magnetron experiments. An EA = 1.2 eV is consistent with most of the available information and is adopted here as the best current value.

INVESTIGATOR	METHOD	$EA(SF_6)$, eV
Lifshitz et al. (5)	Electron-Transfer	<1.18
Compton and Cooper (6)	Collisional Ionization Cs/SF_6	>0.54
Chen et al. (7)	Rate Measurements	>0.7
Fehsenfeld (8)	Electron-Transfer	>0.43 <1.47
Hammond (9)	Solution Electron-Transfer	0.6
Companion (10)	MO Calculations	1.7

From the adopted results, we calculate the primary bond dissociation energy $D^\circ_0(SF_5^--F)$ to be 34.4 kcal/mol which agrees with the value of 24.2 kcal/mol obtained from threshold energies for SF_6^- and SF_5^- measured in collisional ionization studies (6) on the Cs/SF_6 system. ΔHf° at 298.15 K is −320.7 kcal/mol, and the fluoride ion affinity (IA) is found to be IA = 41.3 kcal/mol.

Heat Capacity and Entropy

The six fluorine atoms are assumed to form a regular octahedron around the central sulfur atom, in accordance with observations (11) on the ESR spectrum of SF_6^-. The value of the bond length is taken from theoretical calculations (11). This value (1.72 Å) is intermediate between the bond lengths for SF_6 (1) and XeF_6 (12) and therefore appears to be a reasonable estimate. The principal moments of inertia are: $I_A = I_B = I_C = 3.7323 \times 10^{-38}$ g cm^2.

MO calculations (11) in the INDO approximation indicate that the unpaired electron occupies a totally symmetric antibonding orbital (A_{1g}). Thus, we predict that the bonding in SF_6^- is somewhat weaker than that in the neutral molecule. Additional support for this is provided by the fact that the mean S-F bond energy (products $S(g)+F^-(g)+5F(g)$) in SF_6^- is 8.5 kcal/mol less than that in SF_6 (1). Due to the weaker bonding in SF_6^-, all vibrational frequencies are expected to show a lowering relative to those for SF_6 (1). Very recently, Barefield and Guillory (13) have assigned an absorption band at 594 cm^{-1} observed in the matrix-isolated infrared spectra of NO, Na, and K photoionized in the presence of SF_6 as the ν_4 fundamental of SF_6^-. This represents a lowering of 21.3 cm^{-1} from the gas-phase frequency for SF_6 (1). The other infrared active mode (ν_3) for SF_6^- expected to lie near 925 cm^{-1} was not observed but was believed to be hidden beneath the matrix-isolated ν_3 band (937 cm^{-1}) of SF_6. We estimate the eight unobserved fundamentals from the gas-phase values for SF_6 (1).

MO calculations (11) indicate that the ground state electronic configuration is $^2A_{1g}$. There is, however, little information available on the excited states for SF_6^- or for isoelectronic molecules such as ClF_6 and BrF_6. Indirect experimental evidence for the existence of an excited state at 0.5 eV (4033 cm^{-1}) has been reported by Lifshitz et al. (14) from mass spectral studies of charge-transfer reactions. As shown by Fehsenfeld (15), stable excited states are expected to exist only if $D^\circ_0(SF_5^--F) > EA(SF_6)$. Our adopted results give a difference in $D^\circ_0(SF_5^--F)$ and $EA(SF_6)$ of only 0.053 eV, suggesting that perhaps the SF_6^- ion observed by Lifshitz et al. (14) was vibrationally rather than electronically excited. We prefer not to include this level, but if it does exist, our entropies should be increased by 0.41 and 1.0 gibbs/mol at 2000 K and 4500 K, respectively.

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F_6S^-

HYDROGEN FLUORIDE CYCLIC HEPTAMER (H_7F_7) F_7H_7
(IDEAL GAS) GFW=140.044121

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	−9.994	−498.048	−498.048	INFINITE
100	30.601	83.181	162.191	−7.901	−500.898	−486.556	1063.352
200	40.311	107.571	129.205	−4.327	−502.027	−471.702	515.445
298	47.512	125.077	125.077	0.000	−502.520	−456.695	334.762
300	47.628	125.371	125.078	0.088	−502.526	−456.412	332.491
400	52.836	139.833	127.014	5.127	−502.608	−441.015	240.956
500	56.441	152.034	130.830	10.602	−502.394	−425.638	186.044
600	59.091	162.569	135.262	16.384	−501.966	−410.325	149.459
700	61.221	171.843	139.838	22.403	−501.373	−395.095	123.353
800	63.049	180.139	144.367	28.618	−500.645	−379.964	103.800
900	64.670	187.661	148.766	35.006	−499.795	−364.926	88.615
1000	66.124	194.551	153.004	41.547	−498.847	−349.993	76.490
1100	67.427	200.916	157.074	48.226	−497.810	−335.157	66.589
1200	68.591	206.834	160.977	55.028	−496.702	−320.419	58.355
1300	69.628	212.366	164.720	61.940	−495.534	−305.774	51.405
1400	70.548	217.560	168.310	68.949	−494.320	−291.223	45.461
1500	71.364	222.456	171.758	76.046	−493.069	−276.761	40.324
1600	72.088	227.085	175.073	83.219	−491.786	−262.382	35.839
1700	72.729	231.475	178.263	90.461	−490.477	−248.081	31.893
1800	73.299	235.648	181.336	97.763	−489.156	−233.864	28.395
1900	73.806	239.625	184.300	105.118	−487.817	−219.714	25.272
2000	74.258	243.423	187.162	112.522	−486.476	−205.642	22.471
2100	74.662	247.056	189.928	119.968	−485.123	−191.630	19.943
2200	75.024	250.538	192.604	127.453	−483.770	−177.687	17.651
2300	75.348	253.880	195.196	134.972	−482.418	−163.806	15.565
2400	75.641	257.093	197.709	142.522	−481.063	−149.980	13.657
2500	75.905	260.186	200.147	150.099	−479.712	−136.211	11.907
2600	76.144	263.168	202.513	157.702	−478.368	−122.497	10.297
2700	76.361	266.046	204.813	165.327	−477.028	−108.834	8.809
2800	76.558	268.826	207.050	172.973	−475.700	−95.226	7.433
2900	76.738	271.516	209.227	180.638	−474.373	−81.659	6.154
3000	76.902	274.120	211.347	188.320	−473.058	−68.141	4.964
3100	77.052	276.645	213.413	196.018	−471.748	−54.660	3.854
3200	77.190	279.093	215.427	203.730	−470.454	−41.232	2.816
3300	77.317	281.470	217.393	211.456	−469.165	−27.835	1.843
3400	77.434	283.780	219.312	219.193	−467.892	−14.483	0.931
3500	77.542	286.026	221.186	226.942	−466.629	−1.166	0.073
3600	77.642	288.212	223.017	234.701	−465.376	12.117	−0.736
3700	77.734	290.341	224.808	242.470	−464.138	25.362	−1.498
3800	77.820	292.415	226.560	250.248	−462.913	38.575	−2.219
3900	77.900	294.437	228.275	258.034	−461.699	51.758	−2.900
4000	77.974	296.411	229.954	265.828	−460.503	64.905	−3.546
4100	78.044	298.337	231.598	273.629	−459.317	78.027	−4.159
4200	78.108	300.218	233.210	281.436	−458.146	91.120	−4.741
4300	78.169	302.057	234.789	289.250	−456.989	104.184	−5.295
4400	78.226	303.855	236.339	297.070	−455.847	117.222	−5.822
4500	78.279	305.613	237.859	304.895	−454.724	130.228	−6.325
4600	78.329	307.334	239.350	312.726	−453.610	143.218	−6.804
4700	78.376	309.019	240.815	320.561	−452.513	156.181	−7.262
4800	78.420	310.670	242.253	328.401	−451.431	169.120	−7.700
4900	78.461	312.287	243.666	336.245	−450.360	182.039	−8.119
5000	78.501	313.873	245.054	344.093	−449.309	194.932	−8.520
5100	78.538	315.428	246.419	351.945	−448.268	207.809	−8.905
5200	78.573	316.953	247.761	359.800	−447.244	220.661	−9.274
5300	78.606	318.450	249.080	367.659	−446.231	233.498	−9.628
5400	78.637	319.920	250.379	375.522	−445.232	246.312	−9.969
5500	78.667	321.363	251.656	383.387	−444.245	259.110	−10.296
5600	78.696	322.781	252.914	391.255	−443.272	271.890	−10.611
5700	78.722	324.174	254.152	399.126	−442.310	284.651	−10.914
5800	78.748	325.543	255.371	406.999	−441.356	297.398	−11.206
5900	78.772	326.890	256.572	414.875	−440.413	310.130	−11.488
6000	78.795	328.214	257.755	422.754	−439.486	322.837	−11.759

July 31, 1972 (NBS); June 30, 1977

HYDROGEN FLUORIDE CYCLIC HEPTAMER (H_7F_7) (IDEAL GAS) GFW = 140.044121

F_7H_7

Point Group C_7
$S^\circ_{298.15}$ = [125.1 ± 7] gibbs/mol
Ground State Quantum Weight = 1

ΔHf°_0 = −498.0 ± 9 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −502.5 ± 9 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[202](7)
[53](8)
[962](7)
[552](7)
[3060](7)

Interatomic Distance: F-F = [2.5] Å   σ = [7]
Product of the Moments of Inertia: $I_AI_BI_C$ = [1.7977×10^{-111}] g^3 cm^6

Heat of Formation

The enthalpy of 7 HF(g) → H_7F_7(g) was taken as the mean of third law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier (1) measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer (2) measured C_p between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported second law values of ΔH and ΔS. At n = 7 their second law values differed by 7.3 kcal/mol, which was taken as an estimate of error, while the calculated third law values differed by 6.4 kcal/mol. Using ΔHr°_{298} = −46.54 kcal/mol and auxiliary JANAF data (3) gives the heat of formation of H_7F_7(g).

Heat Capacity and Entropy

The molecular structure of H_7F_7 was assumed as planar with the F atoms forming the vertices of a regular heptagon and the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's (4) theoretical molecular-orbital studies on HF polymers. The length of side (F-F axis) was taken from Atoji and Lipscomb's (5) X-ray studies of solid HF (F-F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell (6) determined for HF gaseous polymers by electron diffraction. The low F-bending frequency (53 cm^{-1}) was taken from Boutin et al. (7). The other vibrational frequencies were taken from Kittelberger and Hornig's (8) work on crystalline HF. Huong and Couzi (9) and Smith (10) have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table (11) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (11), we recalculate the table in terms of 1973 fundamental constants (12), 1975 atomic weights (13), and current JANAF reference states for the elements.

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DISULFUR DECAFLUORIDE (S_2F_{10})
(IDEAL GAS) GFW=254.10403

$F_{10}S_2$

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-7.004	-487.751	-487.751	INFINITE
100	16.532	64.965	123.814	-5.885	-490.435	-475.986	1040.251
200	29.850	80.463	98.372	-3.582	-492.418	-460.708	503.432
298	42.228	94.872	94.872	0.000	-493.400	-444.901	326.117
300	42.417	95.133	94.872	0.078	-493.412	-444.601	323.887
400	50.530	108.535	96.644	4.756	-494.779	-428.226	233.969
500	55.625	120.400	100.234	10.083	-495.350	-411.521	179.873
600	58.900	130.851	104.484	15.820	-495.475	-394.737	143.781
700	61.072	140.105	108.925	21.826	-495.309	-377.957	118.002
800	62.564	148.363	113.348	28.012	-520.953	-363.613	99.333
900	63.605	155.795	117.658	34.323	-519.875	-344.005	83.535
1000	64.347	162.537	121.814	40.723	-518.763	-324.526	70.924
1100	64.861	168.695	125.800	47.184	-517.626	-305.157	60.628
1200	65.271	174.357	129.614	53.691	-516.476	-285.892	52.067
1300	65.553	179.593	133.260	60.233	-515.319	-266.722	44.839
1400	65.782	184.459	136.745	66.800	-514.168	-247.644	38.658
1500	65.943	189.004	140.079	73.387	-513.020	-228.647	33.313
1600	66.078	193.264	143.271	79.988	-511.881	-209.727	28.647
1700	66.160	157.272	146.331	86.600	-510.747	-190.873	24.538
1800	66.233	201.056	149.267	93.220	-509.633	-172.093	20.895
1900	66.296	204.639	152.088	99.846	-508.522	-153.366	17.641
2000	66.351	208.041	154.801	106.478	-507.431	-134.707	14.720
2100	66.385	211.279	157.414	113.115	-506.346	-116.095	12.082
2200	66.416	214.368	159.934	119.755	-505.274	-97.537	9.689
2300	66.443	217.321	162.365	126.398	-504.216	-79.029	7.509
2400	66.467	220.149	164.714	133.044	-503.166	-60.564	5.515
2500	66.488	222.863	166.986	139.692	-502.128	-42.143	3.684
2600	66.502	225.471	169.186	146.341	-501.101	-23.763	1.997
2700	66.515	227.981	171.317	152.992	-500.086	-5.423	0.439
2800	66.526	230.400	173.384	159.644	-499.082	12.878	-1.005
2900	66.536	232.735	175.391	166.297	-498.086	31.147	-2.347
3000	66.544	234.991	177.340	172.951	-497.106	49.374	-3.597
3100	66.549	237.173	179.235	179.606	-496.127	67.580	-4.764
3200	66.553	239.285	181.079	186.261	-495.165	85.745	-5.856
3300	66.557	241.333	182.874	192.916	-494.210	103.886	-6.880
3400	66.560	243.320	184.623	199.572	-493.266	121.996	-7.842
3500	66.563	245.250	186.327	206.228	-492.334	140.075	-8.747
3600	66.564	247.125	187.990	212.885	-491.408	158.133	-9.600
3700	66.565	248.949	189.613	219.541	-490.495	176.162	-10.405
3800	66.566	250.724	191.198	226.198	-489.588	194.169	-11.167
3900	66.567	252.453	192.747	232.854	-488.694	212.151	-11.888
4000	66.568	254.138	194.261	239.511	-487.811	230.108	-12.572
4100	66.569	255.782	195.741	246.168	-486.935	248.048	-13.222
4200	66.570	257.386	157.190	252.825	-486.071	265.963	-13.839
4300	66.571	258.953	198.608	259.482	-485.216	283.859	-14.427
4400	66.572	260.483	199.997	266.139	-484.373	301.734	-14.987
4500	66.573	261.979	201.358	272.797	-483.541	319.588	-15.521
4600	66.573	263.443	202.692	279.454	-482.717	337.429	-16.031
4700	66.573	264.874	204.000	286.111	-481.902	355.252	-16.519
4800	66.573	266.276	205.282	292.769	-481.105	373.050	-16.985
4900	66.574	267.649	206.541	299.426	-480.311	390.840	-17.432
5000	66.574	268.994	207.777	306.083	-479.534	408.607	-17.860
5100	66.574	270.312	208.990	312.741	-478.760	426.368	-18.271
5200	66.575	271.605	210.182	319.398	-478.006	444.104	-18.665
5300	66.575	272.873	211.353	326.056	-477.258	461.832	-19.044
5400	66.576	274.117	212.504	332.713	-476.522	479.542	-19.408
5500	66.576	275.339	213.635	339.371	-475.795	497.243	-19.758
5600	66.576	276.538	214.748	346.029	-475.084	514.926	-20.096
5700	66.577	277.717	215.842	352.686	-474.381	532.599	-20.421
5800	66.577	278.875	216.919	359.344	-473.686	550.260	-20.734
5900	66.577	280.013	217.979	366.002	-473.005	567.911	-21.036
6000	66.577	281.132	219.022	372.659	-472.339	585.545	-21.328

Dec. 31, 1977

DISULFUR DECAFLUORIDE (S_2F_{10}) (IDEAL GAS) GFW = 254.10403

ΔHa°_0 = 802.8 ± 11.0 kcal/mol
$S^\circ_{298.15}$ = [94.9 ± 2.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -487.8 ± 7.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -493.4 ± 7.0 kcal/mol

$F_{10}S_2$

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
913 (1)	938 (1)	410 (2)	860 (2)
690 (1)	684 (1)	[150](2)	634 (2)
[642](1)	571 (1)	728 (2)	425 (2)
247 (1)	826 (2)	624 (2)	188 (2)
Torsion	544 (2)	509 (2)	

Point Group: [D_{4d}] σ = 8
Bond Distances: S-F = 1.56 ± 0.02 Å S-S = 2.21 ± 0.03 Å
Bond Angles: F*-S-F* = 90° F*-S-S = 90°
F**-S-S = 180°
(* - equatorial ** - axial)
Product of the Moments of Inertia: $I_AI_BI_C = 8.7456 \times 10^{-112}\ g^3\ cm^6$
Reduced Moment of Inertia: $I_{red} = 1.5354 \times 10^{-38}\ g\ cm^2$
Barrier to Internal Rotation: V = [8.0] kcal/mol

Heat of Formation

The kinetics of the decomposition of gaseous S_2F_{10} have been studied by Trost and McIntosh (1) from 434-455 K. Benson and Bott (2) have reevaluated these kinetic data and have reported two values for the equilibrium constant of the dissociation process $S_2F_{10}(g) = SF_4(g) + SF_6(g)$. Both values refer to a temperature of 444 K. We analyze these two Kp values by the third law method, and we obtain the result ΔHr°_{298} = 19.26±1.4 kcal/mol. The adopted value of $\Delta Hf^\circ_{298}(S_2F_{10},g)$ = -493.4±7.0 kcal/mol is obtained by combining the value of ΔHr° with JANAF heats of formation (3) for SF_4 and SF_6.

The heat of atomization (ΔHa°_0) and bond dissociation energy $D^\circ_0(F_5S\text{-}SF_5)$ are calculated to be 802.8±11.0 kcal/mol and 58.4± 14.0 kcal/mol, respectively. The latter value agrees with an upper limit value of 62.6 kcal/mol for the bond energy of a covalent S-S linkage established from thermochemical data (3) for the S_8 ring.

Heat Capacity and Entropy

The results of electron diffraction experiments (4) show that the S_2F_{10} molecule consists of two SF_5 octahedral groups sharing a common S-S bond. The adopted bond lengths and angles are taken from this study (4). The relative orientation of the two SF_5 groups has not been experimentally established (5-7), but the staggered configuration of D_{4d} symmetry has been predicted to be more stable (8) than the eclipsed form (D_{4h} symmetry). We assume that the point group is D_{4d}. The principal moments of inertia are: $I_A = 6.1416 \times 10^{-38}$ and $I_B = I_C = 1.1933 \times 10^{-37}\ g\ cm^2$.

The vibrational spectra of S_2F_{10} have been studied in detail in three independent investigations (5-7). The reported fundamental frequencies show reasonable agreement but the assignments of the observed fundamentals made by Wilmshurst and Bernstein (5) differ somewhat from those made by Dodd et al. (6). The adopted frequencies and assignments except for the torsion (ν_5) and SF_5 rocking frequency (ν_{12}) are taken from Dodd et al. (6). We estimate the unobserved ν_{12} fundamental at 150 cm^{-1}. Other estimated values that have been reported include 200 cm^{-1} (2) and 37 cm^{-1} (5). The inactive torsional frequency is treated as a hindered internal rotation. We use an estimated potential barrier of 8.0 kcal/mol (5) to calculate heat capacity contributions for hindered rotation from the table of Pitzer and Brewer (9). Contributions below 201 K could not be obtained by this procedure since the values of the ratio V/RT were outside the range of the table. Cp° values between 150-200 K are estimated by graphical interpolation of the hindered rotor Cp° data above 210 K and the corresponding data for a harmonic oscillator (ν_5 = 89 cm^{-1}, 5) below 150 K. This treatment assumes that the internal rotation approaches harmonic oscillation as V/RT >> 1. The uncertainty (±2 gibbs/mol) in the value of S°_{298} includes the possibility that the potential barrier is as low as 4.0 kcal/mol (8) and contains a contribution from the uncertainty due to the two estimated vibrational frequencies.

Previously published thermodynamic functions (10, 11) for S_2F_{10} are based on the assumption that free internal rotation exists in the molecule and on different estimates (5) for the SF_5 rocking fundamentals. Benson and Bott (2) have shown that these earlier estimated frequencies (5) give values for $S^\circ(S_2F_{10},g)$ which are too high by several units. Our treatment of internal rotation is consistent with the interpretation of electron diffraction data (4) which indicates that the rotation is not completely restricted. It should also be noted that the Cp° data reported by Pass (11) are erroneous above 400 K.

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$F_{10}S_2$

IRON (FE) FE

(REFERENCE STATE) GFW=55.847

T, K	gibbs/mol			kcal/mol			
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	-1.077	0.000	0.000	0.000
100	2.892	1.449	11.210	-0.976	0.000	0.000	0.000
200	5.160	4.290	7.056	-0.553	0.000	0.000	0.000
298	5.998	6.529	6.529	0.000	0.000	0.000	0.000
300	6.009	6.567	6.530	0.011	0.000	0.000	0.000
400	6.565	8.370	6.772	0.639	0.000	0.000	0.000
500	7.099	9.889	7.247	1.321	0.000	0.000	0.000
600	7.660	11.232	7.801	2.059	0.000	0.000	0.000
700	8.270	12.456	8.380	2.853	0.000	0.000	0.000
800	9.070	13.609	8.962	3.717	0.000	0.000	0.000
900	10.300	14.741	9.541	4.680	0.000	0.000	0.000
1000	13.010	15.934	10.120	5.815	0.000	0.000	0.000
1100	11.090	17.223	10.711	7.164	0.000	0.000	0.000
1200	8.130	18.278	11.294	8.380	0.000	0.000	0.000
1300	8.330	18.936	11.857	9.203	0.000	0.000	0.000
1400	8.530	19.561	12.385	10.046	0.000	0.000	0.000
1500	8.730	20.156	12.884	10.909	0.000	0.000	0.000
1600	8.930	20.726	13.356	11.792	0.000	0.000	0.000
1700	9.910	21.410	13.808	12.922	0.000	0.000	0.000
1800	10.150	21.983	14.247	13.925	0.000	0.000	0.000
1900	11.000	24.398	14.757	18.318	0.000	0.000	0.000
2000	11.000	24.962	15.253	19.418	0.000	0.000	0.000
2100	11.000	25.499	15.728	20.518	0.000	0.000	0.000
2200	11.000	26.010	16.184	21.618	0.000	0.000	0.000
2300	11.000	26.499	16.622	22.718	0.000	0.000	0.000
2400	11.000	26.967	17.043	23.818	0.000	0.000	0.000
2500	11.000	27.417	17.449	24.918	0.000	0.000	0.000
2600	11.000	27.848	17.841	26.018	0.000	0.000	0.000
2700	11.000	28.263	18.219	27.118	0.000	0.000	0.000
2800	11.000	28.663	18.585	28.218	0.000	0.000	0.000
2900	11.000	29.049	18.940	29.318	0.000	0.000	0.000
3000	11.000	29.422	19.283	30.418	0.000	0.000	0.000
3100	11.000	29.783	19.616	31.518	0.000	0.000	0.000
3200	6.415	56.674	20.467	115.862	0.000	0.000	0.000
3300	6.492	56.873	21.568	116.507	0.000	0.000	0.000
3400	6.570	57.068	22.609	117.160	0.000	0.000	0.000
3500	6.649	57.259	23.596	117.821	0.000	0.000	0.000
3600	6.730	57.448	24.534	118.490	0.000	0.000	0.000
3700	6.813	57.633	25.426	119.167	0.000	0.000	0.000
3800	6.898	57.816	26.276	119.853	0.000	0.000	0.000
3900	6.984	57.997	27.087	120.547	0.000	0.000	0.000
4000	7.073	58.174	27.862	121.250	0.000	0.000	0.000
4100	7.163	58.350	28.603	121.962	0.000	0.000	0.000
4200	7.256	58.524	29.314	122.683	0.000	0.000	0.000
4300	7.351	58.696	29.995	123.413	0.000	0.000	0.000
4400	7.448	58.866	30.649	124.153	0.000	0.000	0.000
4500	7.547	59.034	31.278	124.903	0.000	0.000	0.000
4600	7.647	59.201	31.883	125.662	0.000	0.000	0.000
4700	7.749	59.367	32.466	126.432	0.000	0.000	0.000
4800	7.853	59.531	33.029	127.212	0.000	0.000	0.000
4900	7.959	59.694	33.571	128.003	0.000	0.000	0.000
5000	8.066	59.856	34.095	128.804	0.000	0.000	0.000
5100	8.175	60.017	34.602	129.616	0.000	0.000	0.000
5200	8.285	60.177	35.092	130.439	0.000	0.000	0.000
5300	8.397	60.336	35.567	131.273	0.000	0.000	0.000
5400	8.510	60.494	36.027	132.119	0.000	0.000	0.000
5500	8.625	60.651	36.473	132.975	0.000	0.000	0.000
5600	8.742	60.807	36.907	133.844	0.000	0.000	0.000
5700	8.860	60.963	37.327	134.724	0.000	0.000	0.000
5800	8.981	61.118	37.736	135.616	0.000	0.000	0.000
5900	9.103	61.273	38.134	136.520	0.000	0.000	0.000
6000	9.228	61.427	38.521	137.437	0.000	0.000	0.000

March 31, 1965; March 31, 1978

IRON (Fe) (REFERENCE STATE) GFW = 55.847

FE

0 to 1184 K	Crystal, alpha
1184 to 1665 K	Crystal, gamma
1665 to 1809 K	Crystal, delta
1809 to 3136.39 K	Liquid
3136.39 to 6000 K	Ideal gas, monatomic

See crystal, liquid, and monatomic gas tables for details.

IRON, ALPHA-DELTA (FE) FE
(CRYSTAL) GFW=55.847

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.077	0.000	0.000	0.000
100	2.892	1.449	11.210	-0.976	0.000	0.000	0.000
200	5.160	4.290	7.056	-0.553	0.000	0.000	0.000
298	5.998	6.529	6.529	0.000	0.000	0.000	0.000
300	6.009	6.567	6.530	0.011	0.000	0.000	0.000
400	6.545	8.370	6.772	0.639	0.000	0.000	0.000
500	7.099	9.889	7.247	1.321	0.000	0.000	0.000
600	7.660	11.232	7.801	2.059	0.000	0.000	0.000
700	8.270	12.456	8.380	2.853	0.000	0.000	0.000
800	9.070	13.609	8.962	3.717	0.000	0.000	0.000
900	10.300	14.741	9.541	4.680	0.000	0.000	0.000
1000	13.010	15.934	10.120	5.815	0.000	0.000	0.000
1100	11.090	17.223	10.711	7.164	0.000	0.000	0.000
1200	9.750	18.124	11.292	8.198	-0.182	0.003	-0.000
1300	9.200	18.878	11.847	9.139	-0.064	0.013	-0.002
1400	9.210	19.557	12.374	10.057	0.011	0.016	-0.002
1500	9.430	20.200	12.875	10.988	0.079	0.014	-0.002
1600	9.670	20.814	13.352	11.943	0.151	0.007	-0.001
1700	9.910	21.410	13.808	12.922	0.000	0.000	0.000
1800	10.150	21.983	14.247	13.925	0.000	0.000	0.000
1900	10.390	22.538	14.669	14.952	-3.366	0.167	-0.019
2000	10.630	23.077	15.076	16.003	-3.415	0.355	-0.039
2100	10.870	23.602	15.469	17.078	-3.440	0.544	-0.057
2200	11.110	24.113	15.850	18.177	-3.441	0.734	-0.073

March 31, 1965; March 31, 1978

IRON, ALPHA - DELTA (Fe) (CRYSTAL) GFW = 55.847

FE

$S°_{298.15}$ = 6.529 ± 0.03 cal/(mol K)

T_{t1} = 1042 ± 1 K (Curie temp)

T_{t2} = 1184 ± 3 K (α - γ)

T_{t3} = 1665 ± 3 K (γ - δ)

Tm = 1809 ± 5 K (δ - ℓ)

$\Delta Hf°_0$ = 0 kcal/mol

$\Delta Hf°_{298.15}$ = 0 kcal/mol

$\Delta H°_{t1}$ = 0 kcal/mol

$\Delta H°_{t2}$ = 0.215 ± 0.010 kcal/mol

$\Delta H°_{t3}$ = 0.200 ± 0.020 kcal/mol

ΔHm° = 3.300 ± 0.200 kcal/mol

$\Delta Hs°_{298.15}$ = 99.3 ± 0.3 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The current literature was surveyed by Hultgren (1). Smoothed low temperature heat capacity values are obtained by fitting the data (2 - 7) graphically and with orthogonal polynomials over selected overlapping temperature intervals. Using $S°_{20}$ = 0.0364 cal/(mol K), we integrate over the adopted smoothed heat capacity values to obtain $S°_{298}$ = 6.529 cal/(mol K). An uncertainty of 0.015 cal/(mol K) arises due to the choice of heat capacity values in the region 20-55 K. In this region there is considerable disagreement between the reported heat capacity values of Eucken and Werth (2), Simon and Swain (3), and those of Duyckaerts (4) and Keesom and Kurrelmeyer (5). An additional uncertainty of 0.01 cal/(mol K) results from the differences in the range 50-298 K in the heat capacity data of Kelley (6) and Stepakoff and Kaufman (8).

The heat capacity and enthalpy studies above room temperature are numerous. A bibliography of all known studies (including low temperature studies) is available on request. The adopted heat capacity values above 400 K are those selected by Hultgren (8) and Orr and Chipman (9). The method of orthogonal polynomials is used to join smoothly the low and high temperature heat capacity values. The smooth heat capacity values for metastable α-Fe in the range 1184-1665 K are adjusted from those of Hultgren (8) so as to yield the proper entropy values for γ-Fe. The available heat capacity/enthalpy data show differences up to 10% in Cp° for δ-Fe with the major discrepancies being different slopes in dCp°/dT.

Transition Data

The enthalpies of the α - γ transition at 1184 K and the γ - δ transition at 1665 K are those selected by Hultgren (8) and Orr and Chipman (9). The α and δ phase has a bcc structure whereas the γ phase has a fcc structure.

Melting Data

Refer to the liquid phase table.

Sublimation Data

The value adopted for the heat of sublimation is that selected by Hultgren (8) and is based on a second and third law analysis of sublimation data over γ-Fe and liquid Fe. Refer to the gas phase table for details.

References

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IRON, GAMMA (FE) FE
(CRYSTAL) GFW=55.847

T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.326	8.495	8.495	-0.000	1.861	1.275	-0.935
300	6.330	8.534	8.495	0.012	1.862	1.272	-0.926
400	6.530	10.383	8.746	0.655	1.877	1.072	-0.586
500	6.730	11.861	9.226	1.318	1.858	0.872	-0.381
600	6.930	13.106	9.771	2.001	1.803	0.679	-0.247
700	7.130	14.189	10.327	2.704	1.712	0.499	-0.156
800	7.330	15.154	10.871	3.427	1.571	0.334	-0.091
900	7.530	16.029	11.396	4.170	1.351	0.192	-0.047
1000	7.730	16.833	11.900	4.933	0.979	0.080	-0.018
1100	7.930	17.579	12.383	5.716	0.413	0.021	-0.004
1200	8.130	18.278	12.845	6.519	0.000	0.000	0.000
1300	8.330	18.936	13.289	7.342	0.000	0.000	0.000
1400	8.530	19.561	13.715	8.185	0.000	0.000	0.000
1500	8.730	20.156	14.125	9.048	0.000	0.000	0.000
1600	8.930	20.726	14.519	9.931	0.000	0.000	0.000
1700	9.130	21.274	14.901	10.834	-0.227	0.005	-0.001
1800	9.330	21.801	15.270	11.757	-0.307	0.020	-0.002
1900	9.530	22.311	15.627	12.700	-3.757	0.208	-0.024
2000	9.730	22.805	15.973	13.663	-3.894	0.420	-0.046
2100	9.930	23.284	16.310	14.646	-4.011	0.639	-0.067
2200	10.130	23.751	16.638	15.649	-4.108	0.863	-0.086

March 31, 1978

IRON, GAMMA (Fe) (CRYSTAL) GFW = 55.847

$S°_{298.15}$ = [8.495] cal/(mol K)
T_{t1} = 1184 ± 3 K (α - γ)
T_{t2} = 1665 ± 3 K (γ - δ)

$\Delta Hf°_{298.15}$ = [1.861] kcal/mol Fe
$\Delta H°_{t1}$ = 0.215 ± 0.010 kcal/mol
$\Delta H°_{t2}$ = 0.200 ± 0.020 kcal/mol

Heat of Formation

The heat of formation at 298.15 K is obtained from that of Fe(α) by adding $\Delta H°_{t1}$ and the difference between $H°_{1184} - H°_{298}$ of Fe(α) and Fe(γ).

Heat Capacity and Entropy

A current literature survey by Hultgren (1) yielded approximately twenty heat capacity/enthalpy studies which gave information as to the heat capacity of γ-Fe in the stable and metastable region. A listing of these studies is available on request. *We adopt the heat capacity values chosen by Hultgren (2) and Orr and Chipman (3). These values are based primarily on the* studies by Dench and Kubaschewski (4), Braun and Kohlhaas (5), and Wallace et al. (6). However, all the available heat capacity/enthalpy data show discrepancies up to 5% (in Cp°); with the major discrepancies appearing as different slopes in Cp° vs T plots.

Values are not extended below 298.15 K due to the lack of substantial data is this metastable region. The entropy at 298.15 K is calculated in a manner analogous to that used for the heat of formation.

Transition Data

Refer to the Fe(α,δ) table (7).

References

1. R. Hultgren, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, personal communication.
2. R. Hultgren, et al., "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals, Metals Park, Ohio, 1973.
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7. JANAF Thermochemical Tables: Fe(c,

IRON (FE) FE
(LIQUID) GFW=55.847

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.998	8.308	8.308	-0.000	2.963	2.433	-1.783
300	6.009	8.345	8.308	0.011	2.963	2.429	-1.770
400	6.545	10.147	8.550	0.639	2.963	2.252	-1.230
500	7.099	11.667	9.025	1.321	2.963	2.074	-0.906
600	7.656	13.010	9.579	2.059	2.963	1.896	-0.690
700	8.213	14.232	10.158	2.852	2.962	1.719	-0.537
800	8.770	15.365	10.739	3.701	2.947	1.542	-0.421
900	9.327	16.431	11.313	4.606	2.889	1.369	-0.332
1000	9.884	17.442	11.875	5.567	2.715	1.207	-0.264
1100	10.442	18.410	12.426	6.583	2.382	1.076	-0.214
1200	11.000	19.343	12.964	7.655	2.238	0.960	-0.175
1300	11.000	20.223	13.489	8.755	2.515	0.842	-0.142
1400	11.000	21.038	13.999	9.855	2.772	0.704	-0.110
1500	11.000	21.797	14.494	10.955	3.009	0.547	-0.080
1600	11.000	22.507	14.973	12.055	3.226	0.376	-0.051
1700	11.000	23.174	15.436	13.155	3.196	0.196	-0.025
1800	11.000	23.803	15.883	14.255	3.293	0.017	-0.002
1900	11.000	24.398	16.316	15.355	0.000	0.000	0.000
2000	11.000	24.962	16.734	16.455	0.000	0.000	0.000
2100	11.000	25.499	17.139	17.555	0.000	0.000	0.000
2200	11.000	26.010	17.531	18.655	0.000	0.000	0.000
2300	11.000	26.499	17.910	19.755	0.000	0.000	0.000
2400	11.000	26.967	18.278	20.855	0.000	0.000	0.000
2500	11.000	27.416	18.634	21.955	0.000	0.000	0.000
2600	11.000	27.848	18.981	23.055	0.000	0.000	0.000
2700	11.000	28.263	19.317	24.155	0.000	0.000	0.000
2800	11.000	28.663	19.643	25.255	0.000	0.000	0.000
2900	11.000	29.049	19.961	26.355	0.000	0.000	0.000
3000	11.000	29.422	20.270	27.455	0.000	0.000	0.000
3100	11.000	29.783	20.571	28.555	0.000	0.000	0.000
3200	11.000	30.132	20.865	29.655	-83.244	1.692	-0.116
3300	11.000	30.470	21.151	30.755	-82.789	4.339	-0.287
3400	11.000	30.799	21.430	31.855	-82.342	6.973	-0.448
3500	11.000	31.118	21.702	32.955	-81.903	9.593	-0.599
3600	11.000	31.428	21.968	34.055	-81.472	12.201	-0.741
3700	11.000	31.729	22.228	35.155	-81.049	14.798	-0.874

March 31, 1965; March 31, 1978

IRON (Fe) (LIQUID) GFW = 55.847

$S^\circ_{298.15}$ = [8.308] cal/(mol K)
Tm = 1809 ± 5 K (δ - ℓ)
Tb = 3136.39 K

$\Delta Hf^\circ_{298.15}$ = [2.963] kcal/mol
ΔHm° = 3.3 ± 0.1 kcal/mol
ΔHv° = 83.538 kcal/mol FE

Heat of Formation

The heat of formation at 298.15 K is calculated from that of the combined phase crystal (α-γ-δ) by adding ΔHm° and the difference between $H^\circ_{1809} - H^\circ_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid is taken to be 11.0 cal/(mol K) as in Hultgren (1) and Orr and Chipman (2). We adopt this value in the real liquid region as well as in the extrapolated region to 1200 K and to 3500 K. Below 1200 K, heat capacity values are chosen so as to form a curve which joins smoothly the α-Fe heat capacity values in the range 298 - 500 K. The entropy is calculated in a manner analogous to that used for the heat of formation. A current literature survey (3) revealed numerous heat capacity and enthalpy studies in the liquid region which yielded heat capacity values in the range 8.0 to 12.4 cal/(mol K), as given in the table below. The more recent studies by Braun et al. (10), using a quasi-adiabatic calorimeter suggest Cp° = 10.938 cal/(mol K) whereas the levitation calorimetric enthalpy measurements of Margrave et al. (12,14) suggest 10.29±0.29 and 11.138±0.43 cal/(mol K), respectively.

Melting Data

The adopted Tm and ΔHm° values are those selected by Hultgren (1) and Orr and Chipman (2); 1809±5 K and 3300±100 cal/mol, respectively. Reported values for ΔHm° vary from a low of 2760 to a high of 3865 cal/mol, as given in the table below.

Vaporization Data

The boiling point is calculated from the adopted thermodynamic functions and the chosen heat of sublimation so that the Gibbs energy functions calculated by integration of the crystal-liquid data and by statistical methods for the gas phase are equal at T_b.

Reference	Year	Calorimetric Method	Tm, K	ΔHm° cal/mol	Cp°(ℓ) cal/(mol K)	Measured Region, K
Wust et al. (4)	1918	drop	1801	2760	11.96	373 - 1873
Umino (5)	1926, 1929	mixture	1800	3865	12.398	373 - 1906
Oberhoffer and Grosse (6)	1927	drop	1801	3595	11.2	370 - 1860
Pattison and Willows (7)	1956	mixture	1806	3658	8.0	1273 - 1923
Ferrier and Olette (8)	1962	drop	1809±1	3292±80	11.226	1665 - 2210
Morris et al. (9)	1966	drop	1808	3298±100	9.766	1720 - 1875
Braun et al. (10)	1965 - 1968	quasi adiab.	1809	3442±50	10.038	300 - 1900
Lebedev et al. (11)	1971	exploding wire		3256		
Treverton and Margrave (12)	1971	levitation		3307±70	10.29±0.29	1804 - 2142
Cezairliyan and McClure (13)	1974	pulse	1808±5			
Margrave (14)	1975	levitation	1811	3370±90	11.138±0.43	

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IRON, MONATOMIC (FE) FE
(IDEAL GAS) GFW=55.847

	gibbs/mol			kcal/mol			
T, K	$C_p°$	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	0.000	0.000	INFINITE	-1.637	98.740	98.740	INFINITE
100	5.112	36.948	48.329	-1.138	99.138	95.588	-208.905
200	5.823	40.712	43.666	-0.591	99.262	91.978	-100.507
298	6.136	43.112	43.111	0.000	99.300	88.393	-64.793
300	6.138	43.150	43.112	0.011	99.300	88.325	-64.344
400	6.102	44.915	43.353	0.625	99.286	84.668	-46.260
500	5.949	46.261	43.805	1.228	99.207	81.021	-35.414
600	5.784	47.331	44.307	1.814	99.055	77.396	-28.191
700	5.643	48.212	44.804	2.386	98.833	73.804	-23.042
800	5.529	48.957	45.277	2.944	98.527	70.248	-19.191
900	5.441	49.603	45.723	3.492	98.112	66.736	-16.206
1000	5.375	50.173	46.140	4.033	97.518	63.279	-13.830
1100	5.329	50.683	46.530	4.568	96.704	59.898	-11.900
1200	5.302	51.145	46.896	5.099	96.019	56.578	-10.304
1300	5.291	51.569	47.239	5.629	95.726	53.303	-8.961
1400	5.295	51.961	47.563	6.158	95.412	50.052	-7.813
1500	5.313	52.327	47.868	6.688	95.079	46.823	-6.822
1600	5.343	52.671	48.158	7.221	94.729	43.617	-5.958
1700	5.383	52.996	48.433	7.757	94.135	40.438	-5.199
1800	5.432	53.305	48.695	8.298	93.673	37.293	-4.528
1900	5.487	53.600	48.946	8.864	89.826	34.341	-3.950
2000	5.548	53.883	49.185	9.396	89.278	31.435	-3.435
2100	5.613	54.155	49.416	9.954	88.736	28.556	-2.972
2200	5.681	54.418	49.637	10.518	88.200	25.703	-2.553
2300	5.751	54.672	49.851	11.090	87.672	22.874	-2.174
2400	5.823	54.919	50.057	11.669	87.151	20.068	-1.827
2500	5.896	55.158	50.256	12.255	86.637	17.284	-1.511
2600	5.969	55.390	50.449	12.848	86.130	14.519	-1.220
2700	6.042	55.617	50.636	13.448	85.630	11.775	-0.953
2800	6.116	55.838	50.818	14.056	85.138	9.048	-0.706
2900	6.190	56.054	50.995	14.671	84.653	6.339	-0.478
3000	6.264	56.265	51.167	15.294	84.176	3.647	-0.266
3100	6.339	56.472	51.335	15.924	83.706	0.971	-0.068
3200	6.415	56.674	51.498	16.562	0.000	0.000	0.000
3300	6.492	56.873	51.658	17.207	0.000	0.000	0.000
3400	6.570	57.068	51.815	17.861	0.000	0.000	0.000
3500	6.649	57.259	51.967	18.521	0.000	0.000	0.000
3600	6.730	57.448	52.117	19.190	0.000	0.000	0.000
3700	6.813	57.633	52.264	19.868	0.000	0.000	0.000
3800	6.898	57.816	52.407	20.553	0.000	0.000	0.000
3900	6.984	57.996	52.548	21.247	0.000	0.000	0.000
4000	7.073	58.174	52.687	21.950	0.000	0.000	0.000
4100	7.163	58.350	52.823	22.662	0.000	0.000	0.000
4200	7.256	58.524	52.956	23.383	0.000	0.000	0.000
4300	7.351	58.696	53.088	24.113	0.000	0.000	0.000
4400	7.448	58.866	53.217	24.853	0.000	0.000	0.000
4500	7.547	59.034	53.345	25.603	0.000	0.000	0.000
4600	7.647	59.201	53.470	26.362	0.000	0.000	0.000
4700	7.749	59.367	53.594	27.132	0.000	0.000	0.000
4800	7.853	59.531	53.716	27.912	0.000	0.000	0.000
4900	7.959	59.694	53.836	28.703	0.000	0.000	0.000
5000	8.066	59.856	53.955	29.504	0.000	0.000	0.000
5100	8.175	60.017	54.072	30.316	0.000	0.000	0.000
5200	8.285	60.176	54.188	31.139	0.000	0.000	0.000
5300	8.397	60.335	54.303	31.973	0.000	0.000	0.000
5400	8.510	60.493	54.416	32.819	0.000	0.000	0.000
5500	8.625	60.651	54.528	33.676	0.000	0.000	0.000
5600	8.742	60.807	54.638	34.544	0.000	0.000	0.000
5700	8.860	60.963	54.748	35.424	0.000	0.000	0.000
5800	8.981	61.118	54.857	36.316	0.000	0.000	0.000
5900	9.103	61.273	54.964	37.220	0.000	0.000	0.000
6000	9.228	61.427	55.070	38.137	0.000	0.000	0.000

March 31, 1965; March 31, 1978

ΔHf°_0 = 98.7 ± 0.3 kcal/mol FE

$S^\circ_{298.15}$ = 43.112 ± 0.01 cal/(mol K)

$\Delta Hf^\circ_{298.15}$ = 99.3 ± 0.3 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^5D_4$	0.000	9
$^5D_3$	415.932	7
$^5D_2$	704.004	5
$^5D_1$	888.129	3
$^5D_0$	978.072	1
.	.	.
.	.	.
.	.	.
$^3G^\circ_2$	62081.27	5

Ionization Limit = 63480 cm^{-1}

Heat of Formation

The sublimation and vaporization studies on iron are too numerous to tabulate. A current literature survey by Hultgren yielded approximately thirty investigations (1). As in Hultgren (2), we adopt ΔHf°_{298}(Fe, g) = 99.3±0.3 kcal/mol based on the studies of Morris et al. (3) and Myles and Aldred (4). A complete listing of all vapor pressure studies is available on request. Many of the more recent studies do not provide sufficient information to enable calculation of ΔHf° values via the second and third law approach.

Our second and third law analyses of the vaporization data of Morris et al. (3) and the sublimation data of Myles and Aldred (4) are given below.

Source	No. Pts	Range, K	ΔHr°_{298}, kcal/mol 2nd law	3rd law	drift cal/(mol K)	ΔHf°_{298}(Fe, g) kcal/mol
Fe(ℓ) = Fe(g)	21	1812-1891	96.8±1.1	96.5±0.1	0.1±0.6	99.5
Fe(γ) = Fe(g)	eqn	1450-1650	98.1	97.1	-0.6	99.0

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Reader and Sugar (5). Although we have only listed the ground state, the lowest four excited states, the highest observed excited state, and the ionization limit for Fe(g), all levels listed by Reader and Sugar (5), as well as estimated missing levels, are used in the calculations. The observed levels are too numerous to list completely. Our calculations indicate that for Fe(g) the thermochemical functions are independent of the estimated missing levels (for n = 4, 5, 6, 7) and the cutoff procedure up to 3500 K. The Gibbs energy function is essentially unaffected up to 5200 K. The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cutoff procedures (6). In fact, the inclusion of some higher states (n = 4, 5, 6, 7) and consideration of various cut-off procedures leads to calculational differences in the Gibbs energy function of roughly 0.1 cal/(mol K) or greater at temperatures in excess of 8000 K.

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IRON, UNIPOSITIVE ION (Fe^+)
(IDEAL GAS) GFW=55.84645

FE^+

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.658	280.240		
100							
200							
298	6.230	43.439	43.439	0.000	282.302	269.810	-197.773
300	6.232	43.477	43.439	0.012	282.311	269.732	-196.497
400	6.241	45.274	43.684	0.636	282.805	265.464	-145.041
500	6.198	46.662	44.146	1.258	283.242	261.077	-114.115
600	6.174	47.789	44.662	1.876	283.619	256.607	-93.468
700	6.167	48.741	45.179	2.493	283.938	252.080	-78.702
800	6.163	49.564	45.676	3.110	284.188	247.510	-67.616
900	6.153	50.289	46.149	3.726	284.337	242.916	-58.987
1000	6.133	50.936	46.596	4.340	284.314	238.312	-52.082
1100	6.104	51.520	47.018	4.952	284.074	233.727	-46.437
1200	6.068	52.049	47.415	5.561	283.962	229.150	-41.733
1300	6.029	52.534	47.791	6.166	284.241	224.571	-37.753
1400	5.988	52.979	48.146	6.766	284.496	219.971	-34.339
1500	5.948	53.391	48.482	7.363	284.727	215.354	-31.377
1600	5.910	53.773	48.801	7.956	284.934	210.723	-28.783
1700	5.874	54.130	49.104	8.545	284.889	206.083	-26.493
1800	5.843	54.465	49.392	9.131	284.969	201.445	-24.458
1900	5.815	54.780	49.668	9.714	281.656	196.970	-22.656
2000	5.791	55.078	49.931	10.294	281.633	192.514	-21.037
2100	5.771	55.360	50.183	10.872	281.608	188.059	-19.571
2200	5.754	55.628	50.424	11.448	281.580	183.604	-18.239
2300	5.740	55.884	50.656	12.023	281.552	179.151	-17.023
2400	5.730	56.128	50.879	12.597	281.522	174.700	-15.908
2500	5.723	56.361	51.094	13.169	281.492	170.250	-14.883
2600	5.719	56.586	51.301	13.741	281.461	165.801	-13.937
2700	5.717	56.802	51.500	14.313	281.429	161.352	-13.060
2800	5.718	57.009	51.693	14.885	281.397	156.906	-12.247
2900	5.722	57.210	51.880	15.457	281.366	152.460	-11.490
3000	5.728	57.404	52.061	16.029	281.336	148.016	-10.783
3100	5.737	57.592	52.237	16.602	281.306	143.573	-10.122
3200	5.748	57.775	52.407	17.177	198.032	140.821	-9.617
3300	5.761	57.952	52.572	17.752	198.460	139.027	-9.207
3400	5.777	58.124	52.733	18.329	198.881	137.220	-8.820
3500	5.795	58.292	52.889	18.907	199.295	135.400	-8.455
3600	5.815	58.455	53.042	19.488	199.704	133.569	-8.109
3700	5.837	58.615	53.190	20.071	200.105	131.726	-7.781
3800	5.862	58.771	53.335	20.655	200.501	129.872	-7.469
3900	5.888	58.923	53.476	21.243	200.892	128.009	-7.173
4000	5.917	59.073	53.614	21.833	201.276	126.135	-6.892
4100	5.947	59.219	53.749	22.426	201.654	124.252	-6.623
4200	5.979	59.363	53.881	23.023	202.025	122.358	-6.367
4300	6.014	59.504	54.010	23.622	202.392	120.458	-6.122
4400	6.049	59.643	54.137	24.225	202.752	118.549	-5.888
4500	6.087	59.779	54.261	24.832	203.106	116.631	-5.664
4600	6.125	59.913	54.382	25.443	203.455	114.706	-5.450
4700	6.166	60.045	54.501	26.057	203.795	112.772	-5.244
4800	6.207	60.176	54.618	26.676	204.131	110.832	-5.046
4900	6.250	60.304	54.733	27.299	204.460	108.885	-4.856
5000	6.293	60.431	54.845	27.926	204.783	106.931	-4.674
5100	6.338	60.556	54.956	28.558	205.098	104.971	-4.498
5200	6.383	60.679	55.065	29.194	205.408	103.005	-4.329
5300	6.429	60.801	55.172	29.834	205.712	101.033	-4.166
5400	6.476	60.922	55.278	30.479	206.008	99.054	-4.009
5500	6.523	61.041	55.381	31.129	206.299	97.072	-3.857
5600	6.571	61.159	55.483	31.784	206.581	95.082	-3.711
5700	6.619	61.276	55.584	32.444	206.857	93.089	-3.569
5800	6.667	61.391	55.683	33.108	207.127	91.091	-3.432
5900	6.715	61.506	55.781	33.777	207.389	89.088	-3.300
6000	6.763	61.619	55.877	34.451	207.643	87.061	-3.172

March 31, 1978

IRON, UNIPOSITIVE ION (Fe^+) (IDEAL GAS) GFW = 55.84645

$S^\circ_{298.15}$ = 43.439 ± 0.01 cal/(mol K)

ΔHf°_0 = 280.24 ± 0.3 kcal/mol FE^+
$\Delta Hf^\circ_{298.15}$ = [282.302] kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^6D_{9/2}$	0.00	10
$^6D_{7/2}$	384.77	8
$^6D_{5/2}$	667.64	6
$^6D_{3/2}$	862.63	4
$^6D_{1/2}$	977.03	2
.	.	.
.	.	.
.	.	.
$^2F_{7/2}$	121081.6	8

Ionization Limit = 130524 cm^{-1}

Heat of Formation

The adopted heat of formation ΔHf°_0 is calculated from the equation $Fe(g) = Fe^+(g) + e^-(g)$ with auxiliary data (1), using an ionization potential of IP = 63480±10 cm^{-1} (181.498±0.03 kcal/mol). This ionization potential, as reported by Moore (2) and Reader and Sugar (3) in units of cm^{-1}, is converted to units of kcal/mol using current CODATA fundamental constants (4). The uncertainty in ΔHf°_0 lies mainly in the uncertainty for $\Delta Hf^\circ_0(Fe,g)$.

$\Delta Hf^\circ_{298}(Fe^+,g)$ is obtained from $\Delta Hf^\circ_0(Fe,g)$ by using IP(Fe) with JANAF (1) enthalpies ($H^\circ_0-H^\circ_{298}$) for Fe(g), $Fe^+(g)$, and $e^-(g)$. $\Delta Hr^\circ_{298}(Fe = Fe^+ + e^-)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (5). ΔHf°_{298} should be changed by -1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Reader and Sugar (3). Although we have only listed the ground state, the lowest four excited states, the highest observed excited state, and the ionization limit for $Fe^+(g)$, all levels listed by Reader and Sugar (3), as well as estimated missing levels, are used in our calculations. The observed levels are too numerous to list completely. Our calculations indicate that for $Fe^+(g)$ the thermochemical functions are independent of the cut-off procedure up to 6500 K. The Gibbs energy function is essentially unaffected up to 8000 K. The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 8000 K may require consideration of the higher excited states and utilization of proper fill and cut-off procedures (7).

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FE^+

IRON, UNINEGATIVE ION (Fe^-) FE⁻

(IDEAL GAS) GFW=55.84755

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-1.481	92.970		
100							
200							
298	4.968	42.557	42.557	0.000	91.893	82.639	-60.575
300	4.968	42.588	42.557	0.009	91.882	82.582	-60.160
400	4.968	44.017	42.752	0.506	91.254	79.574	-43.477
500	4.968	45.126	43.120	1.003	90.572	76.732	-33.539
600	4.968	46.031	43.532	1.500	89.834	74.031	-26.966
700	4.968	46.797	43.945	1.996	89.041	71.461	-22.311
800	4.968	47.461	44.344	2.493	88.176	69.008	-18.852
900	4.968	48.046	44.723	2.990	87.213	66.668	-16.189
1000	4.968	48.569	45.082	3.487	86.078	64.443	-14.084
1100	4.968	49.043	45.421	3.984	84.729	62.348	-12.387
1200	4.968	49.475	45.741	4.480	83.514	60.364	-10.994
1300	4.968	49.873	46.044	4.977	82.690	58.468	-9.829
1400	4.968	50.241	46.331	5.474	81.847	56.636	-8.841
1500	4.968	50.583	46.603	5.971	80.984	54.865	-7.994
1600	4.968	50.904	46.862	6.468	80.101	53.152	-7.260
1700	4.968	51.205	47.108	6.964	78.972	51.500	-6.621
1800	4.968	51.489	47.344	7.461	77.968	49.913	-6.060
1900	4.968	51.758	47.569	7.958	73.575	48.549	-5.584
2000	4.968	52.013	47.785	8.455	72.475	47.260	-5.164
2100	4.968	52.255	47.992	8.952	71.375	46.027	-4.790
2200	4.968	52.486	48.191	9.448	70.276	44.846	-4.455
2300	4.968	52.707	48.383	9.945	69.175	43.715	-4.154
2400	4.968	52.918	48.568	10.442	68.075	42.631	-3.882
2500	4.968	53.121	48.746	10.939	66.975	41.593	-3.636
2600	4.968	53.316	48.918	11.436	65.875	40.600	-3.413
2700	4.968	53.504	49.084	11.932	64.776	39.649	-3.209
2800	4.968	53.684	49.245	12.429	63.675	38.738	-3.024
2900	4.968	53.859	49.401	12.926	62.575	37.867	-2.854
3000	4.968	54.027	49.553	13.423	61.475	37.034	-2.698
3100	4.968	54.190	49.700	13.920	60.375	36.237	-2.555
3200	4.968	54.348	49.842	14.416	-23.968	37.168	-2.538
3300	4.968	54.500	49.981	14.913	-24.614	39.089	-2.589
3400	4.968	54.649	50.116	15.410	-25.267	41.029	-2.637
3500	4.968	54.793	50.248	15.907	-25.928	42.988	-2.684
3600	4.968	54.933	50.376	16.404	-26.597	44.966	-2.730
3700	4.968	55.069	50.501	16.900	-27.273	46.964	-2.774
3800	4.968	55.201	50.623	17.397	-27.960	48.979	-2.817
3900	4.968	55.330	50.742	17.894	-28.654	51.013	-2.859
4000	4.968	55.456	50.858	18.391	-29.357	53.064	-2.899
4100	4.968	55.579	50.972	18.888	-30.069	55.133	-2.939
4200	4.968	55.699	51.083	19.384	-30.789	57.221	-2.977
4300	4.968	55.815	51.192	19.881	-31.520	59.325	-3.015
4400	4.968	55.930	51.298	20.378	-32.260	61.446	-3.052
4500	4.968	56.041	51.402	20.875	-33.010	63.583	-3.088
4600	4.968	56.150	51.504	21.372	-33.769	65.739	-3.123
4700	4.968	56.257	51.604	21.868	-34.539	67.911	-3.158
4800	4.968	56.362	51.702	22.365	-35.319	70.099	-3.192
4900	4.968	56.464	51.799	22.862	-36.110	72.302	-3.225
5000	4.968	56.565	51.893	23.359	-36.911	74.523	-3.257
5100	4.968	56.663	51.986	23.855	-37.722	76.761	-3.289
5200	4.968	56.760	52.076	24.352	-38.546	79.013	-3.321
5300	4.968	56.854	52.166	24.849	-39.380	81.282	-3.352
5400	4.968	56.947	52.253	25.346	-40.226	83.566	-3.382
5500	4.968	57.038	52.340	25.843	-41.082	85.867	-3.412
5600	4.968	57.128	52.424	26.339	-41.950	88.183	-3.441
5700	4.968	57.216	52.508	26.836	-42.831	90.514	-3.470
5800	4.968	57.302	52.589	27.333	-43.723	92.861	-3.499
5900	4.968	57.387	52.670	27.830	-44.627	95.223	-3.527
6000	4.968	57.471	52.749	28.327	-45.544	97.601	-3.555

March 31, 1978

IRON, UNINEGATIVE ION (Fe^-) (IDEAL GAS) GFW = 55.84755

Ground State Configuration $^4F_{9/2}$

$S°_{298.15}$ = 42.557 ± 0.1 cal/(mol K)

$\Delta Hf°_0$ = 92.97 ± 4.6 kcal/mol

$\Delta Hf°_{298.15}$ = [91.893] kcal/mol FE⁻

Electronic Levels and Quantum Weights

State	ϵ_j, cm^{-1}	g_j
$^4F_{9/2}$	0	10

Heat of Formation

The heat of formation $\Delta Hf°_0$ is calculated from an adopted electron affinity of Fe(g) of EA=0.25±0.2 eV (5.765±4.61 kcal/mol). This value has been recommended in the critical compilation by Hotop and Lineberger (1) based on a re-evaluation of a semi-empirical extrapolation (Zollweg horizontal analysis). Rosenstock et al. (2) and Massey (3) reference additional extrapolation/interpolation and calculational studies which yielded electron affinities in the range 0.1 - 0.58 eV.

The $\Delta Hf°_0$ value is converted to a $\Delta Hf°_{298}$ value for $Fe^-(g)$ by including enthalpy differences ($H°_0-H°_{298}$) for $Fe^-(g)$, Fe(g), and $e^-(g)$. $\Delta Hr°_{298}$ ($Fe^- = Fe + e^-$) differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (2). $\Delta Hf°_{298}$ should be changed by +1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for $Fe^-(g)$ is given by Hotop and Lineberger (1) and Rosenstock et al. (2). The thermodynamic functions of the negative ion are calculated using the recent CODATA fundamental constants (4) and assuming the $Fe^-(g)$ is an ideal monatomic gas. Lacking any experimental evidence as to the stability of any excited states, we assumed no stable excited states exist.

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FE⁻

PYRRHOTITE ($Fe_{0.877}S$)
(CRYSTAL) GFW=81.038

$FE_{0.877}S$

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.209	-25.412	-25.412	INFINITE
100	6.190	4.437	23.751	-1.931	-25.389	-25.405	55.522
200	10.100	10.133	15.569	-1.087	-25.308	-25.450	27.810
298	11.922	14.531	14.531	0.000	-25.200	-25.541	18.722
300	11.950	14.605	14.532	0.022	-25.198	-25.543	18.608
400	13.420	18.244	15.018	1.291	-25.578	-25.659	14.019
500	14.910	21.399	15.985	2.707	-25.693	-25.667	11.219
600	13.890	24.400	17.129	4.363	-25.533	-25.664	9.348
700	13.280	26.493	18.322	5.720	-25.668	-25.677	8.017
800	12.870	28.238	19.455	7.026	-38.883	-26.863	7.338
900	12.640	29.740	20.516	8.301	-38.903	-25.359	6.158
1000	12.430	31.052	21.506	9.546	-39.116	-23.846	5.211
1100	13.240	32.274	22.429	10.829	-39.486	-22.295	4.430
1200	14.130	33.465	23.300	12.198	-39.589	-20.733	3.776
1300	14.980	34.628	24.126	13.651	-39.312	-19.172	3.223
1400	16.060	35.776	24.918	15.202	-38.955	-17.635	2.753
1500	17.370	36.927	25.680	16.871	-38.496	-16.128	2.350
1600	18.920	38.097	26.419	18.685	-37.911	-14.655	2.002
1700	20.580	39.292	27.141	20.657	-37.438	-13.218	1.699
1800	22.590	40.524	27.850	22.812	-36.625	-11.816	1.435

Sept. 30, 1977

PYRRHOTITE ($Fe_{0.877}S$) (CRYSTAL) GFW = 81.038

$S^\circ_{298.15}$ = 14.53 ± 0.01 gibbs/mol
$T\beta$ = 598 ± 3 K

ΔHf°_0 = -25.4 ± 0.4 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -25.2 ± 0.4 kcal/mol
$\Delta H\beta^\circ$ = 0.095 ± 0.02 kcal/mol

$FE_{0.877}S$

Heat of Formation

The adopted value of ΔHf°_{298} is based on the calorimetric determination of Stolyarova and Bezmen (1) assuming that their reported value refers to 298.15 K. This value came from an average of eight determinations of $\Delta H\overset{\circ}{r}$ for $Fe_{0.877}S(c) + Zn(c) \rightarrow ZnS(c) + 0.877\ Fe(c)$.

In the composition range y = 0.095 to 0.145, Bugli et al. (2) determined $\Delta Hr^\circ_{433} = -14.4(y-0.025)$ kcal/mol for $FeS(c) + yS(\ell) \rightarrow (1+y)Fe_{1/(1+y)}S(c)$. Using $y = x/(1-x)$ we calculate that $\Delta Hr^\circ_{433} = -14.76x + 0.36$ kcal/mol for $(1-x)FeS(c) + xS(\ell) \rightarrow Fe_{1-x}S(c)$ in this same composition range. Using x = 0.123 and auxiliary JANAF data (3), we then calculate $\Delta Hf^\circ_{298}(Fe_{0.877}S,c)$ = -22.1 kcal/mol based on Bugli's data. The difference between this value of ΔHf°_{298} and that of Stolyarova and Bezmen is probably due to different morphology of the products; Bugli et al. state they are uncertain as to the exact nature of their product. Due to the complicated and kinetically slow phase behavior of $Fe_{0.877}S$, it appears they may not have obtained the pure monoclinic product.

Heat Capacity and Entropy

The adopted heat capacities from 6-350 K are based on our analysis of the Cp° data of Gronvold et al. (4). Two small anomalies in the Cp° curve, for which there is no obvious explanation, were observed near 8 and 30 K (4). These lead to entropy increments of 0.003 and 0.03 gibbs/mol, respectively. Since there are no measured Cp° or enthalpy data above 350 K, the Cp° is estimated via the following procedure. Above Tβ, Cp° is estimated as $Cp^\circ(Fe_{0.877}S,c) = Cp^\circ(FeS,c) - 0.123\ Cp^\circ(Fe,c)$ using auxiliary JANAF data (3). Since the Tα transition present in FeS(c,troilite) is not present in pyrrhotite of composition $Fe_{0.877}S$ (3), the heat capacity is assumed to be linear between 350 and 598 K where Cp°_{598} is estimated via the procedure outlined above. Hirone et al. (5) observed non-linear behavior for Cp° of $Fe_{0.90}S$ from 513 to 593 K.

The value of S°_{298} is derived from the appropriate integration of Cp° data assuming S°_6 = 0.0007 gibbs/mol.

Phase Data

The mineral pyrrhotite has a composition range extending from FeS to $Fe_{0.877}S$ ($\sim Fe_7S_8$); the name troilite is reserved for the stoichiometric FeS composition. The data presented in this table refer to the iron poor composition limit which is found to be $Fe_{0.877}S$ below Tβ (6). For stoichiometric FeS there are 3 crystalline polymorphs designated α, β, γ from low to high temperature, where the α-β transition is designated Tα and the β-γ transition is designated Tβ. We retain this nomenclature for $Fe_{0.877}S$ while recognizing that the α phase does not exist for this composition. Hirone et al.(5) found Tβ and ΔHβ° to be independent of composition so we adopt the same values as for FeS(c, troilite) (3). The transition at 411 K (Tα) in FeS was found to be non-existent in compositions containing less iron than $Fe_{0.95}S$ (2), so it will not be present in $Fe_{0.877}S$. The crystal structure of $Fe_{0.877}S$ is hexagonal above Tβ while the stable form below Tβ is monoclinic (6,7). The conversion from hexagonal to monoclinic when cooling through Tβ is kinetically slow and even annealing for several months may not be sufficient for complete conversion (6,7).

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$FE_{0.877}S$

TROILITE (FES)
(CRYSTAL) GFW=87.907

FES

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.250	-24.421	-24.421	INFINITE
100	6.374	4.115	23.788	-1.967	-24.405	-24.371	53.262
200	10.290	9.958	15.467	-1.102	-24.355	-24.356	26.615
298	12.074	14.417	14.417	0.000	-24.300	-24.368	17.862
300	12.111	14.492	14.417	0.022	-24.299	-24.368	17.752
400	21.320	18.896	14.954	1.577	-24.470	-24.400	13.331
500	17.294	23.851	16.339	3.756	-23.905	-24.498	10.708
600	14.826	27.155	17.862	5.576	-23.671	-24.630	8.971
700	14.294	29.398	19.355	7.030	-23.806	-24.780	7.736
800	13.996	31.284	20.731	8.442	-37.022	-26.103	7.131
900	13.931	32.927	21.997	9.837	-37.042	-24.737	6.007
1000	14.098	34.401	23.165	11.236	-37.244	-23.362	5.106
1100	14.498	35.762	24.249	12.664	-37.638	-21.950	4.361
1200	15.132	37.049	25.262	14.144	-37.772	-20.523	3.738
1300	15.998	38.293	26.217	15.698	-37.496	-19.096	3.210
1400	17.397	39.517	27.123	17.351	-37.140	-17.693	2.762
1500	18.429	40.740	27.990	19.125	-36.681	-16.319	2.378
1600	19.993	41.979	28.826	21.044	-36.097	-14.980	2.046
1700	21.791	43.243	29.636	23.132	-35.653	-13.677	1.758
1800	23.822	44.545	30.428	25.410	-34.839	-12.406	1.506

Sept. 30, 1977

TROILITE (FeS) (CRYSTAL) GFW = 87.907

$S°_{298.15}$ = 14.42 ± 0.01 gibbs/mol
Tα = 411 ± 3 K
Tβ = 598 ± 3 K
Tm = 1463 ± 3 K

$\Delta Hf°_0$ = -24.42 ± 0.2 kcal/mol
$\Delta Hf°_{298.15}$ = -24.30 ± 0.2 kcal/mol
ΔHα° = 0.398 ± 0.2 kcal/mol
ΔHβ° = 0.095 ± 0.02 kcal/mol
ΔHm° = 7.52 ± 0.5 kcal/mol

FES

Heat of Formation

The adopted $\Delta Hf°_{298}$ is -24.30±0.2 kcal/mol and is based on our third law analysis of gas phase H_2S/H_2 equilibrium data of (1 - 7). Additional studies of a similar nature are reported by Mills (8). The gas phase equilibrium results are favored over calorimetric (8) and emf (9 - 11) results because of greater certainty in the stoichiometry of the iron sulfide. Of the calorimetric results (8), only those of Adami and King ($\Delta Hf°_{298}$ = -23.89±0.41 kcal/mol) and the annealed sample of Ariya et al. ($\Delta Hf°_{298}$ = -24.4 kcal/mol) are in reasonable agreement with the adopted value. Of the emf results, all refer to less than stoichiometric composition $Fe_{0.95}S$ (9), $Fe_{0.98}S$ (10) or to impure sample, 97.58% (11). $\Delta Hf°_{298}$ has been shown to vary significantly as a function of stoichiometry (12) which is a result of the variation of ΔHα° with composition (12).

					$\Delta Hr°_{298}$, kcal/mol		Drift	$\Delta Hf°_{298}$ †
Investigator	Reaction	Method	Number of Points	Temp. Range, K	2nd law	3rd law	gibbs/mol	kcal/mol
Rosenqvist (1)	C	H_2S/H_2	11	773 - 1257	-17.89±0.41	-19.40±0.53	-1.45±0.40	-24.30±0.6
Blaise (2)	C	"	equation	923 - 1043	-17.87	-19.41±0.14	-1.57	-24.31±0.2
Turkdogan (3)	C	"	3	943 - 1173	-17.24±0.39	-19.40±0.48	-2.03±0.36	-24.30±0.5
Alcock (4)	B	"	equation	720 - 1261	-38.30	-39.68±0.56	-1.38	-24.26±0.6
McCabe (5)	B	"	10	1224 - 1255	-33.76±2.84	-39.70±0.15	4.81±2.3	-24.28±0.2
Sudo (6)	C	"	4	1048 - 1145	-17.39±2.19	-19.51±0.29	-1.95±2.01	-24.41±0.4
Rau (7)	C	"	9	820 - 1257	-19.40±0.23	-19.31±0.20	0.09±0.22	-24.15±0.3
Berner (9)	A	emf	1	298.15		-24.08		-24.08
DeRanter (10)	A	H titration	1	298.15				-20.55
DeRanter (10)	A	emf	1	298.15		-20.56		-20.56
Guldin (11)	B	emf	1	973		36.445		-21.02

†Based on third law analysis (A) Fe(c) + S(c) → FeS(c) (B) Fe(c) + $1/2S_2$(g) → FeS(c) (C) Fe(c) + H_2S(g) → FeS(c) + H_2(g)

Heat Capacity and Entropy

The adopted heat capacities are obtained by merging the Cp° data (7-345 K) of Gronvold et al. (13) and the enthalpy data (356-1488 K) of Coughlin (14). The data are difficult to merge smoothly because of the proximity of the α-β transition at 411 K. *Coughlin gives the composition of his sample as* $FeS_{1.02}$ *and this introduces some uncertainty at the higher temperatures.*

The value of $S°_{298}$ is obtained from the appropriate integration of Cp° values assuming $S°_7$ = 0.0028 gibbs/mol.

Phase Data

The mineral pyrrhotite has a composition range extending from FeS to $Fe_{0.875}S$ (Fe_7S_8); the name troilite is reserved for the stoichiometric FeS composition. The phase diagram (15) of this system shows that the iron-rich limit of this phase corresponds to stoichiometric FeS below ~1370 K; above this temperature only an iron-deficient material exists so that stoichiometric FeS will melt incongruently.

There are two solid state phase transitions, both associated with electronic-magnetic phenomena. The adopted temperature (Tα) of the α-β transition is 411±3K (15). Our analysis of the adopted Cp° data yields ΔHα° = 0.398 kcal/mol; in view of the uncertainties in this data we adopt an uncertainty of ±0.2 kcal/mol in ΔHα°. The adopted temperature (Tβ) of the β-γ transition is 598±3 K (15) and our analysis of Coughlin's high temperature enthalpy data (14) yields ΔHβ° = 0.095±0.02 kcal/mol.

Melting Data

See FeS(l) table.

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FES

IRON MONOSULFIDE (FES)
(LIQUID) GFW=87.907

FES

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.250	-16.567	-16.567	INFINITE
100	6.374	9.490	29.163	-1.967	-16.552	-17.055	37.273
200	10.290	15.334	20.842	-1.102	-16.501	-17.578	19.208
298	12.074	19.792	19.792	0.000	-16.446	-18.117	13.280
300	12.111	19.867	19.793	0.022	-16.445	-18.127	13.205
400	21.320	24.271	20.329	1.577	-16.617	-18.696	10.215
500	17.294	29.227	21.714	3.756	-16.051	-19.332	8.450
600	14.826	32.530	23.238	5.576	-15.818	-20.001	7.285
700	14.294	34.773	24.730	7.030	-15.953	-20.689	6.459
800	13.996	36.659	26.107	8.442	-29.168	-22.550	6.160
900	13.931	38.302	27.372	9.837	-29.189	-21.721	5.275
1000	14.098	39.776	28.540	11.236	-29.390	-20.884	4.564
1100	14.950	41.163	29.625	12.693	-29.756	-20.009	3.975
1200	14.950	42.464	30.641	14.188	-29.875	-19.124	3.483
1300	14.950	43.661	31.597	15.683	-29.658	-18.237	3.066
1400	14.950	44.769	32.499	17.178	-29.460	-17.365	2.711
1500	14.950	45.800	33.352	18.673	-29.280	-16.508	2.405
1600	14.950	46.765	34.160	20.168	-29.120	-15.662	2.139
1700	14.950	47.671	34.929	21.663	-29.269	-14.820	1.905
1800	14.950	48.526	35.661	23.158	-29.238	-13.971	1.696
1900	14.950	49.334	36.359	24.653	-32.895	-12.938	1.488
2000	14.950	50.101	37.027	26.148	-32.934	-11.888	1.299
2100	14.950	50.831	37.667	27.643	-32.980	-10.833	1.127
2200	14.950	51.526	38.282	29.138	-33.033	-9.777	0.971
2300	14.950	52.191	38.872	30.633	-33.091	-8.720	0.829
2400	14.950	52.827	39.440	32.128	-33.156	-7.660	0.698
2500	14.950	53.437	39.988	33.623	-33.227	-6.595	0.577
2600	14.950	54.023	40.517	35.118	-33.303	-5.529	0.465
2700	14.950	54.588	41.027	36.613	-33.385	-4.460	0.361
2800	14.950	55.131	41.522	38.108	-33.472	-3.386	0.264
2900	14.950	55.656	42.000	39.603	-33.565	-2.311	0.174
3000	14.950	56.163	42.464	41.098	-33.663	-1.230	0.090
3100	14.950	56.653	42.913	42.593	-33.766	-0.146	0.010
3200	14.950	57.128	43.350	44.088	-117.299	2.384	-0.163
3300	14.950	57.588	43.775	45.583	-116.949	6.117	-0.405
3400	14.950	58.034	44.188	47.078	-116.608	9.841	-0.633
3500	14.950	58.467	44.589	48.573	-116.275	13.554	-0.846
3600	14.950	58.889	44.981	50.068	-115.952	17.261	-1.048
3700	14.950	59.298	45.362	51.563	-115.637	20.996	-1.238
3800	14.950	59.697	45.734	53.058	-115.332	24.641	-1.417

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IRON MONOSULFIDE (FeS) (LIQUID) GFW = 87.907

$S°_{298.15}$ = 19.79 ± 0.4 gibbs/mol
Tm = 1463 ± 3 K

$ΔHf°_{298.15}$ = -16.45 ± 0.5 kcal/mol
ΔHm° = 7.52 ± 0.5 kcal/mol

FES

Heat of Formation

The adopted value of $ΔHf°_{298}$ is calculated from that of FeS(c) (1) by adding ΔHm° and the enthalpy difference ($H°_{1463}$ - $H°_{298}$) between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of liquid FeS above an assumed glass transition temperature of 1050 K is taken from Vaisburd and Zedina (2). Their constant value of Cp° = 14.95 gibbs/mol is lower than Cp° = 17.8 gibbs/mol which we derive from the enthalpy data of Coughlin (3). The latter value is based on two points separated by only 9 K while the results of Vaisburd and Zedina are quoted as covering the range from the mp to 1723 K. The heat capacity below the glass transition is that of the crystal (1).

The value of $S°_{298}$ is calculated from that of FeS(c) by adding ΔHm°/Tm and the entropy difference ($S°_{1463}$ - $S°_{298}$) between the crystal and liquid.

Melting Data

The adopted melting point of 1463±3 K is taken from the phase diagram of Hansen and Anderko (4). The adopted heat of fusion, ΔHm° = 7.52±0.5 kcal/mol, is from our analysis of the high temperature enthalpy data of Coughlin (3).

References

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FES

IRON MONOSULFIDE (FeS)
(IDEAL GAS) GFW=87.907

FeS

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-2.343	88.401	88.401	INFINITE
100	7.123	51.943	68.397	-1.645	88.832	84.083	-183.762
200	8.394	57.245	61.610	-0.873	88.789	79.331	-86.687
298	9.277	60.785	60.785	0.000	88.615	74.723	-54.773
300	9.287	60.842	60.785	0.017	88.612	74.637	-54.372
400	9.599	63.566	61.154	0.965	87.833	70.036	-38.265
500	9.644	65.716	61.859	1.928	87.183	65.657	-28.698
600	9.598	67.471	62.653	2.891	86.559	61.412	-22.369
700	9.530	68.945	63.449	3.847	85.927	57.270	-17.880
800	9.466	70.214	64.217	4.797	72.248	52.023	-14.212
900	9.411	71.325	64.947	5.741	71.777	49.524	-12.026
1000	9.366	72.314	65.635	6.679	71.115	47.083	-10.290
1100	9.331	73.205	66.283	7.614	70.228	44.728	-8.887
1200	9.304	74.016	66.894	8.546	69.545	42.434	-7.728
1300	9.283	74.760	67.471	9.475	69.197	40.189	-6.756
1400	9.267	75.447	68.017	10.403	68.827	37.972	-5.928
1500	9.255	76.086	68.534	11.329	68.438	35.781	-5.213
1600	9.247	76.683	69.024	12.254	68.028	33.617	-4.592
1700	9.241	77.244	69.492	13.178	67.309	31.485	-4.048
1800	9.238	77.772	69.937	14.102	66.769	29.393	-3.569
1900	9.236	78.271	70.363	15.026	62.540	27.517	-3.165
2000	9.236	78.745	70.770	15.950	61.930	25.688	-2.807
2100	9.238	79.196	71.161	16.873	61.313	23.893	-2.487
2200	9.241	79.625	71.536	17.797	60.689	22.125	-2.198
2300	9.245	80.036	71.896	18.721	60.060	20.385	-1.937
2400	9.250	80.430	72.244	19.646	59.425	18.673	-1.700
2500	9.257	80.808	72.579	20.572	58.784	16.990	-1.485
2600	9.265	81.171	72.902	21.498	58.139	15.330	-1.289
2700	9.274	81.521	73.215	22.425	57.489	13.695	-1.109
2800	9.285	81.858	73.518	23.352	56.835	12.086	-0.943
2900	9.297	82.184	73.811	24.282	56.176	10.499	-0.791
3000	9.312	82.500	74.096	25.212	55.513	8.936	-0.651
3100	9.328	82.805	74.372	26.144	54.847	7.395	-0.521
3200	9.346	83.102	74.640	27.078	-29.247	7.319	-0.500
3300	9.366	83.389	74.901	28.013	-29.456	8.464	-0.561
3400	9.388	83.669	75.154	28.951	-29.673	9.616	-0.618
3500	9.413	83.942	75.402	29.891	-29.895	10.773	-0.673
3600	9.440	84.207	75.642	30.834	-30.124	11.941	-0.725
3700	9.470	84.466	75.877	31.779	-30.359	13.112	-0.774
3800	9.502	84.719	76.107	32.728	-30.600	14.287	-0.822
3900	9.537	84.967	76.331	33.680	-30.847	15.475	-0.867
4000	9.574	85.209	76.550	34.635	-31.101	16.664	-0.910
4100	9.614	85.446	76.764	35.594	-31.359	17.864	-0.952
4200	9.656	85.678	76.973	36.558	-31.625	19.066	-0.992
4300	9.701	85.905	77.178	37.526	-31.897	20.278	-1.031
4400	9.748	86.129	77.379	38.498	-32.174	21.491	-1.067
4500	9.798	86.349	77.576	39.475	-32.458	22.714	-1.103
4600	9.850	86.564	77.769	40.458	-32.747	23.947	-1.138
4700	9.904	86.777	77.959	41.445	-33.043	25.181	-1.171
4800	9.960	86.986	78.145	42.439	-33.345	26.425	-1.203
4900	10.018	87.192	78.327	43.438	-33.653	27.671	-1.234
5000	10.079	87.395	78.506	44.442	-33.966	28.925	-1.264
5100	10.141	87.595	78.683	45.453	-34.285	30.186	-1.294
5200	10.204	87.793	78.856	46.471	-34.611	31.453	-1.322
5300	10.269	87.988	79.026	47.494	-34.941	32.727	-1.350
5400	10.336	88.180	79.194	48.524	-35.279	34.006	-1.376
5500	10.403	88.371	79.359	49.561	-35.620	35.294	-1.402
5600	10.472	88.559	79.522	50.605	-35.968	36.585	-1.428
5700	10.541	88.745	79.682	51.656	-36.321	37.883	-1.452
5800	10.611	88.928	79.840	52.713	-36.679	39.192	-1.477
5900	10.682	89.110	79.995	53.778	-37.043	40.500	-1.500
6000	10.754	89.291	80.149	54.850	-37.411	41.820	-1.523

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IRON MONOSULFIDE (FeS) (IDEAL GAS) GFW = 87.907

D_0° = 76.3 ± 3.5 kcal/mol
$S^\circ_{298.15}$ = [60.8 ± 3.0] gibbs/mol

ΔHf_0° = 88.4 ± 3.9 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 88.6 ± 3.9 kcal/mol

Electronic Levels and Quantum Weights

FeS

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
[0]	[9]	[20481.9]	[9]	[30716.2]	[5]
[436.2]	[7]	[21462.2]	[9]	[30857.8]	[7]
[738.9]	[5]	[21699.9]	[7]	[30886.4]	[9]
[932.4]	[3]	[21857.2]	[5]	[34812.4]	[1]
[1027.3]	[1]	[24558.8]	[11]	[35803.7]	[5]
[19404.8]	[5]	[24940.9]	[9]	[40999.9]	[5]
[20688.4]	[3]	[25142.4]	[7]	[42896.9]	[7]
[21208.5]	[1]	[30088.8]	[7]	[49148.0]	[1]
[20051.1]	[13]	[30356.2]	[13]	[49576.9]	[3]
[20300.8]	[11]	[30725.8]	[3]	[50412.3]	[5]

ω_e = 550 cm^{-1} $\omega_e x_e$ = [2.8] cm^{-1} σ = 1
B_e = [0.198] cm^{-1} α_e = [0.0012] cm^{-1} r_e = [2.05] Å

Heat of Formation

Drowart et al. (1) used a modified Knudsen cell and a mass spectrometric technique to study the equilibrium FeS(g) + Mn(g) = MnS(g) + Fe(g). We adopt a value of D_0° = 76.3±3.5 kcal/mol based on their third law analysis of this equilibrium. With auxiliary JANAF data (2) this yields ΔHf°_{298} = 88.6±3.9 kcal/mol. Trevedi (3) studied the absorption spectrum of FeS and determined D_0° = 93 kcal/mol from the onset of continuous absorption due to photodissociation. This value is likely to be too high in view of the experimental difficulties in determining the exact position of the onset of continuous absorption. Complications arise because of background emission from the furnace. Marquardt and Berkowitz (4) determined an upper limit of D_0° < 77 kcal/mol by mass-spectrometric measurements. These results may be biased since they used ν = 412 cm^{-1} for the vibrational frequency of FeS in determining their free energy functions. A Birge-Sponer extrapolation of the vibrational data to determine D_0° is not meaningful since DeVore and Franzen (5) used the reverse procedure to arrive at the reported value of $\omega_e x_e$.

Heat Capacity and Entropy

With the exception of the observance of one excited state at 17992 cm^{-1} with a vibrational spacing of ~497 cm^{-1} by DeVore and Franzen (5), there is no information on the electronic spectrum of FeS(g). The identity and quantum weight of this state, as well as the ground state, are unknown. As a result, the electronic states are estimated to be identical to those of the Fe^{2+} ion (6) following the procedure of Brewer and Rosenblatt (7) for the transition metal oxides. As stated by Brewer and Rosenblatt (7), this procedure usually overestimates the contribution of electronic states. Nevertheless; it appears to be the best method available. The uncertainty assigned to S°_{298} is based mainly on the uncertainties in this approximation since the presence of the sulfide ion will undoubtedly alter the electronic structure of the iron ion. Levels above 50,000 cm^{-1} are not included since they have a negligible effect on the thermodynamic properties. The vibrational constants are taken from a study of the matrix isolation spectrum by DeVore and Franzen (5). The rotational constants are estimated based on an oxide-sulfide correlation due to Barrow and Cousins (8), $r_{FeS} = 0.237 + 1.116\ r_{FeO}$. The value r_{FeO} = 1.626 Å is taken from Suchard (9). The value of α_e is estimated assuming a Morse potential function using the expression given by Herzberg (10).

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FeS

MARCASITE (FeS_2)
(CRYSTAL) GFW=119.967

FeS_2

T, K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol $-(G^\circ-H^\circ_{298})/T$	kcal/mol $H^\circ-H^\circ_{298}$	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.331	-39.148	-39.148	INFINITE
100	4.605	1.811	23.751	-2.194	-39.442	-38.878	84.967
200	11.807	7.500	14.156	-1.331	-39.787	-38.167	41.707
298	14.912	12.874	12.874	0.000	-40.000	-37.324	27.359
300	14.951	12.966	12.874	0.028	-40.003	-37.307	27.178
400	15.532	17.506	13.483	1.609	-41.248	-36.338	19.854
500	17.315	21.290	14.677	3.306	-42.104	-35.018	15.306
600	17.822	24.492	16.053	5.063	-42.789	-33.532	12.214
700	18.394	27.280	17.461	6.873	-43.368	-31.943	9.973
800	18.802	29.773	18.847	8.740	-69.889	-32.670	8.925
900	19.292	32.016	20.188	10.645	-69.838	-28.020	6.804
1000	19.781	34.073	21.475	12.599	-69.929	-23.372	5.108
1100	20.270	35.982	22.708	14.601	-70.196	-18.697	3.715
1200	20.760	37.766	23.889	16.653	-70.209	-14.020	2.553
1300	21.250	39.447	25.022	18.753	-69.842	-9.353	1.572
1400	21.740	41.040	26.110	20.903	-69.447	-4.713	0.736

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MARCASITE (FeS_2) (CRYSTAL) GFW = 119.967

FeS_2

$S^\circ_{298.15}$ = 12.87 ± 0.03 gibbs/mol

ΔHf°_0 = -39.1 ± 0.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -40.0 ± 0.5 kcal/mol

Heat of Formation

Based on highly accurate adiabatic-shield calorimetry measurements, Gronvold and Westrum (1) reported that the heat of transformation of marcasite to pyrite is -1.05±0.05 kcal/mol at 700 K. The adopted value of ΔHf°_{298} is selected to reproduce this heat of reaction within the reported uncertainty. Lipin et al. (2), based on combustion calorimetry, reported a value of -5.6 kcal/mol for the marcasite-pyrite transformation at 298.15 K. Due to the state of the art in combustion calorimetry at the time of this measurement and uncertainty in the products (oxides of sulfur), this value must have a high uncertainty and is given no weight in our selection process.

Heat Capacity and Entropy

The adopted heat capacities of marcasite are based on our analysis of the Cp° measurements (6 - 700 K) of Gronvold and Westrum (1). Values above 700 K are extrapolated assuming Cp° (marcasite) = Cp° (pyrite) + 0.075 gibbs/mol.

The adopted value of S°_{298} is obtained from the appropriate integration of the adopted Cp° data assuming $S^\circ_{6.06}$ = 0.0008 gibbs/mol.

Phase Data

Marcasite has an orthorhombic structure, V_h^{12} = Pnmm, and exists as stoichiometric FeS_2 within the limits of experimental error (3). Marcasite is known to be metastable with respect to the other known FeS_2 polymorph, cubic pyrite, above 673 K (3); the JANAF Thermochemical Tables (4) indicate it will also be metastable below 673 K. The marcasite to pyrite transformation is kinetically slow at low temperatures and this accounts for the persistence of marcasite in nature. Kjekshus and Rakke (5) found no conversion to pyrite using heat treatments at 573 K for periods up to 14 months. At 673 K the conversion to pyrite is complete in 4 months and is even more rapid (< 1 hour) at 973 K (5). Indications are that the conversion to pyrite will be complete before the pyrite decomposition temperature of 1016 K is reached (3).

References

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PYRITE (FeS_2) FeS_2

(CRYSTAL) GFW=119.967

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.304	-40.121	-40.121	INFINITE
100	4.472	1.695	23.451	-2.176	-40.424	-39.848	87.087
200	11.725	7.303	13.922	-1.324	-40.780	-39.120	42.748
298	14.848	12.647	12.647	0.000	-41.000	-38.256	28.042
300	14.887	12.739	12.648	0.028	-41.003	-38.239	27.857
400	16.455	17.259	13.253	1.602	-42.255	-37.246	20.350
500	17.218	21.021	14.442	3.290	-43.120	-35.900	15.692
600	17.760	24.210	15.811	5.040	-43.812	-34.387	12.525
700	18.238	26.984	17.213	6.839	-44.402	-32.769	10.231
800	18.727	29.451	18.591	8.688	-70.941	-33.466	9.142
900	19.217	31.685	19.924	10.585	-70.898	-28.782	6.989
1000	19.706	33.735	21.204	12.531	-70.997	-24.101	5.267
1100	20.195	35.636	22.431	14.526	-71.271	-19.392	3.853
1200	20.685	37.414	23.606	16.570	-71.292	-14.680	2.674
1300	21.174	39.089	24.733	18.663	-70.932	-9.977	1.677
1400	21.664	40.676	25.816	20.805	-70.545	-5.302	0.828

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PYRITE (FeS_2) (CRYSTAL) GFW = 119.967

FeS_2

$S^\circ_{298.15}$ = 12.65 ± 0.03 gibbs/mol
T_d = 1016 ± 2 K (P $\approx$ 10 atm)
T_d = [906 K] (P = 1 atm S_2)

ΔHf°_0 = -40.1 ± 0.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -41.0 ± 0.5 kcal/mol

Heat of Formation

The adopted value of ΔHf°_{298} = -41.0±0.5 kcal/mol is based on our third law analysis of the equilibrium data of Toulmin and Barton (1). These authors made corrections for the changing stoichiometry of pyrrhotite as a function of temperature in the pyrrhotite-pyrite equilibrium, and also accounted for the changing activity of pyrrhotite as a function of temperature and stoichiometry. These corrections have not been applied to our analysis of the rest of the equilibrium data shown below.

					ΔHr°_{298}, kcal/mol		Drift	$-\Delta Hf^\circ_{298}$
Investigator	Method	Reaction	Range, K	# of points	2nd Law	3rd Law	gibbs/mol	kcal/mol
Toulmin (1)	electrum-tarnish	A	598 - 1016	17†	-71.77±0.12	-71.89±0.16	-0.15±0.15	41.0±0.5
DeRudder (2)	manometric	B	873 - 962	7	-32.47±1.27	-27.74±0.43	5.17±1.38	43.2±0.6
Ugai (3)	gravimetric	B	923 - 1016	equation	-16.70	-26.81±0.93	-10.28	36.0
DeRanter (4)	emf	C	298.15	1		-36.00		42.3±1.0
Schneeberg (5)	emf	B	597 - 711	4	-28.98±1.10	-28.16±0.26	1.26±1.68	43.6±0.5
Rosenqvist (6)	dew point	B	869 - 1030	22	-34.03±1.22	-28.04±0.63	6.35±1.29	43.5±0.7

† Point at 1009 K rejected by statistical test.

(A) $Fe(c) + S_2(g) \rightarrow FeS_2(c,pyrite)$
(B) $1.14\ Fe_{0.877}S(c) + 0.43S_2(g) \rightarrow FeS_2(c,\ pyrite)$
(C) $Fe(c) + 2S(c) \rightarrow FeS_2(c,pyrite)$

The value reported by DeRanter (4) is biased since FeS_2 is a semiconductor and DeRanter acknowledged that semiconductors lead to incorrect results in his emf technique. The other values are believed to be biased because the equilibrium is treated as if the composition ($Fe_{0.877}S$) and activity (a=1) of pyrrhotite remain unchanged.

Heat Capacity and Entropy

The adopted values of Cp° are based on our analysis of the calorimetrically measured values of Gronvold and Westrum, 4 - 346 K (7) and 314 - 688 K (8). At higher temperatures the Cp° values are based on our analysis of the enthalpy data of Coughlin (9), 405 - 980 K, which merges smoothly with the Cp° data of Gronvold and Westrum. Values above 980 K are extrapolated.

The adopted value of S°_{298} is obtained from the appropriate integration of the adopted Cp° data assuming $S^\circ_{4.6}$ = 0.0007 gibbs/mol.

Phase Data

Pyrite has a cubic structure, T_h^6 = Pa3, and exists as stoichiometric FeS_2 within the limits of experimental error (10). The other known FeS_2 polymorph is orthorhombic marcasite which is known to be metastable with respect to pyrite above 673 K (10); the JANAF Thermochemical Tables (11) indicate that pyrite will also be the stable form below 673 K.

Decomposition Data

Pyrite melts incongruently to pyrrhotite, a liquid whose composition is $\sim FeS_4$ (3), and vapor at 1016±2 K at the vapor pressure of the system, ~10 atm (3, 10). Assuming the vapor to be composed only of $S_2(g)$, we calculate (11) a decomposition temperature of 906 K at 1 atm for the process $2.3263\ FeS_2(pyrite) \rightarrow S_2(g) + 2.6525\ Fe_{0.877}S(c)$.

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HYDROGEN, MONATOMIC (H)

H

(IDEAL GAS) GFW=1.0079

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	51.634	51.634	INFINITE
100	4.968	21.964	31.808	-0.984	51.772	50.778	-110.973
200	4.968	25.408	27.846	-0.488	51.947	49.716	-54.327
298	4.968	27.392	27.392	0.000	52.103	48.588	-35.616
300	4.968	27.422	27.392	0.009	52.105	48.566	-35.380
400	4.968	28.852	27.587	0.506	52.255	47.364	-25.878
500	4.968	29.960	27.955	1.003	52.402	46.124	-20.160
600	4.968	30.866	28.367	1.500	52.549	44.854	-16.338
700	4.968	31.632	28.780	1.996	52.695	43.560	-13.600
800	4.968	32.295	29.179	2.493	52.839	42.245	-11.541
900	4.968	32.880	29.558	2.990	52.980	40.913	-9.935
1000	4.968	33.404	29.917	3.487	53.118	39.564	-8.647
1100	4.968	33.877	30.256	3.984	53.252	38.203	-7.590
1200	4.968	34.309	30.576	4.480	53.381	36.829	-6.707
1300	4.968	34.707	30.878	4.977	53.504	35.444	-5.959
1400	4.968	35.075	31.165	5.474	53.623	34.051	-5.315
1500	4.968	35.418	31.437	5.971	53.736	32.649	-4.757
1600	4.968	35.739	31.696	6.468	53.845	31.239	-4.267
1700	4.968	36.040	31.943	6.964	53.948	29.823	-3.834
1800	4.968	36.324	32.179	7.461	54.046	28.401	-3.448
1900	4.968	36.592	32.404	7.958	54.140	26.974	-3.103
2000	4.968	36.847	32.620	8.455	54.229	25.542	-2.791
2100	4.968	37.090	32.827	8.952	54.315	24.106	-2.509
2200	4.968	37.321	33.026	9.448	54.396	22.665	-2.252
2300	4.968	37.542	33.218	9.945	54.473	21.221	-2.016
2400	4.968	37.753	33.402	10.442	54.547	19.774	-1.801
2500	4.968	37.956	33.580	10.939	54.617	18.324	-1.602
2600	4.968	38.151	33.752	11.436	54.684	16.871	-1.418
2700	4.968	38.338	33.919	11.932	54.748	15.415	-1.248
2800	4.968	38.519	34.080	12.429	54.808	13.957	-1.089
2900	4.968	38.693	34.236	12.926	54.866	12.497	-0.942
3000	4.968	38.862	34.387	13.423	54.921	11.035	-0.804
3100	4.968	39.024	34.534	13.920	54.973	9.572	-0.675
3200	4.968	39.182	34.677	14.416	55.023	8.106	-0.554
3300	4.968	39.335	34.816	14.913	55.070	6.639	-0.440
3400	4.968	39.483	34.951	15.410	55.114	5.171	-0.332
3500	4.968	39.627	35.083	15.907	55.156	3.701	-0.231
3600	4.968	39.767	35.211	16.404	55.196	2.231	-0.135
3700	4.968	39.903	35.336	16.900	55.234	0.759	-0.045
3800	4.968	40.036	35.458	17.397	55.268	-0.714	0.041
3900	4.968	40.165	35.577	17.894	55.301	-2.188	0.123
4000	4.968	40.291	35.693	18.391	55.331	-3.662	0.200
4100	4.968	40.413	35.807	18.888	55.360	-5.138	0.274
4200	4.968	40.533	35.918	19.384	55.386	-6.613	0.344
4300	4.968	40.650	36.026	19.881	55.410	-8.090	0.411
4400	4.968	40.764	36.133	20.378	55.432	-9.567	0.475
4500	4.968	40.876	36.237	20.875	55.451	-11.045	0.536
4600	4.968	40.985	36.339	21.372	55.469	-12.522	0.595
4700	4.968	41.092	36.439	21.868	55.484	-14.001	0.651
4800	4.968	41.197	36.537	22.365	55.498	-15.479	0.705
4900	4.968	41.299	36.633	22.862	55.510	-16.958	0.756
5000	4.968	41.399	36.728	23.359	55.519	-18.437	0.806
5100	4.968	41.498	36.820	23.855	55.527	-19.916	0.853
5200	4.968	41.594	36.911	24.352	55.533	-21.395	0.899
5300	4.968	41.689	37.000	24.849	55.538	-22.875	0.943
5400	4.968	41.782	37.088	25.346	55.541	-24.354	0.986
5500	4.968	41.873	37.174	25.843	55.543	-25.834	1.027
5600	4.968	41.962	37.259	26.339	55.543	-27.313	1.066
5700	4.968	42.050	37.342	26.836	55.542	-28.793	1.104
5800	4.968	42.137	37.424	27.333	55.540	-30.272	1.141
5900	4.968	42.222	37.505	27.830	55.537	-31.752	1.176
6000	4.968	42.305	37.584	28.327	55.532	-33.232	1.210

Dec. 31, 1960; Sept. 30, 1965; June 30, 1974;
March 31, 1977

HYDROGEN, MONATOMIC (H) (IDEAL GAS) GFW = 1.0079

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 27.392 ± 0.004 gibbs/mol

ΔHf°_0 = 51.634 ± 0.001 kcal/mol H

$\Delta Hf^\circ_{298.15}$ = 52.103 ± 0.001 kcal/mol

Electronic Level and Quantum Weight

State	ε_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2

Heat of Formation

ΔHf° is the value adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for ΔHf°_{298}(H,g) was derived using $D^\circ_0(H_2)$ = 36118.3±1 cm^{-1} (103.267±0.003 kcal/mol) from Herzberg (2) and auxiliary data from H_2 (3).

Earlier experimental values for $D^\circ_0(H_2)$ were obtained by Herzberg and Monfils (36113.0±0.3 cm^{-1}, 4) and Beutler (36116±6 cm^{-1}, 5). Kolos and Wolniewicz (6) calculated the adiabatic dissociation energy of H_2, corrected for relativistic and radiative effects, to be 36117.4 cm^{-1}.

Heat Capacity and Entropy

The electronic levels for H(g) are given in the compilation by Moore (7). Our calculations indicate that the inclusion of levels through n = 12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the first excited state lies at 82258 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state. The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (8). The value for S°_{298} = 27.392 gibbs/mol agrees with that adopted by CODATA (1) within 0.001 gibbs/mol: the difference is due to the use of more current fundamental constants (9).

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PROTON (H^+) H^+

(IDEAL GAS) GFW=1.00735

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-1.481	365.221		
100							
200							
298	4.968	26.013	26.013	0.000	367.171	362.580	-265.775
300	4.968	26.043	26.013	0.009	367.183	362.552	-264.115
400	4.968	27.473	26.208	0.506	367.829	360.911	-197.190
500	4.968	28.581	26.575	1.003	368.474	359.106	-156.963
600	4.968	29.487	26.988	1.500	369.118	357.173	-130.098
700	4.968	30.253	27.401	1.996	369.759	355.131	-110.875
800	4.968	30.916	27.800	2.493	370.400	352.997	-96.433
900	4.968	31.501	28.179	2.990	371.038	350.783	-85.181
1000	4.968	32.025	28.538	3.487	371.673	348.499	-76.163
1100	4.968	32.498	28.877	3.984	372.304	346.151	-68.773
1200	4.968	32.930	29.197	4.480	372.929	343.745	-62.604
1300	4.968	33.328	29.499	4.977	373.550	341.288	-57.375
1400	4.968	33.696	29.786	5.474	374.165	338.784	-52.886
1500	4.968	34.039	30.058	5.971	374.776	336.235	-48.989
1600	4.968	34.360	30.317	6.468	375.381	333.646	-45.573
1700	4.968	34.661	30.564	6.964	375.980	331.019	-42.555
1800	4.968	34.945	30.800	7.461	376.576	328.357	-39.867
1900	4.968	35.213	31.025	7.958	377.166	325.662	-37.459
2000	4.968	35.468	31.241	8.455	377.753	322.936	-35.288
2100	4.968	35.711	31.448	8.952	378.335	320.182	-33.321
2200	4.968	35.942	31.647	9.448	378.912	317.398	-31.530
2300	4.968	36.163	31.838	9.945	379.486	314.589	-29.892
2400	4.968	36.374	32.023	10.442	380.057	311.756	-28.389
2500	4.968	36.577	32.201	10.939	380.624	308.898	-27.004
2600	4.968	36.772	32.373	11.436	381.188	306.018	-25.723
2700	4.968	36.959	32.540	11.932	381.748	303.116	-24.535
2800	4.968	37.140	32.701	12.429	382.305	300.193	-23.431
2900	4.968	37.314	32.857	12.926	382.860	297.251	-22.401
3000	4.968	37.483	33.008	13.423	383.412	294.290	-21.439
3100	4.968	37.645	33.155	13.920	383.962	291.311	-20.537
3200	4.968	37.803	33.298	14.416	384.507	288.312	-19.691
3300	4.968	37.956	33.437	14.913	385.051	285.298	-18.894
3400	4.968	38.104	33.572	15.410	385.592	282.267	-18.144
3500	4.968	38.248	33.704	15.907	386.132	279.221	-17.435
3600	4.968	38.388	33.832	16.404	386.669	276.158	-16.765
3700	4.968	38.524	33.957	16.900	387.202	273.081	-16.130
3800	4.968	38.657	34.079	17.397	387.734	269.989	-15.528
3900	4.968	38.786	34.198	17.894	388.263	266.884	-14.956
4000	4.968	38.912	34.314	18.391	388.791	263.765	-14.411
4100	4.968	39.034	34.428	18.888	389.316	260.633	-13.893
4200	4.968	39.154	34.539	19.384	389.838	257.488	-13.398
4300	4.968	39.271	34.647	19.881	390.359	254.330	-12.926
4400	4.968	39.385	34.754	20.378	390.878	251.161	-12.475
4500	4.968	39.497	34.858	20.875	391.394	247.980	-12.043
4600	4.968	39.606	34.960	21.372	391.909	244.788	-11.630
4700	4.968	39.713	35.060	21.868	392.420	241.583	-11.233
4800	4.968	39.817	35.158	22.365	392.931	238.368	-10.853
4900	4.968	39.920	35.254	22.862	393.440	235.144	-10.488
5000	4.968	40.020	35.349	23.359	393.947	231.908	-10.137
5100	4.968	40.119	35.441	23.855	394.450	228.662	-9.799
5200	4.968	40.215	35.532	24.352	394.954	225.406	-9.473
5300	4.968	40.310	35.621	24.849	395.456	222.141	-9.160
5400	4.968	40.403	35.709	25.346	395.955	218.866	-8.858
5500	4.968	40.494	35.795	25.843	396.454	215.582	-8.566
5600	4.968	40.583	35.880	26.339	396.950	212.289	-8.285
5700	4.968	40.671	35.963	26.836	397.446	208.987	-8.013
5800	4.968	40.758	36.045	27.333	397.941	205.677	-7.750
5900	4.968	40.843	36.126	27.830	398.435	202.358	-7.496
6000	4.968	40.926	36.205	28.327	398.927	199.030	-7.250

June 30, 1966; March 31, 1977

PROTON (H^+) (IDEAL GAS) GFW = 1.00735

$\Delta Hf^\circ_0 = 365.221 \pm 0.01$ kcal/mol H^+

$S^\circ_{298.15} = 26.013 \pm 0.005$ gibbs/mol $\Delta Hf^\circ_{298.15} = 367.171 \pm 0.01$ kcal/mol

Heat of Formation

The heat of formation is calculated from the equation $H(g) = H^+(g) + e^-(g)$ with auxiliary data (1) using an ionization *potential of IP = 109678.764* cm^{-1} *(313.5873 kcal/mol). This ionization potential, as reported by Moore* (2) *in units of* cm^{-1}, is converted to units of kcal/mol using the current CODATA fundamental constants (3).

Heat Capacity and Entropy

The thermodynamic functions of the proton gas are calculated using the recent CODATA fundamental constants (3) and assumming that the proton is an ideal monatomic gas. Since there is no electron associated with this species, there is only a translational contribution to the thermochemical functions.

References

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3. E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).

H^+

HYDROGEN UNINEGATIVE ION (H^-) H^-
(IDEAL GAS) GFW=1.00845

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	34.241		
100							
200							
298	4.968	26.016	26.016	0.000	33.229	31.612	-23.172
300	4.968	26.047	26.016	0.009	33.223	31.602	-23.022
400	4.968	27.476	26.211	0.506	32.876	31.114	-17.000
500	4.968	28.584	26.579	1.003	32.526	30.714	-13.425
600	4.968	29.490	26.991	1.500	32.176	30.384	-11.067
700	4.968	30.256	27.404	1.996	31.826	30.114	-9.402
800	4.968	30.919	27.803	2.493	31.473	29.893	-8.166
900	4.968	31.504	28.182	2.990	31.117	29.717	-7.216
1000	4.968	32.028	28.541	3.487	30.758	29.580	-6.465
1100	4.968	32.501	28.880	3.984	30.394	29.480	-5.857
1200	4.968	32.934	29.200	4.480	30.027	29.413	-5.357
1300	4.968	33.331	29.503	4.977	29.654	29.377	-4.939
1400	4.968	33.699	29.789	5.474	29.276	29.370	-4.585
1500	4.968	34.042	30.062	5.971	28.892	29.389	-4.282
1600	4.968	34.363	30.321	6.468	28.503	29.435	-4.021
1700	4.968	34.664	30.567	6.964	28.111	29.506	-3.793
1800	4.968	34.948	30.803	7.461	27.712	29.599	-3.594
1900	4.968	35.217	31.028	7.958	27.309	29.715	-3.418
2000	4.968	35.471	31.244	8.455	26.901	29.852	-3.262
2100	4.968	35.714	31.451	8.952	26.489	30.010	-3.123
2200	4.968	35.945	31.650	9.448	26.074	30.188	-2.999
2300	4.968	36.166	31.842	9.945	25.655	30.384	-2.887
2400	4.968	36.377	32.026	10.442	25.231	30.598	-2.786
2500	4.968	36.580	32.204	10.939	24.805	30.831	-2.695
2600	4.968	36.775	32.377	11.436	24.374	31.080	-2.612
2700	4.968	36.962	32.543	11.932	23.942	31.347	-2.537
2800	4.968	37.143	32.704	12.429	23.506	31.629	-2.469
2900	4.968	37.317	32.860	12.926	23.066	31.927	-2.406
3000	4.968	37.486	33.011	13.423	22.625	32.240	-2.349
3100	4.968	37.649	33.158	13.920	22.180	32.567	-2.296
3200	4.968	37.806	33.301	14.416	21.733	32.910	-2.248
3300	4.968	37.959	33.440	14.913	21.284	33.266	-2.203
3400	4.968	38.108	33.575	15.410	20.831	33.636	-2.162
3500	4.968	38.252	33.707	15.907	20.376	34.019	-2.124
3600	4.968	38.392	33.835	16.404	19.919	34.415	-2.089
3700	4.968	38.528	33.960	16.900	19.460	34.825	-2.057
3800	4.968	38.660	34.082	17.397	18.998	35.246	-2.027
3900	4.968	38.789	34.201	17.894	18.534	35.679	-1.999
4000	4.968	38.915	34.317	18.391	18.067	36.124	-1.974
4100	4.968	39.038	34.431	18.888	17.598	36.582	-1.950
4200	4.968	39.157	34.542	19.384	17.129	37.051	-1.928
4300	4.968	39.274	34.651	19.881	16.656	37.531	-1.908
4400	4.968	39.388	34.757	20.378	16.180	38.022	-1.889
4500	4.968	39.500	34.861	20.875	15.703	38.523	-1.871
4600	4.968	39.609	34.963	21.372	15.223	39.035	-1.855
4700	4.968	39.716	35.063	21.868	14.743	39.559	-1.839
4800	4.968	39.821	35.161	22.365	14.259	40.092	-1.825
4900	4.968	39.923	35.257	22.862	13.774	40.635	-1.812
5000	4.968	40.024	35.352	23.359	13.287	41.188	-1.800
5100	4.968	40.122	35.444	23.855	12.799	41.751	-1.789
5200	4.968	40.218	35.535	24.352	12.308	42.324	-1.779
5300	4.968	40.313	35.624	24.849	11.816	42.905	-1.769
5400	4.968	40.406	35.712	25.346	11.322	43.496	-1.760
5500	4.968	40.497	35.798	25.843	10.827	44.097	-1.752
5600	4.968	40.587	35.883	26.339	10.331	44.707	-1.745
5700	4.968	40.674	35.966	26.836	9.833	45.325	-1.738
5800	4.968	40.761	36.048	27.333	9.333	45.952	-1.731
5900	4.968	40.846	36.129	27.830	8.833	46.587	-1.726
6000	4.968	40.929	36.208	28.327	8.332	47.231	-1.720

Sept. 30, 1965; March 31, 1977

HYDROGEN UNINEGATIVE ION (H^-) (IDEAL GAS) GFW = 1.00845

Ground State Configuration $^1S_0$ ΔHf_0° = 34.241 ± 0.001 kcal/mol H^-
$S^\circ_{298.15}$ = 26.016 ± 0.004 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 33.229 ± 0.001 kcal/mol

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.00	1

Heat of Formation

The heat of formation is calculated from an adopted electron affinity of H(g) of EA = 0.754209 eV (17.3923 kcal/mol). This value is based on extensive Hylleraas-type variational calculations on two electron systems (1, 2). This value has been recommended in the critical compilations by Hotop and Lineberger (3) and Rosenstock et al. (4). These calculations are discussed in detail by Massey (8). The former (3) has an excellent discussion on the election affinity of H(g). Experimentally, Dehmer and Chupka (5) have reported EA(H) $\geq$ 0.7540±0.0003 eV.

Heat Capacity and Entropy

The ground state for H^-(g) is reported to be $1s^2\ ^1S_0$ by Hotop and Lineberger (3). The thermodynamic functions of the proton gas are calculated using the recent CODATA fundamental constants (6) and assuming that H^-(g) is an ideal monatomic gas.

A comparison of the isoelectronic sequence - H^-(g), He(g), Li^+(g) - would suggest that stable electronic states may exist at 0.8 EA(H) or roughly 6400 cm^{-1}. This would greatly affect the entropy. However, Pekeris (2) states that he was unable to find any bound states. In addition, Seman and Branscomb (7) state that theoretical and semiempirical evidence suggests that atomic negative ions have very few if any excited states below the continuum. We assume no stable excited states exist.

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TRIIODOSILANE ($SiHI_3$) HI_3SI

(IDEAL GAS) GFW=409.8074

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	−4.573	−15.861	−15.861	INFINITE
100	14.044	71.055	105.784	−3.473	−16.298	−19.905	43.503
200	17.793	82.038	91.372	−1.867	−17.041	−23.230	25.385
298	20.049	89.602	89.602	0.000	−17.800	−26.107	19.137
300	20.081	89.726	89.602	0.037	−17.814	−26.159	19.057
400	21.424	95.703	90.408	2.118	−24.346	−28.623	15.639
500	22.282	100.582	91.970	4.306	−40.336	−28.169	12.313
600	22.894	104.701	93.757	6.566	−40.339	−25.736	9.374
700	23.364	108.267	95.581	8.880	−40.309	−23.304	7.276
800	23.738	111.412	97.367	11.236	−40.258	−20.878	5.703
900	24.041	114.226	99.087	13.625	−40.193	−18.458	4.482
1000	24.289	116.773	100.730	16.042	−40.116	−16.047	3.507
1100	24.493	119.097	102.296	18.482	−40.035	−13.645	2.711
1200	24.662	121.236	103.784	20.940	−39.953	−11.249	2.049
1300	24.803	123.216	105.206	23.413	−39.870	−8.861	1.490
1400	24.921	125.058	106.559	25.899	−39.794	−6.477	1.011
1500	25.021	126.781	107.850	28.397	−39.724	−4.101	0.598
1600	25.107	128.399	109.084	30.903	−39.662	−1.727	0.236
1700	25.180	129.923	110.266	33.418	−51.603	0.748	−0.096
1800	25.243	131.364	111.398	35.939	−51.506	3.825	−0.464
1900	25.297	132.731	112.485	38.466	−51.411	6.896	−0.793
2000	25.345	134.029	113.530	40.998	−51.316	9.960	−1.088
2100	25.387	135.267	114.536	43.535	−51.223	13.024	−1.355
2200	25.423	136.449	115.506	46.075	−51.133	16.079	−1.597
2300	25.456	137.580	116.441	48.619	−51.044	19.133	−1.818
2400	25.485	138.664	117.344	51.166	−50.958	22.185	−2.020
2500	25.510	139.705	118.218	53.716	−50.874	25.227	−2.205
2600	25.533	140.706	119.064	56.268	−50.794	28.271	−2.376
2700	25.554	141.670	119.883	58.823	−50.720	31.310	−2.534
2800	25.573	142.599	120.678	61.379	−50.647	34.349	−2.681
2900	25.590	143.497	121.450	63.937	−50.576	37.384	−2.817
3000	25.605	144.365	122.199	66.497	−50.509	40.411	−2.944
3100	25.619	145.205	122.928	69.058	−50.444	43.442	−3.063
3200	25.632	146.018	123.637	71.621	−50.383	46.471	−3.174
3300	25.643	146.807	124.327	74.184	−50.326	49.499	−3.278
3400	25.654	147.573	124.999	76.749	−50.271	52.521	−3.376
3500	25.664	148.317	125.655	79.315	−50.219	55.545	−3.468
3600	25.673	149.040	126.295	81.882	−142.133	60.822	−3.692
3700	25.681	149.743	126.919	84.450	−141.990	66.456	−3.925
3800	25.689	150.428	127.529	87.018	−141.850	72.090	−4.146
3900	25.696	151.095	128.124	89.587	−141.716	77.718	−4.355
4000	25.702	151.746	128.707	92.157	−141.584	83.339	−4.553
4100	25.709	152.381	129.276	94.728	−141.457	88.964	−4.742
4200	25.714	153.000	129.834	97.299	−141.333	94.583	−4.922
4300	25.720	153.606	130.380	99.871	−141.212	100.194	−5.092
4400	25.725	154.197	130.914	102.443	−141.097	105.805	−5.255
4500	25.729	154.775	131.438	105.016	−140.984	111.423	−5.411
4600	25.734	155.341	131.952	107.589	−140.874	117.031	−5.560
4700	25.738	155.894	132.455	110.162	−140.769	122.633	−5.702
4800	25.742	156.436	132.949	112.736	−140.666	128.237	−5.839
4900	25.745	156.967	133.434	115.311	−140.567	133.842	−5.970
5000	25.749	157.487	133.910	117.885	−140.472	139.436	−6.095
5100	25.752	157.997	134.377	120.460	−140.379	145.035	−6.215
5200	25.755	158.497	134.836	123.036	−140.292	150.628	−6.331
5300	25.758	158.988	135.287	125.611	−140.205	156.226	−6.442
5400	25.761	159.469	135.731	128.187	−140.124	161.819	−6.549
5500	25.763	159.942	136.167	130.764	−140.046	167.405	−6.652
5600	25.766	160.406	136.595	133.340	−139.973	172.992	−6.751
5700	25.768	160.862	137.017	135.917	−139.902	178.585	−6.847
5800	25.770	161.310	137.432	138.494	−139.835	184.171	−6.940
5900	25.772	161.751	137.841	141.071	−139.772	189.753	−7.029
6000	25.774	162.184	138.243	143.648	−139.712	195.340	−7.115

Dec. 31, 1976

TRIIODOSILANE ($SiHI_3$) (IDEAL GAS) GFW = 409.8074

Point Group C_{3v}
$S^\circ_{298.15}$ = [89.60 ± 0.5] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = [−15.86 ± 5] kcal/mol HI_3SI
$\Delta Hf^\circ_{298.15}$ = [−17.8 ± 5] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2190(1)	717(2)
286(1)	399(2)
122(1)	80(2)

Bond Distances: Si-H = [1.50] Å Si-I = [2.435] Å σ = 3
Bond Angles: H-Si-I = [106.81°] I-Si-I = [112°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [1.04795 x 10^{-110}] g^3 cm^6

Heat of Formation

ΔHf°_{298} is estimated by linear interpolation between the values (1) of SiI_4(g) and SiH_4(g). There are no experimental ΔHf° data for SiH_3I, SiH_2I_2, and $SiHI_3$. Data for the iodomethanes (2) have a surprising progression (1, SiH_3I,g); they are of doubtful use in predicting ΔHf° of the iodosilanes. We conclude, as did Hunt and Sirtl (3), that the available data justify only linear interpolation.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3I, SiI_4 and the various bromo-, chloro-, and fluorosilanes (1). The principal moments of inertia are $I_A = I_B = 174.6 \times 10^{-39}$ and $I_C = 343.48 \times 10^{-39}$ g cm^2.

Vibrational frequencies are from liquid-phase Raman spectra of Hengge and Hoefler (4). Infrared data, also presumably for the liquid phase, were reported (4) for ν_1 and ν_4.

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2 (1).

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HI_3SI

IMIDOGEN (NH)
(IDEAL GAS) GFW=15.0146

H N

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-2.060	89.988	89.988	INFINITE
100	6.961	35.688	49.486	-1.380	89.963	89.505	-195.611
200	6.963	40.514	43.931	-0.684	89.989	89.037	-97.294
298	6.966	43.294	43.294	0.000	90.000	88.567	-64.921
300	6.966	43.337	43.294	0.013	90.000	88.558	-64.514
400	6.973	45.342	43.568	0.710	90.001	88.077	-48.123
500	6.994	46.900	44.084	1.408	89.998	87.596	-38.288
600	7.041	48.179	44.663	2.109	89.993	87.116	-31.732
700	7.119	49.270	45.245	2.817	89.987	86.637	-27.049
800	7.223	50.227	45.809	3.534	89.979	86.159	-23.537
900	7.343	51.085	46.349	4.262	89.972	85.683	-20.806
1000	7.471	51.865	46.862	5.003	89.966	85.206	-18.621
1100	7.600	52.583	47.350	5.757	89.963	84.730	-16.834
1200	7.726	53.250	47.814	6.523	89.961	84.255	-15.345
1300	7.845	53.873	48.256	7.302	89.962	83.779	-14.084
1400	7.958	54.458	48.678	8.092	89.963	83.303	-13.004
1500	8.062	55.011	49.082	8.893	89.966	82.827	-12.068
1600	8.158	55.534	49.469	9.704	89.971	82.352	-11.249
1700	8.247	56.032	49.841	10.524	89.976	81.875	-10.526
1800	8.330	56.505	50.198	11.353	89.983	81.398	-9.883
1900	8.407	56.958	50.542	12.190	89.990	80.922	-9.308
2000	8.478	57.391	50.874	13.034	89.998	80.444	-8.790
2100	8.546	57.806	51.194	13.885	90.006	79.966	-8.322
2200	8.609	58.205	51.504	14.743	90.016	79.487	-7.896
2300	8.670	58.589	51.803	15.607	90.026	79.009	-7.507
2400	8.728	58.959	52.094	16.477	90.038	78.530	-7.151
2500	8.783	59.317	52.376	17.353	90.050	78.050	-6.823
2600	8.837	59.662	52.649	18.234	90.062	77.570	-6.520
2700	8.890	59.997	52.915	19.120	90.076	77.089	-6.240
2800	8.941	60.321	53.174	20.012	90.091	76.607	-5.979
2900	8.990	60.636	53.426	20.908	90.108	76.126	-5.737
3000	9.039	60.941	53.671	21.810	90.126	75.644	-5.511
3100	9.087	61.239	53.911	22.716	90.144	75.161	-5.299
3200	9.135	61.528	54.144	23.627	90.164	74.676	-5.100
3300	9.182	61.810	54.372	24.543	90.186	74.193	-4.914
3400	9.228	62.084	54.595	25.463	90.209	73.708	-4.738
3500	9.273	62.353	54.813	26.388	90.234	73.222	-4.572
3600	9.318	62.614	55.026	27.318	90.260	72.735	-4.416
3700	9.363	62.870	55.235	28.252	90.288	72.248	-4.267
3800	9.407	63.121	55.439	29.191	90.317	71.760	-4.127
3900	9.451	63.366	55.639	30.133	90.348	71.272	-3.994
4000	9.495	63.605	55.835	31.081	90.380	70.782	-3.867
4100	9.538	63.840	56.028	32.032	90.414	70.291	-3.747
4200	9.580	64.071	56.216	32.988	90.450	69.800	-3.632
4300	9.623	64.297	56.402	33.948	90.487	69.308	-3.523
4400	9.665	64.518	56.584	34.913	90.527	68.816	-3.418
4500	9.707	64.736	56.762	35.881	90.567	68.321	-3.318
4600	9.749	64.950	56.938	36.854	90.610	67.827	-3.222
4700	9.790	65.160	57.111	37.831	90.653	67.330	-3.131
4800	9.832	65.367	57.281	38.812	90.699	66.834	-3.043
4900	9.873	65.570	57.448	39.798	90.747	66.336	-2.959
5000	9.914	65.770	57.612	40.787	90.797	65.838	-2.878
5100	9.955	65.966	57.774	41.780	90.848	65.338	-2.800
5200	9.996	66.160	57.933	42.778	90.901	64.837	-2.725
5300	10.037	66.351	58.090	43.780	90.957	64.336	-2.653
5400	10.077	66.539	58.245	44.785	91.014	63.833	-2.583
5500	10.118	66.724	58.398	45.795	91.074	63.329	-2.516
5600	10.159	66.907	58.548	46.809	91.136	62.824	-2.452
5700	10.199	67.087	58.696	47.827	91.200	62.318	-2.389
5800	10.240	67.265	58.842	48.849	91.267	61.811	-2.329
5900	10.281	67.440	58.987	49.875	91.336	61.302	-2.271
6000	10.322	67.613	59.129	50.905	91.408	60.792	-2.214

Dec. 31, 1960; Dec. 31, 1965; Dec. 31, 1971;
July 31, 1972 (NBS); June 30, 1977

IMIDOGEN (NH) (IDEAL GAS) GFW = 15.0146

H N

D_0° = 74.1 ± 4 kcal/mol
$S^\circ_{298.15}$ = 43.294 ± 0.01 gibbs/mol
Symmetry Number = 1

ΔHf_0° = 90 ± 4 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 90 ± 4 kcal/mol

Electronic States and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(13, 15)	$X^3\Sigma^-$	0.0	3	1.038	16.666	0.648	3282.09	78.3
(13, 14)	$a^1\Delta$	12590	2	1.041	16.439	[0.7]	3303	55
(13, 16)	$b^1\Sigma^+$	21240	1	1.035	16.7326	0.6049	3347	70.7
(13, 15)	$A^3\Pi$	29777	6	1.036	16.6901	0.7440	3231.0	98.5
(16, 17)	$c^1\Pi$	43345	2	1.1005	14.7985	1.267	2503	194
(16, 17)	$d^1\Sigma^+$	82856	1	1.1165	14.3809	0.6119	2665	71.0

Heat of Formation

The electron impact appearance potential of N_2^+ from HN_3 determined by Franklin et al. (1), leads to a value $\Delta Hf_0^\circ(NH,g)$ = 81.7±0.5 kcal/mol. Reed and Snedden (2) determined the electron impact appearance potential of NH^+ from NH_3. This, combined with the directly measured electron impact ionization potential of NH, 13.1 eV, gives ΔHf_0° = 82.9 kcal/mol. This value of the ionization potential of NH has also been obtained by Foner and Hudson (3). However, all of these electron impact experiments are subject to errors of several tenths of an electron volt or more.

More recently, Seal and Gaydon (4) measured the concentration of NH in reflected shock waves in nitrogen-hydrogen-krypton and ammonia-krypton mixtures. These led to D(NH) = 3.21±0.16 eV, corresponding to $\Delta Hf_0^\circ(NH,g)$ = 90.13±3.7 kcal/mol. Kaskan and Nadler (5) determined NH, NH_3, and OH concentrations in a flat NH_3-D_2-N_2 flame and concluded $\Delta Hf_0^\circ(NH,g)$ = 90±4 kcal/mol. Stedman (6) studied the NH emission spectrum obtained by collision of metastable rare gas atoms with HN_3. Taking the highest level of NH as observed in emission as a limit, he concluded that $\Delta Hf_0^\circ(NH,g) > 80$ kcal/mol. From analogous consideration on N_2 emission observed by collision of metastable argon atoms with HN_3 he concluded that $\Delta Hf_0^\circ(NH,g) \le 94$ kcal/mol.

Quantum chemical calculation of the dissociation energy of small molecules is possible with estimated accuracies of 0.1 to 0.2 eV. A theoretical calculation of the dissociation energy of $NH(X^3\Sigma^-)$, applying the techniques of Wahl and Das (7) has been determined by Stevens (8) to yield D_e = 3.4 eV. This result corroborates the results of Seal and Gaydon and would support $\Delta Hf_0^\circ(NH,g)$ = 90±4 kcal/mol. Theoretical calculations of this type can be used to distinguish between disparate experimental results that differ by more than 0.2 eV.

Heat Capacity and Entropy

The vibrational and rotational constants for the ground and excited states are taken from the sources indicated. The splitting between the $X^3\Sigma^-$ and $a^1\Delta$ states is based on the work of Gilles et al. (14) who observed the $b^1\Sigma^+ - X^3\Sigma^-$ band in emission.

The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\varepsilon_i/T)$. The National Bureau of Standards prepared this table (9) by critical analysis of data existing in 1972 using only the ground electronic state. Using the molecular constants selected here and ΔHf° selected by NBS (9), we recalculate the table in terms of 1973 fundamental constants (10), 1975 atomic weights (11) and current JANAF reference states for the elements.

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H N

HYDROXYL (OH) H O

(IDEAL GAS) GFW=17.0073

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	−2.192	9.175	9.175	INFINITE
100	7.798	35.727	50.399	−1.467	9.195	8.894	−19.438
200	7.356	40.985	44.542	−0.711	9.281	8.557	−9.350
298	7.167	43.881	43.881	0.000	9.318	8.192	−6.005
300	7.165	43.926	43.881	0.013	9.318	8.185	−5.963
400	7.087	45.974	44.161	0.725	9.328	7.806	−4.265
500	7.056	47.552	44.688	1.432	9.320	7.426	−3.246
600	7.057	48.838	45.275	2.137	9.298	7.049	−2.568
700	7.090	49.928	45.864	2.845	9.265	6.677	−2.085
800	7.150	50.878	46.433	3.556	9.225	6.309	−1.724
900	7.233	51.725	46.974	4.275	9.181	5.947	−1.444
1000	7.332	52.492	47.488	5.004	9.137	5.590	−1.222
1100	7.439	53.196	47.976	5.742	9.093	5.238	−1.041
1200	7.549	53.848	48.438	6.491	9.050	4.889	−0.890
1300	7.659	54.456	48.878	7.252	9.010	4.544	−0.764
1400	7.766	55.028	49.297	8.023	8.971	4.202	−0.656
1500	7.867	55.567	49.697	8.805	8.934	3.863	−0.563
1600	7.963	56.078	50.080	9.596	8.899	3.526	−0.482
1700	8.053	56.564	50.447	10.397	8.865	3.191	−0.410
1800	8.137	57.026	50.800	11.207	8.832	2.858	−0.347
1900	8.214	57.468	51.140	12.024	8.800	2.527	−0.291
2000	8.286	57.891	51.467	12.849	8.768	2.198	−0.240
2100	8.353	58.297	51.782	13.682	8.736	1.870	−0.195
2200	8.415	58.687	52.087	14.520	8.703	1.544	−0.153
2300	8.473	59.063	52.383	15.364	8.670	1.219	−0.116
2400	8.526	59.425	52.669	16.214	8.637	0.896	−0.082
2500	8.576	59.774	52.946	17.069	8.602	0.574	−0.050
2600	8.622	60.111	53.215	17.929	8.567	0.254	−0.021
2700	8.665	60.437	53.476	18.794	8.530	−0.065	0.005
2800	8.706	60.753	53.731	19.662	8.492	−0.383	0.030
2900	8.744	61.059	53.978	20.535	8.452	−0.699	0.053
3000	8.780	61.356	54.219	21.411	8.412	−1.014	0.074
3100	8.814	61.645	54.454	22.291	8.369	−1.327	0.094
3200	8.846	61.925	54.683	23.174	8.325	−1.640	0.112
3300	8.877	62.198	54.907	24.060	8.281	−1.950	0.129
3400	8.906	62.463	55.125	24.949	8.233	−2.260	0.145
3500	8.933	62.722	55.338	25.841	8.185	−2.567	0.160
3600	8.959	62.974	55.547	26.736	8.135	−2.874	0.174
3700	8.985	63.220	55.751	27.633	8.084	−3.179	0.188
3800	9.009	63.459	55.951	28.533	8.030	−3.483	0.200
3900	9.032	63.694	56.146	29.435	7.976	−3.785	0.212
4000	9.055	63.923	56.338	30.339	7.920	−4.086	0.223
4100	9.076	64.147	56.526	31.246	7.862	−4.386	0.234
4200	9.098	64.366	56.710	32.154	7.803	−4.683	0.244
4300	9.118	64.580	56.890	33.065	7.742	−4.980	0.253
4400	9.138	64.790	57.067	33.978	7.679	−5.275	0.262
4500	9.157	64.995	57.241	34.893	7.615	−5.569	0.270
4600	9.176	65.197	57.412	35.809	7.549	−5.861	0.278
4700	9.195	65.394	57.580	36.728	7.482	−6.152	0.286
4800	9.213	65.588	57.745	37.648	7.413	−6.441	0.293
4900	9.232	65.778	57.907	38.571	7.343	−6.729	0.300
5000	9.249	65.965	58.066	39.495	7.271	−7.016	0.307
5100	9.267	66.148	58.223	40.421	7.197	−7.300	0.313
5200	9.284	66.328	58.377	41.348	7.122	−7.584	0.319
5300	9.302	66.505	58.528	42.277	7.044	−7.866	0.324
5400	9.319	66.679	58.678	43.208	6.965	−8.147	0.330
5500	9.336	66.851	58.825	44.141	6.885	−8.426	0.335
5600	9.353	67.019	58.970	45.076	6.803	−8.703	0.340
5700	9.370	67.185	59.112	46.012	4.719	−8.979	0.344
5800	9.388	67.348	59.253	46.950	6.634	−9.254	0.349
5900	9.405	67.508	59.392	47.889	6.547	−9.527	0.353
6000	9.422	67.667	59.528	48.831	6.458	−9.799	0.357

Dec. 31, 1960; Mar. 31, 1966; Dec. 31, 1970;
July 31, 1972 (NBS); June 30, 1977

HYDROXYL (OH) (IDEAL GAS) GFW = 17.0073

H O

D_0° = 101.356 ± 0.29 kcal/mol

$S^\circ_{298.15}$ = 43.890 ± 0.01 gibbs/mol*

Symmetry Number = 1

ΔHf_0° = 9.261 ± 0.29 kcal/mol*

$\Delta Hf^\circ_{298.15}$ = 9.318 ± 0.29 kcal/mol

Electronic States and Molecular Constants

State	ε, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0 139.7	2 2	3735.21	82.81	18.871	0.714	0.9706
$A^2\Sigma^+$	32403	2	3184.28	97.84	17.355	0.807	1.0121
$B^2\Sigma^+$	68372	2	940	105	5.54	0.65	1.80
$C^2\Sigma^+$	89420	2	2339	32	4.20	0.16	2.16

Heat of Formation

$\Delta Hf_0^\circ(OH,g)$ was calculated from the relation $\Delta Hf_0^\circ(OH,g) = 1/2\ D_0^\circ(O_2) + 1/2\ D_0^\circ(H_2) - D_0^\circ(OH)$. The values employed were as follows: $D_0^\circ(O_2)$ = 117.967±0.042 kcal/mol and $D_0^\circ(H_2)$ = 103.267±0.003 kcal/mol were taken from the CODATA (1) selection. Barrow (2) in a refinement of the work of Barrow and Downie (3) obtains a value of D_0° for $OH(X^2\Pi_{3/2}) \rightarrow O(^3P_2) + H(^2S_{1/2})$ of 35427 cm^{-1} from an extrapolation of ΔG_v versus v; it was increased to 35450±100 cm^{-1} to account for the fact that ΔG_v yields slightly low values at high v. Fehlenbok (4) obtains a value of $D_e°$ for $OH(B^2\Sigma^+)$ of 1315 cm^{-1} and G(0) for this state of 441 cm^{-1}. Using $T_e(B^2\Sigma^+)$ given by Rosen (5) and the zero point energy of HO (including the Dunham correction, see Herzberg (6)) of 847.0 cm^{-1}, this yields $D_0^\circ(OH)$ = 35451 cm^{-1} with an estimated uncertainty of 100 cm^{-1}. A value of $D_0^\circ(OH)$ = 35450±100 cm^{-1} = 101.356±0.29 kcal/mol was adopted. Combining the above values, one obtains $\Delta Hf_0^\circ(OH,g)$ = 9.261±0.29 kcal/mol which is in good agreement with the last JANAF (7) selection.

A review of earlier work is given in references (7-9).

Heat Capacity and Entropy*

The vibrational and rotational constants of the respective electronic levels were taken from Rosen (5). Comparison of the results of these calculations with those of the more exact treatment given by Haar et al. (10) suggests that errors in the tables due to approximations in our calculations may be neglected above 400 K. Below this, they may be appreciable. It is recommended that $H_0^\circ - H_{298}^\circ$, S_{298}°, and Cp_{298}° be taken as −2.107 kcal/mol, 43.890 gibbs/mol, and 7.144 gibbs/mol, respectively. These errors result from dealing with the ground state $(X^2\pi_i)$ as two separate electronic states separated by 139.7 cm^{-1}.

The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \Sigma_i Q_r^i Q_v^i g_i \exp(-c_2 \varepsilon_i/T)$. The National Bureau of Standards prepared this table (11) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (11), we recalculate the table in terms of 1973 fundamental constants (12), 1975 atomic weights (13), and current JANAF reference states for the elements.

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SULFUR MONOHYDRIDE (SH) HS
(IDEAL GAS) GFW=33.0679

T, K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
0	0.000	0.000	INFINITE	-2.216	33.149	33.149	INFINITE
100	7.214	38.379	53.630	-1.525	33.317	30.978	-67.702
200	7.815	43.610	47.444	-0.767	33.361	28.615	-31.268
298	7.755	46.730	46.730	0.000	33.300	26.295	-19.274
300	7.752	46.778	46.730	0.014	33.298	26.251	-19.124
400	7.578	48.984	47.032	0.781	32.618	23.944	-13.082
500	7.477	50.662	47.597	1.533	32.083	21.837	-9.545
600	7.464	52.023	48.225	2.279	31.622	19.833	-7.224
700	7.517	53.177	48.852	3.028	31.220	17.924	-5.596
800	7.611	54.186	49.457	3.784	17.798	14.782	-4.038
900	7.724	55.089	50.033	4.550	17.771	14.406	-3.498
1000	7.843	55.909	50.580	5.329	17.749	14.034	-3.067
1100	7.959	56.662	51.100	6.119	17.733	13.662	-2.714
1200	8.069	57.359	51.592	6.920	17.723	13.293	-2.421
1300	8.170	58.009	52.061	7.732	17.717	12.926	-2.173
1400	8.263	58.618	52.508	8.554	17.714	12.557	-1.960
1500	8.347	59.191	52.935	9.385	17.713	12.187	-1.776
1600	8.422	59.732	53.343	10.223	17.715	11.820	-1.615
1700	8.491	60.245	53.734	11.069	17.718	11.451	-1.472
1800	8.553	60.732	54.109	11.921	17.722	11.082	-1.346
1900	8.609	61.196	54.470	12.779	17.727	10.714	-1.232
2000	8.661	61.639	54.818	13.643	17.732	10.344	-1.130
2100	8.707	62.063	55.153	14.511	17.737	9.974	-1.038
2200	8.750	62.469	55.476	15.384	17.742	9.606	-0.954
2300	8.790	62.859	55.789	16.261	17.746	9.235	-0.878
2400	8.827	63.234	56.091	17.142	17.751	8.865	-0.807
2500	8.860	63.595	56.384	18.026	17.756	8.495	-0.743
2600	8.892	63.943	56.668	18.914	17.760	8.125	-0.683
2700	8.922	64.279	56.944	19.805	17.763	7.753	-0.628
2800	8.950	64.604	57.212	20.698	17.765	7.381	-0.576
2900	8.976	64.918	57.472	21.595	17.768	7.011	-0.528
3000	9.001	65.223	57.725	22.493	17.769	6.641	-0.484
3100	9.024	65.519	57.972	23.395	17.771	6.270	-0.442
3200	9.047	65.806	58.212	24.298	17.770	5.898	-0.403
3300	9.068	66.084	58.447	25.204	17.770	5.527	-0.366
3400	9.089	66.355	58.675	26.112	17.768	5.157	-0.332
3500	9.109	66.619	58.898	27.022	17.766	4.784	-0.299
3600	9.128	66.876	59.116	27.934	17.764	4.414	-0.268
3700	9.147	67.126	59.330	28.847	17.759	4.044	-0.239
3800	9.165	67.370	59.538	29.763	17.755	3.673	-0.211
3900	9.183	67.609	59.742	30.680	17.749	3.302	-0.185
4000	9.200	67.841	59.941	31.600	17.743	2.934	-0.160
4100	9.217	68.069	60.137	32.520	17.736	2.563	-0.137
4200	9.234	68.291	60.328	33.443	17.728	2.194	-0.114
4300	9.250	68.509	60.516	34.367	17.719	1.823	-0.093
4400	9.267	68.721	60.700	35.293	17.709	1.453	-0.072
4500	9.283	68.930	60.881	36.220	17.698	1.085	-0.053
4600	9.299	69.134	61.058	37.150	17.687	0.715	-0.034
4700	9.316	69.334	61.232	38.080	17.675	0.345	-0.016
4800	9.332	69.531	61.403	39.013	17.663	-0.024	0.001
4900	9.348	69.723	61.571	39.947	17.650	-0.389	0.017
5000	9.365	69.912	61.736	40.882	17.635	-0.760	0.033
5100	9.382	70.098	61.898	41.820	17.621	-1.126	0.048
5200	9.398	70.280	62.057	42.759	17.606	-1.493	0.063
5300	9.415	70.459	62.214	43.699	17.592	-1.861	0.077
5400	9.433	70.635	62.368	44.642	17.576	-2.226	0.090
5500	9.450	70.809	62.520	45.586	17.561	-2.594	0.103
5600	9.468	70.979	62.670	46.532	17.546	-2.959	0.115
5700	9.486	71.147	62.817	47.480	17.531	-3.327	0.128
5800	9.504	71.312	62.962	48.429	17.516	-3.691	0.139
5900	9.523	71.475	63.105	49.380	17.502	-4.060	0.150
6000	9.542	71.635	63.246	50.334	17.488	-4.422	0.161

Dec. 31, 1960; June 30, 1967; July 31, 1972 (NBS); June 30, 1977

SULFUR MONOHYDRIDE (SH) (IDEAL GAS) GFW = 33.0679
HS

D_0° = 84.23 ± 1.2 kcal/mol
$S^\circ_{298.15}$ = 46.74 ± 0.01 gibbs/mol*
Symmetry Number = 1

ΔHf_0° = 33.15 ± 1.2 kcal/mol*
$\Delta Hf^\circ_{298.15}$ = 33.3 ± 1.2 kcal/mol

Electronic States and Molecular Constants

State	ε, cm^{-1}	g_i	ω_e, cm^{-1}	ω_ex_e, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0 377.01	2 2	2689.6	45.5	9.601	0.285	1.345
$A^2\Sigma^+$	30663	2	1979.8	97.66	8.521	0.464	1.423
$B^2\Sigma$	59622	2	2670.6	56.8	8.785	0.259	1.428
$C^2\Delta$	[63900]	4					
$D^2\Delta$	71195	4					
$E^2\Sigma$	71318	2					
$F^2\Delta$	76708	4	[2689.6]	[45.5]	[9.601]	[0.285]	
$G^2\Delta$	79343	4					
$H^2\Delta$	80848	4					

Heat of Formation

The previous JANAF (1) selection for ΔHf°_{298} of HS(g) was Mackle's (2) estimate of 34.6±4 kcal/mol which he derived from the average of three independent determinations. Of these, the uncertainty can be reduced in the determination involving the calculation of ΔHf°_{298} of HS(g) from ΔHf°_{298} of H_2S(g), the ionization potential of HS(g), and the appearance potential of HS^+(g) from H_2S(g). A summary of previous work on the ionization potential is given below. From the spectroscopic and photoionization work we arrive at a value of ΔHf_0° for the reaction $H_2S(g) = HS(g) + H(g)$ of 89.02±1.15 kcal/mol. Using the appropriate thermal functions for each of the species (see tables for H_2S(g), HS(g), and H(g) (1)) and the selected heats of formation of H_2S(g) of -4.90±0.2 kcal/mol (see H_2S(g) table (1)) and H(g) of 52.103±0.001 kcal/mol (8), one obtains 33.3±1.2 kcal/mol for ΔHf°_{298} of HS(g) versus Mackle's (2) value of 33.7±3 kcal/mol for this determination. The new value is preferred because it is based on photoionization rather than electron impact studies.

Source	Method	Potential (eV)
$HS(g) \rightarrow HS^+(g) + e^-(g)$:		
Morrow (3) (1966)	Rydberg Extrapolation	10.40±0.03
Palmer and Loosing (4) (1962)	Electron Impact	10.5 ±0.1
$H_2S(g) \rightarrow HS^+(g) + H(g) + e^-(g)$:		
Dibeler and Liston (5) (1968)	Photoionization	14.27±0.04*
Dibeler and Rosenstock (6) (1963)	Electron Impact	14.43±0.1
Palmer and Lossing (4) (1962)	Electron Impact	14.43±0.1
Neuert and Clasen (7) (1952)	Electron Impact	15.2 ±0.5

*The uncertainty given by the authors was doubled because the threshold value was not corrected to absolute zero.

Heat Capacity and Entropy*

Calculations were made using the vibrational and rotational constants for the respective electronic levels from Rosen (12). Comparison of the results of the more exact treatment of Haar et al. (13) with those given in the previous JANAF (1) calculations (both used the same molecular constants for the ground state) suggests errors in our calculations are negligible above 400 K. Below this, they can be appreciable. In particular, it is recommended that 0.045 kcal/mol, 0.012 gibbs/mol, and -0.028 gibbs/mol be added to our values of $(H_0^\circ - H^\circ_{298})$, S°_{298} and Cp°_{298}. These errors result from dealing with the ground state ($X^2\pi_i$) as two separate electronic states separated by 377.01 cm^{-1}.

The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t\sum_i Q_r^i Q_v^i g_i \exp(-c_2\varepsilon_i/T)$. The National Bureau of Standards prepared this table (9) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (9), we recalculate the table in terms of 1973 fundamental constants (10), 1975 atomic weights (11), and current JANAF reference states for the elements.

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HS

SILICON MONOHYDRIDE (SIH) HSI
(IDEAL GAS) GFW=29,094

T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-2.205	89.600	89.600	INFINITE
100	7.804	39.135	53.839	-1.470	89.891	87.289	-190.770
200	7.371	44.403	47.968	-0.713	90.066	84.595	-92.441
298	7.191	47.306	47.306	0.000	90.024	81.913	-60.044
300	7.190	47.350	47.306	0.013	90.022	81.863	-59.637
400	7.180	49.414	47.587	0.731	89.885	79.162	-43.252
500	7.285	51.026	48.120	1.453	89.714	76.502	-33.439
600	7.451	52.368	48.719	2.190	89.533	73.875	-26.909
700	7.636	53.531	49.325	2.944	89.351	71.281	-22.255
800	7.817	54.562	49.916	3.717	89.171	68.710	-18.771
900	7.983	55.493	50.485	4.507	88.993	66.165	-16.067
1000	8.129	56.342	51.029	5.313	88.816	63.637	-13.908
1100	8.257	57.122	51.548	6.132	88.637	61.128	-12.145
1200	8.369	57.846	52.043	6.964	88.457	58.635	-10.679
1300	8.465	58.520	52.515	7.805	88.272	56.157	-9.441
1400	8.550	59.150	52.967	8.656	88.080	53.694	-8.382
1500	8.624	59.743	53.399	9.515	87.881	51.246	-7.467
1600	8.690	60.301	53.813	10.381	87.673	48.809	-6.667
1700	8.748	60.830	54.211	11.253	75.464	46.493	-5.977
1800	8.801	61.331	54.592	12.130	75.292	44.794	-5.439
1900	8.848	61.809	54.960	13.013	75.122	43.104	-4.958
2000	8.891	62.264	55.314	13.900	74.951	41.424	-4.527
2100	8.931	62.698	55.655	14.791	74.781	39.752	-4.137
2200	8.967	63.115	55.985	15.686	74.609	38.087	-3.784
2300	9.001	63.514	56.303	16.584	74.438	36.431	-3.462
2400	9.033	63.898	56.612	17.486	74.267	34.784	-3.167
2500	9.063	64.267	56.911	18.391	74.094	33.140	-2.897
2600	9.092	64.623	57.201	19.298	73.922	31.506	-2.648
2700	9.119	64.967	57.482	20.209	73.749	29.877	-2.418
2800	9.146	65.299	57.755	21.122	73.575	28.256	-2.206
2900	9.172	65.620	58.021	22.038	73.402	26.642	-2.008
3000	9.198	65.932	58.279	22.957	73.229	25.030	-1.823
3100	9.224	66.234	58.531	23.878	73.056	23.426	-1.652
3200	9.249	66.527	58.776	24.801	72.883	21.830	-1.491
3300	9.275	66.812	59.016	25.728	72.709	20.238	-1.340
3400	9.301	67.089	59.249	26.656	72.537	18.649	-1.199
3500	9.328	67.359	59.477	27.588	72.364	17.066	-1.066
3600	9.355	67.622	59.700	28.522	-19.770	17.746	-1.077
3700	9.383	67.879	59.917	29.459	-19.843	18.790	-1.110
3800	9.412	68.130	60.130	30.398	-19.916	19.836	-1.141
3900	9.442	68.375	60.338	31.341	-19.989	20.881	-1.170
4000	9.473	68.614	60.542	32.287	-20.061	21.931	-1.198
4100	9.505	68.848	60.742	33.236	-20.133	22.979	-1.225
4200	9.538	69.078	60.938	34.188	-20.204	24.032	-1.251
4300	9.573	69.303	61.130	35.143	-20.273	25.086	-1.275
4400	9.608	69.523	61.318	36.102	-20.341	26.140	-1.298
4500	9.645	69.739	61.503	37.065	-20.408	27.201	-1.321
4600	9.684	69.952	61.684	38.032	-20.472	28.260	-1.343
4700	9.723	70.160	61.862	39.002	-20.535	29.320	-1.363
4800	9.764	70.366	62.037	39.976	-20.595	30.380	-1.383
4900	9.806	70.567	62.209	40.955	-20.653	31.444	-1.402
5000	9.850	70.766	62.378	41.938	-20.709	32.504	-1.421
5100	9.894	70.961	62.545	42.925	-20.762	33.574	-1.439
5200	9.940	71.154	62.708	43.917	-20.813	34.638	-1.456
5300	9.987	71.344	62.870	44.913	-20.859	35.706	-1.472
5400	10.034	71.531	63.028	45.914	-20.904	36.771	-1.488
5500	10.083	71.715	63.185	46.920	-20.946	37.839	-1.504
5600	10.133	71.898	63.338	47.931	-20.985	38.910	-1.519
5700	10.184	72.077	63.490	48.946	-21.020	39.983	-1.533
5800	10.235	72.255	63.640	49.967	-21.053	41.051	-1.547
5900	10.287	72.430	63.787	50.993	-21.082	42.120	-1.560
6000	10.340	72.604	63.933	52.025	-21.108	43.190	-1.573

Dec. 31, 1960; Dec. 31, 1969; Dec. 31, 1976

SILICON MONOHYDRIDE (SiH) (IDEAL GAS) GFW = 29.094

D_0° = 68.7 ± 2.0 kcal/mol
$S^\circ_{298.15}$ = 47.306 ± 0.05 gibbs/mol

ΔHf_0° = 89.6 ± 2.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 90.0 ± 2.0 kcal/mol HSI

Electronic Levels and Quantum Weights

Ref	State	ε_i, cm^{-1}	g_i
(1)	$A\ ^2\Pi$	0	2
(1)		142.83	2
(2)	$^4\Sigma^-$	[21510]	4
(1)	$A\ ^2\Delta$	24193.04	4
(2)	$^2\Sigma^-$	[24730]	2
(3)	$C\ ^2\Sigma^+$	31899.8	2
(3)	$B\ ^2\Sigma^+$	31909.7	2
(1)	$D\ ^2\Delta$	48510.11	4
(1)	$E\ ^2\Sigma^+$	52399.19	2

ω_e = 2041.80 cm^{-1} $\omega_e x_e$ = 35.51 cm^{-1} σ = 1
B_e = 7.4996 cm^{-1} α_e = 0.2190 cm^{-1} r_e = 1.5201 Å

Heat of Formation

Verma (4) has derived an upper limit for the dissociation energy of 24680 cm^{-1} (70.6 kcal/mol) from predissociation in the B $^2\Sigma^+$ state. Hildenbrand (5) has applied an ionic-covalent correction to the linear Birge-Sponer extrapolation and obtained D_0° = 70 kcal/mol. Rao and Lakshman (6) have estimated the ground state dissociation energy of 24040 cm^{-1}(68.7 kcal/mol) from an evaluation of the potential energy curves and Franck-Condon factors. This last number, D_0° = 68.7 kcal/mol, is adopted and may be compared with the average per-bond atomization energy of SiH_4(g) of 75.7 kcal/mol. The $D_0^\circ/\Delta Ha_0^\circ$ ratio is 0.227. For SiF/SiF_4 the ratio is 0.230, for $SiCl/SiCl_4$ it is 0.233 and for SiI/SiI_4 it is 0.245 (7). The adopted D_0° and JANAF auxilary data (7) lead to ΔHf_0° = 89.6 kcal/mol. The allowed error of ±2 kcal/mol includes the upper limit value of D_0°.

Heat Capacity and Entropy

The observed and estimated electronic levels are taken from Herzberg et al. (1), Jordan (2), and Bollmark et al. (3) as indicated. Wirsam's (8) ab initio self-consistent-field and configuration-interaction calculations predicted the electronic level for the $^4\Sigma^-$ state at 6430 and 8275 cm^{-1} respectively. Substitution of 6430 cm^{-1} for the adopted Jordan estimate of 21510 cm^{-1} increases the derived entropy starting near 700°K; at 6000 K the entropy is 0.85 gibbs/mol higher.

The rotational and vibrational constants are those selected by Rosen (9). The ground state is treated as two distinct levels because of the splitting of the ground state as expressed by the spin coupling constant (A = 142.83 cm^{-1}). This approximation gives slightly biased results at lower temperatures which are allowed for in the ±0.05 gibbs/mol error assigned to S°_{298}.

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HSI

HYDROGEN, DIATOMIC (H_2) H_2
(REFERENCE STATE - IDEAL GAS) GFW=2.0158

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	−2.024	0.000	0.000	0.000
100	6.729	24.048	37.117	−1.307	0.000	0.000	0.000
200	6.560	28.514	31.829	−0.663	0.000	0.000	0.000
298	6.892	31.207	31.207	0.000	0.000	0.000	0.000
300	6.895	31.250	31.207	0.013	0.000	0.000	0.000
400	6.974	33.247	31.479	0.707	0.000	0.000	0.000
500	6.993	34.806	31.994	1.406	0.000	0.000	0.000
600	7.009	36.082	32.572	2.106	0.000	0.000	0.000
700	7.036	37.164	33.153	2.808	0.000	0.000	0.000
800	7.080	38.107	33.714	3.514	0.000	0.000	0.000
900	7.142	38.944	34.250	4.225	0.000	0.000	0.000
1000	7.219	39.700	34.758	4.943	0.000	0.000	0.000
1100	7.309	40.392	35.239	5.669	0.000	0.000	0.000
1200	7.407	41.033	35.695	6.405	0.000	0.000	0.000
1300	7.510	41.630	36.129	7.151	0.000	0.000	0.000
1400	7.615	42.190	36.542	7.907	0.000	0.000	0.000
1500	7.719	42.719	36.936	8.674	0.000	0.000	0.000
1600	7.821	43.220	37.314	9.451	0.000	0.000	0.000
1700	7.920	43.698	37.675	10.238	0.000	0.000	0.000
1800	8.016	44.153	38.023	11.035	0.000	0.000	0.000
1900	8.106	44.589	38.357	11.841	0.000	0.000	0.000
2000	8.193	45.007	38.679	12.656	0.000	0.000	0.000
2100	8.275	45.409	38.990	13.479	0.000	0.000	0.000
2200	8.354	45.795	39.290	14.311	0.000	0.000	0.000
2300	8.428	46.168	39.581	15.150	0.000	0.000	0.000
2400	8.499	46.529	39.863	15.996	0.000	0.000	0.000
2500	8.566	46.877	40.137	16.849	0.000	0.000	0.000
2600	8.631	47.214	40.403	17.709	0.000	0.000	0.000
2700	8.692	47.541	40.661	18.575	0.000	0.000	0.000
2800	8.752	47.858	40.913	19.448	0.000	0.000	0.000
2900	8.809	48.166	41.157	20.326	0.000	0.000	0.000
3000	8.864	48.466	41.396	21.209	0.000	0.000	0.000
3100	8.917	48.757	41.629	22.098	0.000	0.000	0.000
3200	8.969	49.041	41.856	22.993	0.000	0.000	0.000
3300	9.020	49.318	42.078	23.892	0.000	0.000	0.000
3400	9.069	49.588	42.295	24.797	0.000	0.000	0.000
3500	9.118	49.852	42.507	25.706	0.000	0.000	0.000
3600	9.165	50.109	42.715	26.620	0.000	0.000	0.000
3700	9.212	50.361	42.918	27.539	0.000	0.000	0.000
3800	9.258	50.607	43.117	28.463	0.000	0.000	0.000
3900	9.304	50.848	43.312	29.391	0.000	0.000	0.000
4000	9.349	51.085	43.504	30.324	0.000	0.000	0.000
4100	9.393	51.316	43.691	31.261	0.000	0.000	0.000
4200	9.437	51.543	43.876	32.202	0.000	0.000	0.000
4300	9.480	51.765	44.056	33.148	0.000	0.000	0.000
4400	9.523	51.984	44.234	34.098	0.000	0.000	0.000
4500	9.564	52.198	44.409	35.053	0.000	0.000	0.000
4600	9.605	52.409	44.580	36.011	0.000	0.000	0.000
4700	9.645	52.616	44.749	36.974	0.000	0.000	0.000
4800	9.684	52.819	44.915	37.940	0.000	0.000	0.000
4900	9.722	53.019	45.079	38.910	0.000	0.000	0.000
5000	9.758	53.216	45.239	39.884	0.000	0.000	0.000
5100	9.794	53.410	45.398	40.862	0.000	0.000	0.000
5200	9.827	53.600	45.554	41.843	0.000	0.000	0.000
5300	9.859	53.788	45.707	42.827	0.000	0.000	0.000
5400	9.890	53.972	45.859	43.815	0.000	0.000	0.000
5500	9.918	54.154	46.008	44.805	0.000	0.000	0.000
5600	9.945	54.333	46.155	45.798	0.000	0.000	0.000
5700	9.970	54.509	46.300	46.794	0.000	0.000	0.000
5800	9.992	54.683	46.443	47.792	0.000	0.000	0.000
5900	10.012	54.854	46.584	48.792	0.000	0.000	0.000
6000	10.030	55.022	46.723	49.795	0.000	0.000	0.000

March 31, 1961; March 31, 1977

HYDROGEN (H_2) (REFERENCE STATE - IDEAL GAS) GFW = 2.0158

0 to 6000 K Ideal Gas

H_2

D_0^o = 103.267 ± 0.003 kcal/mol
$S^o_{298.15}$ = 31.207 ± 0.008 gibbs/mol
Ground State Configuration $^1\Sigma_g^+$

ΔHf_0^o = 0 kcal/mol
ΔHf^o_{298} = 0 kcal/mol
Symmetry Number = 2

Vibrational and Rotational Levels (cm^{-1})

Direct Summation of Electronic Ground State:

$$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_o + BZ - DZ^2 + H^2Z^3/(H+LX),$$

where $Z = J(J+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L

$$G = 4403.566Y - 123.8573Y^2 + 1.87269Y^3 - 0.173514Y^4 + 9.93128\times10^{-3}Y^5 - 4.38015\times10^{-4}Y^6$$

$$B = 60.8904 - 3.16997Y + 0.155932Y^2 - 4.60094\times10^{-2}Y^3 + 8.72205\times10^{-3}Y^4$$
$$-9.59207\times10^{-4}Y^5 + 5.31722\times10^{-5}Y^6 - 1.21393\times10^{-6}Y^7$$

$$D = 4.6573\times10^{-2} - 1.5085\times10^{-3}Y - 2.7385\times10^{-4}Y^2 + 1.0242\times10^{-4}Y^3 - 1.172\times10^{-5}Y^4 + 4.684\times10^{-7}Y^5$$

$$H = 5.224\times10^{-5} - 7.240\times10^{-6}Y + 9.619.10^{-7}Y^2 - 4.838\times10^{-8}Y^3$$

$$L = 6.70\times10^{-8} - 1.426\times10^{-8}Y + 1.388\times10^{-9}Y^2$$

v_{max} = 14, J_{max} = 38−32v/v_{max}
Normalized statistical weights = 1/4 (even J) and 3/4 (odd J)

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

These are calculated by direct summation over vibrational-rotational energy levels of the electronic ground state. We performed the direct summation with an extended version of a program written by W. H. Evans and provided through cooperation of D. D. Wagman, both of the U.S. National Bureau of Standards. Contributions of excited states (T_o>90000 cm^{-1}) are negligible at 6000 K. Polynomials G, B, D, and H are our fits of data from Stoicheff (1), Herzberg and Howe (2) and Rank et al. (3, 4). We estimate polynomial L such that our approximation (5, 6) for the infinite series F yields high-J rotational levels in reasonable agreement with the theoretical values of Waech and Bernstein (7). Maximum deviations in our F values are about ±400 cm^{-1}; these occur near $1 \le v \le 4$ and $29 \le J \le 36$ which is far into the extrapolated region of F. Only about one-third of the vibrational-rotational levels have been observed spectroscopically and the theoretical calculations (7, 6) provide the best available extrapolation to high values of J. Accuracy of the thermodynamic functions near 6000 K depends on this extrapolation and on the rotational cutoff procedure. We assume a linear approximation (5) for the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated from theoretical calculations (7, 6). We omit the nuclear-spin contribution (R ln 4) to entropy and gibbs-energy function.

We adopt ortho-para "equilibrium" H_2 as the reference state at all temperatures. The previous JANAF reference state (8) referred to "normal" H_2 (75% ortho and 25% para). Our new reference state has significant changes in Cp°, S°, and $H^o_T-H^o_{298}$ at 100 K and slight changes at 200 K. Use of "equilibrium" H_2 as a reference state was proposed on the NBS H_2 table (9) which discusses three alternatives. Preferred alternatives are either "equilibrium" H_2 or "normal" H_2. "Normal" H_2 is the form always encountered except in low-temperature generation or catalytic ortho-para equilibration. Use of "normal" H_2 involves a possible complication, depending on the choice of zero energy for ortho-H_2. If we chose the lowest allowed level (v=0, J=1 instead of v=0, J=0), then $H^o_{298}-H^o_0$ would be 0.254 kcal/mol less for "normal" than for "equilibrium" H_2. This would change the difference between ΔHf^o_0 and ΔHf^o_{298} for all species involving hydrogen (8, 10). No such change would occur if we chose the lowest level (v=0, J=0) as the energy zero for ortho-H_2. "Equilibrium" H_2 is the form which parallels most substances, i.e., those maintaining equilibrium among all rotational levels (9).

JANAF values and uncertainties at 298.15 K are the same as those selected by CODATA (10). Previous thermochemical tables based on direct-summation calculations of Woolley et al. (6) include that of Gurvich et al. (11) and that of NBS-JANAF (9, 8). Differences of the new JANAF values from the NBS table are greatest near 5300 K, reaching maxima of 0.005 gibbs/mol in S° and 0.018 kcal/mol in $H^o_T-H^o_{298}$. Differences from Gurvich et al. at 6000 K are 0.006 gibbs/mol in S° and 0.030 kcal/mol in $H^o_T-H^o_{298}$. Errors larger than these differences arise from uncertainty in extrapolation of the rotational levels.

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H_2

HYDROGEN, DIATOMIC UNIPOSITIVE ION (H_2^+) H_2^+
(IDEAL GAS) GFW=2.01525

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				−2.051	355.727		
100							
200							
298	7.000	34.001	34.001	0.000	357.235	354.915	−260.156
300	7.001	34.044	34.001	0.013	357.244	354.900	−258.541
400	7.057	36.065	34.276	0.715	357.749	354.043	−193.438
500	7.174	37.651	34.798	1.426	358.258	353.058	−154.319
600	7.342	38.973	35.387	2.152	358.781	351.969	−128.203
700	7.536	40.119	35.983	2.896	359.319	350.791	−109.520
800	7.734	41.139	36.565	3.659	359.873	349.535	−95.487
900	7.923	42.060	37.125	4.442	360.442	348.208	−84.558
1000	8.099	42.905	37.661	5.243	361.022	346.818	−75.796
1100	8.260	43.684	38.174	6.061	361.611	345.370	−68.618
1200	8.405	44.409	38.663	6.895	362.205	343.866	−62.626
1300	8.537	45.087	39.132	7.742	362.803	342.314	−57.547
1400	8.658	45.724	39.580	8.602	363.404	340.716	−53.187
1500	8.769	46.326	40.010	9.473	364.005	339.074	−49.402
1600	8.873	46.895	40.423	10.355	364.607	337.392	−46.085
1700	8.970	47.436	40.819	11.248	365.209	335.673	−43.153
1800	9.063	47.951	41.201	12.149	365.810	333.918	−40.543
1900	9.152	48.443	41.570	13.060	366.412	332.130	−38.203
2000	9.239	48.915	41.925	13.980	367.014	330.310	−36.094
2100	9.324	49.368	42.269	14.908	367.616	328.461	−34.183
2200	9.408	49.804	42.602	15.844	368.216	326.581	−32.442
2300	9.492	50.224	42.924	16.789	368.819	324.675	−30.851
2400	9.576	50.629	43.237	17.743	369.424	322.744	−29.389
2500	9.659	51.022	43.540	18.705	370.030	320.787	−28.043
2600	9.741	51.402	43.835	19.675	370.637	318.805	−26.798
2700	9.822	51.772	44.122	20.653	371.245	316.799	−25.643
2800	9.901	52.130	44.402	21.639	371.855	314.771	−24.569
2900	9.977	52.479	44.675	22.633	372.468	312.722	−23.567
3000	10.050	52.819	44.940	23.634	373.083	310.652	−22.631
3100	10.118	53.149	45.200	24.643	373.700	308.561	−21.753
3200	10.181	53.471	45.453	25.658	374.316	306.448	−20.929
3300	10.238	53.786	45.701	26.679	374.935	304.319	−20.154
3400	10.288	54.092	45.943	27.705	375.553	302.169	−19.423
3500	10.330	54.391	46.181	28.736	376.172	300.002	−18.733
3600	10.365	54.682	46.413	29.771	376.790	297.818	−18.080
3700	10.391	54.967	46.640	30.809	377.405	295.615	−17.461
3800	10.408	55.244	46.863	31.849	378.018	293.396	−16.874
3900	10.417	55.515	47.081	32.890	378.628	291.161	−16.316
4000	10.416	55.778	47.295	33.932	379.234	288.911	−15.785
4100	10.408	56.035	47.505	34.973	379.835	286.645	−15.279
4200	10.390	56.286	47.711	36.013	380.430	284.365	−14.797
4300	10.365	56.530	47.914	37.051	381.019	282.071	−14.336
4400	10.332	56.768	48.112	38.086	381.601	279.763	−13.896
4500	10.291	57.000	48.307	39.117	382.174	277.442	−13.474
4600	10.244	57.226	48.499	40.144	382.740	275.109	−13.070
4700	10.191	57.445	48.687	41.166	383.295	272.762	−12.683
4800	10.132	57.659	48.871	42.182	383.842	270.405	−12.312
4900	10.068	57.868	49.053	43.192	384.379	268.036	−11.955
5000	9.998	58.070	49.231	44.195	384.905	265.657	−11.612
5100	9.925	58.268	49.406	45.191	385.419	263.266	−11.282
5200	9.849	58.460	49.579	46.180	385.924	260.866	−10.964
5300	9.769	58.646	49.748	47.161	386.418	258.457	−10.658
5400	9.687	58.828	49.915	48.134	386.900	256.038	−10.362
5500	9.603	59.005	50.078	49.099	387.372	253.610	−10.077
5600	9.517	59.178	50.239	50.055	387.831	251.174	−9.802
5700	9.430	59.345	50.397	51.002	388.279	248.729	−9.537
5800	9.342	59.508	50.553	51.941	388.717	246.278	−9.280
5900	9.254	59.667	50.706	52.870	389.143	243.819	−9.031
6000	9.165	59.822	50.857	53.791	389.558	241.351	−8.791

Sept. 30, 1977

HYDROGEN DIATOMIC UNIPOSITIVE ION (H_2^+) (IDEAL GAS) GFW = 2.01525

D_0° = 61.128 ± 0.001 kcal/mol (1)
$S^\circ_{298.15}$ = 34.001 ± 0.01 gibbs/mol

ΔHf_0° = 355.727 ± 0.001 kcal/mol H_2^+
$\Delta Hf^\circ_{298.15}$ = [357.235] kcal/mol

Vibrational and Rotational Levels (cm^{-1})

Direct Summation using Energy-Level Equations for the $^2\Sigma_g^+$ Electronic Ground State:

$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_o + BZ - DZ^2 + H^2Z^3/(H+LZ)$,
where $Z = N(N+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L
$G = 2323.23\ Y - 67.39\ Y^2 + 0.93\ Y^3 - 0.029\ Y^4$
$B = 29.946 - 1.594\ Y + 0.032\ Y^2 - 0.0013\ Y^3$ r_e = 1.057 Å (1, 13)
$D = 0.01991 - 0.00087\ Y + 0.00003\ Y^2$; $H = 1.75\text{x}10^{-5} - 6\text{x}10^{-7}\ Y$; and $L = 1.6\text{x}10^{-8}$
v_{max} = 18 and $N_{max} = 41 - 33v/v_{max}$
Electronic statistical weight = 2 and normalized rotational statistical weights = 1/4 (even N) or 3/4 (odd N)

Heat of Formation

The adopted value for the heat of formation of $H_2^+(g)$, ΔHf_0° = 355.727±0.001 kcal/mol, is based on the ionization potential of $H_2(g)$ determined by Herzberg and Jungen (1). These authors studied in high resolution absorption two Rydberg series of ortho- and para-hydrogen which converge to the $X^2\Sigma_g^+$ ground state of $H_2^+(g)$. This ionization potential, IP = 124417.2±0.4 cm^{-1}, is recommended by Rosenstock (2) as the definitive value. The IP or ΔHf_0° value is converted to a ΔHf°_{298} value for $H_2^+(g)$ by including JANAF (3) enthalpy differences ($H_0^\circ - H^\circ_{298}$) for $H_2^+(g)$, $H_2(g)$ and $e^-(g)$. ΔHf°_{298} should not be interpreted as a room-temperature ionization threshold due to inclusion of these enthalpies and to threshold effects noted by Rosenstock et al. (4).

Rosenstock et al. (4) had earlier recommended IP = 15.4256 eV (124418.4 cm^{-1}) based on the spectroscopic studies of Takezawa (5) and Herzberg (6); in both studies the results were derived from extended Rydberg series. The more recent work of Herzberg and Jungen (1) provides a more accurate experimental value for the ionization potential due to the recognition of a pressure shift which was felt to be negligible in the earlier study (6). The theoretical value, IP = 124417.3 cm^{-1}, is in excellent agreement (0.1 cm^{-1}) with our adopted value. This theoretical value, as discussed by Herzberg and Jungen (1), is essentially the value of Hunter and Pritchard (7) with the relativistic and Lamb shift corrections of Jeziorski and Kolos (8) and the nonadiabatic correction of Bunker (9).

Heat Capacity and Entropy

Thermodynamic functions for ortho-para "equilibrium" H_2^+ are calculated, as they were for H_2 (3), by direct summation over energy levels of the electronic ground state. We use 1973 fundamental constants (10) in an extended version of a computer program written by W. H. Evans and provided by D. D. Wagman of the U. S. National Bureau of Standards. Excited electronic states are neglected because they are either repulsive or too high lying (11) to contribute significantly. The electronic statistical weight is taken equal to the multiplicity since we neglect rotational splitting. Assumption of negligible splitting is common practice in theoretical calculation of H_2^+ energy levels (11 - 13) and it is justified thermodynamically by the small splitting constant (14).

Coefficients of the energy-level polynomials are those derived from theoretical levels by Beckel et al. (13). New calculations (15) yield slightly different levels. The polynomials are confirmed by vibrational ($v\leq3$) and rotational ($N\leq4$) levels obtained from Rydberg spectra (1). The value of L was derived (13) from a fit of theoretical levels with v = 0 to 14. Our adopted v_{max}, derived from the G polynomial, is one unit too low (13, 11). Limiting rotational quantum numbers N_{max} are an approximation of values from theoretical calculations (11, 13). The resulting energy-level equations are very approximate near N_{max}, but they do closely reproduce thermodynamic functions (12, 11) calculated directly from energy levels. More accurate equations do not significantly improve the thermodynamic functions up to 6000 K.

We adopt functions closely reproducing those of Iorish and Yungman (12). The effect of slightly different fundamental constants (12) is barely detectable. Our Gibbs-energy function deviates by less than 0.001 gibbs/mol at all temperatures. Cp°, S° and H° begin to deviate near 2000 K; differences range from +0.005 to −0.012 gibbs/mol in Cp°, ±0.001 gibbs/mol in S° and ±5 cal/mol in H°. Cp° of Patch and McBride (11) is slightly lower at 4000 to 6000 K but well within the probable uncertainty. Due to the high thermal energy (∿20% of D_0° at 6000 K), Cp° depends on the number of levels included in the summation. We follow the published references (11, 12) which include contributions from quasibound levels lying above D_0°. At 6000 K these levels contribute 0.42 gibbs/mol to Cp° and 0.05 gibbs/mol to the Gibbs-energy function.

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H_2^+

HYDROGEN, DIATOMIC UNINEGATIVE ION (H_2^-) H_2^-

(IDEAL GAS) GFW=2.01635

T, K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0				-2.040	57.700		
100							
200							
298	7.064	34.330	34.330	0.000	56.255	56.811	-41.643
300	7.066	34.374	34.330	0.013	56.246	56.815	-41.389
400	7.235	36.427	34.609	0.727	55.770	57.077	-31.185
500	7.474	38.066	35.142	1.462	55.309	57.457	-25.114
600	7.728	39.452	35.747	2.223	54.872	57.927	-21.100
700	7.964	40.661	36.365	3.007	54.459	58.471	-18.255
800	8.171	41.738	36.970	3.814	54.063	59.070	-16.137
900	8.349	42.711	37.555	4.641	53.681	59.719	-14.502
1000	8.501	43.599	38.116	5.483	53.309	60.410	-13.202
1100	8.631	44.415	38.652	6.340	52.942	61.138	-12.147
1200	8.744	45.171	39.164	7.209	52.579	61.900	-11.273
1300	8.843	45.875	39.653	8.088	52.216	62.691	-10.539
1400	8.930	46.534	40.122	8.977	51.852	63.510	-9.914
1500	9.009	47.153	40.570	9.874	51.485	64.355	-9.376
1600	9.079	47.736	41.000	10.779	51.115	65.225	-8.909
1700	9.144	48.289	41.412	11.690	50.743	66.119	-8.500
1800	9.204	48.813	41.809	12.607	50.367	67.034	-8.139
1900	9.260	49.312	42.191	13.531	49.987	67.971	-7.818
2000	9.312	49.789	42.559	14.459	49.604	68.927	-7.532
2100	9.361	50.244	42.914	15.393	49.217	69.903	-7.275
2200	9.408	50.681	43.257	16.331	48.828	70.897	-7.043
2300	9.454	51.100	43.589	17.274	48.435	71.909	-6.833
2400	9.497	51.503	43.911	18.222	48.039	72.938	-6.642
2500	9.539	51.892	44.222	19.174	47.641	73.984	-6.468
2600	9.579	52.267	44.524	20.130	47.240	75.045	-6.308
2700	9.619	52.629	44.818	21.090	46.838	76.124	-6.162
2800	9.657	52.979	45.103	22.053	46.432	77.214	-6.027
2900	9.695	53.319	45.381	23.021	46.024	78.321	-5.902
3000	9.732	53.648	45.651	23.992	45.616	79.442	-5.787
3100	9.768	53.968	45.914	24.967	45.205	80.576	-5.681
3200	9.804	54.279	46.171	25.946	44.792	81.724	-5.581
3300	9.839	54.581	46.421	26.928	44.378	82.885	-5.489
3400	9.874	54.875	46.665	27.914	43.962	84.057	-5.403
3500	9.908	55.162	46.904	28.903	43.545	85.243	-5.323
3600	9.942	55.441	47.137	29.895	43.127	86.440	-5.248
3700	9.976	55.714	47.365	30.891	42.708	87.649	-5.177
3800	10.009	55.981	47.588	31.890	42.286	88.869	-5.111
3900	10.042	56.241	47.807	32.893	41.863	90.100	-5.049
4000	10.075	56.496	48.021	33.899	41.439	91.342	-4.991
4100	10.108	56.745	48.231	34.908	41.014	92.595	-4.936
4200	10.140	56.989	48.436	35.920	40.590	93.859	-4.884
4300	10.172	57.228	48.638	36.936	40.162	95.132	-4.835
4400	10.205	57.462	48.836	37.955	39.734	96.416	-4.789
4500	10.237	57.692	49.030	38.977	39.304	97.707	-4.745
4600	10.268	57.917	49.221	40.002	38.875	99.011	-4.704
4700	10.300	58.138	49.408	41.031	38.444	100.323	-4.665
4800	10.332	58.356	49.593	42.062	38.013	101.645	-4.628
4900	10.363	58.569	49.774	43.097	37.580	102.974	-4.593
5000	10.395	58.779	49.952	44.135	37.147	104.313	-4.559
5100	10.426	58.985	50.127	45.176	36.714	105.661	-4.528
5200	10.457	59.187	50.299	46.220	36.280	107.017	-4.498
5300	10.488	59.387	50.469	47.267	35.847	108.382	-4.469
5400	10.519	59.583	50.636	48.318	35.412	109.754	-4.442
5500	10.550	59.777	50.800	49.371	34.978	111.135	-4.416
5600	10.581	59.967	50.962	50.428	34.546	112.525	-4.391
5700	10.612	60.155	51.122	51.487	34.113	113.920	-4.368
5800	10.643	60.339	51.279	52.550	33.681	115.324	-4.345
5900	10.674	60.522	51.434	53.616	33.249	116.735	-4.324
6000	10.705	60.701	51.587	54.685	32.818	118.153	-4.304

Sept. 30, 1977

HYDROGEN, DIATOMIC UNINEGATIVE ION (H_2^-) (IDEAL GAS) GFW = 2.01635

D_0° = 28.2 ± 10 kcal/mol

$S_{298.15}^\circ$ = [34.33 ± 0.1] gibbs/mol

ΔHf_0° = 57.7 ± 10 kcal/mol

$\Delta Hf_{298.15}^\circ$ = [56.255] kcal/mol

H_2^-

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^2\Sigma_u^+$	0	2

ω_e = [1700] cm^{-1}

B_e = [25.3] cm^{-1}

$\omega_e x_e$ = [35] cm^{-1}

α_e = [0.398] cm^{-1}

σ = 2

r_e = [1.15] Å

Heat of Formation

The heat of formation at 0 K for H_2^-(g) is based on the electron affinity (EA) value derived from a Rydberg-Klein-Rees configuration-interaction calculation (1). This study by Sharpe (1) led to EA(H_2) = -2.5 eV. Using auxiliary data (2), we calculate ΔHf_0° = 57.7±10 kcal/mol and $D_0^\circ(H_2^-)$ = 28.2±10 kcal/mol; the latter value assumes dissociation into ground state H(g) and H^-(g). This adopted EA(H_2) value is suggested to be the more reliable value of eight studies considered by Rosenstock et al. (3).

In terms of molecular orbitals, the ground state for H_2^-(g) is the $(1s\sigma_g)^2(2p\sigma_u)$ $^2\Sigma_u^+$ state involving two bonding electrons and one antibonding electron (4). We would expect, however, the ground state to be $(1s\sigma_g)^2(1s\sigma_u)$. As stated by Massey (4), we should expect only a weakly-bound molecule as compared with H_2(g) for which the ground state has no electron in an antibonding orbital. Our calculated EA(H_2) value is consistent with this viewpoint. Further discussion of the H_2^-(g) ion may be found in Massey (4).

ΔHf_0° is converted to ΔHf_{298}° by use of JANAF (2) enthalpies ($H_0^\circ - H_{298}^\circ$) for H_2(g), H_2^-(g), and e^-(g). ΔHf_{298}° should not be interpreted as a room temperature electron affinity due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (3).

Heat Capacity and Entropy

The vibrational constants for H_2^-(g) are estimated to be the same as in the isoelectronic species He_2^+ (5). The internuclear distance is estimated to be ∿8% larger than that for He_2^+(g). The same relationship appeared *to exist for the* (N_2^-, NO, O_2^+) isoelectronic series. B_e is calculated from r_e whereas α_e is calculated assuming a Morse function for the ground state.

The ground and excited electronic states are discussed in detail by Massey (4). No excited state contributions are included in this calculation. By assuming the same force constant to exist for H_2^- as in He_2^+, we would calculate ω_e = 3384 cm^{-1}. This leads to an entropy at 298.15 K which is 0.06 gibbs/mol smaller than our adopted value. The vibrational constants derived by Comer and Read (6) for some resonant state of H_2^- suggests ω_e values of 1500, 2300, and 2800 cm^{-1}. Thus, the ω_e value is very uncertain.

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DIIODOSILANE (SiH_2I_2) H_2I_2Si
(IDEAL GAS) GFW=283.9108

	gibbs/mol			kcal/mol			
T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.565	-6.718	-6.718	INFINITE
100	10.301	64.006	90.628	-2.662	-7.367	-9.779	21.373
200	13.571	72.130	79.486	-1.471	-8.238	-11.863	12.964
298	16.247	78.079	78.079	0.000	-9.100	-13.457	9.865
300	16.289	78.180	78.079	0.030	-9.116	-13.484	9.823
400	18.126	83.134	78.742	1.757	-13.762	-14.683	8.022
500	19.419	87.325	80.051	3.637	-24.648	-13.870	6.063
600	20.410	90.957	81.572	5.631	-24.819	-11.699	4.261
700	21.211	94.165	83.146	7.713	-24.923	-9.502	2.967
800	21.872	97.042	84.707	9.868	-24.975	-7.296	1.993
900	22.419	99.651	86.224	12.084	-24.987	-5.084	1.234
1000	22.875	102.037	87.688	14.349	-24.969	-2.873	0.628
1100	23.255	104.236	89.094	16.656	-24.930	-0.666	0.132
1200	23.572	106.273	90.442	18.998	-24.874	1.538	-0.280
1300	23.839	108.171	91.733	21.369	-24.813	3.736	-0.628
1400	24.065	109.946	92.971	23.764	-24.749	5.931	-0.926
1500	24.257	111.613	94.159	26.181	-24.686	8.120	-1.183
1600	24.420	113.184	95.300	28.615	-24.629	10.306	-1.408
1700	24.561	114.669	96.396	31.064	-36.571	12.594	-1.619
1800	24.682	116.076	97.450	33.526	-36.473	15.483	-1.880
1900	24.788	117.413	98.466	36.000	-36.374	18.366	-2.113
2000	24.880	118.687	99.445	38.483	-36.276	21.244	-2.321
2100	24.961	119.903	100.391	40.975	-36.179	24.119	-2.510
2200	25.032	121.068	101.304	43.475	-36.084	26.986	-2.681
2300	25.095	122.180	102.188	45.982	-35.990	29.852	-2.837
2400	25.151	123.249	103.043	48.494	-35.900	32.715	-2.979
2500	25.201	124.277	103.872	51.012	-35.814	35.568	-3.109
2600	25.246	125.266	104.676	53.534	-35.730	38.424	-3.230
2700	25.287	126.220	105.457	56.061	-35.650	41.273	-3.341
2800	25.323	127.140	106.215	58.591	-35.574	44.122	-3.444
2900	25.356	128.030	106.952	61.125	-35.500	46.969	-3.540
3000	25.386	128.890	107.669	63.662	-35.431	49.807	-3.628
3100	25.413	129.722	108.367	66.202	-35.364	52.647	-3.712
3200	25.438	130.530	109.047	68.745	-35.301	55.487	-3.790
3300	25.461	131.313	109.710	71.290	-35.243	58.326	-3.863
3400	25.481	132.073	110.356	73.837	-35.188	61.157	-3.931
3500	25.501	132.812	110.987	76.386	-35.138	63.992	-3.996
3600	25.518	133.531	111.604	78.937	-127.053	69.080	-4.194
3700	25.535	134.230	112.206	81.490	-126.913	74.525	-4.402
3800	25.550	134.911	112.794	84.044	-126.776	79.970	-4.599
3900	25.564	135.575	113.370	86.600	-126.646	85.408	-4.786
4000	25.577	136.223	113.933	89.157	-126.520	90.842	-4.963
4100	25.589	136.854	114.485	91.715	-126.399	96.275	-5.132
4200	25.600	137.471	115.025	94.274	-126.283	101.706	-5.292
4300	25.610	138.073	115.554	96.835	-126.170	107.129	-5.445
4400	25.620	138.662	116.072	99.396	-126.064	112.551	-5.590
4500	25.629	139.238	116.581	101.959	-125.961	117.976	-5.730
4600	25.638	139.802	117.079	104.522	-125.862	123.400	-5.863
4700	25.646	140.353	117.569	107.086	-125.769	128.816	-5.990
4800	25.654	140.893	118.049	109.651	-125.679	134.231	-6.112
4900	25.661	141.422	118.521	112.217	-125.593	139.648	-6.229
5000	25.667	141.941	118.984	114.783	-125.513	145.055	-6.340
5100	25.674	142.449	119.439	117.351	-125.435	150.470	-6.448
5200	25.680	142.948	119.886	119.918	-125.364	155.876	-6.551
5300	25.685	143.437	120.326	122.486	-125.295	161.289	-6.651
5400	25.691	143.917	120.759	125.055	-125.232	166.693	-6.746
5500	25.696	144.388	121.184	127.625	-125.172	172.095	-6.838
5600	25.701	144.851	121.602	130.194	-125.119	177.498	-6.927
5700	25.705	145.306	122.014	132.765	-125.068	182.907	-7.013
5800	25.709	145.753	122.420	135.335	-125.024	188.307	-7.096
5900	25.714	146.193	122.819	137.907	-124.982	193.707	-7.175
6000	25.717	146.625	123.212	140.478	-124.946	199.107	-7.252

Dec. 31, 1976

DIIODOSILANE (SiH_2I_2) (IDEAL GAS) GFW = 283.9108

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [78.08 ± 0.8] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = [-6.72 ± 5] kcal/mol H_2I_2Si
$\Delta Hf^\circ_{298.15}$ = [-9.1 ± 5] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2205 (1)	[2230](1)
925 (1)	497 (1)
[350](1)	796 (1)
[90](1)	[410](1)
[650](1)	

Bond Distances: Si-H = [1.49] Å Si-I = [2.44] Å σ = [2]
Bond Angles: H-Si-H = [111°] I-Si-I = [110°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [3.0669 x 10^{-112}] g^3 cm^6

Heat of Formation

ΔHf°_{298} is estimated by linear interpolation between the values (1) of $SiI_4(g)$ and $SiH_4(g)$. There are no experimental ΔHf° data for SiH_3I, SiH_2I_2 and $SiHI_3$. Data for the iodomethanes (2) have a surprising progression (1, SiH_3I, g); they are of doubtful use in predicting ΔHf° of the iodosilanes. We conclude, as did Hunt and Sirtl (3), that the available data justify only linear interpolation of ΔHf°.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3I, SiI_4 and the various bromo-, chloro- and flurosilanes (1). The principal moments of inertia are I_A = 10.200 x 10^{-39}, I_B = 168.86 x 10^{-39} and I_C = 178.05 x 10^{-39} g cm^2.

Five vibrational frequencies are estimated by comparison with the dihalo-, monohalo- and trihalosilanes (1) plus $SiHBrI_2$ and $SiHClI_2$ (4). Frequencies ν_1, ν_2 and ν_8 were observed in gas-phase infrared spectra (5), while ν_7 was observed in liquid-phase infrared spectra (6).

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2 (1).

References

1. JANAF Thermochemical Tables: $H_3ISi(g)$, $HI_3Si(g)$, $BrH_3Si(g)$, $Br_2H_2Si(g)$, $Br_3HSi(g)$, $ClH_3Si(g)$, $Cl_2H_2Si(g)$, $Cl_3HSi(g)$ 12-31-76; $FH_3Si(g)$, $F_2H_2Si(g)$, $F_3HSi(g)$, $I_4Si(g)$, $H_4Si(g)$ 6-30-76.
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H_2I_2Si

AMIDOGEN (NH_2)
(IDEAL GAS) GFW=16.0225

H_2N

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.373	46.187	46.187	INFINITE
100	7.949	37.815	53.595	-1.578	45.918	46.450	-101.516
200	7.954	43.325	47.240	-0.783	45.721	47.058	-51.422
298	8.024	46.510	46.510	0.000	45.500	47.760	-35.009
300	8.027	46.560	46.510	0.015	45.495	47.774	-34.803
400	8.221	48.894	46.827	0.827	45.265	48.570	-26.537
500	8.493	50.756	47.433	1.662	45.049	49.420	-21.601
600	8.805	52.332	48.121	2.527	44.858	50.313	-18.326
700	9.143	53.714	48.823	3.424	44.689	51.236	-15.996
800	9.492	54.958	49.514	4.356	44.544	52.182	-14.255
900	9.842	56.096	50.183	5.322	44.420	53.144	-12.905
1000	10.181	57.151	50.827	6.324	44.316	54.119	-11.827
1100	10.503	58.137	51.448	7.358	44.230	55.104	-10.948
1200	10.802	59.064	52.044	8.423	44.159	56.096	-10.216
1300	11.079	59.939	52.618	9.518	44.102	57.092	-9.598
1400	11.333	60.770	53.171	10.638	44.056	58.094	-9.069
1500	11.566	61.560	53.704	11.784	44.020	59.097	-8.610
1600	11.781	62.313	54.219	12.951	43.993	60.104	-8.210
1700	11.981	63.033	54.716	14.139	43.972	61.111	-7.856
1800	12.167	63.724	55.197	15.347	43.959	62.120	-7.542
1900	12.344	64.386	55.664	16.572	43.952	63.129	-7.261
2000	12.511	65.024	56.116	17.815	43.951	64.138	-7.009
2100	12.672	65.638	56.555	19.074	43.956	65.148	-6.780
2200	12.826	66.231	56.981	20.349	43.966	66.156	-6.572
2300	12.975	66.804	57.396	21.639	43.983	67.165	-6.382
2400	13.120	67.360	57.800	22.944	44.007	68.173	-6.208
2500	13.261	67.898	58.193	24.263	44.036	69.179	-6.048
2600	13.397	68.421	58.576	25.596	44.070	70.184	-5.899
2700	13.529	68.929	58.950	26.943	44.112	71.188	-5.762
2800	13.658	69.423	59.316	28.302	44.157	72.189	-5.635
2900	13.782	69.905	59.672	29.674	44.210	73.190	-5.516
3000	13.901	70.374	60.021	31.058	44.270	74.188	-5.405
3100	14.016	70.832	60.363	32.454	44.334	75.185	-5.300
3200	14.126	71.279	60.697	33.861	44.402	76.178	-5.203
3300	14.231	71.715	61.024	35.279	44.477	77.171	-5.111
3400	14.331	72.141	61.345	36.707	44.555	78.160	-5.024
3500	14.426	72.558	61.659	38.145	44.638	79.147	-4.942
3600	14.516	72.966	61.968	39.592	44.724	80.132	-4.865
3700	14.600	73.365	62.270	41.048	44.815	81.114	-4.791
3800	14.679	73.755	62.568	42.512	44.907	82.094	-4.721
3900	14.753	74.137	62.859	43.984	45.003	83.071	-4.655
4000	14.821	74.512	63.146	45.463	45.100	84.046	-4.592
4100	14.884	74.878	63.428	46.948	45.199	85.018	-4.532
4200	14.942	75.238	63.705	48.439	45.300	85.989	-4.474
4300	14.995	75.590	63.977	49.936	45.401	86.956	-4.420
4400	15.044	75.935	64.245	51.438	45.503	87.922	-4.367
4500	15.088	76.274	64.508	52.945	45.604	88.884	-4.317
4600	15.127	76.606	64.768	54.455	45.705	89.845	-4.269
4700	15.162	76.932	65.023	55.970	45.805	90.803	-4.222
4800	15.193	77.251	65.274	57.488	45.905	91.760	-4.178
4900	15.221	77.565	65.522	59.008	46.003	92.714	-4.135
5000	15.245	77.872	65.766	60.532	46.100	93.667	-4.094
5100	15.265	78.175	66.006	62.057	46.194	94.617	-4.055
5200	15.283	78.471	66.243	63.585	46.287	95.565	-4.016
5300	15.297	78.762	66.477	65.114	46.378	96.513	-3.980
5400	15.309	79.048	66.707	66.644	46.466	97.457	-3.944
5500	15.318	79.329	66.934	68.175	46.552	98.401	-3.910
5600	15.324	79.606	67.158	69.708	46.636	99.344	-3.877
5700	15.328	79.877	67.378	71.240	46.717	100.283	-3.845
5800	15.331	80.143	67.596	72.773	46.796	101.223	-3.814
5900	15.331	80.405	67.811	74.306	46.872	102.160	-3.784
6000	15.329	80.663	68.023	75.839	46.945	103.096	-3.755

Dec. 31, 1960; Dec. 31, 1965; July 31, 1972 (NBS); June 30, 1977

AMIDOGEN (NH_2) (IDEAL GAS) GFW = 16.0225

H_2N

Point Group C_{2v}
$S^\circ_{298.15}$ = 46.51 gibbs/mol

ΔHf°_0 = 46.2 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 45.5 ± 1.5 kcal/mol

Electronic Levels (Quantum Weight) and Vibrational Frequencies (Degeneracies)

State	ε, cm^{-1} (g)	ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
$\tilde{X}^2B_1$	0 (2)	[3173] (1)	1497.2 (1)	3220 (1)
$\tilde{A}^2A_1(\pi)$	10249 (2)	3325 (1)	633 (1)	[3220](1)

Bond Distance: N-H = 1.024 Å
σ = 2
Bond Angle: H-N-H = 103°
Product of the Moments of Inertia: $I_AI_BI_C = 8.742 \times 10^{-120}\ g^3cm^6$

Heat of Formation

Direct kinetic studies (1 - 5) on the decomposition of hydrazine, $N_2H_4(g) \underset{k_r}{\overset{k_d}{\rightleftharpoons}} 2NH_2(g)$, give activation energies which suggest $\Delta Hf^\circ_{298}(NH_2) \leq 40$ kcal/mol. The pre-exponential factor suggests $k_r \sim 10^7$-10^8 1/(mol s). This is exceptionally slow for a radical combination reaction (6) and is at variance with the most recent direct measurements of $k_r = 10^{10.8}$ 1/(mol s) (300 K, 1500 mmHg) (7) and $k_r = 10^{9.4}$ 1/(mol s) (300 K, 10 mmHg) (8). A possible explanation for this discrepancy is that the hydrazine decomposition studies have been carried out in the energy dependent region (9, 10). This has been confirmed on the basis of RRKM calculations. With ΔHf°_{298} = 40 kcal/mol, it is not possible to simultaneously reproduce the measured forward (k_d) *and backward* (k_r) *rates by orders of magnitude. With a value of* ΔHf°_{298} = *45.5 kcal/mol, all of the rate data can be fitted* to a factor of three. For higher values of ΔHf°_{298}, the discrepancy increases.

Data on the thermal decomposition of benzylamine from toluene-carrier studies (2, 11) yield ΔHf°_{298} = 36 kcal/mol. This technique, however, has consistently yielded erroneous rate parameters (12). Using their very low pressure pyrolysis technique, Golden et al. (13) find $\Delta Hf^\circ_{298}(NH_2)$ = 47.2 kcal/mol. This is in reasonable agreement with the recommended value.

Heat Capacity and Entropy

The bond distance and angle are from the electronic absorption spectrum as summarized by Herzberg (14). The vibrational frequencies are obtained from Herzberg (14) and from matrix-isolation studies of *Milligan and Jacox* (15).

The National Bureau of Standards prepared this table (16) by critical analysis of data existing in 1972. Using S°, Cp° and ΔHf° selected by NBS (16), we recalculate the table in terms of current JANAF reference states for the elements.

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H_2N

SULFURIC ACID (H_2SO_4) H_2O_4S

(LIQUID) GFW=98.0734

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	33.125	37.501	37.501	0.000	-194.548	-164.928	120.894
300	33.210	37.706	37.502	0.061	-194.536	-164.744	120.014
400	37.815	47.890	38.859	3.612	-194.198	-154.913	84.639
500	42.456	56.826	41.575	7.626	-193.283	-145.189	63.461
600	47.096	64.977	44.805	12.103	-191.873	-135.694	49.426
700	51.737	72.586	48.236	17.045	-189.989	-126.449	39.479
800	56.377	79.797	51.734	22.451	-200.710	-118.786	32.453
900	61.017	86.705	55.238	28.320	-197.618	-108.738	26.405
1000	65.658	93.374	58.720	34.654	-194.097	-99.046	21.646

Dec. 31, 1960; Dec. 31, 1966; Sept. 30, 1977

SULFURIC ACID (H_2SO_4) (LIQUID) GFW = 98.0734

$S^\circ_{298.15}$ = 37.501 ± 0.02 gibbs/mol

Tm = 283.46 ± 0.05 K

Tb = [610] K

$\Delta Hf^\circ_{298.15}$ = -194.548 ± 0.16 kcal/mol

ΔHm° = 2.560 ± 0.03 kcal/mol

ΔHv° = [13.9] kcal/mol

H_2O_4S

Heat of Formation

The heat of combustion (ΔHc°_{298}) of rhombic sulfur to aqueous sulfuric acid, S(c, rhombic) + 3/2 O_2(g) + H_2O(l) = H_2SO_4 (n H_2O), has been determined by many investigators. Based on the reported combustion data, values of ΔHf°_{298} for liquid H_2SO_4 are derived using tabulated heat of solution and heat of dilution data (1, 2). The value adopted, ΔHf°_{298}(H_2SO_4,l) = -194.548± 0.16 kcal/mol, is that recommended by NBS (2). The uncertainty of ±0.16 kcal/mol not only accounts for the scatter in the combustion data but also the uncertainty arising from conversion of this data to be consistent with the current atomic weights and fundamental constants (∿tens of calories/mol). An uncertainty of -0.08 kcal/mol may exist due to the difference in the heat of formation of $SO_4^=$(aq) as reported by CODATA (11) and NBS (2).

Source	Product	ΔHc°_{298}, kcal/mol	ΔHf°_{298}, kcal/mol
McCullough et al. (3)	H_2SO_4 (70 H_2O)	-143.58±0.09	-194.400
Scott et al. (4)	H_2SO_4 (75 H_2O)	-143.98±0.22	-194.775
Good et al. (5)	H_2SO_4 (115 H_2O)	-143.85±0.06	-194.521
Mansson and Sunner (6)	H_2SO_4 (115 H_2O)	-143.93±0.07	-194.601

Heat Capacity and Entropy

The heat capacity has been measured experimentally (7) in the range 15 - 300 K and has been summarized by Giauque et al. (1). Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda (8) based on experimental data (0 - 300°C). These temperature-dependent values are corrected to current atomic weights, converted from IPTS-48 to IPTS-68, and adjusted graphically in the region 290-350 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used for extrapolation of the heat capacity values to 1000 K.

Other heat capacity studies on sulfuric acid and its aqueous solutions are too numerous to mention. However, a recent compilation (9) summarizes much of the work and shows that our adopted heat capacity values for sulfuric acid and its hydrates from room temperature to ∿80°C are consistent with the available literature.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, S°_{15} = 0.269 cal/(mol K) and addition of the entropy of melting.

Melting Data

The melting point and heat of melting have been measured calorimetrically by Rubin and Giauque (7). The value for Tm used by Giauque et al (1) in their re-evaluation and correlation of aqueous sulfuric acid properties was slightly different; the change was 0.07 K. Many other studies have also reported melting data but they are too numerous to mention.

Vaporization Data

Tb is the temperature at which ΔGr° approaches zero for the reaction H_2SO_4(l) = H_2SO_4(g). ΔHv° is calculated as the difference in the respective ΔHf° values at Tb.

According to Luchinskii (10), the total pressure over H_2SO_4(l) reaches one atmosphere at 553 K with a vapor composition of 76.6 mole% SO_3, 22.6 mole% H_2SO_4, and 0.8 mole% H_2O.

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H_2O_4S

SULFURIC ACID (H_2SO_4) H2O4S
(IDEAL GAS) GFW=98.0734

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.905	-172.378	-172.378	INFINITE
100	10.062	55.496	86.124	-3.063	-173.805	-168.374	367.976
200	15.739	64.267	73.089	-1.764	-174.935	-162.474	177.541
298	20.019	71.388	71.388	0.000	-175.700	-156.183	114.484
300	20.089	71.512	71.388	0.037	-175.712	-156.062	113.689
400	23.383	77.765	72.218	2.219	-176.743	-149.409	81.632
500	25.831	83.259	73.888	4.685	-177.376	-142.497	62.285
600	27.644	88.137	75.864	7.364	-177.764	-135.481	49.348
700	29.018	92.506	77.935	10.200	-177.986	-128.391	40.085
900	30.978	100.051	82.037	16.213	-190.877	-114.009	27.685
1000	31.714	103.354	84.006	19.348	-190.555	-105.484	23.053
800	30.098	96.454	80.007	13.157	-191.156	-122.567	33.483
1200	32.883	109.245	87.734	25.814	-189.812	-88.539	16.125
1100	32.341	106.407	85.906	22.552	-190.198	-96.996	19.271
1300	33.355	111.896	89.492	29.126	-189.403	-80.114	13.468
1400	33.768	114.384	91.182	32.483	-188.977	-71.724	11.196
1500	34.131	116.726	92.807	35.878	-188.537	-63.365	9.232
1600	34.451	118.939	94.372	39.307	-188.087	-55.035	7.517
1700	34.734	121.036	95.879	42.767	-187.627	-46.732	6.008
1800	34.986	123.029	97.333	46.253	-187.164	-38.458	4.669
1900	35.209	124.927	98.736	49.763	-186.698	-30.209	3.475
2000	35.409	126.738	100.091	53.294	-186.231	-21.985	2.402
2100	35.587	128.470	101.401	56.844	-185.766	-13.785	1.435
2200	35.747	130.129	102.670	60.411	-185.303	-5.605	0.557
2300	35.891	131.721	103.898	63.993	-184.845	2.552	-0.242
2400	36.021	133.252	105.090	67.589	-184.390	10.690	-0.973
2500	36.139	134.725	106.246	71.197	-183.940	18.810	-1.644
2600	36.245	136.144	107.369	74.816	-183.497	26.911	-2.262
2700	36.342	137.514	108.460	78.446	-183.059	34.995	-2.833
2800	36.430	138.837	109.521	82.084	-182.631	43.061	-3.361
2900	36.510	140.117	110.554	85.731	-182.209	51.116	-3.852
3000	36.584	141.356	111.560	89.386	-181.795	59.155	-4.309
3100	36.651	142.557	112.541	93.048	-181.387	67.179	-4.736
3200	36.713	143.721	113.497	96.716	-180.989	75.191	-5.135
3300	36.770	144.852	114.430	100.390	-180.596	83.191	-5.509
3400	36.823	145.950	115.341	104.070	-180.214	91.179	-5.861
3500	36.871	147.018	116.231	107.755	-179.838	99.154	-6.191
3600	36.917	148.058	117.101	111.444	-179.470	107.121	-6.503
3700	36.958	149.070	117.951	115.138	-179.112	115.077	-6.797
3800	36.997	150.056	118.783	118.836	-178.760	123.021	-7.075
3900	37.033	151.017	119.598	122.537	-178.416	130.958	-7.339
4000	37.067	151.955	120.395	126.242	-178.079	138.890	-7.589
4100	37.098	152.871	121.176	129.951	-177.750	146.808	-7.825
4200	37.127	153.765	121.941	133.662	-177.428	154.723	-8.051
4300	37.155	154.639	122.691	137.376	-177.116	162.625	-8.265
4400	37.181	155.494	123.427	141.093	-176.810	170.524	-8.470
4500	37.205	156.330	124.149	144.812	-176.513	178.416	-8.665
4600	37.227	157.148	124.858	148.534	-176.224	186.297	-8.851
4700	37.249	157.949	125.553	152.257	-175.943	194.175	-9.029
4800	37.269	158.733	126.236	155.983	-175.669	202.047	-9.199
4900	37.288	159.502	126.907	159.711	-175.403	209.917	-9.363
5000	37.306	160.255	127.567	163.441	-175.148	217.774	-9.519
5100	37.322	160.994	128.215	167.172	-174.900	225.632	-9.669
5200	37.338	161.719	128.852	170.905	-174.661	233.484	-9.813
5300	37.353	162.430	129.479	174.640	-174.431	241.328	-9.951
5400	37.368	163.129	130.096	178.376	-174.211	249.173	-10.084
5500	37.381	163.814	130.703	182.113	-174.000	257.011	-10.213
5600	37.394	164.488	131.300	185.852	-173.799	264.846	-10.336
5700	37.406	165.150	131.888	189.592	-173.608	272.677	-10.455
5800	37.418	165.801	132.467	193.333	-173.428	280.504	-10.570
5900	37.429	166.440	133.038	197.076	-173.256	288.327	-10.680
6000	37.440	167.070	133.600	200.819	-173.098	296.154	-10.787

Dec. 31, 1966; Sept. 30, 1977

SULFURIC ACID (H_2SO_4) (IDEAL GAS) GFW = 98.0734

ΔHf°_0 = -172.4 ± 2 kcal/mol H2O4S
$\Delta Hf^\circ_{298.15}$ = -175.7 ± 2 kcal/mol

$S^\circ_{298.15}$ = [71.39 ± 0.5] gibbs/mol
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[3500](1)	[380](1)	883(1)
1223(1)	[265](1)	[400](1)
1138(1)	[390](1)	1450(1)
834(1)	3610(1)	[265](1)
550(1)	1159(1)	568(1)

Point Group C_{2v} σ = 2
Bond Distances: S-O = [1.42] Å S-OH = [1.55] Å O-H = [0.97] Å
Bond Angles: O-S-O = [109.47122]° S-O-H = [105]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [4.5092 x 10^{-114}] g^3 cm^6

Heat of Formation

The vapor phase equilibria of the H_2SO_4, H_2O, and SO_3 system have been determined by PVT studies by Bodenstein and Katayama (5) and Suvorov et al. (4) and by vapor pressure measurements by Luchinskii (3). Using the reported equilibrium values (after correcting a few typographical errors) for the reaction $H_2SO_4(g) = H_2O(g) + SO_3(g)$, we calculate ΔHf°_{298} using a second and third law analysis and auxiliary data (6). The results are tabulated below. We adopt $\Delta Hf^\circ_{298}(H_2SO_4,g)$ = -175.7±2 kcal/mol which is the median of the three values derived from the third law ΔHr°_{298}. The analysis of vaporization data of Thomas and Ramsey (1) and Abel (2) leads to ΔHf°_{298} values within 2 kcal/mol of our adopted value.

Source	Temp., K	No. Pts	Reaction	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	$\Delta Hf^\circ_{298}(H_2SO_4,g)$* kcal/mol
(1)	463-493	4	A	18.1±0.1	20.5±0.1	4.9±0.2	-174.0
(2)	523-673	7	A	17.7±0.2	19.7±0.4	3.3±0.3	-174.8
(2)	298-603	9	B	24.2±0.3	23.4±0.5	-1.6±0.1	-175.8
(3)	333-473	8	B	23.7±0.1	23.5±0.1	-0.6±0.3	-175.9
(4)	583-785	40	B	25.1±0.4	23.3±0.3	-2.7±0.7	-175.7
(5)	596-756	53	B	23.3±0.6	23.0±0.5	-0.4±0.9	-175.4

* ΔHf°_{298} is calculated using the third law ΔHr°_{298}

Reaction: A) $H_2SO_4(\ell) = H_2SO_4(g)$ B) $H_2SO_4(g) = H_2O(g) + SO_3(g)$

Heat Capacity and Entropy

The molecular structure of $H_2SO_4(g)$ is assumed to be tetrahedral with differing bond lengths for S-O and S-OH. This adopted structure is consistent with the X-ray and electron diffraction studies on $H_2SO_4(c)$ by Pascard (7) and Pascard-Billy (8), respectively, and the X-ray scattering study on $H_2SO_4(\ell)$ by Weidner et al. (9). The latter study gave results which could be interpreted by models having point symmetry C_2 and C_{2v}. In both models, the sulfur-oxygen bond distances are equivalent within the experimental uncertainty. For the C_{2v} model, the O-S-O bond angles coincide with the tetrahedral angle. In the C_2 model these angles are split, but not as extremely as in $H_2SO_4(c)$ (7, 8). The OH distance and the S-O-H angle are taken from those for $H_2O(g)$. The three principal moments of inertia are: $I_A = 14.98 \times 10^{-39}$, $I_B = 17.01 \times 10^{-39}$, and $I_C = 17.70 \times 10^{-39}$ g cm^2.

The vibrational frequencies are from the infrared studies of Chackalackal and Stafford (10) and the comparisons of Giguere and Savoie (11). The infrared studies led to the assignment of nine vibrational frequencies while the remaining six were estimated (10) by comparison with the infrared frequencies for the crystal and Raman frequencies for the liquid.

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H2O4S

HYDROGEN SULFIDE (H_2S)
(IDEAL GAS) GFW=34.0758

H_2S

T, K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔG°	
0	0.000	0.000	INFINITE	-2.381	-4.204	-4.204	INFINITE
100	7.949	40.359	56.219	-1.586	-4.290	-5.625	12.292
200	7.978	45.872	49.827	-0.791	-4.532	-6.879	7.517
298	8.172	49.151	49.151	0.000	-4.900	-7.975	5.846
300	8.176	49.202	49.151	0.015	-4.908	-7.994	5.824
400	8.504	51.597	49.476	0.849	-5.867	-8.938	4.883
500	8.889	53.536	50.100	1.718	-6.635	-9.616	4.203
600	9.306	55.193	50.813	2.628	-7.282	-10.149	3.697
700	9.737	56.660	51.546	3.580	-7.832	-10.558	3.296
800	10.162	57.988	52.269	4.575	-21.368	-12.183	3.328
900	10.567	59.209	52.973	5.612	-21.480	-11.027	2.478
1000	10.943	60.342	53.654	6.687	-21.564	-9.861	2.155
1100	11.281	61.401	54.311	7.799	-21.621	-8.689	1.726
1200	11.584	62.396	54.944	8.943	-21.657	-7.511	1.368
1300	11.853	63.334	55.553	10.115	-21.676	-6.330	1.064
1400	12.092	64.221	56.141	11.312	-21.682	-5.149	0.804
1500	12.303	65.063	56.708	12.532	-21.677	-3.971	0.578
1600	12.491	65.863	57.255	13.772	-21.662	-2.789	0.381
1700	12.658	66.625	57.784	15.030	-21.640	-1.610	0.207
1800	12.808	67.353	58.296	16.303	-21.614	-0.434	0.053
1900	12.941	68.049	58.791	17.590	-21.583	0.744	-0.086
2000	13.063	68.716	59.271	18.891	-21.548	1.917	-0.210
2100	13.171	69.356	59.736	20.203	-21.511	3.089	-0.321
2200	13.270	69.971	60.187	21.525	-21.473	4.261	-0.423
2300	13.360	70.563	60.625	22.856	-21.434	5.429	-0.516
2400	13.444	71.133	61.051	24.197	-21.392	6.597	-0.601
2500	13.520	71.684	61.466	25.545	-21.350	7.763	-0.679
2600	13.590	72.215	61.869	26.900	-21.309	8.926	-0.750
2700	13.655	72.729	62.262	28.263	-21.266	10.088	-0.817
2800	13.715	73.227	62.645	29.631	-21.226	11.246	-0.878
2900	13.771	73.709	63.018	31.005	-21.185	12.406	-0.935
3000	13.824	74.177	63.382	32.385	-21.144	13.565	-0.988
3100	13.874	74.631	63.738	33.770	-21.103	14.721	-1.038
3200	13.921	75.073	64.085	35.160	-21.065	15.875	-1.084
3300	13.965	75.502	64.425	36.554	-21.026	17.028	-1.128
3400	14.007	75.919	64.756	37.953	-20.989	18.182	-1.169
3500	14.047	76.326	65.081	39.356	-20.953	19.332	-1.207
3600	14.085	76.722	65.399	40.762	-20.918	20.483	-1.243
3700	14.122	77.108	65.710	42.173	-20.885	21.634	-1.278
3800	14.156	77.485	66.015	43.586	-20.854	22.781	-1.310
3900	14.190	77.854	66.314	45.004	-20.823	23.929	-1.341
4000	14.223	78.213	66.607	46.424	-20.795	25.078	-1.370
4100	14.254	78.565	66.895	47.848	-20.767	26.224	-1.398
4200	14.285	78.909	67.177	49.275	-20.741	27.371	-1.424
4300	14.314	79.245	67.453	50.705	-20.717	28.514	-1.449
4400	14.343	79.575	67.725	52.138	-20.695	29.660	-1.473
4500	14.371	79.897	67.992	53.574	-20.675	30.805	-1.496
4600	14.397	80.213	68.254	55.012	-20.656	31.948	-1.518
4700	14.423	80.523	68.512	56.453	-20.639	33.090	-1.539
4800	14.450	80.827	68.765	57.897	-20.623	34.232	-1.559
4900	14.475	81.125	69.015	59.343	-20.609	35.378	-1.578
5000	14.500	81.418	69.260	60.792	-20.597	36.518	-1.596
5100	14.523	81.706	69.501	62.243	-20.587	37.662	-1.614
5200	14.548	81.988	69.738	63.697	-20.577	38.804	-1.631
5300	14.571	82.265	69.972	65.153	-20.568	39.946	-1.647
5400	14.594	82.538	70.202	66.611	-20.562	41.088	-1.663
5500	14.616	82.806	70.429	68.071	-20.556	42.229	-1.678
5600	14.639	83.069	70.652	69.534	-20.551	43.373	-1.693
5700	14.661	83.329	70.873	70.999	-20.547	44.512	-1.707
5800	14.682	83.584	71.089	72.466	-20.543	45.654	-1.720
5900	14.705	83.835	71.303	73.936	-20.538	46.793	-1.733
6000	14.725	84.082	71.514	75.407	-20.536	47.937	-1.746

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965;
July 31, 1972 (NBS); June 30, 1977

HYDROGEN SULFIDE (H_2S) (IDEAL GAS) GFW = 34.0758

H_2S

Point Group C_{2v}
$S^\circ_{298.15}$ = 49.15 gibbs/mol
Ground State Quantum Weight = 1

$\Delta Hf^\circ_0 = -4.20 \pm 0.2$ kcal/mol
$\Delta Hf^\circ_{298.15} = -4.90 \pm 0.2$ kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
2614.6 (1)
1182.7 (1)
2626.5 (1)

Bond Distance: S-H = 1.328 Å
$\sigma = 2$
Bond Angle: H-S-H = 92.2°
Product of the Moments of Inertia: $I_AI_BI_C = 4.69 \times 10^{-119}\ g^3\ cm^6$

Heat of Formation

The heats of formation of $H_2S(g)$ determined by various workers including those reviewed in the previous JANAF analysis (1) were recalculated with the results shown below. No weight was given to the work performed prior to 1934 and less weight was given to the work of Kapustinskii and Kankovskii (7) because of the difficulty of establishing the state of the products.

Source	Reaction*	ΔHf°_{298} (kcal/mol)	
		[from (1)]	Recalculated
Thomsen (2, 1882)	$H_2S(g) + HI_3(aq) = 3\ HI(aq) + S(amph)$	----	-4.4, -5.1 if S(rhombic)
Thomsen (3, 1882)	*$H_2S(g) + O_2(g) = SO_2(g) + H_2SO_4 \cdot H_2O$	----	-2.0
Pollitzer (4, 1909)	$H_2S(g) + I_2(c) = 2\ HI(g) + S(rh)$	----	-4.7, -4.0 if S(amph)
Lewis and Randall (5, 1918)	$3\ S(\ell) + 2\ H_2O(g) = SO_2(g) + 2\ H_2S(g)$	----	-3.6±0.2
Zeumer and Roth (6, 1934)	*$H_2S(g) + O_2(g) = SO_2(g) + H_2SO_4 \cdot H_2O$	-4.80±0.15	-4.89±0.24
Kapustinskii and Kankovskii (7, 1958)	*$H_2S(g) + 3/2\ O_2(g) = SO_2(g) + H_2O(\ell) + S(rh)$	-4.94±0.8	-4.92±0.08

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*Equations which are not balanced involve two reactions occurring in various proportions.

Heat Capacity and Entropy

The thermodynamic functions were taken from the JANAF table for $H_2S(g)$ dated Dec. 31, 1965 (1). These in turn were taken from Gordon (8) except below 298 K where they were calculated by the rigid-rotor, harmonic-oscillator approximation. Gordon had calculated Cp° from 298 K to 6000 K by a method which takes into account second-order corrections for vibrational anharmonicity, vibration-rotation interaction, and centrifugal stretching. The spectroscopic constants used were taken from Allen and Plyler (9).

The National Bureau of Standards prepared this table (10) by critical analysis of data existing in 1972. Using ΔHf° selected by NBS (10), we recalculate the table in terms of current JANAF reference states for the elements.

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IODOSILANE (SiH_3I) H_3ISi

(IDEAL GAS) GFW=158.0142

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	−2.887	1.995	1.995	INFINITE
100	8.306	53.723	74.578	−2.085	1.230	0.336	−0.734
200	10.496	60.081	65.859	−1.156	0.385	−0.248	0.271
298	13.002	64.749	64.749	0.000	−0.500	−0.369	0.270
300	13.045	64.829	64.749	0.024	−0.516	−0.368	0.268
400	15.108	68.877	65.287	1.436	−3.238	−0.127	0.070
500	16.725	72.429	66.367	3.031	−8.998	1.210	−0.529
600	18.048	75.599	67.646	4.772	−9.323	3.283	−1.196
700	19.157	78.467	68.990	6.633	−9.549	5.404	−1.687
800	20.089	81.087	70.341	8.597	−9.495	7.55C	−2.063
900	20.872	83.500	71.671	10.646	−9.778	9.713	−2.359
1000	21.528	85.734	72.967	12.767	−9.810	11.880	−2.596
1100	22.077	87.813	74.223	14.948	−9.807	14.049	−2.791
1200	22.538	89.754	75.437	17.180	−9.776	16.217	−2.954
1300	22.926	91.574	76.609	19.453	−9.728	18.380	−3.090
1400	23.254	93.285	77.740	21.763	−9.670	20.541	−3.207
1500	23.533	94.899	78.831	24.103	−9.611	22.698	−3.307
1600	23.771	96.426	79.883	26.468	−9.554	24.849	−3.394
1700	23.976	97.873	80.899	28.856	−21.493	27.106	−3.485
1800	24.153	95.249	81.881	31.262	−21.391	29.959	−3.638
1900	24.307	100.559	82.830	33.686	−21.286	32.809	−3.774
2000	24.442	101.809	83.747	36.123	−21.181	35.654	−3.896
2100	24.560	103.005	84.636	38.573	−21.077	38.494	−4.006
2200	24.664	104.150	85.497	41.035	−20.975	41.327	−4.105
2300	24.756	105.248	86.332	43.506	−20.875	44.157	−4.196
2400	24.838	106.303	87.143	45.985	−20.778	46.985	−4.279
2500	24.911	107.319	87.929	48.473	−20.687	49.802	−4.354
2600	24.976	108.297	88.694	50.967	−20.596	52.622	−4.423
2700	25.035	109.241	89.438	53.468	−20.511	55.435	−4.487
2800	25.088	110.152	90.161	55.974	−20.430	58.247	−4.546
2900	25.136	111.033	90.866	58.485	−20.352	61.059	−4.602
3000	25.180	111.886	91.553	61.001	−20.279	63.860	−4.652
3100	25.220	112.713	92.222	63.521	−20.208	66.663	−4.700
3200	25.256	113.514	92.875	66.045	−20.143	69.467	−4.744
3300	25.289	114.292	93.512	68.572	−20.084	72.268	−4.786
3400	25.319	115.047	94.134	71.103	−20.027	75.062	−4.825
3500	25.347	115.781	94.742	73.636	−19.977	77.861	−4.862
3600	25.373	116.496	95.337	76.172	−111.893	82.911	−5.033
3700	25.397	117.191	95.918	78.711	−111.755	88.321	−5.217
3800	25.419	117.869	96.487	81.251	−111.621	93.726	−5.391
3900	25.439	118.529	97.044	83.794	−111.495	99.129	−5.555
4000	25.458	119.174	97.589	86.339	−111.373	104.528	−5.711
4100	25.476	119.803	98.123	88.886	−111.257	109.923	−5.859
4200	25.492	120.417	98.647	91.434	−111.148	115.318	−6.001
4300	25.508	121.017	99.160	93.984	−111.043	120.705	−6.135
4400	25.522	121.603	99.663	96.536	−110.944	126.092	−6.263
4500	25.535	122.177	100.157	99.089	−110.851	131.481	−6.386
4600	25.548	122.738	100.642	101.643	−110.762	136.868	−6.503
4700	25.560	123.288	101.118	104.198	−110.681	142.250	−6.615
4800	25.571	123.826	101.586	106.755	−110.603	147.630	−6.722
4900	25.581	124.354	102.045	109.313	−110.530	153.012	−6.825
5000	25.591	124.870	102.496	111.872	−110.463	158.382	−6.923
5100	25.600	125.377	102.940	114.431	−110.402	163.765	−7.018
5200	25.609	125.875	103.376	116.991	−110.345	169.137	−7.109
5300	25.617	126.362	103.805	119.552	−110.293	174.517	−7.196
5400	25.625	126.841	104.227	122.115	−110.248	179.885	−7.280
5500	25.632	127.312	104.643	124.677	−110.207	185.256	−7.361
5600	25.639	127.773	105.052	127.241	−110.172	190.626	−7.440
5700	25.644	128.227	105.454	129.805	−110.142	196.003	−7.515
5800	25.652	128.673	105.851	132.370	−110.119	201.371	−7.588
5900	25.658	129.112	106.241	134.936	−110.100	206.739	−7.658
6000	25.664	129.543	106.626	137.502	−110.086	212.107	−7.726

Dec. 31, 1976

IODOSILANE (SiH_3I)   (IDEAL GAS)   GFW = 158.0142

Point Group C_{3v}
$S^\circ_{298.15}$ = 64.75 ± 0.06 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = [+2.0 ± 4] kcal/mol H_3ISi
$\Delta Hf^\circ_{298.15}$ = [-0.5 ± 4] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2192(1)	2206(2)
903(1)	941(2)
362(1)	592(2)

Bond Distances: Si-H = 1.486 ± 0.008 Å   Si-I = 2.437 Å   σ = 3
Bond Angles: H-Si-H = 110.42° ± 0.5°   H-Si-I = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_AI_BI_C = 2.8344 \times 10^{-117}$ g^3 cm^6

Heat of Formation

ΔHf°_{298} is estimated by linear interpolation between the values (1) of SiI_4(g) and SiH_4(g). There are no experimental ΔHf° data for SiH_3I, SiH_2I_2 and $SiHI_3$. It is difficult to justify a nonlinear interpolation scheme such as that adopted for the chlorosilanes (1). A cubic interpolation fits ΔHf° data for the chloromethanes and has been proposed for bromomethanes and iodomethanes (2). Experimental ΔHf° values do not seem to exist for CI_4, CBr_4 and $CHBr_3$, while published values for CBr_4 and $CHBr_3$ are the subject of controversy (1, SiH_3Br,g). Moreover, the cubic scheme proposed (2) for CH_nI_{4-n} is surprisingly different from those of the other halomethanes (2); i.e, the first differences in ΔHf° exhibit a minimum instead of a maximum. These uncertainties preclude use of the iodomethanes for predicting ΔHf° of the iodosilanes. Hunt and Sirtl (3) also concluded that linear interpolation of ΔHf° is all that is justified by available data.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley et al. (4) for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structural determinations (5). The principal moments of inertia are $I_A = 0.9970 \times 10^{-39}$ and $I_B = I_C = 26.1729 \times 10^{-39}$ g cm^2.

Vibrational frequencies are from gas-phase infrared spectra (6, 7). Assignments are consistent with liquid-phase Raman spectra (8, 9) which yield slightly lower values for most of the frequencies.

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3I (10). Comparison of the halosilanes (11) and halomethanes (10, 11) suggests that the lowest excited state of SiH_3I is at ≥30000 cm^{-1}. Contributions from this state should be unimportant.

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H_3ISi

AMMONIA (NH_3) H_3N

(IDEAL GAS) GFW=17.0304

	gibbs/mol			kcal/mol			
T, K	$C_p°$	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	0.000	0.000	INFINITE	-2.401	-9.299	-9.299	INFINITE
100	7.955	37.221	53.322	-1.610	-9.930	-8.137	17.782
200	8.068	42.753	46.810	-0.811	-10.445	-6.143	6.712
298	8.521	46.048	46.048	0.000	-10.970	-3.920	2.873
300	8.533	46.101	46.048	0.016	-10.980	-3.876	2.824
400	9.253	48.650	46.391	0.904	-11.482	-1.430	0.781
500	10.050	50.801	47.063	1.869	-11.917	1.134	-0.496
600	10.825	52.702	47.847	2.913	-12.279	3.779	-1.377
700	11.557	54.426	48.666	4.032	-12.576	6.480	-2.023
800	12.245	56.015	49.486	5.223	-12.816	9.219	-2.518
900	12.894	57.495	50.295	6.480	-13.005	11.985	-2.910
1000	13.502	58.885	51.085	7.800	-13.149	14.770	-3.228
1100	14.068	60.199	51.854	9.179	-13.253	17.567	-3.490
1200	14.591	61.446	52.602	10.612	-13.324	20.373	-3.710
1300	15.071	62.633	53.329	12.096	-13.365	23.182	-3.897
1400	15.510	63.766	54.034	13.625	-13.380	25.995	-4.058
1500	15.909	64.850	54.719	15.197	-13.374	28.807	-4.197
1600	16.271	65.889	55.385	16.806	-13.348	31.618	-4.319
1700	16.599	66.885	56.032	18.450	-13.306	34.427	-4.426
1800	16.896	67.842	56.662	20.125	-13.251	37.233	-4.521
1900	17.165	68.763	57.275	21.828	-13.183	40.037	-4.605
2000	17.408	69.650	57.872	23.557	-13.106	42.836	-4.681
2100	17.627	70.505	58.453	25.309	-13.019	45.631	-4.749
2200	17.825	71.329	59.020	27.081	-12.927	48.421	-4.810
2300	18.004	72.126	59.572	28.873	-12.828	51.208	-4.866
2400	18.166	72.896	60.111	30.682	-12.724	53.990	-4.916
2500	18.314	73.640	60.638	32.506	-12.616	56.768	-4.963
2600	18.445	74.361	61.152	34.344	-12.507	59.541	-5.005
2700	18.564	75.059	61.654	36.194	-12.394	62.311	-5.044
2800	18.674	75.737	62.145	38.056	-12.282	65.074	-5.079
2900	18.769	76.394	62.625	39.929	-12.168	67.835	-5.112
3000	18.858	77.031	63.095	41.810	-12.053	70.593	-5.143
3100	18.936	77.651	63.554	43.700	-11.940	73.346	-5.171
3200	19.006	78.253	64.004	45.597	-11.829	76.094	-5.197
3300	19.069	78.839	64.445	47.501	-11.718	78.841	-5.221
3400	19.123	79.409	64.877	49.411	-11.610	81.583	-5.244
3500	19.172	79.964	65.300	51.325	-11.505	84.323	-5.265
3600	19.216	80.505	65.715	53.245	-11.403	87.059	-5.285
3700	19.252	81.032	66.122	55.168	-11.305	89.793	-5.304
3800	19.284	81.546	66.521	57.095	-11.211	92.524	-5.321
3900	19.310	82.047	66.913	59.025	-11.122	95.252	-5.338
4000	19.331	82.536	67.297	60.957	-11.038	97.978	-5.353
4100	19.349	83.014	67.675	62.891	-10.958	100.703	-5.368
4200	19.361	83.480	68.045	64.826	-10.884	103.426	-5.382
4300	19.371	83.936	68.410	66.763	-10.816	106.146	-5.395
4400	19.375	84.381	68.768	68.700	-10.754	108.867	-5.407
4500	19.377	84.817	69.119	70.638	-10.699	111.583	-5.419
4600	19.373	85.243	69.465	72.576	-10.650	114.301	-5.430
4700	19.367	85.659	69.805	74.513	-10.609	117.016	-5.441
4800	19.357	86.067	70.140	76.449	-10.574	119.732	-5.451
4900	19.343	86.466	70.469	78.384	-10.547	122.446	-5.461
5000	19.325	86.856	70.793	80.317	-10.527	125.161	-5.471
5100	19.300	87.239	71.112	82.248	-10.516	127.873	-5.480
5200	19.300	87.614	71.425	84.178	-10.511	130.587	-5.488
5300	19.300	87.981	71.734	86.108	-10.511	133.301	-5.497
5400	19.300	88.342	72.039	88.038	-10.518	136.014	-5.505
5500	19.300	88.696	72.338	89.968	-10.528	138.728	-5.512
5600	19.300	89.044	72.633	91.898	-10.542	141.443	-5.520
5700	19.300	89.386	72.924	93.828	-10.562	144.156	-5.527
5800	19.300	89.721	73.211	95.758	-10.585	146.871	-5.534
5900	19.300	90.051	73.494	97.688	-10.612	149.586	-5.541
6000	19.300	90.376	73.772	99.618	-10.644	152.300	-5.547

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965;
July 31, 1972 (NBS); June 30, 1977

Point Group C_{3v}
$S°_{298.15}$ = 46.048 ± 0.006 gibbs/mol
Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -9.30 ± 0.1 kcal/mol
$\Delta Hf°_{298.15}$ = -10.97 ± 0.1 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
3506 (1)	1022 (1)	3577 (2)	1691 (2)

Bond Length: N-H = 1.0124 Å
σ(external) = 3
Bond Angle: 106.67°
σ(internal) = 2
Product of the Moments of Inertia: $I_AI_BI_C = 3.4824 \times 10^{-119}\ g^3cm^6$

Heat of Formation

Second and third law analyses of equilibrium data for the reaction $1/2N_2(g)+3/2H_2(g) = NH_3(g)$ cited in the previous JANAF evaluation (1) plus more recent work of Schulz and Schaefer (6) were made using the revised thermal functions for $NH_3(g)$. All of the previously cited work in reaction calorimetry plus the early work of Berthelot (7, 8) and Thomsen (9) were reevaluated. No significant differences in the third law calculations of the equilibrium data or in the corrections to the flow calorimetry data of Haber and Tamaru (12) and Wittig and Schmatz (13) were found. Thus, the 0.1 kcal discrepancy between the results of the equilibrium and reaction calorimetry measurements remains unresolved. The previous JANAF selection (1) for $\Delta Hf°_{298}$ of $NH_3(g)$ was adopted. A recent evaluation (14) which includes new indirect calorimetry (unpublished) further confirms this selection.

Source	Method	$\Delta Hf°_{298}$ kcal/mol	$\Delta Hf°_{298}$ kcal/mol*	$\Delta S°_{298}$(obs.-calc.)* (e.u.)
Larson, Dodge (2, 1923)	$\overset{\circ}{Kp}$(4) from Kp(10-1,000 atm, 600-800 K)	-10.88	-10.70±0.11	+0.24±0.15[a]
Haber et al. (3, 1915)	$\overset{\circ}{Kp}$(4) from Kp(30 atm, 800-1200 K)	-10.86	-10.88±0.15	-0.02±0.15[b]
Haber, Maschke (5, 1915)	Kp(1 atm, 900-1400 K)	-10.85	-10.62±0.22	0.20±0.19[c]
Schulz, Schaefer (6, 1966)	Kp(1 atm, 567-673 K)	-10.87	-10.78±0.20	0.14±0.3[d]
Berthelot (7, 1880)	Indirect; Reaction of Br_2(aq) and NH_3(aq)	-11.4		
Berthelot (8, 1880)	Indirect; Reaction of O_2(g) with NH_3(g)	-12.1		
Thomsen (9, 1882)	Indirect; Reaction of O_2(g) with NH_3(g)	-11.9		
Becker, Roth (10, 1934)	Indirect; Heat of combustion oxalates	-11.00±0.15		
Haber et al. (11, 1915)	Flow calorimetry at 298 K	-11.10±0.05		
Haber, Tamaru (12, 1915)	Flow calorimetry (739-932 K)	-10.97±0.008		
Wittig, Schmatz (13, 1959)	Flow calorimetry at 832 K	-10.99±0.05		

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*Second law analysis assuming ΔCp (gibbs/mol) equals (a) -2.672+0.00591(T-700), (b) -1.236+0.00404(T-1000), (c) -0.855+0.00305(T-1100), (d) -3.287+0.00651(T-600).

Heat Capacity and Entropy

The thermodynamic functions differ from those of the 1965 JANAF table (1) in being taken directly from the later and more complete work of Haar (15). Haar treated in detail the contribution of the highly anharmonic out-of-plane vibrational mode, including its large coupling with rotation and its coupling with the other vibrational modes. Haar's values of $C_p°$ pass through a shallow maximum between 4000 and 5000 K; they were extrapolated from 5000 to 6000 K by assuming a constant value (19.300 gibbs/mol). A summary of Haar's estimated uncertainties and of the differences of the 1965 table from the present table (in gibbs/mol) is as follows:

	Uncertainties (Haar, 15)		1965 Table minus This Table	
T, K	Cp°	S°	Cp°	S°
1000	0.006	0.006	-0.034	-0.033
3000	0.10	0.06	+0.142	-0.122
5000	0.6	0.4	+1.775	+0.265

The National Bureau of Standards prepared this table (16) by critical analysis of data existing in 1972. Using the results of Haar (15) and ΔHf° selected by NBS (16), we recalculate the table in terms of R=1.987192 cal/(mol K) (17) and current JANAF reference states for the elements.

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SULFURIC ACID, MONOHYDRATE ($H_2SO_4 \cdot H_2O$) H_4O_5S
(LIQUID) GFW=116.0886

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	51.214	50.555	50.555	0.000	−269.508	−227.170	166.518
300	51.276	50.872	50.556	0.095	−269.482	−226.908	165.300
400	54.626	66.082	52.607	5.390	−268.449	−212.924	116.334
500	58.227	78.658	56.593	11.033	−266.969	−199.208	87.072
600	61.827	89.592	61.200	17.035	−265.111	−185.823	67.685
700	65.427	99.393	65.968	23.398	−262.898	−172.755	53.936
800	69.028	108.365	70.714	30.121	−273.407	−161.317	44.069
900	72.628	116.703	75.366	37.283	−270.219	−147.495	35.816
1000	76.228	124.542	79.895	44.644	−266.721	−134.042	29.294

Sept. 30, 1977

SULFURIC ACID, MONOHYDRATE ($H_2SO_4 \cdot H_2O$) (LIQUID) GFW = 116.0886

$S^\circ_{298.15}$ = 50.555 ± 0.05 gibbs/mol
Tm = 281.63 ± 0.05 K

$\Delta Hf^\circ_{298.15}$ = −269.508 ± 0.2 kcal/mol
ΔHm° = 4.652 ± 0.010 kcal/mol

H_4O_5S

Heat of Formation

The heat of formation of the monohydrate of sulfuric acid is derived from the heat of solution data of Giauque et al. (1). We calculate ΔHf°_{298} using ΔHr°_{298} = −6.645 kcal/mol for the solution process $H_2SO_4(\ell) + H_2O(\ell) = H_2SO_4 \cdot H_2O(\ell)$ and auxiliary data for H_2SO_4 (2) and H_2O (3).

Heat Capacity and Entropy

The heat capacity has been measured experimentally (4) in the range 15 - 300 K and has been re-analyzed and summarized by Giauque et al. (1). Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda (5) based on experimental data (273 - 573 K). These temperature-dependent values are corrected to current atomic weights, converted from IPTS-48 to IPTS-68, and adjusted graphically in the region 290 - 390 K so as to provide smoothly varying heat capacity values. In the region above 390 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy of 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and S°_{15} = 0.190 cal/(mol K).

Melting Data

The melting point and heat of melting have been measured calorimetrically by Rubin and Giauque (4). The values used by Giauque et al. (1) in their re-evaluation and correlation of aqueous sulfuric acid properties were slightly different from those reported by Rubin and Giauque (4); the changes were 0.01 K in the melting point and 6 cal/mol in the heat of melting. In addition, the value for Tm is corrected from IPTS-48 to IPTS-68.

References

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H_4O_5S

SULFURIC ACID, DIHYDRATE ($H_2SO_4 \cdot 2H_2O$) H_6O_6S
(LIQUID) GFW=134.1038

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	62.493	66.056	66.056	0.000	-341.085	-286.759	210.197
300	62.637	66.443	66.057	0.116	-341.057	-286.422	208.456
400	70.417	85.528	68.407	6.766	-339.716	-268.452	146.673
500	78.198	102.077	73.679	14.199	-337.513	-250.878	109.657
600	85.979	117.022	79.675	22.408	-334.526	-233.817	85.167
700	93.759	130.860	86.010	31.395	-330.779	-217.295	67.841
800	101.540	143.888	92.438	41.140	-339.351	-202.651	55.361
900	109.320	156.297	98.849	51.763	-333.821	-185.888	45.130
1000	117.101	168.217	105.193	63.024	-327.576	-169.737	37.104

Sept. 30, 1977

$S^\circ_{298.15}$ = 66.056 ± 0.10 gibbs/mol
Tm = 233.70 ± 0.05 K

$\Delta Hf^\circ_{298.15}$ = -341.085 ± 0.2 kcal/mol
ΔHm° = 4.360 ± 0.04 kcal/mol

H_6O_6S

Heat of Formation

The heat of formation of the dihydrate of sulfuric acid is derived from the heat of solution data of Giauque et al. (1). We calculate ΔHf°_{298} for the dihydrate using ΔHr°_{298} = -9.907 kcal/mol for the solution process $H_2SO_4(\ell) + 2\ H_2O(\ell) = H_2SO_4 \cdot 2\ H_2O(\ell)$ and auxiliary data for H_2SO_4 (2) and H_2O (3).

Heat Capacity and Entropy

The heat capacity has been measured experimentally (4) in the range 15 - 300 K and has been summarized by Giauque et al. (1). Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda (5) based on experimental data (273 - 573 K). These temperature-dependent values are corrected to current atomic weights, converted from IPTS-48 to IPTS-68, and adjusted graphically in the region 290 - 310 K so as to provide smoothly varying heat capacity values. In the region above 310 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and S°_{15} = 0.363 cal/(mol K).

Melting Data

The melting point and heat of melting have been measured calorimetrically by Rubin and Giauque (4). The melting point adopted in this table differs from that reported by Rubin and Giauque (4) by 0.02 K. This is due to the re-analysis of the data by Giauque et al. (1) and a conversion of the resulting Tm value from IPTS-48 to IPTS-68.

References

1. W. F. Giauque, E. W. Horning, J. E. Kunzler, and T. R. Rubin, J. Am. Chem. Soc. 82, 62 (1960).
2. JANAF Thermochemical Tables: $H_2SO_4(\ell)$, 9-30-77.
3. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
4. T. R. Rubin and W. F. Giauque, J. Am. Chem. Soc. 74, 800 (1952).
5. Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

H_6O_6S

SULFURIC ACID, TRIHYDRATE ($H_2SO_4 \cdot 3H_2O$) H_8O_7S
(LIQUID) GFW=152.1190

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	76.270	82.550	82.550	0.000	-411.186	-345.168	253.011
300	76.325	83.022	82.552	0.141	-411.152	-344.759	251.153
400	83.127	105.878	85.620	8.103	-409.550	-322.910	176.427
500	90.017	125.168	91.647	16.760	-407.186	-301.513	131.789
600	96.908	142.189	98.678	26.107	-404.139	-280.692	102.226
700	103.798	157.645	106.013	36.142	-400.434	-260.331	81.278
800	110.689	171.955	113.372	46.866	-409.152	-241.876	66.077
900	117.579	185.390	120.635	58.280	-403.870	-221.278	53.733
1000	124.470	198.135	127.752	70.382	-397.975	-201.298	43.993

Sept 30, 1977

SULFURIC ACID, TRIHYDRATE ($H_2SO_4 \cdot 3\ H_2O$) (LIQUID) GFW = 152.1190

$S°_{298.15}$ = 82.550 ± 0.10 gibbs/mol
Tm = 236.78 ± 0.05 K

$\Delta Hf°_{298.15}$ = -411.186 ± 0.2 kcal/mol
ΔHm° = 5.736 ± 0.05 kcal/mol

H_8O_7S

Heat of Formation

The heat of formation of the trihydrate of sulfuric acid is derived from the heat of solution data of Giauque et al. (1). We calculate $\Delta Hf°_{298}$ for the trihydrate using $\Delta Hr°_{298}$ = -11.693 kcal/mol for the solution process $H_2SO_4(\ell) + 3\ H_2O(\ell) = H_2SO_4 \cdot 3\ H_2O(\ell)$ and auxiliary data for H_2SO_4 (2) and H_2O (3).

Heat Capacity and Entropy

The heat capacity has been measured experimentally (4,5) in the range 15-300 K and has been summarized by Giauque et al. (1). Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda (6) based on experimental data (273-573 K). These temperature-dependent values are corrected to current atomic weights and converted from IPTS-48 to IPTS-68. Of the five hydrates of sulfuric acid (mono-, di-, tri-, tetra-, and hemihexa-) only in the case of the trihydrate is there a serious discrepancy in the heat capacity values (at ambient temperature) between Giauque et al. (6) and Kharbanda (7). Assuming that the data of Giauque et al. (1) are correct and that the linear dependence suggested by the nomograph of Kharbanda (6) is correct, we have shifted the data derived from the nomograph by 0.78 gibbs/mol to obtain a smooth junction of the low temperature and high temperature heat capacity data. The data are extrapolated linearly to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°_{15}$ = 0.398 cal/(mol K).

Melting Data

The melting point and heat of melting have been measured calorimetrically by Hornung and Giauque (5). The melting point adopted in this table differs from that reported by Hornung and Giauque (5) by 0.02 K. This is due to the re-analysis of the data by Giauque et al. (1) and a conversion of the resulting Tm value from IPTS-48 to IPTS-68.

References

1. W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Am. Chem. Soc. 82, 62 (1960).
2. JANAF Thermochemical Tables: $H_2SO_4(\ell)$, 9-30-77.
3. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
4. J. E. Kunzler and W. F. Giauque, J. Am. Chem. Soc 74, 797 (1952).
5. E. W. Hornung and W. F. Giauque, J. Am. Chem. Soc 77, 2983 (1955).
6. Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

SULFURIC ACID, TETRAHYDRATE ($H_2SO_4 \cdot 4H_2O$) $H_{10}O_8S$
(LIQUID) GFW=170.1342

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	92.354	99.079	99.079	0.000	−480.688	−402.988	295.394
300	92.447	99.651	99.081	0.171	−480.644	−402.507	293.222
400	98.081	127.001	102.772	9.691	−478.533	−374.824	205.884
500	103.861	149.508	109.930	19.789	−475.792	−351.706	153.729
600	109.642	168.955	118.182	30.464	−472.494	−327.109	119.177
700	115.422	184.290	126.495	41.717	−468.463	−303.263	94.675
800	121.202	202.080	135.145	53.548	−477.379	−281.173	76.812
900	126.983	216.689	143.403	65.957	−472.219	−256.953	62.396
1000	132.763	230.367	151.423	78.945	−466.570	−233.331	50.994

Sept. 30, 1977

SULFURIC ACID, TETRAHYDRATE ($H_2SO_4 \cdot 4H_2O$) (LIQUID) GFW = 170.1342

$S^\circ_{298.15}$ = 99.079 ± 0.10 gibbs/mol
Tm = 244.90 ± 0.05 K

$\Delta Hf^\circ_{298.15}$ = −480.688 ± 0.2 kcal/mol
ΔHm° = 7.324 ± 0.06 kcal/mol

$H_{10}O_8S$

Heat of Formation

The heat of formation of the tetrahydrate of sulfuric acid is derived from the heat of solution data of Giauque et al. (1). We calculate ΔHf°_{298} for the tetrahydrate using ΔHr°_{298} = −12.880 kcal/mol for the solution process $H_2SO_4(\ell)$+ 4 $H_2O(\ell)$ = $H_2SO_4 \cdot 4\ H_2O(\ell)$ and auxiliary data for H_2SO_4 (2) and H_2O (3).

Heat Capacity and Entropy

The heat capacity has been measured experimentally (4) in the range 15-300 K and has been summarized by Giauque et al. (1). Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda (5) based on experimental data (273-573 K). These temperature-dependent values are corrected to current atomic weights, converted from IPTS-48 to IPTS-68, and adjusted graphically in the region 300-330 K so as to provide smoothly varying heat capacity values. In the region above 330 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy of 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and S°_{15} = 0.687 cal/(mol K).

Melting Data

The melting point and heat of melting have been measured calorimetrically by Hornung and Giauque (4). The values adopted in this table for Tm and ΔHm° differ from those reported by Hornung and Giauque (4) by 0.02 K and 2 cal/mol, respectively. This is due to the re-analysis of this data by Giauque et al. (1) and a conversion of the resulting Tm value from IPTS-48 to IPTS-68.

References

1. W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Am. Chem. Soc. 82, 62 (1960).
2. JANAF Thermochemical Tables: $H_2SO_4(\ell)$, 9-30-77.
3. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
4. E. W. Hornung and W. F. Giauque, J. Am. Chem. Soc. 77, 2983 (1955).
5. Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

SULFURIC ACID, HEMIHEXAHYDRATE $H_{15}O_{10.5}S$
(LIQUID) GFW=215.1722

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	136.309	140.498	140.498	0.000	-653.265	-619.750	454.283
300	136.389	141.342	140.501	0.252	-653.160	-619.546	451.333
400	139.409	180.993	145.887	14.043	-648.250	-609.152	332.820
500	142.419	212.425	156.157	28.134	-643.643	-599.922	262.222
600	145.429	238.657	167.780	42.526	-639.158	-591.597	215.486
700	148.439	261.301	179.559	57.220	-634.657	-584.080	182.330
800	151.450	281.319	191.051	72.214	-643.143	-578.347	157.995
900	154.460	299.331	202.098	87.510	-638.146	-570.549	138.546
1000	157.470	315.761	212.655	103.106	-633.055	-563.305	123.108

Sept. 30, 1977

SULFURIC ACID, HEMIHEXAHYDRATE ($H_2SO_4 \cdot 6.5H_2O$) (LIQUID) GFW = 215.1722

$S^\circ_{298.15}$ = 140.498 ± 0.15 gibbs/mol

Tm = 220.30 ± 0.05 K

$\Delta Hf^\circ_{298.15}$ = -653.265 ± 0.2 kcal/mol

ΔHm° = 8.154 ± 0.08 kcal/mol

$H_{15}O_{10.5}S$

Heat of Formation

The heat of formation of the hemihexahydrate of sulfuric acid is derived from the heat of solution data of Giauque et al. (1). We calculate ΔHf°_{298} for the hemihexahydrate using ΔHr°_{298} = -14.669 kcal/mol for the solution process $H_2SO_4(\ell) + 6.5H_2O(\ell) = H_2SO_4 \cdot 6.5H_2O(\ell)$ and auxiliary data for H_2SO_4 (2) and H_2O (3).

Heat Capacity and Entropy

The heat capacity has been measured experimentally (4) in the range 15-300 K and has been summarized by Giauque et al. (1). Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda (5) based on experimental data (273-573 K). These temperature-dependent values are corrected to current atomic weights, converted from IPTS-48 to IPTS-68, and adjusted graphically in the region 300-320 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and S°_{15} = 0.721 cal/(mol K).

Melting Data

The melting point and heat of melting have been measured calorimetrically by Hornung et al. These data were re-evaluated by Giauque et al. (1). We have adopted the revised values and have also corrected Tm to the IPTS-68.

References

1. W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Am. Chem. Soc. 82, 62 (1960).
2. JANAF Thermochemical Tables: $H_2SO_4(\ell)$, 9-30-77.
3. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
4. E. W. Hornung, T. E. Brackett, and W. F. Giauque, J. Am. Chem. Soc. 78, 5747 (1956).
5. Om. P. Kharbanda, Ind. Chemist 31, 538 (1955).

HELIUM, MONATOMIC (HE) HE

(REFERENCE STATE - IDEAL GAS) GFW=4.00260

	gibbs/mol			kcal/mol			
T, °K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	0.000	0.000	INFINITE	-1.481	0.000	0.000	0.000
100	4.968	24.698	34.542	-0.984	0.000	0.000	0.000
200	4.968	28.141	30.579	-0.488	0.000	0.000	0.000
298	4.968	30.125	30.125	0.000	0.000	0.000	0.000
300	4.968	30.156	30.125	0.009	0.000	0.000	0.000
400	4.968	31.585	30.320	0.506	0.000	0.000	0.000
500	4.968	32.693	30.688	1.003	0.000	0.000	0.000
600	4.968	33.599	31.100	1.500	0.000	0.000	0.000
700	4.968	34.365	31.513	1.996	0.000	0.000	0.000
800	4.968	35.028	31.912	2.493	0.000	0.000	0.000
900	4.968	35.614	32.291	2.990	0.000	0.000	0.000
1000	4.968	36.137	32.650	3.487	0.000	0.000	0.000
1100	4.968	36.610	32.989	3.984	0.000	0.000	0.000
1200	4.968	37.043	33.309	4.480	0.000	0.000	0.000
1300	4.968	37.440	33.612	4.977	0.000	0.000	0.000
1400	4.968	37.809	33.899	5.474	0.000	0.000	0.000
1500	4.968	38.151	34.171	5.971	0.000	0.000	0.000
1600	4.968	38.472	34.430	6.468	0.000	0.000	0.000
1700	4.968	38.773	34.676	6.964	0.000	0.000	0.000
1800	4.968	39.057	34.912	7.461	0.000	0.000	0.000
1900	4.968	39.326	35.137	7.958	0.000	0.000	0.000
2000	4.968	39.581	35.353	8.455	0.000	0.000	0.000
2100	4.968	39.823	35.560	8.952	0.000	0.000	0.000
2200	4.968	40.054	35.759	9.448	0.000	0.000	0.000
2300	4.968	40.275	35.951	9.945	0.000	0.000	0.000
2400	4.968	40.486	36.135	10.442	0.000	0.000	0.000
2500	4.968	40.689	36.314	10.939	0.000	0.000	0.000
2600	4.968	40.884	36.486	11.436	0.000	0.000	0.000
2700	4.968	41.071	36.652	11.932	0.000	0.000	0.000
2800	4.968	41.252	36.813	12.429	0.000	0.000	0.000
2900	4.968	41.426	36.969	12.926	0.000	0.000	0.000
3000	4.968	41.595	37.121	13.423	0.000	0.000	0.000
3100	4.968	41.758	37.268	13.920	0.000	0.000	0.000
3200	4.968	41.916	37.410	14.416	0.000	0.000	0.000
3300	4.968	42.068	37.549	14.913	0.000	0.000	0.000
3400	4.968	42.217	37.684	15.410	0.000	0.000	0.000
3500	4.968	42.361	37.816	15.907	0.000	0.000	0.000
3600	4.968	42.501	37.944	16.404	0.000	0.000	0.000
3700	4.968	42.637	38.069	16.900	0.000	0.000	0.000
3800	4.968	42.769	38.191	17.397	0.000	0.000	0.000
3900	4.968	42.898	38.310	17.894	0.000	0.000	0.000
4000	4.968	43.024	38.426	18.391	0.000	0.000	0.000
4100	4.968	43.147	38.540	18.888	0.000	0.000	0.000
4200	4.968	43.266	38.651	19.384	0.000	0.000	0.000
4300	4.968	43.383	38.760	19.881	0.000	0.000	0.000
4400	4.968	43.498	38.866	20.378	0.000	0.000	0.000
4500	4.968	43.609	38.970	20.875	0.000	0.000	0.000
4600	4.968	43.718	39.072	21.372	0.000	0.000	0.000
4700	4.968	43.825	39.172	21.868	0.000	0.000	0.000
4800	4.968	43.930	39.270	22.365	0.000	0.000	0.000
4900	4.968	44.032	39.367	22.862	0.000	0.000	0.000
5000	4.968	44.133	39.461	23.359	0.000	0.000	0.000
5100	4.968	44.231	39.553	23.855	0.000	0.000	0.000
5200	4.968	44.328	39.644	24.352	0.000	0.000	0.000
5300	4.968	44.422	39.734	24.849	0.000	0.000	0.000
5400	4.968	44.515	39.821	25.346	0.000	0.000	0.000
5500	4.968	44.606	39.907	25.843	0.000	0.000	0.000
5600	4.968	44.696	39.992	26.339	0.000	0.000	0.000
5700	4.968	44.784	40.075	26.836	0.000	0.000	0.000
5800	4.968	44.870	40.157	27.333	0.000	0.000	0.000
5900	4.968	44.955	40.238	27.830	0.000	0.000	0.000
6000	4.968	45.038	40.317	28.327	0.000	0.000	0.000

March 31, 1977

HELIUM, MONATOMIC (He) (REFERENCE STATE - IDEAL GAS) GFW = 4.00260

0 to 6000K Ideal Gas

Ground State Configuration $^1S_0$
$S°_{298.15}$ = 30.125 ± 0.003 gibbs/mol
T_b = 4.215 K

$\Delta Hf°_0$ = 0 kcal/mol
$\Delta Hf°_{298.15}$ = 0 kcal/mol

HE

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Martin (1). All predicted levels have been observed through n = 4 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (2) has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 159,000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of proper fill and cutoff procedures (2).

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations (3). The tables agree within the estimated uncertainty with those by Hultgren et al. (4) and McBride et al. (5). The estimated uncertainty is due to uncertainties in the gram formula weight and fundamental constants which are based on the 1971 scale (6) and the 1973 values (7), respectively.

The thermodynamic functions reported here are calculated assuming that helium gas obeys Boltzmann statistics. In fact helium is a Bose-Einstein gas (4). *However, the differences in thermal* properties between the two are very small except at extremely low temperature (8,9). At 298.15 K the difference in Cp° amounts to only 0.001 gibbs/mol and will be less at higher temperatures. Since Cp° is the most sensitive of the thermodynamic properties the differences are well within the stated uncertainty. At temperatures below approximately 50 K the differences may become significant and Bose-Einstein statistics should be used.

Phase Data

The boiling point (T_b) is taken from Hultgren et al. (4). This value should prove reasonably accurate, although it has not been evaluated by the present authors, and is furnished for the convenience of the reader. Unlike other elements, helium does not solidify at any temperature under standard conditions (1 atm. pressure). As a result of the low value of T_b the reference state for helium is chosen to be the ideal gas at all temperatures down to 0 K. This may differ from the choice of other authors. The tables of Hultgren et al. (4), among others, use appropriate condensed states of helium as reference states and will differ from the present work at low temperature.

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HE

HELIUM UNIPOSITIVE ION (HE^+) HE^+
(IDEAL GAS) GFW=4.00205

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0				-1.481	566.999		
100							
200							
298	4.968	31.502	31.502	0.000	568.480	566.582	-415.310
300	4.968	31.533	31.502	0.009	568.489	566.570	-412.741
400	4.968	32.962	31.697	0.506	568.986	565.856	-309.165
500	4.968	34.071	32.065	1.003	569.483	565.016	-246.965
600	4.968	34.976	32.477	1.500	569.980	564.076	-205.462
700	4.968	35.742	32.890	1.996	570.477	563.053	-175.791
800	4.968	36.405	33.289	2.493	570.973	561.958	-153.518
900	4.968	36.991	33.668	2.990	571.470	560.801	-136.179
1000	4.968	37.514	34.027	3.487	571.967	559.589	-122.296
1100	4.968	37.988	34.366	3.984	572.464	558.327	-110.928
1200	4.968	38.420	34.686	4.480	572.961	557.021	-101.446
1300	4.968	38.817	34.989	4.977	573.457	555.672	-93.416
1400	4.968	39.186	35.276	5.474	573.954	554.285	-86.527
1500	4.968	39.528	35.548	5.971	574.451	552.863	-80.551
1600	4.968	39.849	35.807	6.468	574.947	551.407	-75.318
1700	4.968	40.150	36.053	6.964	575.445	549.921	-70.696
1800	4.968	40.434	36.289	7.461	575.941	548.406	-66.585
1900	4.968	40.703	36.514	7.958	576.438	546.862	-62.903
2000	4.968	40.958	36.730	8.455	576.935	545.293	-59.586
2100	4.968	41.200	36.937	8.952	577.431	543.698	-56.583
2200	4.968	41.431	37.136	9.448	577.929	542.080	-53.850
2300	4.968	41.652	37.328	9.945	578.425	540.440	-51.353
2400	4.968	41.863	37.512	10.442	578.922	538.778	-49.062
2500	4.968	42.066	37.691	10.939	579.419	537.095	-46.952
2600	4.968	42.261	37.863	11.436	579.915	535.391	-45.003
2700	4.968	42.448	38.029	11.932	580.413	533.670	-43.197
2800	4.968	42.629	38.190	12.429	580.909	531.930	-41.518
2900	4.968	42.804	38.346	12.926	581.406	530.172	-39.954
3000	4.968	42.972	38.498	13.423	581.903	528.397	-38.493
3100	4.968	43.135	38.645	13.920	582.399	526.604	-37.125
3200	4.968	43.293	38.787	14.416	582.897	524.797	-35.842
3300	4.968	43.445	38.926	14.913	583.393	522.974	-34.635
3400	4.968	43.594	39.061	15.410	583.890	521.135	-33.498
3500	4.968	43.738	39.193	15.907	584.387	519.282	-32.425
3600	4.968	43.878	39.321	16.404	584.883	517.415	-31.411
3700	4.968	44.014	39.446	16.900	585.381	515.534	-30.451
3800	4.968	44.146	39.568	17.397	585.877	513.640	-29.541
3900	4.968	44.275	39.687	17.894	586.374	511.733	-28.676
4000	4.968	44.401	39.803	18.391	586.870	509.811	-27.854
4100	4.968	44.524	39.917	18.888	587.367	507.879	-27.072
4200	4.968	44.644	40.028	19.384	587.865	505.935	-26.326
4300	4.968	44.760	40.137	19.881	588.361	503.979	-25.615
4400	4.968	44.875	40.243	20.378	588.858	502.011	-24.935
4500	4.968	44.986	40.347	20.875	589.354	500.030	-24.284
4600	4.968	45.095	40.449	21.372	589.851	498.040	-23.662
4700	4.968	45.202	40.549	21.868	590.348	496.039	-23.066
4800	4.968	45.307	40.647	22.365	590.845	494.028	-22.493
4900	4.968	45.409	40.744	22.862	591.342	492.005	-21.944
5000	4.968	45.510	40.838	23.359	591.838	489.972	-21.416
5100	4.968	45.608	40.930	23.855	592.336	487.931	-20.909
5200	4.968	45.705	41.021	24.352	592.832	485.879	-20.421
5300	4.968	45.799	41.111	24.849	593.329	483.817	-19.950
5400	4.968	45.892	41.198	25.346	593.826	481.746	-19.497
5500	4.968	45.983	41.284	25.843	594.322	479.665	-19.060
5600	4.968	46.073	41.369	26.339	594.820	477.577	-18.638
5700	4.968	46.161	41.452	26.836	595.316	475.479	-18.231
5800	4.968	46.247	41.534	27.333	595.813	473.372	-17.837
5900	4.968	46.332	41.615	27.830	596.310	471.257	-17.456
6000	4.968	46.415	41.694	28.327	596.806	469.132	-17.088

March 31, 1977

HELIUM UNIPOSITIVE ION (He^+) (IDEAL GAS) GFW = 4.00205

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 31.502 ± 0.003 gibbs/mol

ΔHf°_0 = 566.998 ± 0.001 kcal/mol HE^+

$\Delta Hf^\circ_{298.15}$ = 568.480 ± 0.003 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^2S_{1/2}$	0	2

Heat of Formation

The ionization limit of neutral helium (198310.76±0.01 cm^{-1}) reported by Moore (1) is adopted as ΔHf°_0 for $He^+(g)$. The ionization limit is converted from cm^{-1} to kcal/mol using the factor, 1 cm^{-1} = 2.859144 x 10^{-3} kcal/mol, which is derived from the latest CODATA fundamental constants (2). The uncertainity in the ionization limit corresponds to an uncertainty of ±0.00003 kcal/mol in ΔHf°_0. The value of ΔHf°_{298} is derived from ΔHf°_0 using auxiliary JANAF data (3).

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights by Moore (4) is complete to n = 15. Our calculations indicate that any reasonable method of including these levels and cutting off the summation in the partition function (5) has no effect on the thermodynamic functions to 6000 K. This is a result of high energy of these levels; the first excited level is over 329,000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state. The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (5).

The thermodynamic functions reported here agree with those by Green et al. (6) and Hilsenrath et al. (7) within the limits of the uncertainty.

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HE^+

SILICON MONOIODIDE (SiI) ISi

(IDEAL GAS) GFW=154.9905

T, °K	gibbs/mol			kcal/mol			Log Kp
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	
0	0.000	0.000	INFINITE	-2.375	74.930	74.930	INFINITE
100	7.277	51.635	68.368	-1.673	75.203	70.861	-154.865
200	8.541	57.067	61.478	-0.882	75.125	66.538	-72.710
298	9.330	60.646	60.646	0.000	74.959	62.357	-45.709
300	9.339	60.703	60.646	0.017	74.955	62.279	-45.370
400	9.617	63.437	61.017	0.968	72.813	58.152	-31.773
500	9.651	65.589	61.724	1.933	67.472	54.996	-24.039
600	9.603	67.345	62.519	2.896	67.419	52.504	-19.124
700	9.537	68.821	63.317	3.853	67.341	50.024	-15.618
800	9.477	70.090	64.086	4.803	67.242	47.556	-12.992
900	9.427	71.203	64.816	5.748	67.123	45.104	-10.953
1000	9.387	72.194	65.505	6.689	66.987	42.664	-9.326
1100	9.357	73.087	66.154	7.626	66.835	40.239	-7.995
1200	9.335	73.901	66.767	8.561	66.670	37.828	-6.889
1300	9.319	74.647	67.344	9.493	66.494	35.431	-5.957
1400	9.307	75.337	67.891	10.425	66.304	33.049	-5.159
1500	9.300	75.979	68.409	11.355	66.103	30.681	-4.470
1600	9.296	76.579	68.901	12.285	65.891	28.327	-3.869
1700	9.295	77.143	69.370	13.214	53.674	26.091	-3.354
1800	9.296	77.674	69.816	14.144	53.495	24.474	-2.972
1900	9.299	78.177	70.243	15.074	53.315	22.866	-2.630
2000	9.303	78.654	70.652	16.004	53.135	21.269	-2.324
2100	9.309	79.108	71.044	16.934	52.955	19.680	-2.048
2200	9.315	79.541	71.420	17.865	52.775	18.099	-1.798
2300	9.324	79.955	71.782	18.797	52.595	16.527	-1.570
2400	9.333	80.352	72.131	19.730	52.415	14.964	-1.363
2500	9.343	80.734	72.468	20.664	52.236	13.406	-1.172
2600	9.355	81.100	72.793	21.599	52.057	11.856	-0.997
2700	9.369	81.454	73.107	22.535	51.878	10.313	-0.835
2800	9.384	81.795	73.411	23.473	51.700	8.779	-0.685
2900	9.401	82.124	73.706	24.412	51.523	7.249	-0.546
3000	9.420	82.443	73.992	25.353	51.347	5.723	-0.417
3100	9.441	82.752	74.270	26.296	51.173	4.205	-0.296
3200	9.464	83.052	74.539	27.241	51.000	2.695	-0.184
3300	9.490	83.344	74.802	28.189	50.829	1.188	-0.079
3400	9.519	83.628	75.057	29.139	50.660	-0.314	0.020
3500	9.551	83.904	75.306	30.093	50.493	-1.811	0.113
3600	9.586	84.174	75.549	31.050	-41.632	-1.046	0.064
3700	9.625	84.437	75.785	32.010	-41.694	0.081	-0.005
3800	9.667	84.694	76.016	32.975	-41.753	1.212	-0.070
3900	9.713	84.946	76.242	33.944	-41.809	2.342	-0.131
4000	9.763	85.192	76.463	34.917	-41.860	3.475	-0.190
4100	9.816	85.434	76.679	35.896	-41.908	4.608	-0.246
4200	9.874	85.671	76.890	36.881	-41.951	5.743	-0.299
4300	9.936	85.904	77.097	37.871	-41.988	6.878	-0.350
4400	10.002	86.134	77.300	38.868	-42.021	8.014	-0.398
4500	10.072	86.359	77.499	39.872	-42.046	9.157	-0.445
4600	10.146	86.581	77.694	40.883	-42.065	10.294	-0.489
4700	10.225	86.800	77.885	41.901	-42.077	11.431	-0.532
4800	10.308	87.016	78.073	42.928	-42.081	12.570	-0.572
4900	10.394	87.230	78.258	43.963	-42.078	13.710	-0.611
5000	10.485	87.441	78.439	45.007	-42.066	14.845	-0.649
5100	10.580	87.649	78.618	46.060	-42.046	15.986	-0.685
5200	10.679	87.856	78.794	47.123	-42.017	17.122	-0.720
5300	10.782	88.060	78.966	48.196	-41.977	18.260	-0.753
5400	10.889	88.263	79.137	49.280	-41.928	19.397	-0.785
5500	10.999	88.463	79.304	50.374	-41.869	20.529	-0.816
5600	11.113	88.663	79.470	51.480	-41.800	21.664	-0.845
5700	11.230	88.860	79.633	52.597	-41.720	22.799	-0.874
5800	11.350	89.057	79.794	53.726	-41.630	23.930	-0.902
5900	11.473	89.252	79.952	54.867	-41.528	25.056	-0.928
6000	11.599	89.446	80.109	56.020	-41.414	26.185	-0.954

Dec. 31, 1976

SILICON MONOIODIDE (SiI) (IDEAL GAS) GFW = 154.9905

ISi

D_0° = 57.3 ± 8 kcal/mol

$S^\circ_{298.15}$ = 60.65 ± 0.10 gibbs/mol

Symmetry Number = 1

ΔHf°_0 = 74.9 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 75.0 ± 10 kcal/mol

Electronic Levels and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(1)	X $^2\Pi_{1/2}$	0	2	2.45	0.123	[0.001]	363.2	1.25
(1,6)	$^2\Pi_{3/2}$	650	2	2.45	0.123	[0.001]	358.5	1.1
(1)	A' $^4\Sigma_{1/2}$	20939.1	4	2.50	0.118	[0.001]	275.3	5.6
(1)	A $^2\Sigma^+$	21204.9	2	2.95	0.085	[0.001]	208.3	1.66
(1)	B $^2\Sigma^+$	32380.3	2	[2.45]	[0.123]	[0.001]	471.0	0.9
(6)	C $^2\Pi$	42710	4	[2.45]	[0.123]	[0.001]	485	3.5

Heat of Formation

The adopted value is ΔHf°_{298} = 75.0±10 kcal/mol. The value is based on a Birge-Sponer extrapolation of the $A^2\Sigma$ state by Billingsley (1) who obtains a dissociation limit of 69.76 kcal/mol. Correction for the ionic character of the bond according to Hildenbrand (2) yields D_0° = 57.3 kcal/mol which, with auxiliary JANAF data (3), gives the adopted value. An uncertainity of ±10 kcal/mol is assigned to ΔHf°_{298} due to the approximate nature of Birge-Sponer extrapolations based on data from the first few vibrational levels only. The adopted value of D_0° = 57.3±8 kcal/mol is in good agreement with D_0° = 56.9 and 61.8 kcal/mol obtained in a similar manner from the A' $^4\Sigma^-$ state and ground state data, respectively. The value is also in reasonable agreement with D_0° = 72.4 and 65±10 kcal/mol obtained by theoretical and empirical procedures, respecitvely (4, 5). The upper limit for D_0° = 4.02 ev (92.7 kcal/mol) is based on the observed predissociation of the $B^2\Sigma$ state (1). The adopted value of D_0° is also in good agreement with the average (per bond) heat of atomization of SiI_4(g) of 58.6 kcal/mol (3).

Heat Capacity and Entropy

Electronic levels and molecular constants are taken from the studies by Oldershaw and Robinson (6) and Billingsley (1). Several systems above 40,000 cm^{-1} have been observed by Oldershaw and Robinson (7) but are not included since their states and degeneracies are not known. They would make only a minor contribution to the thermodynamic properties at 6000°K and a negligible contribution at lower temperatures. Of more importance is the uncertainity in the value of the ground state spin splitting constant and the energy of the A' $^4\Sigma^-$ state. Billingsley (1) interprets the observed A'-X emission spectrum as terminating at the upper level of the split ground state and calculates the ground state splitting of 646.4 cm^{-1} from the observation of one absorption line. Lakshminarayana and Haranath (8) observe a second emission series 650.3 cm^{-1} to the red of that observed by Billingsley, and although the ground state splittings are in agreement, this would place the A' state approximately 650 cm^{-1} lower than reported. We favor Billingsley's interpretation while recognizing the need for additional work to resolve this paradox. In addition the B' $^2\Delta$ state observed for the other silicon monohalides (3) is not observed for SiI. It's energy is difficult to predict due to the rapidly dropping energy of this state across the series and the possible misidentification of this state for SiBr. Accordingly, we have assigned an uncertainty of ±0.1 gibbs/mol to S°_{298} to account for this uncertainty. Since no information is available on the rotational constants for the B and C states the ground state B_e = .123 cm^{-1} was used in our calculations. Likewise, values of α_e = .001 cm^{-1} are estimated for all states. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant (A = 650 cm^{-1}). This leads to slightly biased results at low temperature; the stated uncertainty in S°_{298} should account for this also. All molecular constants have been corrected to reflect the natural abundance of Si.

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ISi

SILICON DIIODIDE (SiI_2) I_2Si

(IDEAL GAS) GFW=281.8945

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-3.296	22.727	22.727	INFINITE
100	10.344	63.776	87.690	-2.391	22.839	18.011	-39.362
200	12.272	71.619	77.862	-1.249	22.522	13.295	-14.528
298	13.055	76.688	76.688	0.000	22.100	8.853	-6.489
300	13.065	76.768	76.688	0.024	22.091	8.771	-6.389
400	13.407	80.580	77.205	1.350	17.738	4.540	-2.480
500	13.580	83.592	78.192	2.700	7.021	2.262	-0.989
600	13.677	86.078	79.305	4.063	6.919	1.318	-0.480
700	13.738	88.191	80.427	5.434	6.806	0.394	-0.123
800	13.777	90.028	81.515	6.810	6.681	-0.514	0.140
900	13.805	91.652	82.553	8.189	6.544	-1.405	0.341
1000	13.825	93.108	83.537	9.571	6.397	-2.280	0.498
1100	13.839	94.426	84.468	10.954	6.238	-3.141	0.624
1200	13.851	95.631	85.349	12.339	6.069	-3.986	0.726
1300	13.859	96.740	86.183	13.724	5.890	-4.816	0.810
1400	13.866	97.767	86.974	15.111	5.700	-5.632	0.879
1500	13.872	98.724	87.726	16.497	5.498	-6.436	0.938
1600	13.877	99.620	88.441	17.885	5.287	-7.223	0.987
1700	13.881	100.461	89.124	19.273	-6.929	-7.893	1.015
1800	13.884	101.254	89.776	20.661	-7.108	-7.944	0.965
1900	13.887	102.005	90.400	22.050	-7.288	-7.986	0.919
2000	13.889	102.718	90.998	23.438	-7.470	-8.019	0.876
2100	13.892	103.395	91.573	24.827	-7.652	-8.041	0.837
2200	13.895	104.042	92.125	26.217	-7.835	-8.057	0.800
2300	13.897	104.659	92.657	27.606	-8.020	-8.062	0.766
2400	13.901	105.251	93.169	28.996	-8.205	-8.058	0.734
2500	13.904	105.818	93.664	30.386	-8.392	-8.050	0.704
2600	13.909	106.364	94.142	31.777	-8.579	-8.032	0.675
2700	13.914	106.889	94.604	33.168	-8.768	-8.008	0.648
2800	13.921	107.395	95.052	34.560	-8.957	-7.974	0.622
2900	13.929	107.884	95.486	35.953	-9.146	-7.936	0.598
3000	13.938	108.356	95.907	37.346	-9.337	-7.894	0.575
3100	13.949	108.813	96.316	38.740	-9.528	-7.842	0.553
3200	13.962	109.256	96.714	40.136	-9.718	-7.783	0.532
3300	13.976	109.686	97.100	41.533	-9.909	-7.718	0.511
3400	13.993	110.104	97.477	42.931	-10.100	-7.650	0.492
3500	14.011	110.509	97.843	44.331	-10.290	-7.575	0.473
3600	14.032	110.904	98.201	45.733	-102.441	-5.238	0.318
3700	14.055	111.289	98.549	47.138	-102.530	-2.538	0.150
3800	14.080	111.664	98.889	48.544	-102.619	0.166	-0.010
3900	14.107	112.030	99.222	49.954	-102.707	2.872	-0.161
4000	14.136	112.388	99.546	51.366	-102.794	5.578	-0.305
4100	14.167	112.737	99.864	52.781	-102.880	8.290	-0.442
4200	14.200	113.079	100.175	54.199	-102.964	11.003	-0.573
4300	14.234	113.414	100.479	55.621	-103.045	13.714	-0.697
4400	14.271	113.741	100.776	57.046	-103.126	16.430	-0.816
4500	14.309	114.062	101.068	58.475	-103.203	19.155	-0.930
4600	14.349	114.377	101.354	59.908	-103.277	21.874	-1.039
4700	14.390	114.686	101.634	61.345	-103.349	24.593	-1.144
4800	14.432	114.990	101.909	62.786	-103.418	27.316	-1.244
4900	14.476	115.288	102.179	64.232	-103.483	30.042	-1.340
5000	14.520	115.581	102.444	65.681	-103.547	32.765	-1.432
5100	14.566	115.869	102.705	67.136	-103.605	35.494	-1.521
5200	14.612	116.152	102.961	68.594	-103.663	38.220	-1.606
5300	14.658	116.431	103.212	70.058	-103.714	40.951	-1.689
5400	14.705	116.705	103.460	71.526	-103.764	43.682	-1.768
5500	14.752	116.975	103.703	72.999	-103.810	46.409	-1.844
5600	14.799	117.242	103.942	74.477	-103.853	49.140	-1.918
5700	14.847	117.504	104.178	75.959	-103.893	51.876	-1.989
5800	14.894	117.763	104.410	77.446	-103.930	54.609	-2.058
5900	14.940	118.018	104.638	78.938	-103.963	57.339	-2.124
6000	14.987	118.269	104.863	80.434	-103.994	60.075	-2.188

Dec. 31, 1976; Dec. 31, 1977

SILICON DIIODIDE (SiI_2) (IDEAL GAS) GFW = 281.8945

ΔHa°_0 = 135.2 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = [76.69 ± 1.0] gibbs/mol

ΔHf°_0 = 22.7 ± 2.0 kcal/mol I_2Si

$\Delta Hf^\circ_{298.15}$ = 22.1 ± 2.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$^1A_1$]	0	[1]
[$^3B_1$]	[20000]	[3]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[350](1)
[90](1)
[350](1)

Point Group: [C_{2v}] [σ=2]

Bond Distance: Si-I = [2.44] Å

Bond Angle: I-Si-I = [113°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.4192×10^{-112}] g^3 cm^6

Heat of Formation

An equilibrium system involving $SiI_2(g)$ has been studied by Schäfer et al. (1) and Wolf and Herbst (2). They both used a flow technique in an argon atmosphere. A second and third law analysis of their results (reported only in equation form) is summarized below. As in the case of $SiCl_2(g)$ and $SiBr_2(g)$ (3), there is acceptable agreement between the third law results of these two studies. Using the mean ΔHf°_{298}, we calculate and adopt $\Delta Hf^\circ_{298}(SiI_2,g)$ = 22.1 kcal/mol. This corresponds to ΔHa°_0 = 135.2 kcal/mol and an average bond energy of 67.6 kcal/mol. In comparison, the average bond energy of $SiI_4(g)$ is 58.6 kcal/mol. This implies that the average bond energy is 15% stronger in SiI_2 than in SiI_4.

			ΔHr°_{298}, SiI or kcal/mol		drift	$\Delta Hf^\circ_{298}(g)$*
Source	Reaction	Range, K	2nd law	3rd law	gibbs/mol	kcal/mol
(1)	$SiI_4(g) = SiI_2(g) + 2I(g)$	1361-1526	98.92	101.04	1.46	23.60
(2)	$Si(c) + I_2(g) = SiI_2(g)$	1300-1470	3.21	5.14	1.38	20.60
(4)	$SiI_4(g) + Si(c) = 2SiI_2(g)$	1173-1373	83.90	68.09	-12.42	20.84

*Based on third law ΔHr°_{298} value and auxiliary data (3).

Uchimura et al. (4) also studied $SiI_2(g)$. An analysis of their equilibrium data yields $\Delta Hf^\circ_{298}(SiI_2,g)$ = 20.84 kcal/mol which is in good agreement with our adopted value. However, because of the large drift (-12.42 gibbs/mol), no weight was given to this study.

Heat Capacity and Entropy

The Si-I bond distance is assumed to be the same as in SiH_2I_2 (3). The bond angle is estimated to be 113° based on the trend observed in SiF_2, $SiCl_2$, and $SiBr_2$ (3). C_{2v} symmetry is also assumed to be consistent with the other three silicon dihalides. The principal moments of inertia are $I_A = 7.615 \times 10^{-39}$, $I_B = 174.5 \times 10^{-39}$, and $I_C = 182.1 \times 10^{-39}$ g cm^2.

The vibrational frequencies are estimated based on trends observed in the SiX_2 and SiH_2X_2 species, where X = F, Cl Br, and I (3). As suggested by SiF_2 and $SiCl_2$, an electronic excited state is included at 20000 cm^{-1}.

References

1. H. Schäfer, H. Bruderrick, and B. Morcher, Z. Anorg. Allg. Chem. 352, 122 (1967).
2. E. Wolf and C. Herbst, Z. Chem. 7, 34 (1967).
3. JANAF Thermochemical Tables: Si(g), 3-31-67; I(g), 6-30-74; $SiH_2F_2(g)$ and $SiI_4(g)$, 6-30-76, $SiBr_4(g)$, $SiH_2X_2(g)$, X = Cl, Br, I, 12-31-76; $SiF_2(g)$, $SiCl_2(g)$, and $SiBr_2(g)$, 12-31-77.
4. K. Uchimura, T. Takuma, M. Yuizumi, and T. Kunugi, Denki Kagaku 35, 876 (1967).

SILICON TRIIODIDE (SiI_3)
(IDEAL GAS) GFW=408.7990

I_3Si

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-4.440	9.500	9.500	INFINITE
100	14.050	72.416	105.814	-3.340	9.443	4.480	-9.791
200	17.178	83.258	92.045	-1.757	8.977	-0.308	0.337
298	18.449	90.391	90.391	0.000	8.440	-4.755	3.485
300	18.464	90.505	90.391	0.034	8.429	-4.836	3.523
400	19.029	95.904	91.123	1.912	2.042	-8.965	4.898
500	19.316	100.184	92.522	3.831	-13.867	-10.203	4.460
600	19.480	103.722	94.103	5.772	-13.840	-9.475	3.451
700	19.581	106.733	95.697	7.725	-13.820	-8.748	2.731
800	19.648	109.352	97.244	9.687	-13.810	-8.024	2.192
900	19.694	111.469	98.721	11.654	-13.811	-7.301	1.773
1000	19.727	113.746	100.121	13.625	-13.821	-6.577	1.437
1100	19.752	115.627	101.446	15.599	-13.843	-5.852	1.163
1200	19.771	117.347	102.701	17.575	-13.875	-5.125	0.933
1300	19.786	118.930	103.889	19.553	-13.914	-4.393	0.739
1400	19.798	120.397	105.017	21.532	-13.970	-3.658	0.571
1500	19.807	121.763	106.088	23.512	-14.034	-2.921	0.426
1600	19.815	123.042	107.108	25.494	-14.109	-2.175	0.297
1700	19.821	124.243	108.081	27.475	-26.189	-1.322	0.170
1800	19.827	125.376	109.011	29.458	-26.232	0.142	-0.017
1900	19.831	126.448	109.900	31.441	-26.278	1.608	-0.185
2000	19.835	127.466	110.754	33.424	-26.324	3.076	-0.336
2100	19.839	128.433	111.573	35.408	-26.372	4.549	-0.473
2200	19.842	129.356	112.360	37.392	-26.422	6.020	-0.598
2300	19.844	130.238	113.118	39.376	-26.474	7.497	-0.712
2400	19.847	131.083	113.849	41.361	-26.527	8.977	-0.817
2500	19.849	131.893	114.555	43.345	-26.583	10.455	-0.914
2600	19.850	132.672	115.237	45.330	-26.640	11.938	-1.003
2700	19.852	133.421	115.897	47.315	-26.700	13.422	-1.086
2800	19.853	134.143	116.536	49.301	-26.761	14.913	-1.164
2900	19.855	134.840	117.155	51.286	-26.824	16.402	-1.234
3000	19.856	135.513	117.756	53.272	-26.889	17.890	-1.303
3100	19.857	136.164	118.339	55.257	-26.956	19.385	-1.367
3200	19.858	136.794	118.906	57.243	-27.024	20.882	-1.426
3300	19.858	137.405	119.457	59.229	-27.096	22.382	-1.482
3400	19.859	137.998	119.994	61.215	-27.168	23.880	-1.535
3500	19.860	138.574	120.517	63.201	-27.242	25.384	-1.585
3600	19.861	139.133	121.026	65.187	-119.280	29.145	-1.769
3700	19.861	139.678	121.523	67.173	-119.260	33.265	-1.965
3800	19.862	140.207	122.008	69.159	-119.240	37.389	-2.150
3900	19.862	140.723	122.481	71.145	-119.225	41.511	-2.324
4000	19.863	141.226	122.943	73.131	-119.211	45.629	-2.493
4100	19.863	141.717	123.395	75.118	-119.200	49.753	-2.652
4200	19.864	142.195	123.837	77.104	-119.191	53.874	-2.803
4300	19.864	142.663	124.269	79.090	-119.183	57.990	-2.947
4400	19.864	143.119	124.693	81.077	-119.179	62.109	-3.085
4500	19.865	143.566	125.107	83.063	-119.176	66.237	-3.217
4600	19.865	144.002	125.513	85.050	-119.174	70.357	-3.343
4700	19.865	144.430	125.911	87.036	-119.174	74.473	-3.463
4800	19.866	144.848	126.301	89.023	-119.177	78.595	-3.578
4900	19.866	145.257	126.684	91.009	-119.180	82.718	-3.689
5000	19.866	145.659	127.059	92.996	-119.187	86.834	-3.795
5100	19.866	146.052	127.428	94.983	-119.194	90.956	-3.898
5200	19.866	146.438	127.790	96.969	-119.206	95.074	-3.996
5300	19.867	146.816	128.145	98.956	-119.216	99.198	-4.090
5400	19.867	147.188	128.495	100.943	-119.230	103.322	-4.182
5500	19.867	147.552	128.838	102.929	-119.246	107.438	-4.269
5600	19.867	147.910	129.175	104.916	-119.265	111.558	-4.354
5700	19.867	148.262	129.507	106.903	-119.285	115.685	-4.436
5800	19.868	148.667	129.833	108.889	-119.308	119.807	-4.514
5900	19.868	148.947	130.154	110.876	-119.332	123.925	-4.590
6000	19.868	149.281	130.470	112.863	-119.359	128.052	-4.664

Dec. 31, 1977

SILICON TRIIODIDE (SiI_3) (IDEAL GAS) GFW = 408.7990

ΔHa_0° = [174 ± 15] kcal/mol
$S^\circ_{298.15}$ = [90.39 ± 2.0] gibbs/mol
Ground State Quantum Weight = [2]

ΔHf_0° = [9.5 ± 15] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [8.4 ± 15] kcal/mol

I_3Si

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[286](1)
[122](1)
[399](2)
[80](2)

Point Group: = [C_{3v}]
σ = [3]
Bond Distance: Si-I − [2.435] Å
Bond Angle: I-Si-I = [112°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [10.3866 x 10^{-111}] g^3 cm^6

Heat of Formation

The heat of formation of $SiI_3(g)$ is based on an assumed average bond energy of 58±5 kcal/mol (1). This average bond energy is that of $SiI_4(g)$, i.e. $\Delta Ha_0^\circ(SiI_4,g)/4$. The rationale for this assumption is based on the same relationship existing for the silicon chloride and fluoride species (1).

Heat Capacity and Entropy

The molecular structure is assumed to be identical to the SiI_3 group in $SiHI_3$ (1). From this structure we estimate the following principal moments of inertia: $I_A = I_B = 173.89 \times 10^{-39}$, and $I_C = 343.48 \times 10^{-39}$ g cm^2. The vibrational frequencies are assumed to be those of the SiI_3 group in $SiHI_3(g)$.

References

1. JANAF Thermochemical Tables: $SiI_4(g)$, $SiCl_3(g)$, and $SiF_3(g)$, 12-31-77; $SiHI_3(g)$, 12-31-76.

I_3Si

SILICON TETRAIODIDE (SiI_4) I_4Si
(LIQUID) GFW=535.7035

T, K	gibbs/mol Cp°	S°	-(G°-H°298)/T	kcal/mol H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	38.193	70.342	70.342	0.000	-41.731	-44.810	32.846
303	38.211	70.578	70.342	0.071	-41.718	-44.829	32.458
400	39.198	81.706	71.853	3.941	-48.698	-45.706	24.972
500	40.185	90.559	74.738	7.910	-68.319	-43.123	18.849
600	41.172	97.972	78.009	11.978	-66.613	-38.245	13.930
700	42.159	104.393	81.329	16.145	-64.829	-33.656	10.508

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$S^\circ_{298.15}$ = 70.342 gibbs/mol
Tm = 393.65 ± 3.0 K (120.5°C)
Tb = 575.8 K

$\Delta Hf^\circ_{298.15}$ = -41.731 kcal/mol
ΔHm° = 4.7 ± 0.5 kcal/mol
ΔHv° = 11.53 kcal/mol

I_4Si

Heat of Formation

The heat of formation of $SiI_4(\ell)$ is calculated from that of $SiI_4(c)$ by adding ΔHm°, the heat of melting, and the enthalpy difference ($H^\circ_{393.65}-H^\circ_{298}$) between the crystal and liquid.

Heat Capacity and Entropy

Kurosawa et al. (1) measured the heat capacity of SiI_4 from the melting point to the boiling point (unspecified). No data was presented but rather smoothed results were represented by an equation, linear in T. This equation is extrapolated to 700K and to 298.15 K. S°_{298} is obtained in a manner analogous to that used for ΔHf°_{298}.

Vaporization Data

Tb is calculated as that temperature for which ΔGr° = 0 for the process $SiI_4(\ell) = SiI_4(g)$. ΔHv° is calculated as the difference between the ΔHf° values for the ideal gas and the liquid at Tb. The vaporization studies near T_b are discussed in the $SiI_4(g)$ table; they yielded normal boiling points (p = 760 mm Hg) of 574.7 K (2) and 573.7 K (3). The normal boiling point should be slightly lower than our calculated Tb which corresponds to f = 760 mm Hg.

References

1. T. Kurosawa, R. Hasegawa, and T. Yagihashi, Trans. Japan Inst. Metals 6, 229 (1965); Trans. Natl. Res. Metals (Tokyo) 7, 222 (1965).
2. H. C. Andersen and L. H. Belz, J. Am. Chem. Soc 75, 4828 (1953).
3. K. Uchimura, T. Takuma, M. Yuizumi, and T. Kunugi, Denki Kagaku 35, 876 (1967).

SILICON TETRAIODIDE (SiI_4) I_4Si
(IDEAL GAS) GFW=535.7035

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-5.784	-25.107	-25.107	INFINITE
100	18.785	75.879	119.684	-4.380	-25.225	-29.806	65.140
200	22.478	90.197	101.664	-2.293	-25.775	-34.179	37.349
298	24.037	99.506	99.506	0.000	-26.400	-38.175	27.983
300	24.056	99.655	99.506	0.044	-26.413	-38.247	27.863
400	24.764	106.684	100.460	2.490	-34.818	-41.817	22.848
500	25.126	112.253	102.281	4.986	-55.912	-41.563	18.167
600	25.333	116.854	104.338	7.510	-55.750	-38.711	14.100
700	25.462	120.770	106.412	10.050	-55.593	-35.883	11.203
800	25.547	124.176	108.425	12.601	-55.444	-33.077	9.036
900	25.606	127.188	110.345	15.159	-55.306	-30.289	7.355
1000	25.648	129.888	112.167	17.721	-55.178	-27.516	6.014
1100	25.680	132.335	113.891	20.288	-55.060	-24.757	4.919
1200	25.704	134.570	115.522	22.857	-54.954	-22.007	4.008
1300	25.723	136.628	117.068	25.429	-54.855	-19.264	3.239
1400	25.738	138.535	118.534	28.002	-54.771	-16.529	2.580
1500	25.750	140.311	119.927	30.576	-54.698	-13.802	2.011
1600	25.760	141.973	121.254	33.152	-54.635	-11.074	1.513
1700	25.769	143.535	122.519	35.728	-66.579	-8.249	1.061
1800	25.776	145.009	123.728	38.305	-66.486	-4.820	0.585
1900	25.781	146.402	124.885	40.883	-66.396	-1.397	0.161
2000	25.786	147.725	125.994	43.462	-66.307	2.019	-0.221
2100	25.791	148.983	127.059	46.040	-66.221	5.436	-0.566
2200	25.795	150.183	128.083	48.620	-66.137	8.843	-0.878
2300	25.798	151.330	129.069	51.199	-66.056	12.251	-1.164
2400	25.801	152.428	130.020	53.779	-65.976	15.656	-1.426
2500	25.803	153.481	130.937	56.359	-65.900	19.053	-1.666
2600	25.805	154.493	131.824	58.940	-65.825	22.450	-1.887
2700	25.807	155.467	132.682	61.521	-65.754	25.843	-2.092
2800	25.809	156.406	133.512	64.101	-65.686	29.239	-2.282
2900	25.811	157.311	134.317	66.682	-65.619	32.627	-2.459
3000	25.812	158.186	135.098	69.264	-65.555	36.009	-2.623
3100	25.814	159.033	135.857	71.845	-65.494	39.395	-2.777
3200	25.815	159.852	136.594	74.426	-65.435	42.779	-2.922
3300	25.816	160.647	137.311	77.008	-65.379	46.162	-3.057
3400	25.817	161.417	138.009	79.589	-65.326	49.539	-3.184
3500	25.818	162.166	138.688	82.171	-65.274	52.919	-3.304
3600	25.819	162.893	139.351	84.753	-157.187	58.550	-3.554
3700	25.819	163.600	139.996	87.335	-157.042	64.538	-3.812
3800	25.820	164.289	140.627	89.917	-156.899	70.527	-4.056
3900	25.821	164.960	141.242	92.499	-156.761	76.511	-4.288
4000	25.821	165.613	141.843	95.081	-156.625	82.485	-4.507
4100	25.822	166.251	142.431	97.663	-156.492	88.467	-4.716
4200	25.823	166.873	143.005	100.245	-156.362	94.440	-4.914
4300	25.823	167.481	143.567	102.828	-156.233	100.404	-5.103
4400	25.823	168.075	144.118	105.410	-156.110	106.369	-5.283
4500	25.824	168.655	144.657	107.992	-155.988	112.343	-5.456
4600	25.824	169.223	145.184	110.575	-155.867	118.304	-5.621
4700	25.825	169.778	145.702	113.157	-155.750	124.258	-5.778
4800	25.825	170.322	146.209	115.740	-155.635	130.216	-5.929
4900	25.825	170.854	146.707	118.322	-155.523	136.174	-6.074
5000	25.826	171.376	147.195	120.905	-155.414	142.122	-6.212
5100	25.826	171.887	147.674	123.487	-155.306	148.072	-6.345
5200	25.826	172.389	148.145	126.070	-155.203	154.016	-6.473
5300	25.826	172.881	148.607	128.653	-155.099	159.966	-6.596
5400	25.827	173.363	149.061	131.235	-155.001	165.914	-6.715
5500	25.827	173.837	149.507	133.818	-154.904	171.849	-6.829
5600	25.827	174.303	149.945	136.401	-154.811	177.786	-6.938
5700	25.827	174.760	150.377	138.983	-154.721	183.729	-7.045
5800	25.828	175.209	150.801	141.566	-154.633	189.667	-7.147
5900	25.828	175.651	151.219	144.149	-154.547	195.597	-7.265
6000	25.828	176.085	151.629	146.732	-154.465	201.535	-7.341

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ΔHa°_0 = 234.2 ± 5 kcal/mol
$S^\circ_{298.15}$ = 99.51 ± 0.05 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -25.1 ± 4.0 kcal/mol I_4Si
$\Delta Hf^\circ_{298.15}$ = -26.4 ± 4.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
165.9(1)	404(3)
57.4(2)	88.8(3)

Point Group: T_d σ = 12
Bond Distance: Si-I = 2.43 ± 0.02 Å
Bond Angle: I-Si-I = 109.47122°
Products of the Moments of Inertia: $I_AI_BI_C = 3.6529 \times 10^{-110}$ g^3 cm^6

Heat of Formation

The sublimation, vaporization, and decomposition studies on SiI_4 are summarized in the following table. The vapor pressure data from the sublimation and vaporization studies are corrected for vapor non-ideality by means of the equation $\Delta G^\circ/T = -R\ln p - Bp/T$. The Berthelot equation of state and critical constants Tc = 850 K and Pc = 42.1 atm as suggested by Lapidus et al. (1) are used to calculate B.

			ΔHr°_{298}, kcal/mol		drift	$\Delta Hf^\circ_{298}(g)$*
Ref/Eqn	No. of data pts.	Range, K	2nd law	3rd law	gibbs/mol	kcal/mol
2A	13	343-396	16.23±0.32	18.82±0.28	6.9±0.9	-26.48
3A	eqn (flow)	373-392	18.75	19.08	0.9	-26.22
3A	eqn (static)	370-395	18.33	19.08	2.0	-26.22
3B	eqn (static)	398-425	15.68	15.49	-0.5	-26.24
4B	10	399-572	15.50±0.06	15.38±0.05	-0.2±0.1	-26.35
5B	eqn	393-573	14.82	15.27	0.9	-26.46
6C	6	1313-1513	59.09±1.14	59.91±0.26	0.6±0.8	-30.-06
7C	eqn	1300-1470	59.44	59.84	0.3	-29.99

*Based on 3rd law.

Equations: A) $SiI_4(c) = SiI_4(g)$ B) $SiI_4(\ell) = SiI_4(g)$ C) $SiI_4(g) = Si(c) + 2I_2(g)$

The third law results of the sublimation and vaporization studies (reactions A and B) perhaps imply a better agreement among the studies than actually exists. For example, the vaporization studies of Andersen and Belz (4) and Uchimura et al. (5) agree very well near Tb but diverge by up to 33% as T decreases to Tm. The vapor pressure results of Bartsch and Wolf (3) cover a very small temperature range and lie 10-15% lower than those of Andersen and Belz (4) and Krichevskii et al. (2). In addition, the decomposition studies (reaction C) suggest a $\Delta Hf^\circ_{298}(g)$ value 3.6 kcal/mol more negative than the vapor pressure studies.

We adopt $\Delta Hf^\circ_{298}(g)$ = -26.4 kcal/mol based primarily on Andersen and Belz (4) and Krichevskii et al. (2). Anderson and Belz (4) are also given primary weight in our selection of $S^\circ_{298}(c)$. We assign an uncertainty of ±4 kcal/mol to include the possibility that the decomposition studies (6,7) may be correct.

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark and Rippon (8), who recorded the Raman spectra in the vapor phase (210°C). The spectral data were interpreted in terms of a tetrahedral structure. This structure is consistent with the electron diffraction data of Liston and Sutton (9) which suggested a tetrahedral structure with a Si-I bond distance of 2.43±0.02Å. We adopt this bond distance. The principal moments of inertia are $I_A = I_B = I_C = 3.3180 \times 10^{-39}$ g cm^2.

Shimanouchi, in a recent compilation of molecular vibrational frequencies (10), suggested somewhat different values (168, 63, 405, 94 cm^{-1}), based on earlier infrared and Raman studies by Delwaulle (11) and Delwaulle and Francois (12). Much literature has been published on the inter-relationships between force constants and vibrational frequencies. Since the majority of this work was published prior to the Clark and Rippon study (8), it will not be further discussed or referenced. The same situation exists for temperature dependent thermochemical tabulations for $SiI_4(g)$.

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I_4Si

POTASSIUM SULFATE, ALPHA (α-K_2SO_4) K_2O_4S
(CRYSTAL) GFW=174.2542

T, K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0	0.000	0.000	INFINITE	-6.079	-341.109	-341.109	INFINITE
100	18.928	14.725	66.297	-5.157	-342.567	-333.760	729.421
200	26.450	30.436	44.675	-2.848	-343.283	-324.639	354.744
298	31.386	41.956	41.956	0.000	-343.620	-315.406	231.196
300	31.469	42.150	41.957	0.058	-343.624	-315.231	229.642
400	35.289	51.743	43.239	3.402	-345.428	-305.504	166.917
500	38.416	59.959	45.780	7.090	-345.627	-295.498	129.160
600	41.235	67.205	48.758	11.068	-345.467	-285.479	103.984
700	44.543	73.812	51.872	15.358	-344.965	-275.516	86.019
800	47.710	79.966	55.003	19.971	-357.132	-266.848	72.898
857	49.515	83.312	56.775	22.742	---- ALPHA-BETA TRANSITION ----		
900	50.876	85.769	58.102	24.900	-355.694	-255.644	62.078
1000	54.043	91.293	61.147	30.146	-353.988	-244.617	53.460
1100	57.210	96.592	64.130	35.709	-389.824	-231.726	46.039
1200	60.376	101.706	67.049	41.588	-387.086	-217.470	39.606

Dec. 31, 1971; June 30, 1978

POTASSIUM SULFATE (α-K_2SO_4) (CRYSTAL) GFW = 174.2542

$S^\circ_{298.15}$ = 41.956 ± 0.2 cal/(mol K)
$T_t(\alpha \rightarrow \beta)$ = 857 ± 1 K

ΔHf°_0 = -341.11 ± 0.1 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -343.62 ± 0.1 kcal/mol
$\Delta Ht^\circ(\alpha \rightarrow \beta)$ = 2.020 ± 0.100 kcal/mol

K_2O_4S

Heat of Formation

Shibata et al. (1) *measured the emf of the cell: K (amalgam, 0.2201%)|K_2SO_4(sat. soln.), Hg_2SO_4|Hg* at 298-303 K. From their results at 298 K, correcting the observed voltage for the formation of the K-amalgam, and converting to absolute volts, we have E_{cell} = 3.59172 volts for the reaction at 298 K, 2 K(c) + Hg_2SO_4(c) = 2 Hg(ℓ) + K_2SO_4(c). From this voltage, we calculate ΔGr°_{298} = -165.656 kcal/mol. Taking $\Delta Gf^\circ_{298}(Hg_2SO_4, c)$ = -149.658 kcal/mol (2) and reference entropies from (3), we calculate $\Delta Gf^\circ_{298}(K_2SO_4, c)$ = -315.314 kcal/mol and $\Delta Hf^\circ_{298}(K_2SO_4, c)$ = -343.525±0.2 kcal/mol.

The heat of solution at infinite dilution, $\Delta Hsoln^\circ_{298}(K_2SO_4, c)$ = 5.677±0.020 kcal/mol, adopted in this tabulation is based on our reanalysis of the heat of solution measurements of Mishchenko and Pronina (4), Tsvetkov and Rabinovich (5), Romanova and Samoilov (6), Cohen and Kooy (7), Brönsted (8), Samoilov et al. (9), and Gritsus et al. (10). Heats of dilution are taken from Lange and Streeck (11). When this result is combined with heats of formation of the infinitely dilute ions from CODATA (2), we obtain $\Delta Hf^\circ_{298}(K_2SO_4, \infty H_2O)$ = -337.940±0.10 kcal/mol and $\Delta Hf^\circ_{298}(K_2SO_4, c)$ = -343.617±0.10 kcal/mol.

The solubility of K_2SO_4(c) in water at 298 K has been measured by many workers (4, 12, 14, 15, 16). When the solubility of 0.6919 molal is combined with the activity coefficient data of Stokes (13), we obtain ΔGr°_{298} = 2423±20 cal/mol for the reaction $K_2SO_4(c) = 2\ K^+(\infty H_2O) + SO_4^{-2}(\infty H_2O)$. When this result is combined with heats of formation and entropies from (3), we obtain $\Delta Hf^\circ_{298}(K_2SO_4, c)$ = -343.595±0.2 kcal/mol.

We adopt the value of ΔHf°_{298} obtained from the heat of solution measurements.

Heat Capacity and Entropy

Low temperature heat capacities of $K_2SO_4(c, \alpha)$ have been measured by Moore and Kelley (17) from 52.7-295.4 K and by Paukov (18) from 12.5-299.5 K. The heat capacities reported by Moore and Kelley are systematically lower by about 0.5% than those of Paukov. Our adopted value of S°_{298} = 41.956±0.2 cal/(mol K) is based on $S^\circ_{12.5}$ = 0.068 cal/(mol K) (18) and $H^\circ_{12.5}-H^\circ_0$ = 0.640 cal/mol derived from a Debye T^3-law extrapolation.

Heat capacity data measured by adiabatic calorimetry in the range 298.5-773.7 K have been reported by Shmidt (19). In addition, drop calorimetric measurements have been reported by the following workers; Shomate and Naylor (20), Dworkin and Bredig (21), Denielou et al. (22), and Rubinchik et al. (23). The heat capacity and enthalpy curves between 298 K and 857 K are obtained by orthogonal polynomial curve-fitting of all the data listed above. These data are in good agreement.

Transition Data

$K_2SO_4(c, \alpha)$ is the low-temperature form of potassium sulfate (sometimes denoted K_2SO_4 II). The mineral is known as arcanite and exists in the form of orthorhombic crystals (space group D^{16}_{2h}-Pnma, 24). The orthorhombic-to-hexagonal transition temperature for K_2SO_4 is selected as 857±1 K from the calorimetric work of Dworkin and Bredig (21) and Rubinchik et al. (23) and the polymorphism study of Pistorius and Rapoport (25). The enthalpy of transition is determined by taking the difference between the adopted enthalpy curves of α- and β-K_2SO_4 extrapolated to 857 K.

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K_2O_4S

POTASSIUM SULFATE, BETA (β-K_2SO_4) K_2O_4S
(CRYSTAL) GFW=174.2542

T, K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	33.120	45.956	45.956	0.000	-340.402	-313.381	229.711
300	33.160	46.161	45.956	0.061	-340.403	-313.213	228.172
400	35.100	55.966	47.280	3.474	-342.138	-303.903	166.042
500	37.040	64.007	49.844	7.081	-342.418	-294.312	128.642
600	38.990	70.932	52.794	10.883	-342.434	-284.683	103.694
700	40.930	77.088	55.833	14.879	-342.226	-275.071	85.880
800	42.870	82.680	58.844	19.069	-354.816	-266.703	72.859
857	43.977	85.669	60.530	21.544	---- ALPHA-BETA TRANSITION ----		
900	44.810	87.842	61.783	23.453	-353.923	-255.740	62.101
1000	46.750	92.663	64.633	28.031	-352.885	-244.885	53.519
1100	48.700	97.211	67.389	32.803	-389.512	-232.093	46.112
1200	50.640	101.531	70.056	37.770	-387.486	-217.860	39.677
1300	52.580	105.661	72.637	42.931	-385.486	-203.790	34.260
1342	53.390	107.344	73.697	45.157	------------ MELTING ----------		
1400	54.520	109.629	75.139	48.286	-383.511	-189.877	29.641
1500	56.460	113.456	77.566	53.835	-381.198	-176.126	25.661

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POTASSIUM SULFATE (β-K_2SO_4) (CRYSTAL) GFW = 174.2542

$S^\circ_{298.15}$ = [45.956] cal/(mol K)
Tt($\alpha \rightarrow \beta$) = 857 ± 1 K
Tm($\beta \rightarrow \ell$) = 1342 ± 1 K

$\Delta Hf^\circ_{298.15}$ = [-340.402] kcal/mol
ΔHt°($\alpha \rightarrow \beta$) = 2.020 ± 0.100 kcal/mol
ΔHm°($\beta \rightarrow \ell$) = 8.220 kcal/mol

K_2O_4S

Heat of Formation

The ΔHf°_{298}(K_2SO_4, c, β) is calculated from ΔHf°_{298}(K_2SO_4, c, α) = -343.62 kcal/mol by adding the heat of transition ($\alpha \rightarrow \beta$) and the difference between H°_{857}-H°_{298} for the alpha and beta crystalline forms (1).

Heat Capacity and Enthalpy

High temperature enthalpy measurements by drop calorimetry were carried out by Shomate and Naylor (2, 872.4-1258.8 K), Rubinchik et al. (3, 859.0-1340.7 K) Dworkin and Bredig (4, 868.5-979.9 K), and Denielou et al. (5, 864-1300 K). The data of (2) are systematically higher by about 0.5% than the data from (3, 4, 5). Cp° values are derived from the smoothed curves and extrapolated to 298 K and 1500 K. S°_{298} is calculated in a manner analogous to that of the heat of formation.

Transition Data

The high temperature β-modification of K_2SO_4 is of hexagonal structure, space group D^3_{3d}-P3ml (6). The transition from the low temperature orthorhombic pseudohexagonal modification occurs at 857±1 K (1).

Melting Data

The adopted melting point of 1342 K was determined by Shomate and Naylor (2) and Rubinchik et al. (3). The heat of fusion, ΔHm° = 8.220±0.400 kcal/mol, is calculated from the difference between the smoothed relative enthalpy of the liquid (see K_2SO_4(ℓ) table) and the adopted enthalpy value for the β-crystalline form at Tm.

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K_2O_4S

POTASSIUM SULFATE (K_2SO_4)
(LIQUID) GFW=174.2542

K_2O_4S

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	31.386	50.551	50.551	0.000	-333.095	-307.443	225.359
300	31.469	50.745	50.551	0.058	-333.098	-307.284	223.853
400	35.289	60.338	51.834	3.402	-334.903	-298.417	163.045
500	38.416	68.554	54.375	7.090	-335.102	-289.270	126.438
600	41.235	75.800	57.353	11.068	-334.941	-280.111	102.029
700	44.543	82.407	60.466	15.358	-334.439	-271.007	84.611
800	47.710	88.563	63.598	19.972	ASSUMED		
800	48.150	88.563	63.598	19.972	GLASS TRANSITION		
900	48.150	94.234	66.693	24.787	-345.282	-252.851	61.400
1000	48.150	99.307	69.705	29.602	-344.007	-242.650	53.030
1100	48.150	103.897	72.608	34.417	-380.591	-230.527	45.801
1200	48.150	108.086	75.393	39.232	-378.917	-216.957	39.513
1300	48.150	111.940	78.058	44.047	-377.263	-203.529	34.216
1342	48.150	113.471	79.142	46.069	MELTING		
1400	48.150	115.508	80.607	48.862	-375.628	-190.225	29.695
1500	48.150	118.830	83.046	53.677	-374.009	-177.037	25.794
1600	48.150	121.938	85.380	58.492	-372.408	-163.959	22.395
1700	48.150	124.857	87.618	63.307	-370.822	-150.982	19.410
1800	48.150	127.609	89.764	68.122	-369.252	-138.095	16.767
1900	48.150	130.213	91.825	72.937	-367.700	-125.296	14.412
2000	48.150	132.682	93.806	77.752	-366.161	-112.575	12.301
2100	48.150	135.032	95.714	82.567	-364.641	-99.933	10.400
2200	48.150	137.272	97.552	87.382	-363.140	-87.363	8.679
2300	48.150	139.412	99.326	92.197	-361.656	-74.863	7.114
2400	48.150	141.461	101.039	97.012	-360.191	-62.426	5.685
2500	48.150	143.427	102.696	101.827	-358.748	-50.051	4.375
2600	48.150	145.315	104.299	106.642	-357.322	-37.726	3.171
2700	48.150	147.132	105.852	111.457	-355.920	-25.464	2.061
2800	48.150	148.884	107.358	116.272	-354.543	-13.250	1.034
2900	48.150	150.573	108.819	121.087	-353.190	-1.082	0.082
3000	48.150	152.206	110.238	125.902	-351.862	11.033	-0.804

Dec. 31, 1971; June 30, 1978

POTASSIUM SULFATE (K_2SO_4) (LIQUID) GFW = 174.2542

$S°_{298.15}$ = [50.551] cal/(mol K)
Tm(β → ℓ) = 1342 ± 1 K
Td = 2567 K

$\Delta Hf°_{298.15}$ = [-333.095] kcal/mol
ΔHm°(β → ℓ) = 8.220 kcal/mol

K_2O_4S

Heat of Formation

The adopted value of $\Delta Hf°_{298}(K_2SO_4, \ell) = -333.095 \pm 0.5$ kcal/mol is obtained from $\Delta Hf°_{298}(K_2SO_4, c, \beta)$ by adding ΔHm° and the difference between $H°_{1342}-H°_{298}$ for the crystal and liquid (1).

Heat Capacity and Entropy

Enthalpies for $K_2SO_4(\ell)$ have been measured by drop calorimetry by Shomate and Naylor (1358-1698 K, 2), Denielou et al. (1350-1550 K, 3), and Rubinchik et al. (single point at 1344.84 K, 4). A constant heat capacity of 48.15 cal/(mol K) is selected above a hypothetical glass transition at 800 K. Below the glass transition, the heat capacity is taken as that of the orthorhombic crystal. The $S°_{298}(K_2SO_4, \ell) = 50.551 \pm 1.0$ cal/(mol K) is calculated in a manner analogous to that of the heat of formation.

Melting Data

See K_2SO_4(c, β) table for details.

Vaporization and Decomposition Data

$K_2SO_4(\ell)$ can vaporize to the gaseous monomer $K_2SO_4(g)$ or decompose according to $K_2SO_4(\ell) = 2\ K(g) + SO_2(g) + O_2(g)$. Vaporization pressures from the two processes are of comparable magnitude in the vicinity of the melting point (6). *Recent experimental data for vaporization of K_2SO_4(c) (5, 6) are in good agreement with dissociation pressures and the heat of* reaction calculated from the JANAF Thermochemical Tables (1). Molecular vaporization data are discussed on the $K_2SO_4(g)$ table (1). Tb = 2975 K is the calculated temperature at which the Gibbs energy difference is zero for the reaction $K_2SO_4(\ell) = K_2SO_4(g)$. Td = 2567 K is the temperature at which the Gibbs energy difference is zero for the reaction $K_2SO_4(\ell) = 2\ K(g) + SO_2(g) + O_2(g)$. Decomposition to the oxides of potassium produces significantly lower decomposition pressures than decomposition to the metal. Significant decomposition can occur in the presence of water vapor according to $K_2SO_4(\ell) + H_2O(g) = 2\ KOH(g) + SO_2(g) + 1/2\ O_2(g)$.

References for $K_2SO_4(\ell)$

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References for $K_2SO_4(g)$

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POTASSIUM SULFATE (K_2SO_4) (ALPHA-BETA-LIQUID) GFW=174.2542

K_2O_4S

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-6.079	-341.109	-341.109	INFINITE
100	18.928	14.725	66.297	-5.157	-342.567	-333.760	729.421
200	26.450	30.436	44.675	-2.848	-343.283	-324.639	354.744
298	31.386	41.956	41.956	0.000	-343.620	-315.406	231.196
300	31.469	42.150	41.957	0.058	-343.624	-315.231	229.642
400	35.269	51.743	43.239	3.402	-345.428	-305.504	166.917
500	38.416	59.959	45.780	7.090	-345.627	-295.498	129.160
600	41.235	67.205	48.758	11.068	-345.467	-285.479	103.984
700	44.543	73.812	51.872	15.358	-344.965	-275.516	86.019
800	47.710	79.966	55.003	19.971	-357.132	-266.848	72.898
857	49.515	83.312	56.775	22.742			
857	43.977	85.669	56.775	24.762	---- ALPHA-BETA TRANSITION ----		
900	44.810	87.842	58.208	26.671	-353.923	-255.740	62.101
1000	46.750	92.663	61.415	31.249	-352.885	-244.885	53.519
1100	48.700	97.211	64.464	36.021	-389.512	-232.093	46.112
1200	50.640	101.531	67.374	40.988	-387.686	-217.860	39.677
1300	52.580	105.661	70.162	46.149	-385.686	-203.790	34.260
1342	53.390	107.346	71.299	48.375			
1342	48.150	113.471	71.299	56.595	------------ MELTING ----------		
1400	48.150	115.509	73.089	59.387	-375.628	-190.225	29.695
1500	48.150	118.831	76.029	64.202	-374.009	-177.038	25.794
1600	48.150	121.938	78.802	69.017	-372.408	-163.959	22.395
1700	48.150	124.857	81.426	73.832	-370.822	-150.982	19.410
1800	48.150	127.609	83.916	78.647	-369.252	-138.095	16.767
1900	48.150	130.213	86.285	83.462	-367.700	-125.296	14.412
2000	48.150	132.682	88.544	88.277	-366.161	-112.575	12.301
2100	48.150	135.032	90.702	93.092	-364.641	-99.933	10.400
2200	48.150	137.272	92.768	97.907	-363.140	-87.363	8.679
2300	48.150	139.412	94.750	102.722	-361.656	-74.863	7.114
2400	48.150	141.461	96.654	107.537	-360.191	-62.426	5.685
2500	48.150	143.427	98.486	112.352	-358.748	-50.051	4.375
2600	48.150	145.315	100.251	117.167	-357.322	-37.726	3.171
2700	48.150	147.132	101.954	121.982	-355.920	-25.464	2.061
2800	48.150	148.884	103.599	126.797	-354.543	-13.250	1.034
2900	48.150	150.573	105.190	131.612	-353.190	-1.082	0.082
3000	48.150	152.206	106.730	136.427	-351.862	11.033	-0.804

June 30, 1978

POTASSIUM SULFATE (K_2SO_4) (ALPHA-BETA-LIQUID) GFW = 174.2542

K_2O_4S

0 to 857 K Crystal, alpha
857 to 1342 K Crystal, beta
1342 to Td K Liquid

Refer to the single phase tables for the alpha, beta, liquid phases for details.

POTASSIUM SULFATE (K_2SO_4) K_2O_4S
(IDEAL GAS) GFW=174.2542

	gibbs/mol			kcal/mol			
T, K	$C_p°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log Kp
0	0.000	0.000	INFINITE	-5.369	-258.279	-258.279	INFINITE
100	15.480	65.272	107.450	-4.218	-259.508	-255.755	558.944
200	21.602	77.999	89.731	-2.347	-260.662	-251.530	274.856
298	25.987	87.486	87.486	0.000	-261.500	-246.861	180.952
300	26.057	87.647	87.487	0.048	-261.514	-246.770	179.769
400	29.240	95.607	88.550	2.822	-263.888	-241.509	131.952
500	31.442	102.383	90.656	5.863	-264.734	-235.816	103.074
600	32.960	108.259	93.111	9.088	-265.327	-229.971	83.766
700	34.021	113.424	95.652	12.440	-265.763	-224.042	69.948
800	34.781	118.019	98.166	15.882	-279.101	-219.258	59.898
900	35.339	122.149	100.605	19.390	-279.084	-211.777	51.426
1000	35.758	125.896	102.950	22.946	-279.068	-204.300	44.649
1100	36.079	129.319	105.194	26.538	-316.875	-194.776	38.698
1200	36.330	132.470	107.337	30.159	-316.395	-183.695	33.455
1300	36.530	135.386	109.384	33.803	-315.912	-172.659	29.026
1400	36.691	138.099	111.339	37.464	-315.431	-161.655	25.235
1500	36.823	140.635	113.209	41.140	-314.951	-150.687	21.955
1600	36.932	143.015	114.998	44.828	-314.477	-139.753	19.089
1700	37.023	145.257	116.713	48.526	-314.008	-128.849	16.564
1800	37.100	147.376	118.358	52.232	-313.547	-117.969	14.323
1900	37.165	149.383	119.938	55.945	-313.097	-107.118	12.321
2000	37.222	151.291	121.459	59.665	-312.653	-96.285	10.521
2100	37.270	153.108	122.923	63.389	-312.224	-85.477	8.896
2200	37.313	154.843	124.335	67.119	-311.808	-74.690	7.420
2300	37.350	156.503	125.697	70.852	-311.406	-63.922	6.074
2400	37.383	158.093	127.014	74.588	-311.020	-53.171	4.842
2500	37.411	159.620	128.288	78.328	-310.652	-42.437	3.710
2600	37.437	161.087	129.522	82.071	-310.298	-31.710	2.665
2700	37.460	162.501	130.717	85.815	-309.967	-21.005	1.700
2800	37.481	163.863	131.877	89.562	-309.658	-10.309	0.805
2900	37.499	165.179	133.003	93.311	-309.371	0.380	-0.029
3000	37.516	166.451	134.096	97.062	-309.107	11.053	-0.805
3100	37.531	167.681	135.160	100.815	-308.870	21.723	-1.531
3200	37.545	168.873	136.195	104.568	-308.660	32.386	-2.212
3300	37.557	170.028	137.203	108.323	-308.479	43.038	-2.850
3400	37.569	171.150	138.185	112.080	-308.333	53.685	-3.451
3500	37.579	172.239	139.142	115.837	-308.220	64.331	-4.017
3600	37.589	173.298	140.076	119.596	-308.146	74.978	-4.552
3700	37.598	174.328	140.988	123.355	-308.115	85.616	-5.057
3800	37.606	175.330	141.879	127.115	-308.130	96.256	-5.536
3900	37.614	176.307	142.749	130.876	-308.193	106.898	-5.990
4000	37.621	177.260	143.600	134.638	-308.310	117.547	-6.422
4100	37.627	178.189	144.432	138.400	-308.490	128.194	-6.833
4200	37.633	179.095	145.247	142.163	-308.734	138.850	-7.225
4300	37.639	179.981	146.045	145.927	-309.049	149.510	-7.599
4400	37.644	180.846	146.826	149.691	-309.443	160.177	-7.956
4500	37.649	181.692	147.591	153.456	-309.919	170.861	-8.298
4600	37.654	182.520	148.342	157.221	-310.488	181.546	-8.625
4700	37.658	183.330	149.077	160.986	-311.153	192.251	-8.940
4800	37.662	184.123	149.799	164.752	-311.921	202.973	-9.241
4900	37.666	184.899	150.508	168.519	-312.799	213.708	-9.532
5000	37.669	185.660	151.203	172.285	-313.793	224.458	-9.811
5100	37.673	186.406	151.886	176.053	-314.905	235.242	-10.081
5200	37.676	187.138	152.557	179.820	-316.146	246.039	-10.341
5300	37.679	187.856	153.216	183.588	-317.515	256.859	-10.592
5400	37.682	188.560	153.864	187.356	-319.017	267.707	-10.835
5500	37.684	189.251	154.501	191.124	-320.653	278.586	-11.070
5600	37.687	189.930	155.128	194.893	-322.423	289.498	-11.298
5700	37.689	190.597	155.744	198.661	-324.327	300.442	-11.519
5800	37.692	191.253	156.351	202.431	-326.365	311.417	-11.734
5900	37.694	191.897	156.948	206.200	-328.532	322.438	-11.944
6000	37.696	192.531	157.536	209.969	-330.827	333.497	-12.147

June 30, 1978

POTASSIUM SULFATE (K_2SO_4) (IDEAL GAS) GFW = 174.2542

$\Delta Ha_0° = 367.0 \pm 4.0$ kcal/mol
$S°_{298.15} = 87.486 \pm 4.0$ cal/(mol K)
Ground State Quantum Weight = [1]

$\Delta Hf_0° = -258.3 \pm 4.0$ kcal/mol
$\Delta Hf°_{298.15} = -261.5 \pm 4.0$ kcal/mol

K_2O_4S

Vibrational Frequencies, Symmetry, and Degeneracies

	ω, cm^{-1}			ω, cm^{-1}			ω, cm^{-1}	
A_1	962	(1)	B_1	[450]	(1)	E	1098	(2)
	[458]	(1)	B_2	1124	(1)		613	(2)
	[190]	(1)		639	(1)		[230]	(2)
				[262]	(1)		[62]	(2)

Point Group D_{2d} $\sigma = 4$
Bond Distances: S-O = 1.47 Å K-O = 2.45 Å
Bond Angles: O-S-O = 109.47° O-K-O = 68.67°
Product of the Moments of Inertia: $I_AI_BI_C = 2.6263 \times 10^{-112}$ g^3 cm^6

Heat of Formation

The adopted value of the heat of formation is based on JANAF analyses of the vaporization data given below. Earlier data on the vaporization of K_2SO_4 is extremely discordant (for a review, see 10). Dissociation and other reactions play an important role in K_2SO_4 vaporization (see $K_2SO_4(\ell)$ table).

Torsion-effusion studies on the vaporization of $K_2SO_4(g)$ by Lau et al. (3) showed an orifice dependence which was reproduced in four separate runs. Plante et al. (2) did not observe this orifice size dependence in their effusion study, obtaining similar total pressures in two separate experiments. Calculated dissociation pressures were subtracted in both studies to obtain $K_2SO_4(g)$ pressures. Similar results were obtained by Efimova and Gorokhov (1). We have corrected the effusion data of Kosugi (11) for dissociation. The third law heats of sublimation from the three studies (1, 2, 3) are in very good agreement indicating similar $K_2SO_4(g)$ pressures. The studies of Lau et al. (3) and Efimova and Gorokhov (1) yield second law heats of sublimation (from $K_2SO_4(c, \beta)$) some 6 kcal/mol greater than our calculated third law heats.

Lau et al. (3) and Efimova and Gorokhov (1) also carried out mass spectrometric measurements of the $K_2SO_4^+$ ion intensity as a function of temperature. The second law heats of sublimation of Lau et al. (3) obtained in two separate mass spectrometric experiments tend to corroborate their second law heats from the torsion-effusion measurements. The second law heats of Efimova and Gorokhov (1) as well as that of Ficalora et al. (12) are more in line with our third law effusion values. Kosugi (11) did not observe the $K_2SO_4^+$ ion in his mass spectrometric experiments. The appearance potential of $K_2SO_4^+$ has been measured as 7.4±0.5 eV (12), 8.4±0.3 eV (3) and 8.0 eV (1).

We have discounted the transpiration experiments of Halstead (13) and Dubois and Millet (14). The calculated third law $\Delta Hr°$(298 K) may have an uncertainty of 3 kcal/mol since the JANAF free energy functions are partially based on the estimated molecular constants of $K_2SO_4(g)$. *Our adopted $\Delta Hf°$ is based on a weighted average of the third law results from* (1, 2, 3).

Source	Method	Reaction[a]	Range T/K	No. of Points	δS^b cal/(mol K)	ΔHr_{298}/(kcal/mol) 2nd Law	3rd Law	$\Delta Hf°_{298}(K_2SO_4, g)^c$ kcal/mol
Efimova (1)	effusion	A	1171-1331	equation	4.38	84.77	79.02±0.11	-261.38±1.5
Lau et al. (3)	torsion-effusion	A	1180-1274	37	5.18	85.36	78.93±0.45	-261.47±1.5
Plante (2)	effusion	A	1166-1322	26	-1.42±0.8	77.03±0.9	78.78±0.42	-261.62±1.5
Plante(2)	effusion	A	1196-1321	15	-0.76±2.0	77.87±2.0	78.83±0.51	-261.57±1.0
Halstead	effusion	A	1180-1340	equation	1.07	75.75	74.38±0.15	-266.02±1.0
Kosugi (11)	effusion	B	1409-1530	12	2.70±2.8	73.67±4.2	69.66±0.76	-263.43±2.0
Efimova (1)	mass spec	A	1171-1331	?	--	78.0 ±1.0	--	-262.4 ±2
Lau et al. (3)	mass spec	A	1183-1248	9	--	84.12±2.02	--	-256.28±2.0
Lau et al. (3)	mass spec	A	1180-1314	10	--	81.96±0.40	--	-258.44±1.5
Ficalora (12)	mass spec	A	1080-1230	?	--	79.8 ±2.0	--	-260.6 ±4

[a] Reactions: A) $K_2SO_4(c, \beta) = K_2SO_4(g)$ B) $K_2SO_4(\ell) = K_2SO_4(g)$

[b] $\delta S = \Delta Sr°_{298}$(2nd law) - $\Delta Sr°_{298}$(3rd law) [c] 3rd law $\Delta Hr°_{298}$ is used to derive $\Delta Hf°_{298}(K_2SO_4, g)$ if possible.

Heat Capacity and Entropy

The adopted structure (D_{2d} symmetry) is based on the high temperature electron diffraction study of Spiridonov and Lutoshkin (5). *This symmetry is supported by the similar work of* Ugarov et al. (4) on Cs_2SO_4 and the IR and Raman study of Atkins and Gingerich (7) on K_2SO_4 and Na_2SO_4. The molecule can be pictured as having a central sulfur atom surrounded at the corners of a tetrahedron by four oxygen atoms with bridging potassium atoms between two pairs of oxygens forming two planar mutually perpendicular KO_2S rings. The sulphate core is fairly rigid while the metal atoms undergo large amplitude motions. The internuclear distances of 1.47 Å for S-O and 2.45 Å for K-O are from (5) as are the O-S-O and O-K-O angles. The principal moments of inertia are $I_A = 15.309 \times 10^{-39}$ and $I_B = I_C = 130.976 \times 10^{-39}$ g cm^2.

Atkins and Gingerich (7) have observed the infrared and Raman spectra of K_2SO_4 and Na_2SO_4 isolated in oxygen and nitrogen matrices at 12 K. Five of the eleven fundamental frequencies were observed in this work. Good agreement exists between these observations and the frequencies adopted by Gurvich et al. (6). The two other sulphate-ion group fundamentals are taken from the Raman study of Davies and Sandford (9). The low-frequency fundamentals involving the metal atoms are taken from the infrared study of Belyaeva et al. (8). These authors observed the spectra of K_2SO_4, Rb_2SO_4, and Cs_2SO_4 isolated in Ar, Kr, and Xe matrices at 4.2 K. Uncertainties in the location of the gas phase frequencies may contribute 4 cal/(mol K) to $S°_{298}$.

References

See $K_2SO_4(\ell)$ table.

K_2O_4S

DIPOTASSIUM MONOSULFIDE (K_2S)
(CRYSTAL) GFW=110.2566

T, K	gibbs/mol			kcal/mol			
	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.850	27.500	27.500	0.000	-90.000	-86.707	63.557
300	17.860	27.610	27.500	0.033	-90.003	-86.686	63.150
400	18.480	32.833	28.208	1.850	-91.913	-85.311	46.611
500	19.100	37.024	29.566	3.729	-92.458	-83.596	36.539
600	19.720	40.561	31.111	5.670	-92.826	-81.785	29.790
700	20.350	43.648	32.686	7.673	-93.055	-79.901	24.946
800	20.970	46.406	34.231	9.739	-106.238	-79.281	21.658
900	24.750	49.020	35.728	11.963	-105.876	-75.929	18.438
1000	37.300	52.169	37.206	14.962	-104.760	-72.650	15.878
1100	34.020	56.061	38.749	19.043	-140.396	-67.501	13.411
1200	34.020	59.021	40.317	22.445	-138.432	-60.959	11.102
1300	34.020	61.744	41.862	25.847	-136.469	-54.583	9.176
1400	34.020	64.265	43.373	29.249	-134.508	-48.357	7.549
1500	34.020	66.612	44.845	32.651	-132.548	-42.273	6.159
1600	34.020	68.808	46.275	36.053	-130.588	-36.316	4.960
1700	34.020	70.870	47.662	39.455	-128.631	-30.487	3.919
1800	34.020	72.815	49.005	42.857	-126.675	-24.770	3.007
1900	34.020	74.654	50.307	46.259	-124.723	-19.161	2.204
2000	34.020	76.399	51.569	49.661	-122.772	-13.655	1.492

March 31, 1978

ΔHf°_0 = Unknown
$S^\circ_{298.15}$ = 27.5 ± 4 gibbs/mol
$\Delta Hf^\circ_{298.15}$ = -90 ± 3 kcal/mol
Tt = 1050 ± 10 K (diffuse lambda transition)
ΔHt° = 0 kcal/mol
Tm = 1221 ± 10 K
ΔHm° = 3.86 ± 0.04 kcal/mol

Heat of Formation

Experimental measurements leading to the heat of formation of $K_2S(c)$ are summarized below.

Source	Reaction	ΔHf°_{298}, kcal/mol
Sabatier (1)	ΔHsoln $K_2S(c)$ and K(c); ΔHn KOH(aq) + $H_2S(aq)$	-103.4
Rengade and Costeanu (2)		-87.3
Letoffe et al. (3)	$H_2SO_4(1100\ H_2O) + K_2S(c) = K_2SO_4(\text{soln.}) + H_2S(g)$	-92.1[a]

a. The authors' value of -91.1±0.9 kcal/mol is changed by new ΔHf°_{298} values for $H_2SO_4(1100\ H_2O)$, $K_2SO_4(c)$, and $H_2S(g)$ (4, 5).

Since Sabatier himself has expressed reservations because of impure material, we eliminate his value and adopt the average of the other two values, $\Delta Hf^\circ_{298}(K_2S,c)$ = -90±3 kcal/mol.

Heat Capacity and Entropy

The heat capacity is taken from the drop calorimetry of Dworkin and Bredig (384 to 1260 K, 6). Between 298 and 820 K, the observed enthalpy differences, $H_T-H_{298.15}$, and the constraint of passing through zero at 298.15 K are fit by a linear least ssquares technique; $C_p = 15.99 + 6.22\times10^{-3}T$ gibbs/mol (298-820 K). The heat capacity in the observed diffuse lambda transition region, 820-1100 K, was adjusted to properly reproduce the observed enthalpies. The sharp heat capacity maximum occurs at 1050 K (6) and 46.60 gibbs/mol. From 1100 K to the melting point, 1221 K (7), the heat capacity was found to be constant at 34.02 gibbs/mol (6).

Freeman (8) has estimated $S^\circ_{298}(K_2S,c)$ = 27 gibbs/mol; Voronin (9) also has estimated 27 gibbs/mol. Kelley's additive entropy constants give 28.0. We adopt $S^\circ_{298}(K_2S,c)$ = 27.5±4 gibbs/mol.

Transition and Melting Data

A crystal II to crystal I transition at 419.6 K with a heat change of 0.085 kcal/mol has been listed (10) from Bridgman (11). However, West (12) found no change in the x-ray powder diffraction pattern over the 298-473 K range. Although not definitive because of the small heat change listed, the drop calorimetric enthalpy measurements of Dworkin and Bredig (6) do not show this transition. Therefore, we do not indicate any solid state transition at 419.6 K.

The diffuse lambda transition has been discussed above.

A melting point of 1221 K was determined by thermal analysis (cooling curves) of the K-K_2S system by Dworkin and Bredig (7). This is considerably higher than earlier values of 1108 K (13) and 1185 K (14), but it is confirmed by their drop calorimetric measurements (6). A melting point of 1221±10 K is adopted with ΔHm° = 3.86±0.04 kcal/mol (6).

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DIPOTASSIUM MONOSULFIDE (K_2S) K_2S
(LIQUID) GFW=110.2566

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.850	33.741	33.741	0.000	-82.817	-81.385	59.656
300	17.860	33.851	33.741	0.033	-82.820	-81.375	59.281
400	18.480	39.074	34.449	1.850	-84.730	-80.624	44.051
500	19.100	43.265	35.806	3.729	-85.275	-79.533	34.763
600	19.720	46.802	37.352	5.670	-85.643	-78.346	28.537
700	20.350	49.889	38.927	7.673	-85.872	-77.086	24.067
800	20.970	52.646	40.472	9.739	-99.055	-77.091	21.060
900	24.130	55.412	41.978	12.090	-98.566	-74.371	18.059
1000	24.130	57.954	43.451	14.503	-98.036	-71.712	15.672
1100	24.130	60.254	44.876	16.916	-135.340	-67.057	13.323
1200	24.130	62.354	46.246	19.329	-134.365	-60.891	11.090
1300	24.130	64.285	47.560	21.742	-133.391	-54.808	9.214
1400	24.130	66.073	48.820	24.155	-132.419	-48.798	7.618
1500	24.130	67.738	50.026	26.568	-131.448	-42.861	6.245
1600	24.130	69.295	51.182	28.981	-130.477	-36.984	5.052
1700	24.130	70.758	52.291	31.394	-129.509	-31.174	4.008
1800	24.130	72.138	53.356	33.807	-128.542	-25.417	3.086
1900	24.130	73.442	54.379	36.220	-127.579	-19.714	2.268
2000	24.130	74.680	55.363	38.633	-126.617	-14.060	1.536
2100	24.130	75.857	56.311	41.046	-125.660	-8.457	0.880
2200	24.130	76.980	57.225	43.459	-124.709	-2.896	0.288
2300	24.130	78.052	58.108	45.872	-123.763	2.617	-0.249
2400	24.130	79.079	58.960	48.285	-122.823	8.092	-0.737
2500	24.130	80.064	59.785	50.698	-121.893	13.527	-1.182
2600	24.130	81.011	60.583	53.111	-120.970	18.929	-1.591
2700	24.130	81.921	61.357	55.524	-120.059	24.288	-1.966
2800	24.130	82.799	62.107	57.937	-119.163	29.615	-2.312
2900	24.130	83.646	62.835	60.350	-118.279	34.918	-2.631
3000	24.130	84.464	63.543	62.763	-117.410	40.184	-2.927

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DIPOTASSIUM MONOSULFIDE (K_2S) (LIQUID) GFW = 110.2566

$S^\circ_{298.15}$ = [33.741] gibbs/mol
T_m = 1221 ± 10 K

$\Delta Hf^\circ_{298.15}$ = [-82.817] kcal/mol
ΔHm° = 3.86 ± 0.04 kcal/mol K_2S

Heat of Formation

$\Delta Hf^\circ_{298}(K_2S,\ell)$ is obtained from that of the crystal (1) by adding ΔHm° and the difference between $(H^\circ_{1221} - H^\circ_{298})$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was derived from drop calorimetric enthalpy measurements by Dworkin and Bredig (2, 1221–1260 K) and is constant at 24.13 gibbs/mol over the range measured. A glass transition temperature is assumed at 820 K with Cp = 24.13 above this temperature and Cp equal to that of the crystal below this temperature.

The entropy is obtained in a manner similar to that for the heat of formation.

References

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2. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 72, 1277 (1968).

KRYPTON, MONATOMIC (KR) KR
(REFERENCE STATE - IDEAL GAS) GFW=83.80

T, °K	$C_p°$	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-1.481	0.000	0.000	0.000
100	4.968	33.764	43.608	-0.984	0.000	0.000	0.000
200	4.968	37.207	39.645	-0.488	0.000	0.000	0.000
298	4.968	39.191	39.191	0.000	0.000	0.000	0.000
300	4.968	39.222	39.191	0.009	0.000	0.000	0.000
400	4.968	40.651	39.386	0.506	0.000	0.000	0.000
500	4.968	41.759	39.754	1.003	0.000	0.000	0.000
600	4.968	42.665	40.166	1.500	0.000	0.000	0.000
700	4.968	43.431	40.579	1.996	0.000	0.000	0.000
800	4.968	44.094	40.978	2.493	0.000	0.000	0.000
900	4.968	44.680	41.357	2.990	0.000	0.000	0.000
1000	4.968	45.203	41.716	3.487	0.000	0.000	0.000
1100	4.968	45.677	42.055	3.984	0.000	0.000	0.000
1200	4.968	46.109	42.375	4.480	0.000	0.000	0.000
1300	4.968	46.506	42.678	4.977	0.000	0.000	0.000
1400	4.968	46.875	42.965	5.474	0.000	0.000	0.000
1500	4.968	47.217	43.237	5.971	0.000	0.000	0.000
1600	4.968	47.538	43.496	6.468	0.000	0.000	0.000
1700	4.968	47.839	43.742	6.964	0.000	0.000	0.000
1800	4.968	48.123	43.978	7.461	0.000	0.000	0.000
1900	4.968	48.392	44.203	7.958	0.000	0.000	0.000
2000	4.968	48.647	44.419	8.455	0.000	0.000	0.000
2100	4.968	48.889	44.626	8.952	0.000	0.000	0.000
2200	4.968	49.120	44.825	9.448	0.000	0.000	0.000
2300	4.968	49.341	45.017	9.945	0.000	0.000	0.000
2400	4.968	49.552	45.201	10.442	0.000	0.000	0.000
2500	4.968	49.755	45.380	10.939	0.000	0.000	0.000
2600	4.968	49.950	45.552	11.436	0.000	0.000	0.000
2700	4.968	50.137	45.718	11.932	0.000	0.000	0.000
2800	4.968	50.318	45.879	12.429	0.000	0.000	0.000
2900	4.968	50.492	46.035	12.926	0.000	0.000	0.000
3000	4.968	50.661	46.187	13.423	0.000	0.000	0.000
3100	4.968	50.824	46.334	13.920	0.000	0.000	0.000
3200	4.968	50.982	46.476	14.416	0.000	0.000	0.000
3300	4.968	51.134	46.615	14.913	0.000	0.000	0.000
3400	4.968	51.283	46.750	15.410	0.000	0.000	0.000
3500	4.968	51.427	46.882	15.907	0.000	0.000	0.000
3600	4.968	51.567	47.010	16.404	0.000	0.000	0.000
3700	4.968	51.703	47.135	16.900	0.000	0.000	0.000
3800	4.968	51.835	47.257	17.397	0.000	0.000	0.000
3900	4.968	51.964	47.376	17.894	0.000	0.000	0.000
4000	4.968	52.090	47.492	18.391	0.000	0.000	0.000
4100	4.968	52.213	47.606	18.888	0.000	0.000	0.000
4200	4.968	52.333	47.717	19.384	0.000	0.000	0.000
4300	4.968	52.449	47.826	19.881	0.000	0.000	0.000
4400	4.968	52.564	47.932	20.378	0.000	0.000	0.000
4500	4.968	52.675	48.036	20.875	0.000	0.000	0.000
4600	4.968	52.784	48.138	21.372	0.000	0.000	0.000
4700	4.968	52.891	48.238	21.868	0.000	0.000	0.000
4800	4.968	52.996	48.336	22.365	0.000	0.000	0.000
4900	4.968	53.098	48.433	22.862	0.000	0.000	0.000
5000	4.968	53.199	48.527	23.359	0.000	0.000	0.000
5100	4.968	53.297	48.619	23.855	0.000	0.000	0.000
5200	4.968	53.394	48.710	24.352	0.000	0.000	0.000
5300	4.968	53.488	48.800	24.849	0.000	0.000	0.000
5400	4.968	53.581	48.887	25.346	0.000	0.000	0.000
5500	4.968	53.672	48.973	25.843	0.000	0.000	0.000
5600	4.968	53.762	49.058	26.339	0.000	0.000	0.000
5700	4.968	53.850	49.141	26.836	0.000	0.000	0.000
5800	4.968	53.936	49.223	27.333	0.000	0.000	0.000
5900	4.968	54.021	49.304	27.830	0.000	0.000	0.000
6000	4.968	54.104	49.383	28.327	0.000	0.000	0.000

March 31, 1977

KRYPTON, MONATOMIC (Kr) (REFERENCE STATE - IDEAL GAS) GFW = 83.80

0 to 6000 K Ideal Gas

Ground State Configuration $^1S_0$
$S°_{298.15}$ = 39.191 ± 0.005 gibbs/mol
T_{tr} = 115.78 K
T_b = 119.80 K

$\Delta Hf°_0$ = 0 kcal/mol
$\Delta Hf°_{298.15}$ = 0 kcal/mol

KR

Electronic Levels and Quantum Weights

state	ε_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore (1). All predicted levels have been observed for n=4 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (2) has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is nearly 80,000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of proper fill and cutoff procedures (2).

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations (3). The tables agree within the estimated uncertainty with those by Hultgren et al. (4) and Hilsenrath et al. (5). The estimated uncertainty is due to uncertainties in the gram formula weight and fundamental constants which are based on the 1971 scale (6) and the 1973 values (7), respectively.

Phase Data

The triple point (T_{tr}) and boiling point (T_b) are taken from Hultgren et al. (4). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values of T_{tr} and T_b the reference state for krypton is chosen to be the ideal gas at all temperatures down to 0 K. This may differ from the choice of other authors. The tables of Hultgren (4), among others, use appropriate condensed states of krypton as reference states and will differ from the present work at low temperatures.

References

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KR

KRYPTON UNIPOSITIVE ION (Kr^+) Kr^+
(IDEAL GAS) GFW=83.79945

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0				-1.481	322.839		
100							
200							
298	4.968	41.946	41.946	0.000	324.320	322.011	-236.037
300	4.968	41.977	41.946	0.009	324.329	321.997	-234.571
400	4.968	43.406	42.141	0.506	324.826	321.145	-175.463
500	4.968	44.514	42.509	1.003	325.323	320.167	-139.943
600	4.968	45.420	42.921	1.500	325.820	319.089	-116.227
700	4.970	46.186	43.334	1.997	326.317	317.928	-99.260
800	4.974	46.850	43.733	2.494	326.814	316.696	-86.516
900	4.982	47.436	44.112	2.991	327.311	315.401	-76.589
1000	4.994	47.962	44.471	3.490	327.810	314.051	-68.635
1100	5.012	48.438	44.811	3.990	328.310	312.651	-62.117
1200	5.034	48.875	45.132	4.493	328.813	311.205	-56.677
1300	5.060	49.279	45.435	4.997	329.317	309.717	-52.067
1400	5.089	49.655	45.723	5.505	329.825	308.191	-48.110
1500	5.120	50.007	45.997	6.015	330.335	306.628	-44.675
1600	5.152	50.339	46.258	6.529	330.848	305.029	-41.664
1700	5.184	50.652	46.508	7.045	331.365	303.401	-39.004
1800	5.215	50.949	46.746	7.565	331.885	301.741	-36.636
1900	5.245	51.232	46.975	8.088	332.408	300.052	-34.513
2000	5.273	51.502	47.195	8.614	332.934	298.335	-32.600
2100	5.299	51.760	47.406	9.143	333.462	296.592	-30.866
2200	5.323	52.007	47.610	9.674	333.994	294.824	-29.288
2300	5.344	52.244	47.806	10.207	334.527	293.032	-27.844
2400	5.364	52.472	47.996	10.743	335.063	291.217	-26.519
2500	5.381	52.691	48.179	11.280	335.600	289.379	-25.297
2600	5.395	52.902	48.357	11.819	336.138	287.518	-24.168
2700	5.408	53.106	48.529	12.359	336.679	285.639	-23.121
2800	5.418	53.303	48.696	12.900	337.220	283.739	-22.146
2900	5.427	53.493	48.858	13.442	337.762	281.819	-21.238
3000	5.433	53.678	49.016	13.986	338.306	279.881	-20.389
3100	5.439	53.856	49.169	14.529	338.848	277.923	-19.593
3200	5.443	54.029	49.318	15.073	339.393	275.950	-18.846
3300	5.445	54.196	49.463	15.618	339.938	273.959	-18.143
3400	5.446	54.359	49.605	16.162	340.482	271.952	-17.481
3500	5.446	54.516	49.743	16.707	341.027	269.928	-16.855
3600	5.446	54.670	49.878	17.251	341.570	267.888	-16.263
3700	5.444	54.819	50.009	17.796	342.116	265.835	-15.702
3800	5.442	54.964	50.138	18.340	342.660	263.766	-15.170
3900	5.439	55.106	50.263	18.884	343.204	261.683	-14.664
4000	5.435	55.243	50.386	19.428	343.747	259.584	-14.183
4100	5.431	55.377	50.506	19.971	344.290	257.474	-13.724
4200	5.427	55.508	50.624	20.514	344.834	255.351	-13.287
4300	5.422	55.636	50.739	21.057	345.377	253.214	-12.870
4400	5.416	55.760	50.852	21.598	345.918	251.064	-12.470
4500	5.411	55.882	50.962	22.140	346.459	248.901	-12.088
4600	5.405	56.001	51.070	22.681	347.000	246.727	-11.722
4700	5.399	56.117	51.176	23.221	347.541	244.542	-11.371
4800	5.393	56.231	51.281	23.760	348.080	242.345	-11.034
4900	5.387	56.342	51.383	24.300	348.620	240.137	-10.710
5000	5.381	56.451	51.483	24.838	349.157	237.917	-10.399
5100	5.375	56.557	51.581	25.376	349.696	235.687	-10.100
5200	5.369	56.661	51.678	25.913	350.233	233.447	-9.811
5300	5.362	56.764	51.773	26.450	350.770	231.196	-9.533
5400	5.356	56.864	51.866	26.985	351.305	228.935	-9.265
5500	5.350	56.962	51.958	27.521	351.840	226.662	-9.007
5600	5.344	57.058	52.048	28.055	352.375	224.383	-8.757
5700	5.337	57.153	52.137	28.589	352.909	222.092	-8.515
5800	5.331	57.246	52.224	29.123	353.443	219.793	-8.282
5900	5.325	57.337	52.310	29.656	353.976	217.484	-8.056
6000	5.319	57.426	52.395	30.188	354.507	215.165	-7.837

March 31, 1977

KRYPTON UNIPOSITIVE ION (Kr^+) (IDEAL GAS) GFW = 83.79945

Ground State Configuration $^2P_{3/2}$
$S^\circ_{298.15}$ = 41.946 ± 0.005 gibbs/mol

ΔHf°_0 = 322.839 ± 0.006 kcal/mol Kr^+
$\Delta Hf^\circ_{298.15}$ = 324.320 ± 0.006 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	5371.00	2

Heat of Formation

The ionization limit of neutral krypton (112914.5 cm^{-1}) reported by Moore (1) is adopted as ΔHf°_0 for Ne^+(g). The ionization limit is converted from cm^{-1} to kcal/mol using the factor, 1 cm^{-1} = 2.859144×10^{-3} kcal/mol, which is derived from the latest CODATA fundamental constants (2). The uncertainty in the ionization limit is estimated to be ±2 cm^{-1} which corresponds to an uncertainty of ±0.006 kcal/mol in the heat of formation. The value of ΔHf°_{298} is derived from ΔHf°_0 using auxiliary JANAF data (3).

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights by Moore (4) is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (5) has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 109,000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore (1). The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (5).

The thermodynamic functions reported here agree with those by Green et al. (6) and Hilsenrath et al. (7) within the limits of the uncertainty.

References

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LITHIUM NITRIDE (Li_3N) (CRYSTAL) GFW=34.8297

Li_3N

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.680	-37.659	-37.659	INFINITE
100	5.307	2.417	27.484	-2.507	-38.189	-35.995	78.666
200	13.245	8.701	16.471	-1.554	-38.905	-33.500	36.607
298	17.989	14.960	14.960	0.000	-39.330	-30.747	22.538
300	18.055	15.072	14.960	0.033	-39.336	-30.695	22.361
400	20.817	20.675	15.706	1.988	-39.593	-27.771	15.173
500	23.169	25.575	17.189	4.188	-41.999	-24.567	10.738
600	25.437	30.001	18.969	6.619	-42.063	-21.069	7.674
700	27.624	34.087	20.841	9.273	-41.873	-17.584	5.490
800	29.727	37.914	22.738	12.141	-41.452	-14.141	3.863
900	31.749	41.533	24.627	15.215	-40.830	-10.762	2.613
1000	33.688	44.979	26.491	18.488	-40.015	-7.463	1.631
1100	35.538	48.278	28.323	21.951	-39.010	-4.254	0.845
1200	37.311	51.647	30.119	25.594	-37.831	-1.147	0.209
1300	39.000	54.500	31.877	29.410	-36.479	1.856	-0.312

Dec. 31, 1960; Sept. 30, 1966; March 31, 1978

LITHIUM NITRIDE (Li_3N) (CRYSTAL) GFW = 34.8297

ΔHf°_0 = -37.66 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 14.96 ± 0.03 cal/(mol K)

$\Delta Hf^\circ_{298.15}$ = -39.33 ± 0.26 kcal/mol

Tm = 1086 K

Li_3N

Heat of Formation

The adopted heat of formation for $Li_3N(c)$ is derived from the solution calorimetric study of O'Hare and Johnson (1). The reported values have been revised by Osborne and Flotow (2) to correct for the current atomic weight of lithium to give ΔHf°_{298} = -39.33±0.26 kcal/mol. This uncertainty is derived from the experimental studies.

Previous studies on the measurement of the heat of reaction of lithium with nitrogen (4) and the heat of solution of Li_3N *in water (3) are currently thought to be less reliable (1). Both these studies* (3, 4) yielded ΔHf°_{298} values of approximately -47 kcal/mol. Yonco et al. (5) studied the solubility of nitrogen in liquid lithium (468-714 K) and the equilibrium pressure of nitrogen over solid Li_3N (933-1051 K). A second and third law analysis of their reported ΔGf°(T) values supports our adopted S°_{298} value, to within 0.1 cal/(mol K), but suggests a third law ΔHf°_{298} value which is more positive by roughly 1.5 kcal/mol than our adopted value. Emf measurements (823-973 K) of Bonomi et al. (6) gave ΔGf°(T) values which are also more positive than our adopted values by roughly 2 kcal/mol at 900 K. These are suspect since $Li_9N_2Cl_3$ may be involved in the reaction (6). A second and third law analysis of this latter data suggests a S°_{298} value which is 1.8 cal/(mol K) smaller than our adopted value and a third law ΔHf°_{298} value which is more positive by 2 kcal/mol than our adopted value. The S°_{298} discrepancy is very difficult to reconcile without a unreasonable change in the heat capacity values.

Heat Capacity and Entropy

The thermal functions adopted are those tabulated by Osborne and Flotow (2). These authors determined the heat capacity of a well characterized sample of Li_3N between 5 and 350 K. They used the results of Satoh (7), ice calorimetric data from 273 to 773 K, to extend the heat capacity results to 773 K and then extrapolate to 1086 K, the melting point of Li_3N (1, 5).

As a check, the low temperature experimental heat capacity values are smoothed by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. This fitting procedure gave an S°_{298} identical to that reported by Osborne and Flotow (2). The ice calorimetric data of Satoh (7) are not extensive enough to reliably define the entire heat capacity dependence from 350 to 1086 K, however the three data prints at 373 K, 578 K, and 773 K are sufficient to define a reasonable temperature dependence.

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Li_3N

MAGNESIUM MONOSULFIDE (MgS) MgS

(CRYSTAL) GFW=56.365

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.992	-82.372	-82.372	INFINITE
100	5.420	2.610	20.666	-1.806	-82.504	-82.238	179.729
200	9.590	7.910	12.988	-1.016	-82.669	-82.014	89.620
298	10.890	12.030	12.030	0.000	-82.630	-81.603	59.816
300	10.910	12.097	12.030	0.020	-82.631	-81.596	59.442
400	11.380	15.304	12.464	1.136	-83.229	-81.222	44.377
500	11.700	17.879	13.298	2.291	-83.655	-80.673	35.262
600	11.930	20.034	14.246	3.473	-83.998	-80.044	29.155
700	12.080	21.885	15.208	4.674	-84.290	-79.360	24.777
800	12.190	23.505	16.146	5.887	-97.562	-79.835	21.810
900	12.300	24.947	17.045	7.112	-97.537	-77.620	18.849
1000	12.400	26.248	17.902	8.347	-99.665	-75.226	16.440
1100	12.511	27.436	18.715	9.592	-99.669	-72.783	14.460
1200	12.620	28.529	19.488	10.849	-99.690	-70.339	12.810
1300	12.727	29.543	20.223	12.116	-99.731	-67.891	11.413
1400	12.830	30.490	20.923	13.394	-130.155	-64.960	10.141
1500	12.924	31.379	21.591	14.682	-129.826	-60.314	8.788
1600	13.020	32.216	22.229	15.979	-129.492	-55.693	7.607
1700	13.124	33.008	22.840	17.286	-129.151	-51.089	6.568
1800	13.220	33.761	23.426	18.604	-128.803	-46.508	5.647
1900	13.300	34.478	23.989	19.929	-128.449	-41.946	4.825
2000	13.390	35.162	24.530	21.264	-128.089	-37.402	4.087
2100	13.496	35.818	25.052	22.608	-127.723	-32.878	3.422
2200	13.600	36.449	25.556	23.963	-127.349	-28.369	2.818
2300	13.701	37.055	26.043	25.328	-126.966	-23.877	2.269
2400	13.800	37.641	26.514	26.703	-126.576	-19.405	1.767
2500	13.894	38.206	26.971	28.088	-126.179	-14.949	1.307
2600	13.990	38.753	27.413	29.482	-125.774	-10.505	0.883
2700	14.090	39.282	27.843	30.886	-125.362	-6.081	0.492
2800	14.190	39.797	28.261	32.300	-124.941	-1.672	0.130
2900	14.290	40.296	28.667	33.724	-124.513	2.724	-0.205
3000	14.390	40.783	29.063	35.158	-124.078	7.104	-0.517

Dec. 31, 1960; Dec. 31, 1971; Sept. 30, 1977

MAGNESIUM MONOSULFIDE (MgS) (CRYSTAL) GFW = 56.365

$S^\circ_{298.15}$ = 12.03 ± 0.1 gibbs/mol

ΔHf°_0 = -82.4 ± 1.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -82.63 ± 1.0 kcal/mol

MgS

Heat of Formation

Sabatier (1) determined ΔHr°_{286} = -37.8±1.0 kcal/mol while Mourlot (2) determined ΔHr°_{291} = -38.0±1.0 kcal/mol for MgS(c) + 2HCl(100 H_2O,aq) → $MgCl_2$(100 H_2O,aq) + H_2S(aq). We derive ΔHf°_{298}(MgS,c) = -83.0±2.0 kcal/mol and ΔHf°_{298}(MgS,c) = -82.8±2.0 kcal/mol respectively based on the following auxiliary data: ΔHf°_{298}(HCl·100 H_2O,aq) = -39.657 kcal/mol (3), ΔHf°_{298}(H_2S,aq) = -9.5 kcal/mol (3), and ΔHf°_{298}($MgCl_2$·100 H_2O,aq) = -190.59 kcal/mol (4). The uncertainty reflects the correction to 298.15 K and the ambiguity of the exact solution composition. Von Wartenberg (5) measured ΔHr°_{293} = -33.95±0.79 kcal/mol for MgS(c) + 2HCl(30 H_2O,aq) → $MgCl_2$(30 H_2O,aq) + H_2S(g). We derive ΔHf°_{298}(MgS,c) = -82.0±1.0 kcal/mol based on the following auxiliary data: ΔHf°_{298}(HCl·30 H_2O,aq) = -39.357 kcal/mol (3), ΔHf°_{298}(H_2S,g) = -4.90 kcal/mol (3), and ΔHf°_{298}($MgCl_2$·30 H_2O,aq) = -189.78 kcal/mol (4).

Kapustinskii and Korshunov (6) performed calorimetric measurements of the heat of formation of MgS(c) from the pure elements. They determined ΔHf°_{298} = -84.33±0.27 kcal/mol for Mg(c) + S(c,rhombic) = MgS(c).

Our analyses of equilibrium studies of Curlock and Pidgeon (7) and of Dewing and Richardson (8) are given below. The two studies are in reasonable agreement. The third law ΔHr°_{298} may be in error by as much as 0.5 kcal/mol since the free energy functions employed in the calculations are partially based on estimated high temperature C°_p values.

Source	Method	Reaction[a]	Temp T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}, kcal/mol 2nd law	3rd law	ΔHf°_{298}[c] (MgS,c) kcal/mol
(7)Curlock	Equilibrium	A	1180 - 1483	6	-0.60±0.45	-8.49±0.59	-9.19±0.24	-81.59±0.4
(8)Dewing	Equilibrium	A	1267 - 1768	6	-2.23±0.22	-5.53±0.38	-8.73±1.01	-82.05±1.2

[a] Reactions: A) MgS(c) + H_2O(g) = MgO(c) + H_2S(g)

[b] $\delta S = \Delta S_{298}$ (2nd law) - ΔS_{298} (3rd law)

[c] 3rd law ΔHr°_{298} is used to derive ΔHf°_{298}(MgS,c)

Our adopted value is based on a weighted average of all the data.

Heat Capacity and Entropy

Stull et al. (9) measured the low temperature heat capacities in an adiabatic calorimeter from 15 - 320 K. Their smooth values are adopted in the tabulation. The entropy S°_{298} = 12.03±0.1 gibbs/mol is based on S° = 0.010 gibbs/mol at 15 K (9). The C°_p values above 320 K are estimated by graphical extrapolation combined with method B of Kubaschewski et al. (10).

Melting Data

MgS melts above 2300 K (11) and no other literature melting data are available.

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MgS

MAGNESIUM MONOSULFIDE (MGS) MGS

(IDEAL GAS) GFW=56.365

	gibbs/mol			kcal/mol			
T, K	$C_p°$	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.210	34.750	34.750	INFINITE
100	7.020	45.649	60.783	-1.513	35.129	31.090	-67.947
200	7.657	50.692	54.603	-0.782	34.905	27.003	-29.507
298	8.269	53.866	53.866	0.000	34.710	23.264	-17.053
300	8.281	53.917	53.866	0.015	34.704	23.193	-16.896
400	9.075	56.399	54.199	0.880	33.855	19.424	-10.613
500	10.259	58.545	54.857	1.844	33.238	15.887	-6.944
600	11.567	60.533	55.639	2.936	32.805	12.461	-4.539
700	12.605	62.399	56.473	4.148	32.524	9.095	-2.839
800	13.169	64.125	57.323	5.441	19.332	4.563	-1.247
900	13.287	65.686	58.167	6.767	19.458	2.710	-0.658
1000	13.102	67.078	58.990	8.088	17.416	1.025	-0.224
1100	12.758	68.312	59.783	9.382	17.461	-0.617	0.123
1200	12.361	69.405	60.540	10.638	17.439	-2.261	0.412
1300	11.969	70.379	61.260	11.855	17.348	-3.899	0.655
1400	11.612	71.253	61.943	13.033	-13.176	-5.048	0.788
1500	11.300	72.043	62.590	14.178	-12.990	-4.474	0.652
1600	11.033	72.763	63.204	15.295	-12.836	-3.913	0.535
1700	10.807	73.425	63.786	16.386	-12.711	-3.358	0.432
1800	10.618	74.037	64.339	17.457	-12.610	-2.812	0.341
1900	10.460	74.607	64.864	18.511	-12.527	-2.270	0.261
2000	10.328	75.140	65.365	19.550	-12.463	-1.731	0.189
2100	10.218	75.641	65.843	20.577	-12.414	-1.197	0.125
2200	10.126	76.114	66.299	21.594	-12.378	-0.662	0.066
2300	10.050	76.563	66.735	22.603	-12.351	-0.129	0.012
2400	9.986	76.989	67.154	23.605	-12.334	0.400	-0.036
2500	9.933	77.396	67.555	24.601	-12.326	0.929	-0.081
2600	9.889	77.784	67.941	25.592	-12.324	1.461	-0.123
2700	9.853	78.157	68.313	26.579	-12.329	1.991	-0.161
2800	9.824	78.515	68.671	27.562	-12.339	2.520	-0.197
2900	9.800	78.859	69.016	28.544	-12.353	3.052	-0.230
3000	9.781	79.191	69.350	29.523	-12.373	3.583	-0.261
3100	9.767	79.511	69.673	30.500	-12.397	4.116	-0.290
3200	9.756	79.821	69.985	31.476	-12.425	4.648	-0.317
3300	9.749	80.121	70.288	32.451	-12.457	5.182	-0.343
3400	9.745	80.412	70.581	33.426	-12.493	5.719	-0.368
3500	9.743	80.695	70.866	34.400	-12.534	6.253	-0.390
3600	9.743	80.969	71.143	35.375	-12.579	6.791	-0.412
3700	9.746	81.236	71.412	36.349	-12.630	7.331	-0.433
3800	9.750	81.496	71.674	37.324	-12.685	7.872	-0.453
3900	9.756	81.750	71.929	38.299	-12.746	8.411	-0.471
4000	9.763	81.997	72.178	39.275	-12.813	8.955	-0.489
4100	9.771	82.238	72.420	40.252	-12.887	9.500	-0.506
4200	9.780	82.473	72.657	41.229	-12.968	10.046	-0.523
4300	9.791	82.704	72.888	42.208	-13.057	10.595	-0.538
4400	9.802	82.929	73.113	43.187	-13.154	11.147	-0.554
4500	9.814	83.149	73.334	44.168	-13.259	11.702	-0.568
4600	9.827	83.365	73.550	45.150	-13.373	12.259	-0.582
4700	9.840	83.577	73.761	46.134	-13.496	12.817	-0.596
4800	9.854	83.784	73.967	47.118	-13.632	13.379	-0.609
4900	9.868	83.987	74.170	48.104	-13.777	13.942	-0.622
5000	9.882	84.187	74.368	49.092	-13.932	14.510	-0.634
5100	9.897	84.383	74.563	50.081	-14.100	15.077	-0.646
5200	9.912	84.575	74.753	51.071	-14.281	15.653	-0.658
5300	9.928	84.764	74.940	52.063	-14.473	16.233	-0.669
5400	9.943	84.950	75.124	53.057	-14.679	16.810	-0.680
5500	9.959	85.132	75.304	54.052	-14.898	17.397	-0.691
5600	9.975	85.312	75.482	55.049	-15.132	17.985	-0.702
5700	9.991	85.488	75.656	56.047	-15.380	18.583	-0.712
5800	10.007	85.662	75.827	57.047	-15.643	19.176	-0.723
5900	10.023	85.833	75.995	58.048	-15.923	19.783	-0.733
6000	10.039	86.002	76.160	59.051	-16.218	20.386	-0.743

Dec. 31, 1960; June 30, 1971; Sept. 30, 1977

MAGNESIUM MONOSULFIDE (MgS) (IDEAL GAS) GFW = 56.365

D_0^o = [66 ± 16] kcal/mol
$S^o_{298.15}$ = 53.9 ± 1.0 gibbs/mol
Symmetry Number = 1

ΔHf_0^o = [34.75 ± 16] kcal/mol
$\Delta Hf^o_{298.15}$ = [34.71 ± 16] kcal/mol

MGS

Electronic and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	a_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(1)	$X^1\Sigma^+$	0.0	1	2.1425	0.26570	0.00174	526.47	2.681
(2)	$^3\Pi$	[2000.]	6	[2.27]	[0.237]	[0.0015]	[430]	[2.2]
(3)	$^1\Pi$	[3000.]	2	[2.27]	[0.237]	[0.0015]	[430]	[2.2]
(1, 2)	$^3\Sigma^+$	[17000.]	3	[2.1956]	[0.2530]	[0.00153]	[493.20]	[2.313]
(1)	$A^1\Sigma^+$	23036.98	1	2.1956	0.2530	0.00153	495.20	2.313

Heat of Formation

Colin et al. (1) searched unsuccessfully for gaseous MgS in a Knudsen effusion mass-spectrometric experiment. They set the upper limit D_0^o(MgS,g) = 55 kcal/mol. There are no other equilibrium or positive mass spectrometric data involving MgS(g); consequently D_0^o(MgS,g) must be estimated. The Birge-Sponer extrapolation is of little utility in this case. Gaydon (2) has gone into great detail concerning the problems inherent in linear-Birge-Sponer extrapolations (LBX) on the oxides and sulfides of the alkaline earths. The normal LBX yields D_0^o(MgS,g) = 73 kcal/mol. When adjusted for ionic character with the Hildenbrand correction (3), D_0^o(MgS,g) = 65 kcal/mol. The $^1\Sigma$ ground state of MgS cannot dissociate into ground state atoms. After correcting for the excited atomic products, D_0^o(MgS,g) = 42 kcal/mol. A more reliable method of estimation is that of Hauge and Margrave (4) based on the observation that the ratio $D_{MS}K_{MO}/D_{MO}K_{MS}$ is very similar for elements within a given group. Based on data involving known bond energies and force constants of the gaseous diatomic oxides and sulfides, we calculate D_0^o(MgS,g) = 78±10 kcal/mol. Dissociation energies of the alkaline earth monoxides were taken from Srivastava (5), dissociation energies for the alkaline earth sulfides were taken from the JANAF Thermochemical Tables (6) and force constants were calculated from spectroscopic data of Barrow and Cousins (7). Further comparisons of vapor pressures and heats of sublimation for the other alkaline earth oxides and sulfides (6) suggest lower values of D_0^o(MgS,g) than the Hauge and Margrave method leads to. We adopt D_0^o(MgS,g) ≤ 66±16 kcal/mol. Using Auxiliary JANAF data (6), we calculate ΔHf^o_{298}(MgS,g) = 34.71±16 kcal/mol.

Heat Capacity and Entropy

The spectroscopic constants of the observed states, taken from Marcano and Barrow (8) for the isotopic species $Mg^{24}S^{32}$, are corrected to account for the natural abundances of the elements. *Other low-lying electronic states and their vibrational-*rotational constants are estimated in isoconfigurational groups by analogy with MgO (6) and from trends observed in the known states of the other alkaline-earth oxides and sulfides (6). Uncertainty in the energy and molecular constants for the estimated states may contribute significantly, perhaps as much as 1.0 gibbs/mol to the entropy at 298 K.

The ground state of gaseous MgS is taken as $^1\Sigma^+$. There should be low-lying triplet states. A $^1\Pi$ state is predicted for MgS at 3000 cm^{-1} based on experimentally observed $^1\Pi$ states for MgO (9), BeO (6), and BeS (10). The corresponding triplet, $^3\Pi$, is assumed to lie 1000 cm^{-1} lower in energy based on trends in the triplet-singlet splitting observed by Field (11) for the alkaline-earth oxides. Similar trends in the triplet-singlet splitting of the isoconfigurational Σ states are used to place the $^3\Sigma^+$ state 6000 cm^{-1} below the experimentally observed (8) $A^1\Sigma^+$ state. By analogy with MgO (6) we do not feel that a $^1\Delta$ state exists below 25000 cm^{-1}. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\varepsilon_i/T)$.

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MGS

MOLYBDENUM (Mo) (REFERENCE STATE) GFW = 95.94

Mo

0 - 2896 K Crystal
2896 - 4956.79 K Liquid
4956.59 - 6000 K Ideal Gas, Monatomic

See Mo(c), Mo(ℓ), and Mo(g) tables for details

Mo

MOLYBDENUM (Mo)
(REFERENCE STATE) GFW=95.94

Mo

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	-1.096	0.000	0.000	0.000
100	3.226	1.679	11.462	-0.978	0.000	0.000	0.000
200	5.140	4.655	7.345	-0.538	0.000	0.000	0.000
298	5.720	6.836	6.836	0.000	0.000	0.000	0.000
300	5.726	6.872	6.836	0.011	0.000	0.000	0.000
400	5.994	8.558	7.064	0.597	0.000	0.000	0.000
500	6.178	9.917	7.503	1.207	0.000	0.000	0.000
600	6.324	11.056	8.003	1.832	0.000	0.000	0.000
700	6.448	12.041	8.511	2.471	0.000	0.000	0.000
800	6.558	12.909	9.008	3.121	0.000	0.000	0.000
900	6.666	13.688	9.485	3.782	0.000	0.000	0.000
1000	6.781	14.396	9.941	4.455	0.000	0.000	0.000
1100	6.907	15.048	10.376	5.139	0.000	0.000	0.000
1200	7.048	15.655	10.791	5.836	0.000	0.000	0.000
1300	7.204	16.225	11.187	6.549	0.000	0.000	0.000
1400	7.376	16.765	11.567	7.278	0.000	0.000	0.000
1500	7.565	17.280	11.931	8.025	0.000	0.000	0.000
1600	7.768	17.775	12.280	8.791	0.000	0.000	0.000
1700	7.988	18.252	12.618	9.579	0.000	0.000	0.000
1800	8.227	18.716	12.944	10.389	0.000	0.000	0.000
1900	8.482	19.167	13.259	11.225	0.000	0.000	0.000
2000	8.760	19.609	13.566	12.087	0.000	0.000	0.000
2100	9.058	20.044	13.864	12.977	0.000	0.000	0.000
2200	9.379	20.472	14.155	13.899	0.000	0.000	0.000
2300	9.720	20.897	14.439	14.853	0.000	0.000	0.000
2400	10.088	21.318	14.717	15.844	0.000	0.000	0.000
2500	10.490	21.738	14.989	16.872	0.000	0.000	0.000
2600	10.966	22.158	15.257	17.944	0.000	0.000	0.000
2700	11.561	22.583	15.520	19.069	0.000	0.000	0.000
2800	12.326	23.017	15.780	20.262	0.000	0.000	0.000
2900	9.000	26.427	16.041	30.119	0.000	0.000	0.000
3000	9.000	26.732	16.393	31.019	0.000	0.000	0.000
3100	9.000	27.028	16.731	31.919	0.000	0.000	0.000
3200	9.000	27.313	17.057	32.819	0.000	0.000	0.000
3300	9.000	27.590	17.372	33.719	0.000	0.000	0.000
3400	9.000	27.859	17.677	34.619	0.000	0.000	0.000
3500	9.000	28.120	17.971	35.519	0.000	0.000	0.000
3600	9.000	28.373	18.257	36.419	0.000	0.000	0.000
3700	9.000	28.620	18.534	37.319	0.000	0.000	0.000
3800	9.000	28.860	18.802	38.219	0.000	0.000	0.000
3900	9.000	29.094	19.063	39.119	0.000	0.000	0.000
4000	9.000	29.322	19.317	40.019	0.000	0.000	0.000
4100	9.000	29.544	19.563	40.919	0.000	0.000	0.000
4200	9.000	29.761	19.804	41.819	0.000	0.000	0.000
4300	9.000	29.972	20.038	42.719	0.000	0.000	0.000
4400	9.000	30.179	20.266	43.619	0.000	0.000	0.000
4500	9.000	30.382	20.488	44.519	0.000	0.000	0.000
4600	9.000	30.579	20.706	45.419	0.000	0.000	0.000
4700	9.000	30.773	20.918	46.319	0.000	0.000	0.000
4800	9.000	30.962	21.125	47.219	0.000	0.000	0.000
4900	9.000	31.148	21.328	48.119	0.000	0.000	0.000
5000	12.680	59.832	21.773	190.292	0.000	0.000	0.000
5100	13.006	60.086	22.522	191.577	0.000	0.000	0.000
5200	13.325	60.342	23.247	192.893	0.000	0.000	0.000
5300	13.639	60.599	23.949	194.242	0.000	0.000	0.000
5400	13.948	60.856	24.630	195.621	0.000	0.000	0.000
5500	14.252	61.115	25.291	197.031	0.000	0.000	0.000
5600	14.552	61.375	25.933	198.471	0.000	0.000	0.000
5700	14.847	61.635	26.557	199.941	0.000	0.000	0.000
5800	15.140	61.896	27.164	201.441	0.000	0.000	0.000
5900	15.430	62.157	27.755	202.969	0.000	0.000	0.000
6000	15.719	62.419	28.331	204.527	0.000	0.000	0.000

Dec. 31, 1966; March 31, 1978

Mo

MOLYBDENUM (Mo) Mo
(CRYSTAL) GFW=95.94

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.096	0.000	0.000	0.000
100	3.226	1.679	11.462	-0.978	0.000	0.000	0.000
200	5.140	4.655	7.345	-0.538	0.000	0.000	0.000
298	5.720	6.836	6.836	0.000	0.000	0.000	0.000
300	5.726	6.872	6.836	0.011	0.000	0.000	0.000
400	5.994	8.558	7.064	0.597	0.000	0.000	0.000
500	6.178	9.917	7.503	1.207	0.000	0.000	0.000
600	6.324	11.056	8.003	1.832	0.000	0.000	0.000
700	6.448	12.041	8.511	2.471	0.000	0.000	0.000
800	6.558	12.909	9.008	3.121	0.000	0.000	0.000
900	6.666	13.688	9.485	3.782	0.000	0.000	0.000
1000	6.781	14.396	9.941	4.455	0.000	0.000	0.000
1100	6.907	15.048	10.376	5.139	0.000	0.000	0.000
1200	7.048	15.655	10.791	5.836	0.000	0.000	0.000
13C0	7.204	16.225	11.187	6.549	0.000	0.000	0.000
1400	7.376	16.765	11.567	7.278	0.000	0.000	0.000
15CC	7.565	17.280	11.931	8.025	0.000	0.000	0.000
1600	7.768	17.775	12.280	8.791	0.000	0.000	0.000
17C0	7.988	18.252	12.618	9.579	0.000	0.000	0.000
1800	8.227	18.716	12.944	10.389	0.000	0.000	0.000
1900	8.482	19.167	13.259	11.225	0.000	0.000	0.000
2000	8.760	19.609	13.566	12.087	0.000	0.000	0.000
2100	9.058	20.044	13.864	12.977	0.000	0.000	0.000
2200	9.379	20.472	14.155	13.899	0.000	0.000	0.000
2300	9.720	20.897	14.439	14.853	0.000	0.000	0.000
2400	10.088	21.318	14.717	15.844	0.000	0.000	0.000
2500	10.490	21.738	14.989	16.872	0.000	0.000	0.000
2600	10.966	22.158	15.257	17.944	0.000	0.000	0.000
2700	11.561	22.583	15.520	19.069	0.000	0.000	0.000
2800	12.326	23.017	15.780	20.262	0.000	0.000	0.000
2900	13.138	23.463	16.037	21.538	-8.583	0.012	-0.001
3000	13.951	23.922	16.292	22.890	-8.129	0.301	-0.022
3100	14.763	24.393	16.546	24.326	-7.593	0.573	-0.040
3200	15.576	24.875	16.799	25.843	-6.976	0.827	-0.056
3300	16.389	25.366	17.051	27.441	-6.278	1.060	-0.070

Dec. 31, 1966; March 31, 1978

MOLYBDENUM (Mo) (CRYSTAL) GFW = 95.94

Mo

$S^\circ_{298.15}$ = 6.836 ± 0.012 cal/(mol K)
Tm = 2896 ± 8 K

ΔHf°_0 = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol
ΔHm° = 8.6 ± 1.3 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 157.5 ± 0.9 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities of Mo(c) have been measured by Clusius and Franzosini (1) between 16 and 256 K (63 measured Cp points). The reported Cp values are smoothed by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. This fitting procedure also includes the smoothed Cp° values (275-335 K) reported in the critical evaluation by Ditmars et al. (2) so as to provide smoothly varying heat capacity values in the range 256-275 K. The data of Simon and Zeidler (3), 15-238 K, are as much as 2.5% high below 78 K and as much as 1% low above 78 K.

Below 20 K several investigators (4, 5, 6, 7) have determined the heat capacity. Heiniger et al. (8) have summarized and critically reviewed this work as well as other studies. These sources give S°_{20} values in the range 0.021-0.025 cal/(mol K). Adopting S°_{20} = 0.024 cal/(mol K) and combining this with our analysis of the Clusius and Franzosoni work (1), we calculate S°_{298} = 6.836±0.012 cal/(mol K). This result agrees with the review of the heat capacity data (T <298.15 K) by Reilly and Furukawa (9) for Brewer (10).

The high temperature heat capacity values, 273-2800 K, are those selected by Ditmars et al. (2). This study reports three recent NBS heat capacity/enthalpy studies covering the 270-2800 K on NBS Standard Reference Material No. 781. In addition, the report contains a bibliography of publications on the high temperature enthalpy and heat capacity of crystalline molybdenum. A graphical comparison of the NBS results with those of all the principal investigators and critical evaluation is also given in the publication. These results are linearly extrapolated from 2800 K to 3300 K. The high temperature heat capacity values adopted by Brewer (10), based on IPTS-48, are within 0.1% of the NBS results between 298 and 900 K and are 0.2 to 0.3% higher between 1000 and 1400 K. Between 1500 and 1900 K, the difference is less than 0.1%. From 2000 to 2300 K, the values are 0.2 to 0.3% lower and are 0.1% low to 0.2% high between 2400 to 2700 K. The value at 2800 K is 0.5% lower than our adopted value. At 2800 K, the entropy difference is 0.004 cal/(mol K) with the JANAF value being smaller.

Melting Data

Refer to the Mo(ℓ) table.

Sublimation Data

Eight sublimation studies are discussed on the Mo(g) table.

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Mo

MOLYBDENUM (MO)　　　　MO
(LIQUID) GFW=95.94

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	5.720	10.312	10.312	0.000	9.935	8.899	-6.523
300	5.726	10.347	10.312	0.011	9.935	8.892	-6.478
400	5.994	12.034	10.540	0.597	9.935	8.545	-4.669
500	6.178	13.392	10.979	1.207	9.935	8.197	-3.583
600	6.324	14.532	11.478	1.832	9.935	7.850	-2.859
700	6.448	15.516	11.987	2.471	9.935	7.502	-2.342
800	6.558	16.385	12.483	3.121	9.935	7.155	-1.955
900	6.666	17.163	12.961	3.782	9.935	6.808	-1.653
1000	6.781	17.871	13.417	4.455	9.935	6.459	-1.412
1100	6.907	18.523	13.852	5.139	9.935	6.112	-1.214
1200	7.048	19.130	14.267	5.836	9.935	5.765	-1.050
1300	7.204	19.700	14.663	6.549	9.935	5.417	-0.911
1400	7.376	20.241	15.042	7.278	9.935	5.069	-0.791
1500	7.565	20.756	15.406	8.025	9.935	4.722	-0.688
1600	7.768	21.250	15.756	8.791	9.935	4.375	-0.598
1700	7.988	21.728	16.093	9.579	9.935	4.027	-0.518
1800	8.227	22.191	16.419	10.389	9.935	3.680	-0.447
1900	8.482	22.643	16.735	11.225	9.935	3.331	-0.383
2000	8.760	23.085	17.041	12.087	9.935	2.984	-0.326
2100	9.058	23.519	17.340	12.977	9.935	2.637	-0.274
2200	9.000	23.941	17.630	13.884	9.920	2.289	-0.227
2300	9.000	24.341	17.913	14.784	9.866	1.944	-0.185
2400	9.000	24.724	18.189	15.684	9.775	1.601	-0.146
2500	9.000	25.092	18.458	16.584	9.647	1.263	-0.110
2600	9.000	25.445	18.720	17.484	9.475	0.931	-0.078
2700	9.000	25.784	18.975	18.384	9.250	0.607	-0.049
2800	9.000	26.112	19.224	19.284	8.957	0.291	-0.023
2900	9.000	26.427	19.467	20.184	0.000	0.000	0.000
3000	9.000	26.732	19.704	21.084	0.000	0.000	0.000
3100	9.000	27.028	19.936	21.984	0.000	0.000	0.000
3200	9.000	27.313	20.162	22.884	0.000	0.000	0.000
3300	9.000	27.590	20.383	23.784	0.000	0.000	0.000
3400	9.000	27.859	20.599	24.684	0.000	0.000	0.000
3500	9.000	28.120	20.810	25.584	0.000	0.000	0.000
3600	9.000	28.373	21.017	26.484	0.000	0.000	0.000
3700	9.000	28.620	21.219	27.384	0.000	0.000	0.000
3800	9.000	28.860	21.417	28.284	0.000	0.000	0.000
3900	9.000	29.094	21.611	29.184	0.000	0.000	0.000
4000	9.000	29.322	21.801	30.084	0.000	0.000	0.000
4100	9.000	29.544	21.987	30.984	0.000	0.000	0.000
4200	9.000	29.761	22.169	31.884	0.000	0.000	0.000
4300	9.000	29.972	22.348	32.784	0.000	0.000	0.000
4400	9.000	30.179	22.524	33.684	0.000	0.000	0.000
4500	9.000	30.382	22.696	34.584	0.000	0.000	0.000
4600	9.000	30.579	22.865	35.484	0.000	0.000	0.000
4700	9.000	30.773	23.032	36.384	0.000	0.000	0.000
4800	9.000	30.962	23.195	37.284	0.000	0.000	0.000
4900	9.000	31.148	23.355	38.184	0.000	0.000	0.000
5000	9.000	31.330	23.513	39.084	-141.273	1.237	-0.054
5100	9.000	31.508	23.668	39.984	-141.658	4.090	-0.175
5200	9.000	31.683	23.821	40.884	-142.074	6.952	-0.292
5300	9.000	31.854	23.970	41.784	-142.523	9.822	-0.405
5400	9.000	32.023	24.118	42.684	-143.002	12.701	-0.514
5500	9.000	32.188	24.263	43.584	-143.512	15.589	-0.619

Dec. 31, 1966; March 31, 1978

MOLYBDENUM (Mo)　　　　(LIQUID)　　　　GFW = 95.94

$S°_{298.15}$ = [10.312] cal/(mol K)　　　　$\Delta Hf°_{298.15}$ = [9.935] kcal/mol　　Mo

Tm = 2896 ± 8 K　　　　ΔHm° = 8.6 ± 1.3 kcal/mol

Tb = 4956.59 K　　　　ΔHv° = 141.117 kcal/mol

Heat of Formation

The heat of formation is obtained from that of the crystal by addition of ΔHm° and the difference between $H°_{2896}-H°_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

Enthalpy measurements via levitation calorimetry by Treverton and Margrave (3) were over a sufficient range of temperature, 2692-3112 K, to establish Cp°(ℓ) = 8.19 cal/(mol K). The enthalpy measurements of Berezin et al. (2) in the liquid region (14 pts., 2890-2925 K) are insufficient to define a liquid phase heat capacity value. Shaner et al. (5) and Dikhter and Lebedev (6) have reported Cp°(ℓ) values of 16.7 cal/(mol K) and 14.0 cal/(mol K), respectively, using pulse heating techniques.

We adopt Cp°(ℓ) =.9.0 cal/(mol K) as did Brewer (9). This value implies a heavier weighting of the drop calorimetric studies rather than the pulse heating techniques. The magnitude of the difference of the Cp°(ℓ) values derived from the various studies (3, 5, 6) suggests further study in this area. A glass transition is assumed at 2150 K below which the heat capacity is assumed to be that of the crystal. The entropy is calculated in a manner analogous to the heat of formation.

Melting Data

The adopted melting point, Tm = 2896±8 K, is derived from the recent experimental study and critical evaluation of earlier data by Kenisarin et al. (1).

Berezin et al. (2) have measured the enthalpy of crystal and liquid molybdenum by levitation calorimetry in the range 1962-2869 K and 2890-2925 K, respectively. They reported ΔHm° = 8.741±0.314 kcal/mol at an assumed melting temperature of 2890 K. Correcting these results to Tm = 2896 K yields 8.693±0.314 kcal/mol. Shaner et al. (5), using a pulse-heating technique, reported enthalpy measurements (1978-4450 K) which gave ΔHm° = 8.553 kcal/mol at a melting point of 2883 K.

Treverton and Margrave (3) also used levitation calorimetry to measure the liquid phase enthalpy of molybdenum in the range 2693-3115 K. Using the enthalpy value for the liquid at the melting point as determined by Treverton and Margrave (3) and the enthalpy value for the crystal at the melting point as determined by our adopted functions, we calculate ΔHm° = 7.264 kcal/mol. Lebedev et al. (7) reported ΔHm° = 9.864 kcal/mol (exploding wire technique) while Kostekov et al. (8) found ΔHm° = 6.095 kcal/mol (drop technique).

We adopt ΔHm° = 8.6±1.3 kcal/mol, which corresponds to ΔSm° = 2.97 cal/(mol K). This ΔSm° appears high for a metal with a bcc (A2) structure; however, this value is supported by the studies of Berezin et al. (2) and Shaner et al. (5). Brewer (9) selected a value of ΔHm° = 8.54±0.3 kcal/mol (IPTS-48).

Vaporization Data

The boiling point and heat of vaporization are calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Koch and Anable (4) have measured the vapor pressure of liquid molybdenum by a Langmuir free-evaporation method. They measured 16 data points in the range 2895-2995 K. A second and third law analysis gives $\Delta Hv°_{298}$ values of 136.8±18.4 and 147.7±1.7 kcal/mol, respectively. This corresponds to our adopted value of $\Delta Hv°_{298}$ = 147.565 kcal/mol. Note, however, that there is a significant difference between the second and third law results.

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MOLYBDENUM, MONATOMIC (MO) Mo

(IDEAL GAS) GFW=95.94

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	157.115	157.115	INFINITE
100	4.968	38.034	47.878	-0.984	157.494	153.858	-336.252
200	4.968	41.478	43.915	-0.488	157.550	150.186	-164.113
298	4.968	43.461	43.461	0.000	157.500	146.580	-107.445
300	4.968	43.492	43.461	0.009	157.498	146.512	-106.733
400	4.968	44.921	43.656	0.506	157.409	142.864	-78.056
500	4.968	46.030	44.024	1.003	157.296	139.239	-60.861
600	4.968	46.935	44.436	1.500	157.168	135.640	-49.406
700	4.968	47.701	44.849	1.996	157.025	132.063	-41.231
800	4.968	48.365	45.248	2.493	156.872	128.508	-35.106
900	4.968	48.950	45.628	2.990	156.708	124.972	-30.347
1000	4.968	49.473	45.986	3.487	156.532	121.455	-26.544
1100	4.969	49.947	46.325	3.984	156.345	117.956	-23.435
1200	4.970	50.379	46.645	4.481	156.145	114.475	-20.849
1300	4.972	50.777	46.948	4.978	155.929	111.011	-18.662
1400	4.977	51.146	47.235	5.475	155.697	107.564	-16.791
1500	4.985	51.489	47.507	5.973	155.448	104.135	-15.172
1600	4.998	51.811	47.766	6.472	155.181	100.723	-13.758
1700	5.016	52.115	48.013	6.973	154.894	97.328	-12.512
1800	5.043	52.402	48.249	7.476	154.587	93.951	-11.407
1900	5.079	52.676	48.475	7.982	154.257	90.590	-10.420
2000	5.125	52.937	48.692	8.492	153.905	87.248	-9.534
2100	5.183	53.189	48.900	9.007	153.530	83.925	-8.734
2200	5.254	53.432	49.100	9.529	153.130	80.620	-8.009
2300	5.340	53.667	49.294	10.058	152.705	77.334	-7.348
2400	5.440	53.896	49.481	10.597	152.253	74.066	-6.745
2500	5.556	54.121	49.662	11.147	151.775	70.818	-6.191
2600	5.689	54.341	49.838	11.709	151.265	67.590	-5.681
2700	5.838	54.559	50.008	12.285	150.716	64.382	-5.211
2800	6.005	54.774	50.175	12.877	150.115	61.195	-4.776
2900	6.190	54.988	50.337	13.487	140.868	58.042	-4.374
3000	6.391	55.201	50.496	14.116	140.597	55.191	-4.021
3100	6.610	55.414	50.651	14.766	140.347	52.349	-3.691
3200	6.846	55.628	50.803	15.439	140.120	49.514	-3.382
3300	7.099	55.842	50.952	16.136	139.917	46.685	-3.092
3400	7.367	56.058	51.099	16.859	139.740	43.863	-2.819
3500	7.649	56.276	51.244	17.610	139.591	41.045	-2.563
3600	7.946	56.495	51.387	18.389	139.470	38.232	-2.321
3700	8.254	56.717	51.528	19.199	139.380	35.420	-2.092
3800	8.574	56.941	51.668	20.040	139.321	32.612	-1.876
3900	8.902	57.168	51.806	20.914	139.295	29.804	-1.670
4000	9.239	57.398	51.943	21.821	139.302	26.996	-1.475
4100	9.582	57.630	52.079	22.762	139.343	24.188	-1.289
4200	9.928	57.865	52.213	23.738	139.419	21.379	-1.112
4300	10.278	58.103	52.348	24.748	139.529	18.567	-0.944
4400	10.628	58.343	52.481	25.793	139.674	15.753	-0.782
4500	10.978	58.586	52.614	26.874	139.855	12.934	-0.628
4600	11.326	58.831	52.747	27.989	140.070	10.112	-0.480
4700	11.671	59.079	52.879	29.139	140.320	7.284	-0.339
4800	12.013	59.328	53.011	30.323	140.604	4.450	-0.203
4900	12.349	59.579	53.142	31.541	140.922	1.610	-0.072
5000	12.680	59.832	53.273	32.793	0.000	0.000	0.000
5100	13.006	60.086	53.404	34.077	0.000	0.000	0.000
5200	13.325	60.342	53.535	35.394	0.000	0.000	0.000
5300	13.639	60.599	53.666	36.742	0.000	0.000	0.000
5400	13.948	60.856	53.797	38.121	0.000	0.000	0.000
5500	14.252	61.115	53.928	39.531	0.000	0.000	0.000
5600	14.551	61.375	54.058	40.971	0.000	0.000	0.000
5700	14.847	61.635	54.189	42.441	0.000	0.000	0.000
5800	15.140	61.896	54.320	43.941	0.000	0.000	0.000
5900	15.430	62.157	54.450	45.469	0.000	0.000	0.000
6000	15.719	62.419	54.581	47.027	0.000	0.000	0.000

Dec. 31, 1966; March 31, 1978

ΔHf_0° = 157.1 ± 0.9 kcal/mol Mo

$S^\circ_{298.15}$ = 43.461 ± 0.01 cal/(mol K)

$\Delta Hf^\circ_{298.15}$ = 157.5 ± 0.9 kcal/mol

Electronic Levels and Quantum Weight

State	ε_i, cm^{-1}	g_i
$^7S_3$	0	7
$^5S_2$	10768.33	5
⋮	⋮	⋮
$^6S_{5/2}(Mo^+)$	57144.26	7

Ionization limit = 57260 cm^{-1}

Heat of Formation

The heat of formation at 298.15 K for Mo(g) is simply the heat of sublimation at 298.15 K; i.e. Mo(c) = Mo(g). The following table summarizes the analysis of the numerous sublimation studies by a second and third law calculation., All temperatures have been corrected to IPTS-68. All studies are based on the Langmuir effusion method.

			ΔHs°_{298}, kcal/mol		Drift
Reference	Points	Range, K	2nd Law	3rd Law	cal/(mol K)
1	eqn	1201-2396	159.8	158.5	-0.7
2	9	2068-2500	162.2±3.8	156.2±1.4	-2.6±1.6
3	12	2144-2537	158.4±2.6	157.8±0.8	-0.3±1.1
4	9	2154-2466	146.8±1.4	158.4±1.2	5.1±0.6
5	eqn	1601-2297	131.7	148.8	8.8
6	12	2089-2493	156.8±1.6	156.9±0.6	0.1±0.7
7	10	2293-2673	152.4±4.1	158.2±1.4	2.3±1.6

A mass spectrometric study of the heat of sublimation of molybdenum (8) yielded ΔHs°_{2500} = 144.1±2.2 kcal/mol; correcting to 298.15 K, we calculate ΔHs°_{298} = 149.8 kcal/mol.

We adopt ΔHs°_{298}= 157.5±0.9 kcal/mol from a consideration of five studies (1, 2, 3, 6, 7). Brewer (12) has adopted a value 0.2 kcal/mol less positive; however his vapor pressure analysis is based on the 1948 temperature scale.

Heat Capacity and Entropy

The electronic energy levels are given in the compilations by Moore (9, 10). Although we have only listed the ground state, first excited state, highest observed excited state, and the ionization limit for Mo(g), all levels listed by Moore (9, 10), as well as estimated levels, are used in our calculations. The observed levels are too numerous to list completely. An examination of the estimates for missing levels suggests that they all lie above 20000 cm^{-1}. Our calculations indicate that for Mo(g) the thermochemical functions are independent of the estimated missing levels (for n = 5, 6, 7), the cut-off procedure, and the inclusion of n = 6, 7 levels up to 3000 K. The free energy function is essentially unaffected up to 4000 K. The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut-off procedures (11). In fact, the inclusion of some higher states (n = 5, 6, 7) and consideration of various cut-off procedures leads to calculational differences in the free energy function of roughly 0.1 cal/(mol K) or greater at temperatures in excess of 7600 K. The thermal functions adopted here are the same as those of Brewer (12).

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Mo

MOLYBDENUM, UNIPOSITIVE ION (Mo^+) Mo^+
(IDEAL GAS) GFW=95.93945

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	320.830		
100							
200							
298	4.968	43.155	43.155	0.000	322.696	310.380	-227.512
300	4.968	43.186	43.155	0.009	322.703	310.303	-224.053
400	4.968	44.615	43.350	0.506	323.111	306.109	-167.248
500	4.968	45.723	43.718	1.003	323.495	301.813	-131.921
600	4.968	46.629	44.130	1.500	323.864	297.443	-108.342
700	4.968	47.395	44.543	1.996	324.217	293.010	-91.481
800	4.968	48.058	44.942	2.493	324.561	288.529	-78.821
900	4.968	48.643	45.321	2.990	324.894	284.005	-68.965
1000	4.968	49.167	45.680	3.487	325.215	279.444	-61.072
1100	4.968	49.640	46.019	3.984	325.525	274.852	-54.607
1200	4.969	50.073	46.339	4.480	325.820	270.232	-49.215
1300	4.970	50.470	46.642	4.977	326.101	265.588	-44.649
1400	4.972	50.839	46.928	5.474	326.366	260.923	-40.731
1500	4.977	51.182	47.201	5.972	326.614	256.240	-37.334
1600	4.986	51.503	47.460	6.470	326.843	251.542	-34.359
1700	4.999	51.806	47.707	6.969	327.050	246.828	-31.731
1800	5.020	52.092	47.942	7.470	327.238	242.104	-29.395
1900	5.050	52.365	48.168	7.973	327.402	237.369	-27.303
2000	5.091	52.625	48.384	8.480	327.544	232.627	-25.420
2100	5.145	52.874	48.592	8.992	327.663	227.879	-23.715
2200	5.214	53.115	48.792	9.510	327.755	223.124	-22.165
2300	5.300	53.349	48.985	10.035	327.823	218.367	-20.749
2400	5.405	53.576	49.172	10.570	327.864	213.607	-19.451
2500	5.528	53.799	49.353	11.117	327.880	208.846	-18.257
2600	5.672	54.019	49.528	11.677	327.865	204.085	-17.155
2700	5.837	54.236	49.698	12.252	327.811	199.325	-16.134
2800	6.022	54.452	49.864	12.845	327.708	194.568	-15.186
2900	6.228	54.667	50.026	13.457	318.960	189.827	-14.306
3000	6.453	54.881	50.184	14.091	319.191	185.371	-13.504
3100	6.696	55.097	50.339	14.748	319.445	180.906	-12.754
3200	6.957	55.314	50.491	15.431	319.724	176.432	-12.050
3300	7.233	55.532	50.641	16.140	320.030	171.949	-11.388
3400	7.522	55.752	50.788	16.878	320.365	167.457	-10.764
3500	7.823	55.974	50.933	17.645	320.729	162.955	-10.175
3600	8.133	56.199	51.076	18.443	321.124	158.442	-9.619
3700	8.450	56.426	51.218	19.272	321.549	153.916	-9.091
3800	8.770	56.656	51.358	20.133	322.007	149.380	-8.591
3900	9.092	56.888	51.496	21.026	322.497	144.831	-8.116
4000	9.412	57.122	51.634	21.951	323.019	140.269	-7.664
4100	9.729	57.358	51.771	22.908	323.573	135.694	-7.233
4200	10.040	57.597	51.907	23.897	324.158	131.104	-6.822
4300	10.342	57.836	52.042	24.916	324.774	126.500	-6.429
4400	10.634	58.078	52.176	25.965	325.420	121.882	-6.054
4500	10.913	58.320	52.310	27.043	326.095	117.249	-5.694
4600	11.177	58.562	52.443	28.147	326.796	112.600	-5.350
4700	11.426	58.806	52.576	29.277	327.522	107.935	-5.019
4800	11.658	59.049	52.709	30.432	328.274	103.255	-4.701
4900	11.872	59.291	52.840	31.609	329.048	98.560	-4.396
5000	12.068	59.533	52.972	32.806	188.569	95.085	-4.156
5100	12.244	59.774	53.103	34.021	188.995	93.210	-3.994
5200	12.401	60.013	53.233	35.254	189.409	91.328	-3.838
5300	12.538	60.251	53.364	36.501	189.804	89.438	-3.688
5400	12.656	60.486	53.493	37.761	190.182	87.541	-3.543
5500	12.756	60.719	53.623	39.032	190.540	85.637	-3.403
5600	12.837	60.950	53.751	40.311	190.875	83.726	-3.268
5700	12.900	61.178	53.880	41.598	191.189	81.810	-3.137
5800	12.946	61.402	54.007	42.891	191.479	79.888	-3.010
5900	12.976	61.624	54.135	44.187	191.744	77.963	-2.888
6000	12.992	61.842	54.261	45.486	191.982	76.032	-2.769

Dec. 31, 1966; March 31, 1978

MOLYBDENUM, UNIPOSITIVE ION (Mo^+) (IDEAL GAS) GFW = 95.93945

ΔHf°_0 = 320.83 ± 0.9 kcal/mol Mo^+

$S^\circ_{298.15}$ = 43.155 ± 0.01 cal/(mol K) $\Delta Hf^\circ_{298.15}$ = [322.696] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0	6
$^6D_{1/2}$	11783.36	2
.	.	.
$^2F^\circ_{5/2}$	86566.24	6

ionization limit = 130300 cm^{-1}

Heat of Formation

The adopted heat of formation ΔHf°_0 is calculated from the equation Mo(g) = $Mo^+(g) + e^-(g)$ with auxiliary data (1), using an ionization potential of IP = 57260±10 cm^{-1} (163.715±0.03 kcal/mol). This ionization potential, as reported by Moore (2) in units of cm^{-1}, is converted to units of kcal/mol using current CODATA fundamental constants (3). The uncertainty in ΔHf°_0 lies mainly in the uncertainty for ΔHf°_0(Mo,g). Brewer (7) has used the same IP value.

$\Delta Hf^\circ_{298}(Mo^+,g)$ is obtained from ΔHf°_0(Mo,g) by using IP(Mo) with JANAF (1) enthalpies ($H^\circ_0-H^\circ_{298}$) for Mo(g), $Mo^+(g)$, and $e^-(g)$. $\Delta Hr^\circ_{298}(Mo = Mo^+ + e^-)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (4). ΔHf°_{298} should be changed by -1.481 kcal/mol if it is to be used in the ion convention *which excludes the enthalpy of the electron.*

Heat Capacity and Entropy

The electronic energy levels are given in the compilations by Moore (2, 5). Although we have only listed the ground state, first excited state, highest observed excited state, and the ionization limit for $Mo^+(g)$, all levels listed by Moore (2, 5), as well as estimated missing levels, are used in our calculations. The observed levels are too numerous to list completely. An examination of the estimates for missing levels suggests that they all lie above 50000 cm^{-1}. Our calculations indicate that for $Mo^+(g)$ the thermochemical functions are independent of the estimated missing levels (for n = 4, 5) and the cut-off procedure up to 4200 K. The free energy function is essentially unaffected up to 6300 K. The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut-off procedures (6). In fact, the inclusion of some higher state (n = 4, 5) and consideration of various cut-off procedures leads to calculational differences in the free energy function of roughly 0.1 cal/(mol K) or greater at temperatures in excess of 8000 K. The thermal functions adopted here are the same as those of Brewer (7).

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MOLYBDENUM, UNINEGATIVE ION (Mo^-) Mo^-
(IDEAL GAS) GFW=95.94055

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	134.055		
100							
200							
298	4.968	43.155	43.155	0.000	132.959	123.618	-90.613
300	4.968	43.186	43.155	0.009	132.948	123.560	-90.012
400	4.968	44.615	43.350	0.506	132.362	120.518	-65.847
500	4.968	45.723	43.718	1.003	131.752	117.627	-51.414
600	4.968	46.629	44.130	1.500	131.127	114.860	-41.837
700	4.968	47.395	44.543	1.996	130.488	112.200	-35.030
800	4.968	48.058	44.942	2.493	129.838	109.632	-29.950
900	4.968	48.643	45.321	2.990	129.177	107.146	-26.018
1000	4.968	49.167	45.680	3.487	128.504	104.733	-22.889
1100	4.968	49.640	46.019	3.984	127.820	102.389	-20.342
1200	4.968	50.073	46.339	4.480	127.123	100.109	-18.232
1300	4.968	50.470	46.642	4.977	126.410	97.886	-16.456
1400	4.968	50.838	46.928	5.474	125.681	95.718	-14.942
1500	4.968	51.181	47.201	5.971	124.934	93.604	-13.638
1600	4.968	51.502	47.460	6.468	124.168	91.541	-12.504
1700	4.968	51.803	47.706	6.964	123.380	89.526	-11.509
1800	4.968	52.087	47.942	7.461	122.570	87.558	-10.631
1900	4.968	52.356	48.167	7.958	121.734	85.634	-9.850
2000	4.968	52.610	48.383	8.455	120.872	83.756	-9.152
2100	4.968	52.853	48.590	8.952	119.982	81.923	-8.526
2200	4.968	53.084	48.789	9.448	119.060	80.132	-7.960
2300	4.968	53.305	48.981	9.945	118.106	78.385	-7.448
2400	4.968	53.516	49.165	10.442	117.115	76.678	-6.982
2500	4.968	53.719	49.343	10.939	116.087	75.014	-6.558
2600	4.968	53.914	49.516	11.436	115.015	73.392	-6.169
2700	4.968	54.101	49.682	11.932	113.890	71.814	-5.813
2800	4.968	54.282	49.843	12.429	112.697	70.276	-5.485
2900	4.968	54.456	49.999	12.926	102.840	68.795	-5.184
3000	4.968	54.625	50.150	13.423	101.940	67.436	-4.927
3100	4.968	54.788	50.297	13.920	101.040	66.507	-4.689
3200	4.968	54.945	50.440	14.416	100.140	65.408	-4.467
3300	4.968	55.098	50.579	14.913	99.240	64.337	-4.261
3400	4.968	55.247	50.714	15.410	98.340	63.292	-4.068
3500	4.968	55.391	50.846	15.907	97.440	62.274	-3.889
3600	4.968	55.531	50.974	16.404	96.540	61.283	-3.720
3700	4.968	55.667	51.099	16.900	95.640	60.316	-3.563
3800	4.968	55.799	51.221	17.397	94.740	59.374	-3.415
3900	4.968	55.928	51.340	17.894	93.840	58.454	-3.276
4000	4.968	56.054	51.456	18.391	92.940	57.558	-3.145
4100	4.968	56.177	51.570	18.888	92.040	56.684	-3.022
4200	4.968	56.296	51.681	19.384	91.140	55.834	-2.905
4300	4.968	56.413	51.790	19.881	90.240	55.004	-2.796
4400	4.968	56.527	51.896	20.378	89.340	54.194	-2.692
4500	4.968	56.639	52.000	20.875	88.440	53.405	-2.594
4600	4.968	56.748	52.102	21.372	87.540	52.637	-2.501
4700	4.968	56.855	52.202	21.868	86.640	51.889	-2.413
4800	4.968	56.960	52.300	22.365	85.740	51.159	-2.329
4900	4.968	57.062	52.396	22.862	84.840	50.447	-2.250
5000	4.968	57.163	52.491	23.359	-57.333	50.991	-2.229
5100	4.968	57.261	52.583	23.855	-58.618	53.170	-2.278
5200	4.968	57.357	52.674	24.352	-59.934	55.375	-2.327
5300	4.968	57.452	52.763	24.849	-61.283	57.604	-2.375
5400	4.968	57.545	52.851	25.346	-62.662	59.861	-2.423
5500	4.968	57.636	52.937	25.843	-64.072	62.143	-2.469
5600	4.968	57.726	53.022	26.339	-65.512	64.452	-2.515
5700	4.968	57.813	53.105	26.836	-66.982	66.785	-2.561
5800	4.968	57.900	53.187	27.333	-68.482	69.144	-2.605
5900	4.968	57.985	53.268	27.830	-70.010	71.530	-2.650
6000	4.968	58.068	53.347	28.327	-71.568	73.942	-2.693

March 31, 1978

MOLYBDENUM, UNINEGATIVE ION (Mo^-) (IDEAL GAS) GFW = 95.94055

Ground State Configuration $^6S_{5/2}$
$S^\circ_{298.15}$ = 43.155 ± 0.1 cal/(mol K)

ΔHf°_0 = 134.055 ± 4.6 kcal/mol Mo^-
$\Delta Hf^\circ_{298.15}$ = [132.959] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0	6

Heat of Formation

The heat of formation ΔHf°_0 is calculated from an adopted electron affinity of Mo(g) of EA=1.0±0.2 eV (23.06±4.61 kcal/mol). This value has been recommended in the critical compilation by Hotop and Lineberger (1) based on the self-surface ionization study by Scheer (2) and a re-evaluation of a semi-empirical extrapolation (Zollweg horizontal analysis) by Hotop and Lineberger (1). Rosenstock et al. (3) and Massey (4) reference additional extrapolation/interpolation studies which yielded electron affinities in the range 0.86 - 1.3 eV.

ΔHf°_{298} (Mo^-,g) is obtained from ΔHf°_0 (Mo,g) by using EA (Mo,g) with JANAF (6) enthalpies ($H^\circ_0 - H^\circ_{298}$) for Mo^-(g), Mo(g), and e^-(g). ΔHr°_{298} ($Mo^- = Mo + e^-$) differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (3). ΔHf°_{298} should be changed by +1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Mo^-(g) is given by Hotop and Lineberger (1) and Rosenstock et al. (3). The thermodynamic functions of the negative ion are calculated using the recent CODATA fundamental constants (5) and assuming the Mo^-(g) is an ideal monatomic gas. Lacking any experimental evidence as to the stability of any excited states, we assumed no stable excited states exist.

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MOLYBDENUM DISULFIDE (MoS_2)

(CRYSTAL) GFW=160.06

MoS_2

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.528	-65.324	-65.324	INFINITE
100	5.748	3.105	26.314	-2.321	-65.563	-65.107	142.290
200	12.390	9.497	16.271	-1.373	-65.841	-64.532	70.516
298	15.190	14.955	14.955	0.000	-66.000	-63.852	46.804
300	15.220	15.049	14.955	0.028	-66.003	-63.839	46.506
400	16.470	19.622	15.570	1.621	-67.196	-63.055	34.451
500	17.150	23.376	16.768	3.304	-68.001	-61.934	27.071
600	17.590	26.543	18.140	5.042	-68.600	-60.659	22.095
700	17.930	29.281	19.540	6.818	-69.063	-59.298	18.513
800	18.220	31.695	20.912	8.626	-95.425	-60.272	16.465
900	18.470	33.855	22.232	10.461	-95.129	-55.893	13.573
1000	18.700	35.813	23.494	12.320	-94.831	-51.551	11.266
1100	18.910	37.605	24.696	14.200	-94.529	-47.237	9.385
1200	19.120	39.260	25.842	16.102	-94.226	-42.951	7.822
1300	19.320	40.798	26.934	18.024	-93.927	-38.691	6.504
1400	19.520	42.237	27.976	19.966	-93.630	-34.453	5.378
1500	19.710	43.591	28.972	21.927	-93.340	-30.236	4.405
1600	19.900	44.869	29.926	23.908	-93.057	-26.038	3.557
1700	20.090	46.081	30.841	25.907	-92.784	-21.858	2.810
1800	20.270	47.234	31.720	27.925	-92.522	-17.694	2.148
1900	20.460	48.335	32.566	29.962	-92.271	-13.544	1.558
2000	20.640	49.389	33.381	32.017	-92.034	-9.406	1.028
2100	20.820	50.401	34.167	34.090	-91.813	-5.280	0.549
2200	21.010	51.374	34.927	36.181	-91.612	-1.165	0.116
2300	21.190	52.312	35.663	38.291	-91.426	2.944	-0.280
2400	21.370	53.217	36.376	40.419	-91.265	7.042	-0.641

June 30, 1978

MOLYBDENUM DISULFIDE (MoS_2) (CRYSTAL) GFW = 160.06

Pearson notation = hP6
$S^\circ_{298.15}$ = 14.96 ± 0.02 cal/(mol K)
Tm = 2023 ± 50 K [P = 1 atm $S_2(g)$]

ΔHf°_0 = -65.3 ± 0.6 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -66.0 ± 0.6 kcal/mol
ΔHm° = unknown

MoS_2

Heat of Formation

The adopted heat of formation is from Brewer (1) and is a weighted average of calorimetric (2) and equilibrium (3) values. O'Hare et al. (2) obtained ΔHf°_{298} = -65.8±1.2 kcal/mol using a fluorine bomb calorimeter. Larson and Elliott (3) studied the equilibrium $MoO_2(c) + 2\ SO_2(g) = MoS_2(c) + 3\ O_2(g)$ via emf technique (1051-1372 K); using auxiliary data (1, 4) Brewer calculated $\Delta Hf^\circ_{298}(MoS_2)$ = -66.64±0.6 kcal/mol from their results. Thermodynamic analysis of other calorimetric and equilibrium measurements (5 - 7) are summarized by O'Hare et al. (2) and Mills (8).

Heat Capacity and Entropy

The adopted values of Cp° are from Brewer (1) and are based on experimental Cp° data (6-346 K) of McBride and Westrum (9) and high temperature enthalpy data (523-1204 K) of Fredrickson and Chasanov (10). Cp° values above 1200 K are extrapolated. The recent enthalpy data (500-1700 K) of Volovik et al. (11) agrees with enthalpies in this table to within ±2% to 2000 K. Older Cp° data of Smith et al. (12) and Anderson (13) contain considerable scatter and are given no weight.

The value of S°_{298} is obtained from the appropriate integration of the adopted Cp° data based on S°_{10} = 0.012 cal/(mol K).

Melting Data

The crystal structure of MoS_2 is (hP6). Mering and Levialdi (14) have shown that nonstoichiometric sulfur-rich modifications (which have essentially the hP6 structure with expansion and distortion of the lattice) can be prepared as metastable compositions up to $MoS_{2.59}$; amorphous metastable phases are obtained with higher sulfur contents. For information on other metastable phases, see (1) and (15). According to Brewer's (1) phase diagram the compositional range of stability decreases as the temperature increases.

Based on Cannon's evidence (16) of a melting point in excess of 2073 K, Brewer (1) adopted a congruent melting point of 2173 K. However, congruent melting is observed only at high sulfur pressures; the melting point of 2173 K corresponds to a $S_2(g)$ pressure of ~4 atm. Incongruent melting points up to 350 K lower may be obtained depending upon the pressure of $S_2(g)$. The adopted melting point is that selected by Brewer (1) for an $S_2(g)$ pressure of 1 atm. Mills (8) adopted a 1 atm value of 1458 K which appears much too low.

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DIMOLYBDENUM TRISULFIDE (Mo_2S_3)

Mo_2S_3

(CRYSTAL) GFW=288.06

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	26.122	27.480	27.480	0.000	-97.300	-94.564	69.317
300	26.168	27.642	27.480	0.048	-97.304	-94.548	68.877
400	28.074	35.454	28.533	2.768	-99.056	-93.540	51.107
500	29.380	41.865	30.577	5.644	-100.217	-92.038	40.229
600	30.449	47.319	32.924	8.637	-101.042	-90.316	32.897
700	31.407	52.085	35.328	11.730	-101.627	-88.480	27.624
800	32.305	56.338	37.693	14.916	-141.021	-90.165	24.632
900	33.168	60.193	39.982	18.190	-140.386	-83.842	20.359
1000	34.010	63.732	42.182	21.549	-139.705	-77.599	16.959
1100	34.838	67.012	44.292	24.991	-138.972	-71.422	14.190
1200	35.656	70.078	46.315	28.516	-138.194	-65.314	11.895
1300	36.468	72.964	48.255	32.123	-137.378	-59.276	9.965
1400	37.275	75.697	50.118	35.810	-136.523	-53.298	8.320
1500	38.078	78.296	51.911	39.577	-135.636	-47.384	6.904
1600	38.878	80.779	53.638	43.425	-134.718	-41.531	5.673
1700	39.676	83.160	55.305	47.353	-133.773	-35.736	4.594
1800	40.473	85.450	56.916	51.360	-132.805	-29.997	3.642
1900	41.268	87.660	58.477	55.447	-131.815	-24.313	2.797
2000	42.062	89.797	59.990	59.614	-130.806	-18.680	2.041
2080	42.697	91.459	61.168	63.004	------------	MELTING	----------
2100	42.856	91.868	61.459	63.860	-129.783	-13.098	1.363
2200	43.648	93.880	62.887	68.185	-128.754	-7.568	0.752
2300	44.440	95.838	64.277	72.590	-127.712	-2.079	0.198
2400	45.232	97.746	65.632	77.073	-126.675	3.359	-0.306

June 30, 1978

Pearson notation = mP10
$S^\circ_{298.15}$ = 27.48 ± 2 cal/(mol K)
Td = 900 ± 40 K
Tm = 2080 ± 20 K

$\Delta Hf^\circ_{298.15}$ = -97.3 ± 2 kcal/mol
ΔHd° = -2.307 kcal/mol
ΔHm° = 31.0 ± 10 kcal/mol

Mo_2S_3

Heat of Formation

The adopted heat of formation is taken from the critical review by Brewer (1). His linear regression analysis of equilibrium data, which is based on Cubicciotti's sigma-plot method (2), yields both ΔHf°_{298} and S°_{298}. The data used in Brewer's analysis are outlined below. Auxiliary data are taken from the JANAF tables (3).

Study	Reaction	Temp. Range, K
McCabe (4)	A	1303 - 1425
Isakova (5)	B	1523 - 1738
Hager and Elliott (6)	C	1366 - 1612
Stubbles and Richardson (7)	C	1119 - 1467
Pouillard and Perrot (8)	C	1030 - 1280
Stubbles and Richardson (7)	D	1270 - 1470
Pouillard and Perrot (8)	D	1030 - 1280

Reactions: (A) $2\ Mo(c) + 3/2S_2(g) = Mo_2S_3(c)$
(B) $2\ MoS_2(c) = Mo_2S_3(c) + 1/2S_2(g)$
(C) $2\ Mo(c) + 3\ H_2S(g) = Mo_2S_3(c) + 3\ H_2(g)$
(D) $2\ MoS_2(c) + H_2(g) = Mo_2S_3(c) + H_2S(g)$

Heat Capacity and Entropy

There are no experimental high temperature heat capacity or enthalpy studies. The adopted heat capacity, which is assumed to represent the high temperature crystal form, is based on the estimate of Gronvold and Westrum (9), $Cp^\circ = 26.36 + 7.88 \times 10^{-3}T - 2.30 \times 10^5/T^2$. The value of S°_{298} is taken from Brewer (1), see above.

Rastogi and Ray (10) measured the low temperature Cp° (80-350 K) but report only Cp°_{298} = 33.2 cal/(mol K). This value apparently refers to the low temperature superstructure crystal form but is not expected to differ significantly from the high temperature form. The reason for the 7 cal/(mol K) discrepancy between the Rastogi-Ray value of Cp°_{298} and that adopted here is not known but it should be mentioned that the Rastogi-Ray value is well above the classical limit of 15R. Insufficient information on sample preparation and calorimetric technique is available to assess the validity of the Rastogi-Ray data.

Phase Data

The crystal structure of Mo_2S_3 is monoclinic and belongs to space group $P2_1/m$ above 310 K (11). Below 310 K all axes are doubled and a superstructure is formed. The heat of transition is reported to be 5 cal/mol (10).

The stability region for Mo_2S_3 is from 900±40 K (1) to the melting point. Below 900 K the material is metastable with respect to disproportionation to Mo(c) and $MoS_2(c)$. However equilibrium is established very slowly below 1100 K (11, 12) and, once prepared, Mo_2S_3 may be quenched and stored indefinitely at room temperature. The heat of decomposition at 900 K (ΔHd°) for the reaction $Mo_2S_3(c) \rightarrow 1/2\ Mo(c) + 3/2\ MoS_2(c)$ is calculated from the JANAF tables (3).

Melting Data

We adopt the congruent melting point from Brewer (1). The heat of melting is estimated assuming an entropy of fusion of ~3 cal/(g-atom K) as suggested by Kubaschewski et al. (13). This gives a heat of fusion of 31 kcal/mol and the uncertainty is estimated to be 10 kcal/mol.

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Mo_2S_3

DIMOLYBDENUM TRISULFIDE (Mo_2S_3) (LIQUID) GFW=288.06

Mo_2S_3

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	26.122	43.301	43.301	0.000	-64.604	-66.585	48.808
300	26.168	43.463	43.301	0.048	-64.608	-66.598	48.516
400	28.074	51.275	44.354	2.768	-66.360	-67.172	36.701
500	29.380	57.686	46.398	5.644	-67.521	-67.252	29.396
600	30.449	63.139	48.745	8.637	-68.346	-67.112	24.445
700	31.407	67.906	51.149	11.730	-68.931	-66.859	20.874
800	32.305	72.159	53.514	14.916	-108.325	-70.126	19.157
900	33.168	76.014	55.803	18.190	-107.690	-65.385	15.877
1000	34.010	79.552	58.003	21.549	-107.009	-60.724	13.271
1100	34.838	82.833	60.113	24.991	-106.276	-56.129	11.152
1200	35.656	85.899	62.136	28.516	-105.498	-51.603	9.398
1300	36.468	88.785	64.076	32.123	-104.683	-47.147	7.926
1400	37.275	91.517	65.939	35.810	-103.827	-42.752	6.674
1450	37.677	92.832	66.844	37.683	ASSUMED		
1450	37.500	92.832	66.844	37.683	GLASS TRANSITION		
1500	37.500	94.104	67.731	39.558	-102.959	-38.419	5.598
1600	37.500	96.524	69.456	43.308	-102.139	-34.144	4.664
1700	37.500	98.797	71.116	47.058	-101.372	-29.918	3.846
1800	37.500	100.941	72.714	50.808	-100.661	-25.737	3.125
1900	37.500	102.968	74.253	54.558	-100.008	-21.592	2.484
2000	37.500	104.892	75.738	58.308	-99.416	-17.480	1.910
2080	37.500	106.363	76.887	61.308	---------- MELTING ----------		
2100	37.500	106.721	77.170	62.058	-98.889	-13.395	1.394
2140	37.500	107.429	77.729	63.558	-------- DECOMPOSITION -------		
2200	37.500	108.466	78.553	65.808	-98.435	-9.337	0.928
2300	37.500	110.133	79.890	69.558	-98.048	-5.293	0.503
2400	37.500	111.729	81.184	73.308	-97.744	-1.269	0.116
2500	37.500	113.260	82.436	77.058	-97.520	2.745	-0.240
2600	37.500	114.730	83.650	80.808	-97.387	6.754	-0.568
2700	37.500	116.146	84.828	84.558	-97.366	10.758	-.871
2800	37.500	117.509	85.971	88.308	-97.484	14.765	-1.152
2900	37.500	118.825	87.081	92.058	-114.936	18.801	-1.417
3000	37.500	120.097	88.161	95.808	-114.477	23.404	-1.705
3100	37.500	121.326	89.211	99.558	-114.021	27.993	-1.973
3200	37.500	122.517	90.233	103.308	-113.568	32.566	-2.224
3300	37.500	123.671	91.229	107.058	-113.118	37.126	-2.459
3400	37.500	124.790	92.200	110.808	-112.671	41.671	-2.679
3500	37.500	125.877	93.146	114.558	-112.227	46.204	-2.885

June 30, 1978

DIMOLYBDENUM TRISULFIDE (Mo_2S_3) (LIQUID) GFW = 288.06

$S^\circ_{298.15}$ = [43.301] cal/(mol K)
Tm = 2080 ± 20 K
Td = 2140 ± 30 K [P = 1 atm S_2(g)]

$\Delta Hf^\circ_{298.15}$ = [-64.604] kcal/mol
ΔHm° = 31.0 ± 10 kcal/mol
ΔHd° = unknown

Mo_2S_3

Heat of Formation

The adopted value of ΔHf°_{298} is obtained from that of Mo_2S_3(c)(1) by addition of the heat of melting and the enthalpy difference ($H^\circ_{2080}-H^\circ_{298}$) for the crystal and liquid.

Heat Capacity and Entropy

A constant liquid Cp° of 7.5 cal/(g-atom K) is assumed which yields a Cp° value of 37.5 cal/(mol K). This value is adopted above an assumed glass transition at 1450 K. The heat capacity of the crystal (1) is assumed below the glass transition. The value of S°_{298} is calculated by a procedure which is analagous to that for ΔHf°_{298}.

Melting Data

See the JANAF table for Mo_2S_3(c)(1).

Decomposition Data

According to Brewer's phase diagram (2), Mo_2S_3 has a very short liquid range at 1 atm S_2(g). We adopt a decomposition temperature of 2140±30 K based on the phase diagram (2). Above this temperature Mo_2S_3(ℓ) decomposes to S_2(g) plus a liquid poorer in sulfur than Mo_2S_3. At higher sulfur pressures, the liquid range is much more extensive.

References

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Mo_2S_3

DIMOLYBDENUM TRISULFIDE (Mo_2S_3) Mo_2S_3
(CRYSTAL - LIQUID) GFW=288.06

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	26.122	27.480	27.480	0.000	-97.300	-94.564	69.317
300	26.168	27.642	27.480	0.048	-97.304	-94.548	68.877
400	28.074	35.454	28.533	2.768	-99.056	-93.540	51.107
500	29.380	41.865	30.577	5.644	-100.217	-92.038	40.229
600	30.449	47.319	32.924	8.637	-101.042	-90.316	32.897
700	31.407	52.085	35.328	11.730	-101.627	-88.480	27.624
800	32.305	56.338	37.693	14.916	-141.021	-90.165	24.632
900	33.168	60.193	39.982	18.190	-140.386	-83.842	20.359
1000	34.010	63.732	42.182	21.549	-139.705	-77.599	16.959
1100	34.838	67.012	44.292	24.991	-138.972	-71.422	14.190
1200	35.656	70.078	46.315	28.516	-138.194	-65.314	11.895
1300	36.468	72.964	48.255	32.123	-137.378	-59.276	9.965
1400	37.275	75.697	50.118	35.810	-136.523	-53.298	8.320
1500	38.078	78.296	51.911	39.577	-135.636	-47.384	6.904
1600	38.878	80.779	53.638	43.425	-134.718	-41.531	5.673
1700	39.676	83.160	55.305	47.353	-133.773	-35.736	4.594
1800	40.473	85.450	56.916	51.360	-132.805	-29.997	3.642
1900	41.268	87.660	58.477	55.447	-131.815	-24.313	2.797
2000	42.062	89.797	59.990	59.614	-130.806	-18.680	2.041
2080	42.697	91.459	61.168	63.004			
2080	37.500	106.363	61.168	94.004	------------ MELTING ----------		
2100	37.500	106.721	61.600	94.754	-98.889	-13.395	1.394
2140	37.500	107.429	62.450	96.254	-------- DECOMPOSITION -------		
2200	37.500	108.466	63.691	98.504	-98.435	-9.337	0.928
2300	37.500	110.133	65.674	102.254	-98.048	-5.293	0.503
2400	37.500	111.729	67.560	106.004	-97.744	-1.269	0.116
2500	37.500	113.260	69.358	109.754	-97.520	2.745	-.240
2600	37.500	114.730	71.075	113.504	-97.387	6.754	-.568
2700	37.500	116.146	72.718	117.254	-97.366	10.758	-.871
2800	37.500	117.509	74.294	121.004	-97.484	14.766	-1.152
2900	37.500	118.825	75.807	124.754	-114.936	18.801	-1.417
3000	37.500	120.097	77.262	128.504	-114.477	23.404	-1.705
3100	37.500	121.326	78.664	132.254	-114.021	27.993	-1.973
3200	37.500	122.517	80.015	136.004	-113.568	32.566	-2.224
3300	37.500	123.671	81.321	139.754	-113.118	37.126	-2.459
3400	37.500	124.790	82.583	143.504	-112.671	41.671	-2.679
3500	37.500	125.877	83.805	147.254	-112.227	46.204	-2.885

June 30, 1978

DIMOLYBDENUM TRISULFIDE (Mo_2S_3) (CRYSTAL-LIQUID) GFW = 288.06

Mo_2S_3

298 to 900 K Metastable Crystal
900 to 2080 K Crystal
2080 to 2140 K Liquid

Refer to the crystal and liquid single phase tables for details.

NITROGEN, MONATOMIC (N) N
(IDEAL GAS) GFW=14.0067

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	112.530	112.530	INFINITE
100	4.968	31.186	41.030	-0.984	112.680	111.470	-243.615
200	4.968	34.630	37.068	-0.488	112.829	110.202	-120.422
298	4.968	36.613	36.613	0.000	112.975	108.882	-79.812
300	4.968	36.644	36.614	0.009	112.978	108.857	-79.301
400	4.968	38.073	36.808	0.506	113.126	107.460	-58.713
500	4.968	39.182	37.176	1.003	113.271	106.027	-46.344
600	4.968	40.088	37.588	1.500	113.412	104.565	-38.087
700	4.968	40.854	38.002	1.996	113.545	103.080	-32.182
800	4.968	41.517	38.400	2.493	113.670	101.576	-27.749
900	4.968	42.102	38.780	2.990	113.788	100.057	-24.297
1000	4.968	42.626	39.139	3.487	113.897	98.525	-21.532
1100	4.968	43.099	39.478	3.984	114.000	96.983	-19.269
1200	4.968	43.531	39.798	4.480	114.097	95.432	-17.380
1300	4.968	43.929	40.100	4.977	114.188	93.873	-15.781
1400	4.968	44.297	40.387	5.474	114.274	92.307	-14.410
1500	4.968	44.640	40.659	5.971	114.356	90.735	-13.220
1600	4.968	44.961	40.918	6.468	114.435	89.158	-12.178
1700	4.968	45.262	41.165	6.964	114.511	87.576	-11.258
1800	4.968	45.546	41.401	7.461	114.583	85.989	-10.440
1900	4.968	45.814	41.626	7.958	114.654	84.399	-9.708
2000	4.969	46.069	41.842	8.455	114.722	82.804	-9.048
2100	4.970	46.312	42.049	8.952	114.788	81.207	-8.451
2200	4.971	46.543	42.248	9.449	114.852	79.606	-7.908
2300	4.972	46.764	42.439	9.946	114.915	78.003	-7.412
2400	4.975	46.975	42.624	10.443	114.977	76.397	-6.957
2500	4.978	47.179	42.802	10.941	115.038	74.788	-6.538
2600	4.982	47.374	42.974	11.439	115.097	73.176	-6.151
2700	4.987	47.562	43.141	11.937	115.156	71.563	-5.793
2800	4.993	47.743	43.302	12.436	115.215	69.947	-5.460
2900	5.001	47.919	43.458	12.936	115.274	68.330	-5.149
3000	5.010	48.088	43.610	13.436	115.332	66.710	-4.860
3100	5.021	48.253	43.757	13.938	115.391	65.089	-4.589
3200	5.034	48.413	43.900	14.441	115.449	63.465	-4.334
3300	5.049	48.568	44.039	14.945	115.510	61.840	-4.095
3400	5.066	48.719	44.174	15.451	115.570	60.212	-3.870
3500	5.085	48.866	44.306	15.958	115.632	58.583	-3.658
3600	5.106	49.009	44.435	16.468	115.695	56.952	-3.457
3700	5.130	49.150	44.560	16.980	115.760	55.320	-3.268
3800	5.155	49.287	44.683	17.494	115.827	53.685	-3.088
3900	5.183	49.421	44.803	18.011	115.896	52.049	-2.917
4000	5.212	49.553	44.920	18.531	115.967	50.411	-2.754
4100	5.244	49.682	45.034	19.053	116.041	48.771	-2.600
4200	5.278	49.808	45.147	19.579	116.118	47.129	-2.452
4300	5.313	49.933	45.257	20.109	116.197	45.486	-2.312
4400	5.351	50.056	45.364	20.642	116.280	43.841	-2.178
4500	5.390	50.176	45.470	21.179	116.366	42.193	-2.049
4600	5.431	50.295	45.573	21.720	116.456	40.544	-1.926
4700	5.473	50.412	45.675	22.265	116.550	38.893	-1.808
4800	5.516	50.528	45.775	22.815	116.647	37.239	-1.696
4900	5.561	50.642	45.873	23.369	116.748	35.584	-1.587
5000	5.607	50.755	45.970	23.927	116.854	33.927	-1.483
5100	5.654	50.867	46.065	24.490	116.964	32.267	-1.383
5200	5.702	50.977	46.158	25.058	117.078	30.605	-1.286
5300	5.751	51.086	46.250	25.631	117.197	28.941	-1.193
5400	5.800	51.194	46.341	26.208	117.320	27.275	-1.104
5500	5.849	51.301	46.430	26.791	117.447	25.606	-1.017
5600	5.899	51.407	46.518	27.378	117.580	23.935	-0.934
5700	5.949	51.512	46.604	27.970	117.716	22.262	-0.854
5800	6.000	51.615	46.690	28.568	117.858	20.586	-0.776
5900	6.050	51.718	46.774	29.170	118.003	18.907	-0.700
6000	6.100	51.821	46.857	29.778	118.154	17.227	-0.627

March 31, 1961; March 31, 1977

NITROGEN, MONATOMIC (N) (IDEAL GAS) GFW = 14.0067

Ground State Configuration $^4S^o_{3/2}$
$S^o_{298.15}$ = 36.613 ± 0.005 gibbs/mol

ΔHf^o_0 = 112.53 ± 0.10 kcal/mol N
$\Delta Hf^o_{298.15}$ = 112.97 ± 0.10 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^4S^o_{3/2}$	0.000	4
$^2D^o_{5/2}$	19224.464	6
$^2D^o_{3/2}$	19233.177	4
$^2P^o_{1/2}$	28838.920	2
$^2P^o_{3/2}$	28839.306	4

Heat of Formation

ΔHf° is based on the D^o_0 value for N_2(g) adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for ΔHf^o_{298} (N,g) is derived using $D^o_0(N_2,g)$ = 78715±50 cm^{-1} (225.057±0.143 kcal/mol) from Buttenbender and Herzberg (2), Tanaka, Ogawa, and Jursa (3), and Telford, Vanderslice, and Wilkinson (4). This is discussed further by Gaydon (5) and Lofthus and Krupenie (6).

Heat Capacity and Entropy

The electronic levels for N(g) are given in the compilation by Moore (7). Our calculations indicate that, except for the five states lying below 29000 cm^{-1}, the inclusion of levels up to n=12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 83284.070 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the lowest lying states (ε_i < 29000 cm^{-1}). The reported uncertainty in S^o_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (8).

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6. A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
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NITROGEN UNIPOSITIVE ION (N^+) N^+

(IDEAL GAS) GFW=14.00615

T, °K	gibbs/mol			kcal/mol			
	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0				-1.701	447.695		
100							
200							
298	5.087	38.166	38.166	0.000	449.841	443.798	-325.308
300	5.086	38.198	38.166	0.009	449.853	443.760	-323.274
400	5.034	39.653	38.365	0.515	450.507	441.631	-241.292
500	5.010	40.773	38.739	1.017	451.155	439.336	-192.031
600	4.997	41.685	39.156	1.517	451.795	436.913	-159.143
700	4.989	42.455	39.574	2.017	452.427	434.381	-135.618
800	4.984	43.120	39.976	2.515	453.051	431.761	-117.950
900	4.981	43.707	40.359	3.013	453.667	429.063	-104.189
1000	4.978	44.232	40.721	3.511	454.274	426.297	-93.166
1100	4.976	44.706	41.062	4.009	454.875	423.470	-84.135
1200	4.975	45.139	41.384	4.507	455.469	420.588	-76.598
1300	4.974	45.537	41.688	5.004	456.058	417.658	-70.214
1400	4.973	45.906	41.976	5.501	456.641	414.682	-64.734
1500	4.973	46.249	42.250	5.999	457.221	411.665	-59.979
1600	4.972	46.570	42.510	6.496	457.797	408.609	-55.813
1700	4.972	46.871	42.758	6.993	458.369	405.516	-52.132
1800	4.972	47.156	42.994	7.490	458.939	402.391	-48.856
1900	4.972	47.424	43.220	7.987	459.507	399.235	-45.922
2000	4.973	47.679	43.437	8.485	460.072	396.048	-43.277
2100	4.974	47.922	43.645	8.982	460.636	392.833	-40.882
2200	4.975	48.153	43.845	9.479	461.196	389.590	-38.702
2300	4.977	48.375	44.037	9.977	461.757	386.323	-36.709
2400	4.980	48.587	44.222	10.475	462.316	383.032	-34.879
2500	4.983	48.790	44.401	10.973	462.875	379.717	-33.194
2600	4.987	48.985	44.573	11.472	463.432	376.379	-31.637
2700	4.991	49.174	44.740	11.970	463.987	373.020	-30.193
2800	4.996	49.355	44.902	12.470	464.543	369.641	-28.851
2900	5.002	49.531	45.058	12.970	465.099	366.242	-27.600
3000	5.009	49.700	45.210	13.470	465.655	362.824	-26.431
3100	5.016	49.865	45.358	13.971	466.210	359.387	-25.336
3200	5.024	50.024	45.501	14.473	466.764	355.931	-24.309
3300	5.032	50.179	45.641	14.976	467.320	352.460	-23.342
3400	5.042	50.329	45.776	15.480	467.875	348.971	-22.431
3500	5.051	50.476	45.908	15.985	468.431	345.466	-21.572
3600	5.062	50.618	46.037	16.490	468.987	341.944	-20.759
3700	5.072	50.757	46.163	16.997	469.543	338.407	-19.989
3800	5.083	50.892	46.286	17.505	470.101	334.856	-19.258
3900	5.095	51.024	46.405	18.014	470.659	331.290	-18.565
4000	5.107	51.154	46.523	18.524	471.217	327.709	-17.905
4100	5.119	51.280	46.637	19.035	471.776	324.115	-17.277
4200	5.131	51.403	46.749	19.547	472.335	320.506	-16.677
4300	5.143	51.524	46.859	20.061	472.896	316.884	-16.106
4400	5.156	51.643	46.966	20.576	473.458	313.250	-15.559
4500	5.169	51.759	47.071	21.092	474.020	309.603	-15.036
4600	5.181	51.872	47.174	21.610	474.584	305.943	-14.535
4700	5.194	51.984	47.276	22.129	475.147	302.270	-14.055
4800	5.207	52.093	47.375	22.649	475.712	298.586	-13.595
4900	5.219	52.201	47.472	23.170	476.277	294.890	-13.153
5000	5.232	52.306	47.568	23.693	476.845	291.183	-12.727
5100	5.244	52.410	47.662	24.216	477.411	287.463	-12.318
5200	5.256	52.512	47.754	24.741	477.979	283.734	-11.925
5300	5.268	52.612	47.845	25.268	478.549	279.993	-11.546
5400	5.280	52.711	47.934	25.795	479.118	276.241	-11.180
5500	5.292	52.808	48.022	26.324	479.689	272.479	-10.827
5600	5.303	52.903	48.108	26.853	480.260	268.706	-10.487
5700	5.314	52.997	48.193	27.384	480.832	264.923	-10.158
5800	5.325	53.090	48.277	27.916	481.405	261.131	-9.840
5900	5.336	53.181	48.359	28.449	481.978	257.328	-9.532
6000	5.347	53.271	48.440	28.983	482.552	253.516	-9.234

March 31, 1977

NITROGEN UNIPOSITIVE ION (N^+) (IDEAL GAS) GFW = 14.00615

Ground State Configuration $^3P_0$

$S°_{298.15}$ = 38.166 ± 0.005 gibbs/mol

$\Delta Hf°_0$ = 447.69 ± 0.1 kcal/mol N^+

$\Delta Hf°_{298.15}$ = 449.84 ± 0.1 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^3P_0$	0.0	1
$^3P_1$	48.7	3
$^3P_2$	130.8	5
$^1D_2$	15316.2	5
$^1S_0$	32688.8	1
$^5S^o_2$	46784.6	5

Heat of Formation

The heat of formation is calculated from the equation $N(g) = N^+(g) + e^-(g)$ with auxiliary data (1), using an ionization potential of IP = 117225.7±0.3 cm^{-1} (335.1651±0.0009 kcal/mol). This ionization potential, as reported by Moore (2) in units of cm^{-1}, is converted to units of kcal/mol using the current CODATA fundamental constants (3). The uncertainty in the ΔHf° values lie mainly in the uncertainty in $D^o_0(N_2,g)$.

Heat Capacity and Entropy

The electronic levels for $N^+(g)$ are given in the compilation by Moore (2). Our calculations indicate that, except for the six states lying below 47000 cm^{-1}, the inclusion of levels up to n=12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the sixth excited state lies at 92237.2 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the lowest lying states (ϵ_i < 47000 cm^{-1}). The reported uncertainty in $S°_{298}$ is due to uncertainties in the gram formula weight, the fundamental constants, and the position of the low lying electronic levels. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (4).

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N^+

NITROGEN UNINEGATIVE ION (N^-) N^-

(IDEAL GAS) GFW=14.00725

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-1.553	114.140		
100							
200							
298	5.021	38.197	38.197	0.000	113.176	110.098	-80.703
300	5.021	38.229	38.198	0.009	113.170	110.079	-80.191
400	4.998	39.669	38.394	0.510	112.825	109.100	-59.609
500	4.988	40.784	38.765	1.009	112.476	108.209	-47.297
600	4.982	41.692	39.179	1.508	112.121	107.388	-39.116
700	4.978	42.460	39.595	2.006	111.759	106.629	-33.291
800	4.976	43.125	39.995	2.503	111.389	105.921	-28.936
900	4.974	43.711	40.376	3.001	111.010	105.260	-25.560
1000	4.973	44.235	40.736	3.498	110.622	104.642	-22.869
1100	4.972	44.709	41.076	3.996	110.229	104.063	-20.675
1200	4.972	45.141	41.397	4.493	109.830	103.521	-18.853
1300	4.971	45.539	41.701	4.990	109.425	103.011	-17.317
1400	4.971	45.907	41.988	5.487	109.014	102.533	-16.006
1500	4.970	46.250	42.261	5.984	108.600	102.084	-14.873
1600	4.970	46.571	42.520	6.481	108.182	101.663	-13.886
1700	4.970	46.872	42.768	6.978	107.761	101.269	-13.019
1800	4.970	47.156	43.004	7.475	107.337	100.899	-12.251
1900	4.969	47.425	43.229	7.972	106.911	100.553	-11.566
2000	4.969	47.680	43.446	8.469	106.481	100.229	-10.952
2100	4.969	47.922	43.653	8.966	106.050	99.927	-10.399
2200	4.969	48.154	43.852	9.463	105.619	99.646	-9.899
2300	4.969	48.375	44.044	9.960	105.185	99.385	-9.444
2400	4.969	48.586	44.229	10.457	104.749	99.142	-9.028
2500	4.969	48.789	44.407	10.953	104.312	98.917	-8.647
2600	4.969	48.984	44.580	11.450	103.873	98.709	-8.297
2700	4.969	49.171	44.746	11.947	103.435	98.520	-7.975
2800	4.969	49.352	44.908	12.444	102.995	98.345	-7.676
2900	4.969	49.526	45.064	12.941	102.553	98.187	-7.400
3000	4.969	49.695	45.215	13.438	102.111	98.044	-7.142
3100	4.969	49.858	45.363	13.935	101.668	97.916	-6.903
3200	4.968	50.015	45.506	14.431	101.225	97.802	-6.679
3300	4.968	50.168	45.645	14.928	100.781	97.702	-6.470
3400	4.968	50.317	45.780	15.425	100.336	97.616	-6.275
3500	4.968	50.461	45.911	15.922	99.890	97.542	-6.091
3600	4.968	50.601	46.040	16.419	99.443	97.480	-5.918
3700	4.968	50.737	46.165	16.916	98.997	97.433	-5.755
3800	4.968	50.869	46.287	17.412	98.550	97.397	-5.602
3900	4.968	50.998	46.406	17.909	98.101	97.372	-5.456
4000	4.968	51.124	46.522	18.406	97.653	97.359	-5.319
4100	4.968	51.247	46.636	18.903	97.204	97.357	-5.190
4200	4.968	51.366	46.747	19.400	96.755	97.367	-5.066
4300	4.968	51.483	46.856	19.897	96.305	97.386	-4.950
4400	4.968	51.598	46.963	20.393	95.855	97.417	-4.839
4500	4.968	51.709	47.067	20.890	95.403	97.457	-4.733
4600	4.968	51.818	47.169	21.387	94.952	97.507	-4.633
4700	4.968	51.925	47.269	21.884	94.501	97.568	-4.537
4800	4.968	52.030	47.367	22.381	94.049	97.638	-4.446
4900	4.968	52.132	47.463	22.878	93.596	97.717	-4.358
5000	4.968	52.233	47.558	23.374	93.143	97.806	-4.275
5100	4.968	52.331	47.650	23.871	92.691	97.904	-4.195
5200	4.968	52.428	47.741	24.368	92.237	98.011	-4.119
5300	4.968	52.522	47.831	24.865	91.783	98.126	-4.046
5400	4.968	52.615	47.918	25.362	91.328	98.250	-3.976
5500	4.968	52.706	48.005	25.858	90.873	98.382	-3.909
5600	4.968	52.796	48.089	26.355	90.419	98.524	-3.845
5700	4.968	52.884	48.173	26.852	89.963	98.672	-3.783
5800	4.968	52.970	48.255	27.349	89.506	98.829	-3.724
5900	4.968	53.055	48.335	27.846	89.049	98.993	-3.667
6000	4.968	53.138	48.415	28.343	88.592	99.165	-3.612

March 31, 1977

NITROGEN UNINEGATIVE ION (N^-) (IDEAL GAS) GFW = 14.00725

Ground State Configuration $^3P_2$
$S°_{298.15}$ = 38.197 ± 0.02 gibbs/mol

$\Delta Hf°_0$ = 114.14 ± 2.0 kcal/mol N^-
$\Delta Hf°_{298.15}$ = 113.18 ± 2.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0	5
$^3P_1$	[63]	3
$^3P_0$	[90]	1

Heat of Formation

The heat of formation is calculated from an adopted electron affinity of N(g) of EA = -0.07±0.08 eV (1.61±1.84 kcal/mol). This value, based on a semiempirical extrapolation, was derived and recommended by Hotop and Lineberger (1). Additional comments and references are given both in Hotop and Lineberger (1), Rosenstock et al. (2), and Massey (3).

Heat Capacity and Entropy

The ground state for $N^-(g)$ is reported to be $2p^4\ ^3P$. We estimate the fine structure separations in the ground state by comparison of isoelectronic series based on $N^-(g)$ [N^-, O, F^+, Ne^{++}, Na^{+++}] and C(g)[C, N^+, O^{++}, F^{+++}]. The uncertainty in $S°_{298}$ in part reflects this estimation. Massey (3) listed the hyperfine splitting of the ground state as 97 and 137 cm^{-1} based on a quadratic isoelectronic extrapolation. This technique led to high values in the case of $O^-(g)$ (5) and is assumed to give high results for $N^-(g)$. The thermodynamic functions of $N^-(g)$ are calculated using the recent CODATA fundamental constant (3) and assuming that $N^-(g)$ is an ideal monatomic gas.

A comparison of the isoelectronic sequence - $N^-(g)$, O(g), $F^+(g)$ - would suggest that stable electronic states may exist at low wave numbers. These states would greatly affect the entropy. As discussed in Hotop and Lineberger (1), no stable excited states have been observed. Thus, we assume no stable states exist.

References

1. H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
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3. H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, 1976.
4. E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).
5. JANAF Thermochemical Tables: $O^-(g)$, 3-31-77.

N^-

NITROGEN, DIATOMIC (N_2)
(REFERENCE STATE - IDEAL GAS) GFW=28.0134

N_2

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.072	0.000	0.000	0.000
100	6.956	38.170	51.955	-1.379	0.000	0.000	0.000
200	6.957	42.991	46.406	-0.683	0.000	0.000	0.000
298	6.961	45.770	45.770	0.000	0.000	0.000	0.000
300	6.961	45.813	45.770	0.013	0.000	0.000	0.000
400	6.991	47.818	46.043	0.710	0.000	0.000	0.000
500	7.070	49.386	46.560	1.413	0.000	0.000	0.000
600	7.196	50.685	47.142	2.126	0.000	0.000	0.000
700	7.350	51.806	47.730	2.853	0.000	0.000	0.000
800	7.513	52.798	48.303	3.596	0.000	0.000	0.000
900	7.670	53.692	48.853	4.355	0.000	0.000	0.000
1000	7.815	54.508	49.378	5.130	0.000	0.000	0.000
1100	7.945	55.259	49.879	5.918	0.000	0.000	0.000
1200	8.060	55.955	50.357	6.718	0.000	0.000	0.000
1300	8.161	56.605	50.813	7.529	0.000	0.000	0.000
1400	8.250	57.213	51.248	8.350	0.000	0.000	0.000
1500	8.328	57.785	51.665	9.179	0.000	0.000	0.000
1600	8.396	58.324	52.065	10.015	0.000	0.000	0.000
1700	8.456	58.835	52.448	10.858	0.000	0.000	0.000
1800	8.508	59.320	52.816	11.706	0.000	0.000	0.000
1900	8.555	59.781	53.171	12.559	0.000	0.000	0.000
2000	8.597	60.221	53.513	13.417	0.000	0.000	0.000
2100	8.634	60.641	53.842	14.279	0.000	0.000	0.000
2200	8.668	61.044	54.160	15.144	0.000	0.000	0.000
2300	8.699	61.430	54.468	16.012	0.000	0.000	0.000
2400	8.726	61.801	54.766	16.883	0.000	0.000	0.000
2500	8.751	62.157	55.055	17.757	0.000	0.000	0.000
2600	8.775	62.501	55.334	18.634	0.000	0.000	0.000
2700	8.796	62.833	55.606	19.512	0.000	0.000	0.000
2800	8.815	63.153	55.870	20.393	0.000	0.000	0.000
2900	8.833	63.463	56.126	21.275	0.000	0.000	0.000
3000	8.850	63.762	56.376	22.159	0.000	0.000	0.000
3100	8.866	64.053	56.619	23.045	0.000	0.000	0.000
3200	8.881	64.335	56.856	23.933	0.000	0.000	0.000
3300	8.895	64.608	57.086	24.821	0.000	0.000	0.000
3400	8.908	64.874	57.312	25.711	0.000	0.000	0.000
3500	8.920	65.132	57.531	26.603	0.000	0.000	0.000
3600	8.932	65.384	57.746	27.496	0.000	0.000	0.000
3700	8.944	65.629	57.956	28.389	0.000	0.000	0.000
3800	8.954	65.867	58.161	29.284	0.000	0.000	0.000
3900	8.965	66.100	58.361	30.180	0.000	0.000	0.000
4000	8.975	66.327	58.558	31.077	0.000	0.000	0.000
4100	8.984	66.549	58.750	31.975	0.000	0.000	0.000
4200	8.993	66.765	58.938	32.874	0.000	0.000	0.000
4300	9.002	66.977	59.123	33.774	0.000	0.000	0.000
4400	9.011	67.184	59.304	34.674	0.000	0.000	0.000
4500	9.020	67.387	59.481	35.576	0.000	0.000	0.000
4600	9.028	67.585	59.655	36.478	0.000	0.000	0.000
4700	9.036	67.779	59.826	37.382	0.000	0.000	0.000
4800	9.045	67.970	59.993	38.286	0.000	0.000	0.000
4900	9.053	68.156	60.158	39.191	0.000	0.000	0.000
5000	9.061	68.339	60.320	40.096	0.000	0.000	0.000
5100	9.070	68.519	60.479	41.003	0.000	0.000	0.000
5200	9.078	68.695	60.635	41.910	0.000	0.000	0.000
5300	9.085	68.868	60.789	42.818	0.000	0.000	0.000
5400	9.093	69.038	60.940	43.727	0.000	0.000	0.000
5500	9.101	69.205	61.089	44.637	0.000	0.000	0.000
5600	9.110	69.369	61.235	45.547	0.000	0.000	0.000
5700	9.119	69.530	61.379	46.459	0.000	0.000	0.000
5800	9.128	69.689	61.521	47.371	0.000	0.000	0.000
5900	9.138	69.845	61.661	48.285	0.000	0.000	0.000
6000	9.148	69.999	61.799	49.199	0.000	0.000	0.000

Dec. 31, 1960; March 31, 1961; Sept. 30, 1965;
March 31, 1977

NITROGEN, DIATOMIC (N_2) (REFERENCE STATE - IDEAL GAS) GFW = 28.0134

0 to 6000 K Ideal Gas

D_0° = 225.06 ± 0.14 kcal/mol
$S^\circ_{298.15}$ = 45.770 ± 0.006 gibbs/mol
Ground State Configuration $^1\Sigma_g^+$

ΔHf_0° = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol
Symmetry Number = 2

N_2

Vibrational and Rotational Levels (cm^{-1})

Direct Summation of Electronic Ground State:

$$E = G - G_o + F = G - G_o + BZ - DZ^2 + \ldots \approx G - G_o + B^2Z/(B+DZ),$$

where $Z = J(J+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, and D

$$G = 2358.583Y - 14.33594Y^2 - 3.767755\times10^{-3}Y^3 + 2.753652\times10^{-4}Y^4 - 2.701198\times10^{-5}Y^5 + 1.749062\times10^{-7}Y^6$$

$$B = 1.998197 - 0.017279Y - 3.283\times10^{-5}Y^2, \quad D = 5.74\times10^{-6}$$

$$v_{max} = 58, \quad J_{max} = 260 - 250v/v_{max}$$

Excited Electronic States - Contributions at 4800-6000 K Calculated
Using First-Order Corrections:

State	ε_i/cm^{-1}	g_i	B_e/cm^{-1}	α_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e x_e/cm^{-1}$
$A^3\Sigma_u^+$	49754.78	3	1.4546	0.01799	1460.638	13.8723
$B^3\Pi_g$	59306.81	6	1.63745	0.017906	1733.391	14.1221
$W^3\Delta_u$	59380.	6	[1.47327]	[0.016656]	1501.4	11.6

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

These are calculated by combining direct summation of vibrational-rotational energy levels of the electronic ground state with an approximate correction for the contribution of three excited states. All spectroscopic constants are from Lofthus and Krupenie (1) except the vibrational polynomial G used in direct summation of the ground state. We revise the G equation (1) so that it converges near D_0° = 78715 cm^{-1} (2, 1). Experimental data are limited to v ≤ 27 and there is uncertainty in the extrapolation to high v values. Methods proposed by Khachkuruzov (3) are used to approximate the infinite-series (F) equation for rotational levels and the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated by comparison with Khachkuruzov (3) and Gurvich et al. (4).

Contributions of excited states begin to appear in Cp° at ~4800 K. We obtain these contributions using the difference between *approximate calculations for four states (X, A, B, and W) and one state (ground state). These approximate calculations* used first-order corrections for anharmonicity and vibrational-rotational interaction. The excited state contribution to Cp° is 0.019 gibbs/mol at 6000 K.

Values and uncertainties at 298.15 K are the same as those selected by CODATA (2). Uncertainties at 6000 K are considerably larger due to uncertainity in the extrapolation of G and F. Comparing our approximate calculation (a) with our adopted values (b) and those (c) of Gurvich et al. (4), we have S°_{6000} = 69.981, 69.999 and 70.005 gibbs/mol and $H_T^\circ - H_0^\circ$ = 51.196, 51.271, and 51.289 kcal/mol.

References

1. A. Lofthus and P. H. Krupenie, J. Phys. Chem. Ref. Data 6, 113 (1977).
2. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
3. G. A. *Khachkuruzov, Opt. Spectrosc.* 30, 455 (1971).
4. L. V. Gurvich, G. A. Khachkuruzov et al., "Thermodynamic Properties of Individual Substances. Volume I. Calculation of the Thermodynamic Properties," English Translation, Reports AD-659660, AD-659659, AD-659679 (avail. NTIS), 1967; Volume II, Russian Edition, Moscow, 1962.

N_2

NITROGEN, DIATOMIC UNIPOSITIVE ION (N_2^+) N_2^+

(IDEAL GAS) GFW=28.01285

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0				-2.072	359.298		
100							
200							
298	6.964	47.216	47.216	0.000	360.779	358.861	-263.048
300	6.964	47.259	47.216	0.013	360.788	358.848	-261.417
400	7.008	49.267	47.489	0.711	361.286	358.127	-195.669
500	7.111	50.841	46.008	1.417	361.786	357.280	-156.165
600	7.261	52.150	48.592	2.135	362.288	356.332	-129.792
700	7.432	53.282	49.183	2.870	362.792	355.299	-110.928
800	7.605	54.286	49.759	3.622	363.298	354.194	-96.760
900	7.767	55.191	50.313	4.390	363.804	353.026	-85.725
1000	7.913	56.017	50.843	5.174	364.310	351.801	-76.885
1100	8.044	56.778	51.348	5.972	364.817	350.526	-69.642
1200	8.162	57.483	51.831	6.783	365.324	349.204	-63.598
1300	8.269	58.140	52.291	7.604	365.831	347.840	-58.476
1400	8.369	58.757	52.731	8.436	366.339	346.437	-54.081
1500	8.466	59.338	53.152	9.278	366.849	344.998	-50.266
1600	8.562	59.887	53.556	10.129	367.361	343.525	-46.923
1700	8.658	60.409	53.944	10.990	367.875	342.018	-43.969
1800	8.756	60.907	54.317	11.861	368.395	340.483	-41.340
1900	8.857	61.383	54.677	12.742	368.920	338.919	-38.984
2000	8.962	61.840	55.023	13.633	369.450	337.326	-36.861
2100	9.069	62.280	55.358	14.534	369.986	335.706	-34.937
2200	9.179	62.704	55.683	15.447	370.530	334.060	-33.185
2300	9.290	63.114	55.997	16.370	371.082	332.391	-31.584
2400	9.402	63.512	56.302	17.305	371.643	330.697	-30.114
2500	9.514	63.898	56.598	18.250	372.211	328.979	-28.759
2600	9.626	64.274	56.886	19.207	372.788	327.238	-27.506
2700	9.735	64.639	57.166	20.176	373.375	325.475	-26.345
2800	9.843	64.995	57.440	21.154	373.969	323.690	-25.265
2900	9.946	65.342	57.706	22.144	374.574	321.884	-24.258
3000	10.046	65.681	57.966	23.144	375.187	320.057	-23.316
3100	10.142	66.012	58.221	24.153	375.807	318.209	-22.433
3200	10.232	66.335	58.469	25.172	376.434	316.340	-21.605
3300	10.317	66.652	58.712	26.199	377.070	314.453	-20.825
3400	10.396	66.961	58.950	27.235	377.713	312.547	-20.090
3500	10.469	67.263	59.184	28.278	378.361	310.620	-19.396
3600	10.536	67.559	59.412	29.329	379.016	308.675	-18.739
3700	10.598	67.849	59.636	30.385	379.675	306.712	-18.116
3800	10.655	68.132	59.856	31.448	380.340	304.731	-17.526
3900	10.707	68.409	60.072	32.516	381.009	302.733	-16.964
4000	10.754	68.681	60.284	33.589	381.682	300.718	-16.430
4100	10.793	68.947	60.492	34.667	382.359	298.685	-15.921
4200	10.829	69.208	60.696	35.748	383.037	296.635	-15.435
4300	10.860	69.463	60.897	36.832	383.718	294.570	-14.971
4400	10.888	69.713	61.095	37.920	384.403	292.490	-14.528
4500	10.912	69.958	61.289	39.010	385.088	290.393	-14.103
4600	10.930	70.198	61.480	40.102	385.775	288.282	-13.696
4700	10.945	70.433	61.668	41.196	386.461	286.153	-13.306
4800	10.958	70.664	61.853	42.291	387.149	284.012	-12.931
4900	10.968	70.890	62.035	43.387	387.837	281.856	-12.571
5000	10.975	71.111	62.215	44.484	388.526	279.687	-12.225
5100	10.978	71.329	62.391	45.582	389.213	277.503	-11.892
5200	10.980	71.542	62.565	46.680	389.901	275.306	-11.571
5300	10.980	71.751	62.736	47.778	390.588	273.097	-11.261
5400	10.978	71.956	62.905	48.876	391.274	270.873	-10.963
5500	10.975	72.158	63.072	49.973	391.958	268.637	-10.674
5600	10.970	72.355	63.236	51.071	392.642	266.389	-10.396
5700	10.964	72.550	63.397	52.167	393.323	264.128	-10.127
5800	10.957	72.740	63.557	53.263	394.004	261.856	-9.867
5900	10.948	72.927	63.714	54.359	394.683	259.571	-9.615
6000	10.937	73.111	63.869	55.453	395.360	257.276	-9.371

Sept. 30, 1977

NITROGEN DIATOMIC UNIPOSITIVE ION (N_2^+) (IDEAL GAS) GFW = 28.01285

Symmetry Number = 2
$S^\circ_{298.15}$ = 47.216 ± 0.01 gibbs/mol

ΔHf°_0 = 359.298 ± 0.01 kcal/mol
$\Delta Hf^\circ_{298.15}$ = [360.779] kcal/mol

N_2^+

Electronic and Molecular Constants

State	g_i	T_o, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	$\omega_e y_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Sigma_g^+$	2	0	2207.00	16.10	-0.040	1.9319	0.0190	1.116384
$A^2\Pi_{ui}$	4	9016.4	1903.53	15.011		1.748	0.020	1.17364
$B^2\Sigma_u^+$	2	25566.0	2419.84	23.19		2.073	0.020	1.07772

Heat of Formation

The adopted value for the heat of formation of N_2^+(g), ΔHf°_0 = 359.298±0.01 kcal/mol is that recommended in a critical review on the energetics of gaseous ions by Rosenstock et al. (1). This value is derived from ionization potentials determined in the spectroscopic studies of Worley (2) and Ogawa and Tanaka (3); the IP values are 125665.8 and 125666.8 cm^{-1} respectively. ΔHf°_{298} (N_2^+,g) is obtained from ΔHf° (N_2,g) by using IP (N_2,g) with JANAF (7) enthalpies (H°_0-H°_{298}) for N_2(g), N_2^+(g), and e^-(g). ΔHr°_{298} for the reaction $N_2(g) = N_2^+(g) + e^-(g)$ differs from a room temperature threshold energy due to the inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (1). ΔHf°_{298} should be changed by -1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The thermal functions are calculated using the program of McBride and Gordon (4). The contributions of vibrational anharmonicity and rotation-vibration interaction are calculated via the procedures given by Pennington and Kobe (5). In this procedure the energy levels are calculated as follows: $\epsilon_i = T_o + G(v) - G(o) + B_vJ(J+1) - D_eJ^2(J+1)^2$ where $G(v) = \omega_e(v+1/2) - \omega_ex_e(v+1/2)^2 + \omega_ey_e(v+1/2)^3$ and $B_v = B_e - \alpha_e(v+1/2)$. When a value of D_e is not available, it is calculated to be $D_e = 4B_e^3/\omega_e^2$. Molecular constant data in the table are from the critical review of Lofthus and Krupenie (6). Electronic levels above 50000 cm^{-1} given by Lofthus and Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K.

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NITROGEN, DIATOMIC UNINEGATIVE ION (N_2^-) N_2^-
(IDEAL GAS) GFW=28.01395

T, K	gibbs/mol Cp°	 S°	 −(G°−H°₂₉₈)/T	kcal/mol H°−H°₂₉₈	 ΔHf°	 ΔGf°	Log Kp
0				−2.073	37.000		
100							
200							
298	6.978	48.859	48.859	0.000	35.520	36.086	−26.452
300	6.978	48.902	48.859	0.013	35.511	36.090	−26.291
400	7.067	50.920	49.134	0.714	35.019	36.357	−19.864
500	7.227	52.513	49.656	1.429	34.533	36.747	−16.062
600	7.424	53.848	50.246	2.161	34.055	37.235	−13.563
700	7.623	55.007	50.845	2.914	33.585	37.803	−11.803
800	7.806	56.038	51.431	3.685	33.116	38.438	−10.501
900	7.967	56.966	51.995	4.474	32.649	39.131	−9.502
1000	8.104	57.813	52.535	5.278	32.181	39.876	−8.715
1100	8.221	58.591	53.051	6.094	31.712	40.668	−8.080
1200	8.321	59.311	53.543	6.921	31.244	41.504	−7.559
1300	8.405	59.980	54.013	7.758	30.772	42.378	−7.124
1400	8.476	60.606	54.462	8.602	30.298	43.288	−6.757
1500	8.538	61.193	54.891	9.453	29.823	44.232	−6.444
1600	8.591	61.746	55.302	10.309	29.347	45.208	−6.175
1700	8.637	62.268	55.697	11.171	28.869	46.214	−5.941
1800	8.678	62.763	56.076	12.037	28.390	47.249	−5.737
1900	8.714	63.233	56.440	12.906	27.909	48.310	−5.557
2000	8.745	63.681	56.791	13.779	27.427	49.395	−5.398
2100	8.773	64.108	57.129	14.655	26.944	50.505	−5.256
2200	8.799	64.517	57.456	15.534	26.462	51.639	−5.130
2300	8.822	64.908	57.772	16.415	25.978	52.794	−5.017
2400	8.843	65.284	58.077	17.298	25.493	53.971	−4.915
2500	8.862	65.646	58.372	18.183	25.007	55.167	−4.823
2600	8.879	65.994	58.659	19.070	24.521	56.382	−4.739
2700	8.895	66.329	58.937	19.959	24.035	57.618	−4.664
2800	8.910	66.653	59.207	20.849	23.548	58.870	−4.595
2900	8.924	66.966	59.469	21.741	23.060	60.141	−4.532
3000	8.937	67.268	59.724	22.634	22.572	61.427	−4.475
3100	8.949	67.562	59.972	23.528	22.084	62.730	−4.422
3200	8.961	67.846	60.213	24.424	21.595	64.049	−4.374
3300	8.972	68.122	60.449	25.321	21.107	65.384	−4.330
3400	8.982	68.390	60.679	26.218	20.618	66.733	−4.290
3500	8.992	68.650	60.903	27.117	20.127	68.096	−4.252
3600	9.002	68.904	61.121	28.017	19.637	69.473	−4.218
3700	9.011	69.151	61.335	28.917	19.149	70.866	−4.186
3800	9.019	69.391	61.544	29.819	18.658	72.270	−4.156
3900	9.028	69.625	61.748	30.721	18.167	73.687	−4.129
4000	9.036	69.854	61.948	31.624	17.677	75.116	−4.104
4100	9.043	70.077	62.144	32.528	17.185	76.558	−4.081
4200	9.051	70.295	62.335	33.433	16.695	78.013	−4.059
4300	9.058	70.508	62.523	34.338	16.204	79.478	−4.039
4400	9.065	70.717	62.707	35.245	15.713	80.956	−4.021
4500	9.072	70.921	62.887	36.151	15.221	82.443	−4.004
4600	9.079	71.120	63.064	37.059	14.729	83.943	−3.988
4700	9.085	71.315	63.237	37.967	14.237	85.453	−3.974
4800	9.092	71.507	63.407	38.876	13.745	86.973	−3.960
4900	9.098	71.694	63.575	39.786	13.253	88.503	−3.947
5000	9.104	71.878	63.739	40.696	12.761	90.045	−3.936
5100	9.110	72.058	63.900	41.606	12.269	91.595	−3.925
5200	9.116	72.235	64.059	42.518	11.776	93.154	−3.915
5300	9.122	72.409	64.215	43.430	11.283	94.725	−3.906
5400	9.128	72.580	64.368	44.342	10.790	96.304	−3.898
5500	9.134	72.747	64.519	45.255	10.296	97.892	−3.890
5600	9.139	72.912	64.667	46.169	9.803	99.491	−3.883
5700	9.145	73.074	64.813	47.083	9.308	101.096	−3.876
5800	9.150	73.233	64.957	47.998	8.814	102.711	−3.870
5900	9.156	73.389	65.099	48.913	8.319	104.333	−3.865
6000	9.161	73.543	65.238	49.829	7.823	105.964	−3.860

Sept. 30, 1977

NITROGEN, DIATOMIC UNINEGATIVE ION (N_2^-) (IDEAL GAS) GFW = 28.01395

D_0° = 190 ± 30 kcal/mol
$S_{298.15}^\circ$ = [48.86 ± 0.1] gibbs/mol

ΔHf_0° = 37 ± 23 kcal/mol
$\Delta Hf_{298.15}^\circ$ = [35.520] kcal/mol

N_2^-

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^2\Pi g$	0	4

ω_e = [1900] cm^{-1}
B_e = [1.691] cm^{-1}

$\omega_e x_e$ = [12.0]
α_e = [0.015] cm^{-1}

σ = 2
r_e = [1.193 ± 0.003] Å

Heat of Formation

The heat of formation at 0 K for $N_2^-(g)$ is based on the electron affinity value (EA) derived from the Rydberg-Klein-type calculations of Gilmore (1). Use of this adopted value, EA(N_2) = −1.6±1.0 eV and auxiliary data (2) leads to ΔHf_0° = 37±23 kcal/mol and D_0° (N_2^-) = 190±30 kcal/mol. Additional discussion on $N_2^-(g)$ may be found in the reviews by Lofthus and Krupenie (3) and Massey (4).

The adopted EA is the only tabulated value for the ground state given in a recent compilation by Rosenstock et al. (5). This compilation contains results through the end of 1973. In support of the adopted value there are two additional studies to consider. First, Massey (4) discusses qualitatively the electronic and molecular structure as follows. The ground state of N_2 has a closed shell configuration. The corresponding configuration for N_2^- is obtained by adding an additional electron in an antibonding Πg 2p orbital. According to Mulliken's rule this reduces the binding energy by about 1.25 eV (∿29 kcal/mol). In contrast to $O_2^-(g)$, in the separated atom limit the ion N_2^- is not stable so that we expect the lowest level of N_2^- will be at least 1.25 eV above that for N_2 as well as occurring at a larger nuclear separation. Second, Birtwistle and Herzenberg (6) developed a theory of vibrational excitation through an intermediate state which predicts that the lowest energies of N_2^- and N_2 are separated by 1.925 eV (∿44 kcal/mol). Comparable results were obtained by Krauss and Mies (7) using a variational method.

ΔHf_0° is converted to ΔHf_{298}° by use of JANAF (2) enthalpies ($H_0 - H_{298}$) for $N_2(g)$, $N_2^-(g)$, and $e^-(g)$. ΔHf_{298}° should not be interpreted as a room-temperature electron affinity due to the inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (5). ΔHf_{298}° should be changed by +1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The vibrational constants are estimated based on trends implied in isoelectronic sequences involving (N_2^-, NO, and O_2^+) and (N_2 and NO^+). The value adopted for ω_e is ∿35 cm^{-1} and ∿65 cm^{-1} lower than those calculated by Krauss and Mies (7) and Birtwistle and Herzenberg (6), respectively.

We adopt the r_e = 1.193±0.003 Å value calculated by Birtwistle and Herzenberg (6) as it agrees with the value suggested from the above isoelectronic series. The calculations of Krauss and Mies (7) suggest r_e = 1.22 Å which, in our estimation, is too high. B_e is calculated from r_e while α_e is estimated from the aforementioned isoelectronic series. This α_e value is the same as one would calculate assuming a Morse potential for the electronic ground state.

No low lying excited states are assumed to exist (3, 4).

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N_2^-

SODIUM SULFATE, V (Na_2SO_4)
(CRYSTAL) GFW=142.03714

NA_2O_4S

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-5.549	-328.959	-328.959	INFINITE
100	15.904	10.306	59.036	-4.873	-330.475	-321.789	703.260
200	25.255	24.620	38.390	-2.754	-331.315	-312.732	341.733
298	30.627	35.754	35.754	0.000	-331.696	-303.517	222.481
300	30.711	35.944	35.755	0.057	-331.699	-303.341	220.981
400	34.680	45.340	37.009	3.332	-333.632	-293.743	160.491
458	36.647	50.167	38.374	5.402	--------	V-IV TRANSITION	------
500	37.980	53.441	39.503	6.969	-333.878	-283.738	124.020
600	40.947	60.631	42.436	10.917	-333.738	-273.716	99.700
700	43.722	67.153	45.508	15.151	-333.272	-263.748	82.345
800	46.378	73.165	48.594	19.657	-345.512	-255.062	69.679
900	48.955	78.777	51.639	24.424	-344.192	-243.831	59.210
1000	51.475	84.066	54.620	29.446	-342.648	-232.760	50.869

Dec. 31, 1966; June 30, 1978

SODIUM SULFATE, V (Na_2SO_4) (CRYSTAL) GFW = 142.03714

$S^\circ_{298.15}$ = 35.754 ± 0.1 cal/(mol K)
Tt(V → IV) = 458 ± 1 K

ΔHf°_0 = -328.96 ± 0.15 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -331.696 ± 0.15 kcal/mol
ΔHt°(V → IV) = 0.061 ± 0.015 kcal/mol

NA_2O_4S

Heat of Formation

Shibata et al. (1) measured the emf of the cell: Na(amalgam, 0.2077%)|Na_2SO_4(sat. soln.), Hg_2SO_4|Hg at 306-310 K. Extrapolating their results to 298 K, correcting the observed voltage for the formation of the Na-amalgam, and converting to absolute volts, we have E_{cell} = 3.33404 volts for the reaction at 298 K, 2 Na(c) + Hg_2SO_4(c) = 2 Hg(ℓ) + Na_2SO_4(c,V). From this voltage we calculate ΔGr°_{298} = -153.77 kcal/mol. Taking ΔGf°_{298}(Hg_2SO_4,c) = -149.66 kcal/mol (2) and reference entropies from (3), we calculate ΔGf°_{298}(Na_2SO_4,c,V) = -303.43 kcal/mol and ΔHf°_{298}(Na_2SO_4,c,V) = -331.60±0.2 kcal/mol.

The heat of solution at infinite dilution, $\Delta Hsoln^\circ_{298}$(Na_2SO_4,c,V) = -570±10 cal/mol adopted in this tabulation is based on our reanalysis of the heat of solution measurements of Gardner et al. (4), Brodale and Giauque (5), Pitzer and Coulter (6), Coughlin (7) as corrected in (5), and Readnour and Cobble (8). When this result is combined with heats of formation of the infinitely dilute ions from CODATA (2), we obtain ΔHf°_{298} (Na_2SO_4, ∞ H_2O) = -332.266±0.13 kcal/mol and ΔHf°_{298}(Na_2SO_4,c,V) = -331.696±0.15 kcal/mol. The experimental $\Delta Hsoln^\circ_{298}$ values and the number of determinations are -582±5 cal/mol, 6(4), -574 cal/mol, 1(5), -564±10 cal/mol, 2(6), -565±30 cal/mol, 5(7, 5), and -567±12 cal/mol, 9(8).

We adopt ΔHf°_{298}(Na_2SO_4,c,V) = -331.696±0.15 kcal/mol) from the heat of solution results for consistency with the other modifications of Na_2SO_4(c)(3).

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(c,V) have been measured by Pitzer and Coulter (6) over the range 13.74-313.44 K and by Shmidt and Sokolov (9) in an adiabatic calorimeter over the temperature range 324.62-503.06 K. Shmidt (10) later carried out additional measurements which he combined with the earlier measurements of Shmidt and Sokolov (9) and reported Cp° values extending from 298.5-503.1 K. We have smoothed the experimental data (6, 9, 10) by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. The data have been smoothly extrapolated to 1000 K. We have given no weight to the calorimetry enthalpy differences measured by Coughlin (7), May (11), and Denielou et al. (12). These measured enthalpies are higher than our calculated enthalpies by 6%, 9%, and 2% respectively at 400 K. The Cp° measurements of Popov and Galchenko (13) from 373-468 K appear to be biased, being too low at 373 K and too high at 468 K. S°_{298} is derived from our combined smooth fit based on S°_{14} = 0.059 cal/(mol K) and $H^\circ_{14}-H^\circ_0$ = 0.620 cal/mol derived from a Debye T^3-law extrapolation.

Transition Data

Na_2SO_4(c,V) is the stable low-temperature modification of anhydrous sodium sulfate which is obtained by crystallization from aqueous solution above 305.55 K under ordinary pressure. The mineral is known as thenardite and exists in the form of orthorhombic crystals (space group Fddd)(15).

Polymorphism studies by Kracek (14) indicated five distinct modifications of anhydrous sodium sulfate, i.e. V, IV, III, II, I. Calorimetric studies of Shmidt and Sokolov (9) as well as the x-ray work of Simanov and Kirkina (15) suggested another form, stable at high temperatures which is labeled as δ. Brodale and Giauque (5) have recently reviewed the relationships among the various crystalline forms of Na_2SO_4(c). Their analysis shows that Na_2SO_4(c,V) is the stable form from 0 to 458 K; Na_2SO_4(c,IV) rather than Na_2SO_4(c,III) is the stable form from 458 to 514 K; Na_2SO_4(c,I) is the form stable from 514 K to the melting point. Na_2SO_4(c,III) is metastable at all temperatures from 0 to 517 K. Na_2SO_4(c,II) is a meta-stable phase intermediate between forms III and I. The phase transitions are sluggish and subject to hysteresis. Forms V, IV, and III can all persist far beyond their stable regions.

The heat of transition ΔHt°_{458}(V → IV) = 61±15 cal/mol is discussed on the table for Na_2SO_4(c,IV)(3). The temperature of the transition is taken from the work of Kracek (14) and Brodale and Giauque (5). The heat of transition from metastable Na_2SO_4(c,V) to metastable Na_2SO_4(c,III) ΔHt°_{517}(V → III) = 1041±20 cal/mol has been discussed on the table for Na_2SO_4(c,III) (3). This compares to ΔHt_{521}(V → III) = 1030±25 cal/mol from Shmidt and Sokolov (9) and ΔHt_{514}(V → III) = 1040±20 cal/mol from (5). The heat of transition from metastable Na_2SO_4(c,V) to metastable Na_2SO_4(c,I) at 512±1 K is obtained by summation of ΔHt(V → III) = 1021 cal/mol and ΔHt(III → I) = 1642 cal/mol (5) to yield ΔHt°_{512}(V → I) = 2663±25 cal/mol, in good agreement with the value measured by Shmidt and Sokolov (9), ΔHt_{521}(V → I) = 2673±5 cal/mol. Brodale and Giauque (5) give ΔHt_{512}(V → I) = *2681±20 cal/mol*.

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NA_2O_4S

SODIUM SULFATE, IV (NA_2SO_4) (CRYSTAL) GFW=142.03714

NA_2O_4S

T, K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	30.627	35.888	35.888	0.000	-331.634	-303.495	222.465
300	30.711	36.078	35.889	0.057	-331.638	-303.320	220.965
400	34.680	45.474	37.143	3.332	-333.570	-293.735	160.487
456	36.647	50.302	38.508	5.402	-------- V-IV TRANSITION ------		
500	37.960	53.575	39.637	6.969	-333.817	-283.744	124.023
514	38.411	54 630	40.031	7.508	-------- IV-I TRANSITION ------		
600	40.947	60.765	42.570	10.917	-333.676	-273.735	99.707
700	43.722	67.287	45.642	15.152	-333.210	-263.780	82.355
800	46.378	73.300	48.728	19.657	-345.450	-255.108	69.691
900	48.955	78.912	51.773	24.424	-344.130	-243.891	59.224
1000	51.475	84.201	54.754	29.446	-342.586	-232.833	50.885

June 30, 1978

SODIUM SULFATE, IV (Na_2SO_4) (CRYSTAL) GFW = 142.03714

$S°_{298.15}$ = [35.887 ± 0.1] cal/(mol K)
Tt(V → IV) = 458 ± 1 K
Tt(IV → I) = 514 ± 1 K

$\Delta Hf°_0$ = [-329.86 kcal/mol]
$\Delta Hf°_{298.15}$ = -331.635 ± 0.15 kcal/mol
ΔHt°(V → IV) = 0.061 ± 0.015 kcal/mol
ΔHt°(IV → I) = 2.607 ± 0.020 kcal/mol

NA_2O_4S

Heat of Formation

Brodale and Giauque (1) determined the heat of solution at infinite dilution $\Delta Hsoln°_{298}(Na_2SO_4,c,IV)$ = -635±1 cal/mol for the process $Na_2SO_4(c,IV) \rightarrow Na_2SO_4(\infty\ H_2O)$. When this result is combined with the heats of formation of the infinitely dilute ions from CODATA (2), we obtain $\Delta Hf°_{298}(Na_2SO_4,\infty\ H_2O)$ = -332.266±0.13 kcal/mol and $\Delta Hf°_{298}(Na_2SO_4,c,IV)$ = -331.631±0.15 kcal/mol. Brodale and Giauque (1) have also determined the difference in $\Delta Hf°_{298}$ between $Na_2SO_4(c,IV)$ and $Na_2SO_4(c,V)$ by direct heat of solution experiments. We prefer to give complete weight to these results using the same calorimeter. $\Delta Hsoln°_{298}(Na_2SO_4,c,V)$ = -574 cal/mol (1) which leads to $\Delta Hr_{298}(V \rightarrow IV)$ = 61±15 cal/mol. When this is combined with auxiliary data for $Na_2SO_4(c,V)$ (3), we obtain $\Delta Hf°_{298}(Na_2SO_4,c,IV)$ = -331.635±0.15 kcal/mol. This value of $\Delta Hf°_{298}$ is adopted in this tabulation.

Heat Capacity and Entropy

The heat capacity of $Na_2SO_4(c,IV)$ has been taken equal to the heat capacity of the V form from 298-514 K (1, 3). The heat of transition (V → IV) adopted here leads to a calculated entropy of transition of 0.133 cal/(mol K) and $S°_{458}(Na_2SO_4,c,IV)$ = 50.304 cal/(mol K). Brodale and Giauque (1) state that the small difference in entropy (between IV and V) means that on the average the heat capacity of $Na_2SO_4(c,IV)$ should exceed the heat capacity of $Na_2SO_4(c,V)$ by only about 0.3% over the range 298-514 K. We calculate $S°_{298}(Na_2SO_4,c,IV)$ = 35.887 cal/(mol K).

Transition Data

$Na_2SO_4(c,IV)$ is the orthorhombic modification of anhydrous sodium sulfate stable from 458-514 K (1, 4). This form can *persist down to low temperatures. The presence of moisture enhances the achievement of equilibrium. A recent Raman and DSC* study has failed to observe the IV modification (8). The (V → IV) transition at 458 K has been discussed previously (see (3) and above), $\Delta Hr_{298}(V \rightarrow IV)$ = 61±15 cal/mol. Since ΔCp = 0 (1, 3), $\Delta Ht°_{458}(V \rightarrow IV)$ = 61±15 cal/mol. The temperature of 458 K for the transition is taken from Kracek (4) and Brodale and Giauque (1).

The transition from $Na_2SO_4(c,IV)$ to $Na_2SO_4(c,I)$ has been found to occur at 514 K (1, 4). The heat of the transition has not been directly measured although Shmidt and Sokolov (5) obtained ΔHt_{516} = 2584±15 cal/mol for a sample of ground Na_2SO_4 which could have been $Na_2SO_4(c,IV)$ (see 1). We adopt the value of the heat of transition $\Delta Ht°_{514}(IV \rightarrow I)$ = 2607±20 cal/mol. This is obtained by summation of ΔHt(IV → III) (1, 3) and ΔHt(III → I) (1, 3), all reduced to 514 K. Other measurements include that of Kreidl and Simon (6) who found $\Delta Ht_{511}(IV \rightarrow I)$ = 2300 kcal/mol and Popov and Galchenko (7) who found ΔHt_{518} = 2586±64 cal/mol on first heating. Later heating apparently converted some sample over to the III modification. Brodale and Giauque (1) give $\Delta Ht_{514}(IV \rightarrow I)$ = 2611 cal/mol.

The heat of transition from metastable $Na_2SO_4(c,IV)$ to metastable $Na_2SO_4(c,III)$ is obtained from heat of solution measurements on the separate crystalline forms. Brodale and Giauque (1) obtained $\Delta Hsoln°_{298}(Na_2SO_4,c,IV)$ = -635±1 cal/mol and $\Delta Hsoln°_{298}(Na_2SO_4,c,III)$ = -1273±4 cal/mol from which $\Delta Hr°_{298}(IV \rightarrow III)$ = 638±10 cal/mol. Combining this result with the difference between $H_{519}-H_{298}$ for $Na_2SO_4(c,IV)$ and $Na_2SO_4(c,III)$ we obtain $\Delta Ht°_{519}(IV \rightarrow III)$ = 988±20 cal/mol. Shmidt and Sokolov (5) have measured the heats of transformation of Na_2SO_4(thenardite) → $Na_2SO_4(c,I)$ and $Na_2SO_4(c,III) \rightarrow Na_2SO_4(c,I)$ calorimetrically from which we obtain ΔHt_{516}(thenardite → III) = 954±20 cal/mol. Brodale and Giauque (1) have speculated that the "ground thenardite" of (5) was actually the IV modification of Na_2SO_4.

References

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NA_2O_4S

SODIUM SULFATE, I (NA_2SO_4) NA_2O_4S
(CRYSTAL) GFW=142.03714

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	38.150	38.297	38.297	0.000	-330.037	-302.616	221.821
300	38.175	38.533	38.298	0.071	-330.027	-302.445	220.328
400	39.378	49.679	39.809	3.948	-331.357	-293.204	160.197
500	40.635	58.602	42.704	7.949	-331.239	-283.680	123.995
514	40.806	59.726	43.152	8.519	--------	IV-I TRANSITION	------
600	41.905	66.121	45.996	12.075	-330.921	-274.194	99.874
700	43.270	72.682	49.349	16.333	-330.431	-264.778	82.666
800	44.760	78.556	52.639	20.734	-342.777	-256.639	70.110
900	46.330	83.919	55.821	25.288	-341.669	-245.936	59.721
1000	47.875	88.880	58.882	29.999	-340.437	-235.364	51.438
1100	49.410	93.516	61.822	34.863	-339.089	-224.924	44.688
1157	50.279	96.033	63.446	37.704	------------	MELTING	----------
1200	50.940	97.880	64.647	39.880	-384.099	-213.694	38.918
1300	52.449	102.017	67.363	45.050	-382.090	-199.573	33.551
1400	53.919	105.958	69.981	50.369	-379.951	-185.614	28.975
1500	55.350	109.727	72.506	55.833	-377.684	-171.810	25.032

Dec. 31, 1966; June 30, 1978

SODIUM SULFATE, I (Na_2SO_4) (CRYSTAL) GFW = 142.03714

S°_{298} = [38.297 ± 1.0] cal/(mol K)
$Tt(III \rightarrow I)$ = 509 ± 1 K
$Tt(IV \rightarrow I)$ = 514 ± 1 K
$Tm(I \rightarrow \ell)$ = 1157 ± 1 K

ΔHf°_{298} = [-330.037 ± 0.2] kcal/mol
$\Delta Ht^\circ(III \rightarrow I)$ = 1.646 ± 0.020 kcal/mol
$\Delta Ht^\circ(IV \rightarrow I)$ = 2.607 ± 0.020 kcal/mol
$\Delta Hm^\circ(I \rightarrow \ell)$ = 5.700 ± 0.10 kcal/mol

NA_2O_4S

Heat of Formation

The heat of formation adopted in this tabulation is obtained from $\Delta Hf^\circ_{298}(Na_2SO_4, c, III)$ by adding $\Delta Ht^\circ_{509}(III \rightarrow I)$ = 1646 cal/mol (1, 2) and the difference between $H^\circ_{509}-H^\circ_{298}$ for Na_2SO_4(c,III) and Na_2SO_4(c,I) (2).

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(c,I) have been measured by Shmidt and Sokolov (3) in an adiabatic calorimeter over the temperature range 538.65 - 1021.75 K. The direct heating measurements of Popov and Galchenko (4) using a heat-flow calorimeter are in substantial agreement. Enthalpy measurements by drop calorimetry have been carried out by Coughlin (5, 515 - 1143 K), Popov and Ginzburg (6, 1173 - 1290 K), May (7, 520 - 1157 K), and by Denielou et al. (8, 516 - 1154 K).

The data of May (7) are not in agreement with the other enthalpy results. The enthalpy data of references (5, 6, 8) are in general agreement but our derived Cp° values are lower than the calorimetric Cp° (3) results below 800 K but show the proper slope. Derived Cp° values from Denielou et al. (8) are in agreement with the calorimetric results above 930 K. All of the experiments seem to show a change in the slope of the Cp° curve near 900 K. We adopt Cp° from 530 - 880 K from (3) and extrapolate smoothly to 1500 K. Cp° values below 530 K are obtained by graphical extrapolation. The entropy, S°_{298}, is calculated in a manner analogous to that of the heat of formation.

Transition Data

Na_2SO_4(c,I) is the hexagonal modification (space group D^3_{3d} or C3m1(9, 10)) of anhydrous sodium sulfate stable from 514 - 1157 K. All the low-temperature modifications (III, IV, V) are converted to the high temperature form between 500 - 530 K (2); $\Delta Ht^\circ_{514}(IV \rightarrow I)$ = 2607 cal/mol (1, 2), $\Delta Ht^\circ_{512}(V \rightarrow I)$ = 2663 cal/mol (1, 2) and $\Delta Ht^\circ_{509}(III \rightarrow I)$ = 1646 cal/mol (1, 2).

A small anomalous region between 963.15 - 993.15 K on the Cp° curve for Na_2SO_4(c,I) was reported by Shmidt and Sokolov (3), who attributed the anomaly to a transition to another phase of Na_2SO_4 which they referred to as the δ-phase. There is not sufficient evidence to warrant our inclusion of the δ-phase.

Melting Data

The heat of melting of $Na_2SO_4(c,I) \rightarrow Na_2SO_4(\ell)$ has been derived from drop calorimetry data by Denielou et al. (8, 5.58±0.13 kcal/mol), Coughlin (5, 5.67±0.1 kcal/mol), Popov and Ginzburg (6, 5.77±0.2 kcal/mol), and May (7, 5.8±0.2 kcal/mol). No mention was made of the δ phase. Based on our selected Cp° values for Na_2SO_4(c,I) and $Na_2SO_4(\ell)$, we derive $\Delta Hm^\circ(I \rightarrow \ell)$ = 5.70±0.10 kcal/mol, using the enthalpy data of Coughlin (5). There is good agreement on the melting temperature which we take as $Tm(I \rightarrow \ell)$ = 1157±1 K.

References

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SODIUM SULFATE, III (NA_2SO_4) NA_2O_4S
(CRYSTAL) GFW=142.03714

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-5.623	-328.325	-328.325	INFINITE
100	16.304	11.439	60.389	-4.895	-329.789	-321.217	702.009
200	25.244	25.853	39.673	-2.764	-330.617	-312.281	341.240
298	30.872	37.024	37.024	0.000	-330.988	-303.187	222.239
300	30.968	37.215	37.025	0.057	-330.991	-303.014	220.742
400	35.885	46.784	38.296	3.395	-332.861	-293.550	160.386
500	41.388	55.351	40.862	7.244	-332.895	-283.710	124.008
509	41.967	56.094	41.125	7.620	------ III-I TRANSITION --------		
600	47.823	63.465	43.957	11.705	-332.242	-273.921	99.774
700	54.257	71.320	47.308	16.809	-330.906	-264.300	82.517
800	60.692	78.986	50.790	22.556	-341.905	-256.111	69.965
900	67.127	86.506	54.342	28.947	-338.961	-245.556	59.628
1000	73.561	93.911	57.929	35.982	-335.404	-235.362	51.438

Dec. 31, 1966; June 30, 1978

SODIUM SULFATE, III (Na_2SO_4) (CRYSTAL) GFW = 142.03714

$\Delta Hf°_0$ = -328.325 ± 0.15 kcal/mol
$S°_{298.15}$ = 37.024 ± 0.1 cal/(mol K)
$\Delta Hf°_{298.15}$ = -330.988 ± 0.15 kcal/mol
Tt (III → I) = 509 ± 1 K
ΔHt° (III → I) = 1.646 ± 0.020 kcal/mol

NA_2O_4S

Heat of Formation

Brodale and Giauque (1) determined the heat of solution at infinite dilution $\Delta Hsoln°_{298}$ (Na_2SO_4,c,III) = -1273±4 cal/mol for the process Na_2SO_4(c,III) → Na_2SO_4(∞ H_2O). When this result is combined with the heats of formation of the infinitely dilute ions from CODATA (2), we obtain $\Delta Hf°_{298}$ (Na_2SO_4, ∞ H_2O) = -332.266±0.13 kcal/mol and $\Delta Hf°_{298}$(Na_2SO_4,c,III) = -330.993±0.15 kcal/mol. Coughlin (3) also measured the heat of solution, $\Delta Hsoln_{303}$(Na_2SO_4,c,III) = -1363±4 cal/mol for the process Na_2SO_4(c,III) → Na_2SO_4(1068 H_2O). Using ΔCp as determined by Coughlin to extrapolate the heat of solution to 298 K gives $\Delta Hsoln_{298}$(Na_2SO_4,c,III) = -1037±20 cal/mol. Extrapolating to infinite dilution using the data of Lange and Streeck (4) and Wallace and Robinson (5) gives $\Delta Hsoln°_{298}$(Na_2SO_4,c,III) = -1282±20 cal/mol. Using the same auxiliary data as above (2) $\Delta Hf°_{298}$(Na_2SO_4,c,III) = -330.984±0.15 kcal/mol. *The heat of solution data of Coughlin (3) as corrected by Brodale and Giauque* (1) leads to $\Delta Hr°_{298}$(V → III) = 716±8 cal/mol. When this is combined with auxiliary data for Na_2SO_4(c,V) (6), we obtain $\Delta Hf°_{298}$(Na_2SO_4,c,III) = -330.980±0.2 kcal/mol. We adopt an intermediate value $\Delta Hf°_{298}$(Na_2SO_4,c,III) = -330.988±0.15 kcal/mol for this tabulation.

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(c,III) have been measured by Brodale and Giauque (1) over the range 13.16 - 297.71 K and by Shmidt and Sokolov (7) in an adiabatic calorimeter over the temperature range 319.03 - 520.56 K. Paukov and Lavrent'eva (8) also measured the low temperature heat capacity of Na_2SO_4(c,III) but their results are intermediate between Na_2SO_4(c,V) and Na_2SO_4(c,III) indicating that their sample may have been converted to as much as two-thirds of the V modification. Coughlin (3) measured enthalpies of Na_2SO_4(c,III) from 370.2 - 514.9 K by drop calorimetry, but his data appear high by 2% at 450 K. Enthalpy measurements of Denielou et al. (9) are in very good agreement with the Cp° measurements of Shmidt and Sokolov (7). We combine the three sets of experimental data (1, 7, 9) by graphical smoothing and by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. Cp° is smoothly extrapolated to 1000 K. $S°_{298}$ is derived from our combined smooth fit based on $S°_{14}$ = 0.100 cal/(mol K) and $H°_{14}-H°_0$ = 1.051 cal/mol derived from a Debye T^3-law extrapolation.

Transition Data

Na_2SO_4(c,III) is the meltable low-temperature orthorhombic modification of anhydrous sodium sulfate which is obtained on cooling, in the absence of moisture, the high-temperature hexagonal form Na_2SO_4(c,I). Na_2SO_4(c,III) is metastable with respect to the two other low-temperature orthorhombic forms *Na_2SO_4(c,V) and Na_2SO_4(c,IV). The space group of Na_2SO_4(c,III) has been* given as Cmcm (10).

The second-order transformation from Na_2SO_4(c,III) to Na_2SO_4(c,I) in which both phases are metastable, has been observed by Shmidt and Sokolov (7) at 521.5 K, ΔHt(III → I) = 1642±20 cal/mol; by Coughlin (3) at 514 K, ΔHt(III → I) = 1680 cal/mol; by Denielou et al. (9) at 515±1 K, ΔHt(III → I) = 1650±90 cal/mol; and by May (11) at 520±5 K, ΔHt(III → I) = 1150 cal/mol. We adopt the transition temperature from the analysis of Brodale and Giauque (1). This is consistent with our analysis which yields $\Delta Ht°_{509}$(III → I) = 1646±20 cal/mol. The heat of transition from metastable Na_2SO_4(c,V) to metastable Na_2SO_4(c,III) has been measured by heat of solution measurements on the separate crystalline forms by Coughlin (3), Brodale and Giauque (1) and Pickering (12). ΔHr_{298}(V → III) = 716±8 cal/mol (1, 3), 699±10 cal/mol (1), 709±10 cal/mol (1, 13), and ΔHr_{294}(V → III) = 708±20 cal/mol (12). Using the heat of transition value from (1) and the difference between $H°_{517}-H°_{298}$ for Na_2SO_4(c,III) and Na_2SO_4(c,V) (6), we obtain $\Delta Ht°_{517}$(V → III) = 1041±20 cal/mol. The heat of transition from metastable Na_2SO_4(c,IV) to metastable Na_2SO_4(c,III) is discussed on the table for Na_2SO_4(c,IV). Our analysis yields $\Delta Ht°_{519}$(IV → III) = 988±20 cal/mol.

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NA_2O_4S

SODIUM SULFATE, DELTA (NA_2SO_4) NA_2O_4S
(CRYSTAL) GFW=142.03714

T, K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	37.240	39.009	39.009	0.000	-329.659	-302.450	221.699
300	37.260	39.239	39.009	0.069	-329.650	-302.280	220.208
400	38.970	50.215	40.494	3.888	-331.039	-293.100	160.140
500	39.735	58.982	43.345	7.819	-330.991	-283.622	123.970
600	41.065	66.342	46.580	11.857	-330.761	-274.166	99.863
700	42.570	72.781	49.872	16.037	-330.350	-264.766	82.663
800	44.385	78.577	53.103	20.379	-342.753	-256.632	70.108
900	46.840	83.942	56.235	24.936	-341.643	-245.931	59.719
986	49.336	88.329	58.844	29.072	----- I-DELTA TRANSITION ------		
1000	49.740	89.027	59.262	29.765	-340.292	-235.366	51.438
1100	52.680	93.907	62.191	34.888	-338.687	-224.952	44.693
1170	54.654	97.218	64.188	38.645	----------- MELTING ----------		
1200	55.470	98.612	65.031	40.297	-383.304	-213.777	38.934
1300	58.050	103.155	67.790	45.974	-380.788	-199.749	33.580
1400	60.450	107.547	70.474	51.903	-378.040	-185.926	29.024
1500	62.460	111.788	73.088	58.051	-375.087	-172.305	25.104

Dec. 31, 1966; June 30, 1978

SODIUM SULFATE, δ (Na_2SO_4) (CRYSTAL) GFW = 142.03714

$S^\circ_{298.15}$ = [39.009] cal/(mol K)
Tt(I → δ) = [986] K
Tm(δ → ℓ) = [1170] K

$\Delta Hf^\circ_{298.15}$ =[-329.659] kcal/mol
ΔHt°(I → δ) = [0.120] kcal/mol
ΔHm°(δ → ℓ) = [5.100] kcal/mol

NA_2O_4S

Heat of Formation

The heat of formation adopted in this tabulation is obtained from ΔHf°_{298} for Na_2SO_4(c,I) by adding ΔHt°(I → δ) and the difference between $H^\circ_{986}-H^\circ_{298}$ for Na_2SO_4(c,I) and Na_2SO_4(c,δ) (2).

Heat Capacity and Entropy

Heat capacities in the range 900 - 1010 K were measured by Shmidt and Sokolov (1) in an adiabatic calorimeter. We have graphically extrapolated these data down to 298.15 K, paralleling the Cp° data of Na_2SO_4(c,I), and extended the data smoothly to 1500 K. Our calculated enthalpies are biased by some 300 cal/mol above the experimental results (for the I phase) of Denielou et al. (3) and Coughlin (4). See the discussion in the Na_2SO_4(c,I) table (2).

Transition Data

The existence of Na_2SO_4(c, δ) is based on the work of Shmidt and Sokolov (1) who found an anomolous region in the heat capacity curve of Na_2SO_4(c,I) between 963 - 993 K. Popov and Ginzburg (5) also observed a sharp change in the heat capacity above 837.6 K. Simanov and Kirkina (6) have observed an orthorhombic modification of Na_2SO_4 at 993 K by X-ray diffraction. As noted above, our calculated enthalpies do not agree with measured enthalpies above 980 K. The evidence for the existence of the δ-phase is not conclusive. We have deleted the δ-phase from our combined phase table for Na_2SO_4. The heat of transition ΔHt°_{986}(I → δ) = 120±10 cal/mol is obtained by graphical integration of the area between the measured Cp° curve from (1) and the adopted Cp° curve for Na_2SO_4(c,I)(2). The temperature of the transition is assumed to be 986 K.

Melting Data

Based on our selected Cp° values for Na_2SO_4(c,δ) and Na_2SO_4(ℓ), we derive ΔHm°(δ → ℓ) = 5.10±0.10 kcal/(mol) using the experimental liquid enthalpies from Denielou et al. (3) and Coughlin (4). Tm(δ → ℓ) = 1170 K is the calculated temperature at which ΔGr° = 0 for Na_2SO_4(c,δ) → Na_2SO_4(ℓ).

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SODIUM SULFATE (NA_2SO_4) NA2O4S

(LIQUID) GFW=142.03714

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	38.150	43.326	43.326	0.000	-324.178	-298.257	218.625
300	38.175	43.562	43.326	0.071	-324.168	-298.095	217.159
400	39.378	54.707	44.838	3.948	-325.498	-289.357	158.095
500	40.635	63.631	47.733	7.949	-325.380	-280.335	122.533
600	41.905	71.150	51.025	12.075	-325.062	-271.352	98.838
700	43.270	77.711	54.378	16.333	-324.572	-262.439	81.936
800	44.760	83.584	57.668	20.733	ASSUMED		
800	47.092	83.584	57.668	20.733	GLASS TRANSITION		
900	47.092	89.131	60.861	25.442	-335.656	-244.614	59.400
1000	47.092	94.093	63.941	30.152	-334.425	-234.564	51.263
1100	47.092	98.581	66.889	34.861	-333.232	-224.639	44.631
1157	47.092	100.960	68.510	37.545	MELTING		
1200	47.092	102.678	69.703	39.570	-378.550	-213.903	38.956
1300	47.092	106.448	72.387	44.279	-377.002	-200.244	33.664
1400	47.092	109.938	74.946	48.988	-375.473	-186.706	29.146
1500	47.092	113.187	77.388	53.698	-373.960	-173.275	25.246
1600	47.092	116.226	79.722	58.407	-372.464	-159.946	21.847
1700	47.092	119.081	81.954	63.116	-370.980	-146.706	18.860
1800	47.092	121.773	84.092	67.825	-369.514	-133.557	16.216
1900	47.092	124.319	86.143	72.534	-368.062	-120.487	13.859
2000	47.092	126.734	88.112	77.244	-366.625	-107.495	11.746
2100	47.092	129.032	90.007	81.953	-365.200	-94.576	9.842
2200	47.092	131.223	91.831	86.662	-363.791	-81.721	8.118
2300	47.092	133.316	93.589	91.371	-362.395	-68.932	6.550
2400	47.092	135.320	95.287	96.080	-361.014	-56.200	5.118
2500	47.092	137.243	96.927	100.790	-359.645	-43.532	3.806
2600	47.092	139.090	98.513	105.499	-358.290	-30.911	2.598
2700	47.092	140.867	100.049	110.208	-356.950	-18.347	1.485
2800	47.092	142.579	101.537	114.917	-355.625	-5.831	0.455
2900	47.092	144.232	102.981	119.626	-354.314	6.642	-0.501
3000	47.092	145.828	104.383	124.336	-353.020	19.064	-1.389

Dec. 31, 1966; June 30, 1978

SODIUM SULFATE (Na_2SO_4) (LIQUID) GFW = 142.03714

$S^\circ_{298.15}$ = [43.326] cal/(mol K)
Tm(I → ℓ) = 1157 ± 1 K
Td = 2500 K

$\Delta Hf^\circ_{298.15}$ = [-324.178] kcal/mol
ΔHm°(I → ℓ) = 5.700 ± 0.10 kcal/mol

NA2O4S

Heat of Formation

The heat of formation adopted in this tabulation is obtained from $\Delta Hf^\circ_{298}(Na_2SO_4,c,I)$ by adding ΔHm° and the difference between $H^\circ_{1157}-H^\circ_{298}$ for $Na_2SO_4(c,I)$ and $Na_2SO_4(\ell)$(5).

Heat Capacity and Entropy

The enthalpies for $Na_2SO_4(\ell)$ have been measured by drop calorimetry in the temperature range 1164.7-1826.2 K by Coughlin (1), 1173.3-1502.6 K by Denielou (2), 1157-1500 K by May (3) and 1173.4-1280.2 K *by Popov and Ginzburg (4). The more recent* studies (1, 2, 4) are in very good agreement. The study of May (4) appears biased, being 1% low at 1200 K and 2% high at 1500 K. *We have adopted heat capacities derived from the enthalpy data of Coughlin (1) over the range 1157-1800 K.* The data have been extended to 800 K and 3000 K. Below an assumed glass transition temperature of 800 K, the heat capacities are taken to be identical to those of the I phase. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

The heat of melting of $Na_2SO_4(c,I) \rightarrow Na_2SO_4(\ell)$ has been discussed in the $Na_2SO_4(c,I)$ table (5). Kelley (6) had previously reported ΔHm°_{1157} = 5.83 kcal/mol from data on binary systems. We prefer the results from direct calorimetric measurements.

Vaporization and Decomposition Data

Vaporization data on $Na_2SO_4(\ell)$ is somewhat discordant due primarily to the extent to which the vapor is dissociated. $Na_2SO_4(\ell)$ can decompose according to various mechanisms, the most significant of which is the reaction $Na_2SO_4(\ell) = 2\ Na(g) + SO_2(g) + O_2(g)$. Recent experimental data (7, 8, 9) are in good agreement with dissociation pressures and the heat of reaction calculated from the JANAF Thermochemical Tables (5). Decomposition to the oxides of sodium produces lower decomposition pressures than decomposition to the metal. In the presence of water vapor, significant decomposition can occur according to $Na_2SO_4(\ell) + H_2O(g) = 2\ NaOH(g) + SO_2(g) + 1/2\ O_2(g)$(10). Molecular vaporization data are discussed in the $Na_2SO_4(g)$ table (5). Td = 2500 K is the calculated temperature at which the Gibbs *energy difference is zero for the reaction* $Na_2SO_4(\ell) = 2\ Na(g) + SO_2(g) + O_2(g)$.

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NA2O4S

SODIUM SULFATE (Na_2SO_4) NA_2O_4S
(V-IV-I-LIQUID) GFW=142.03714

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-5.549	-328.959	-328.959	INFINITE
100	15.904	10.306	59.036	-4.873	-330.475	-321.789	703.260
200	25.255	24.620	38.390	-2.754	-331.315	-312.732	341.733
298	30.627	35.754	35.754	0.000	-331.696	-303.517	222.481
300	30.711	35.944	35.755	0.057	-331.699	-303.341	220.981
400	34.680	45.340	37.009	3.332	-333.632	-293.743	160.491
458	36.647	50.169	38.374	5.402			
458	36.647	50.302	38.374	5.463	-------- V-IV TRANSITION ------		
500	37.980	53.575	39.514	7.030	-333.817	-283.744	124.023
514	38.411	54.630	39.912	7.565			
514	40.806	59.726	39.912	10.185	-------- IV-I TRANSITION ------		
600	41.905	66.121	43.232	13.734	-330.921	-274.194	99.874
700	43.270	72.682	46.980	17.991	-330.432	-264.778	82.666
600	44.760	78.556	50.566	22.392	-342.777	-256.639	70.110
900	46.330	83.919	53.978	26.947	-341.669	-245.936	59.721
1000	47.875	88.880	57.223	31.657	-340.437	-235.364	51.438
1100	49.410	93.515	60.314	36.522	-339.089	-224.924	44.688
1157	50.279	96.033	62.006	39.370			
1157	47.092	100.960	62.006	45.070	------------ MELTING ----------		
1200	47.092	102.678	63.439	47.088	-378.550	-213.903	38.956
1300	47.092	106.448	66.604	51.797	-377.002	-200.244	33.664
1400	47.092	109.938	69.576	56.506	-375.473	-186.706	29.146
1500	47.092	113.187	72.376	61.215	-373.960	-173.275	25.246
1600	47.092	116.226	75.023	65.925	-372.464	-159.946	21.847
1700	47.092	119.081	77.532	70.634	-370.980	-146.706	18.860
1800	47.092	121.773	79.915	75.343	-369.514	-133.557	16.216
1900	47.092	124.319	82.186	80.052	-368.062	-120.487	13.859
2000	47.092	126.734	84.353	84.761	-366.625	-107.495	11.746
2100	47.092	129.032	86.427	89.471	-365.200	-94.576	9.842
2200	47.092	131.223	88.413	94.180	-363.791	-81.721	8.118
2300	47.092	133.316	90.321	98.889	-362.395	-68.932	6.550
2400	47.092	135.320	92.154	103.598	-361.014	-56.200	5.118
2500	47.092	137.242	93.919	108.307	-359.645	-43.532	3.806
2600	47.092	139.089	95.621	113.017	-358.290	-30.911	2.598
2700	47.092	140.867	97.265	117.726	-356.950	-18.347	1.485
2800	47.092	142.579	98.853	122.435	-355.625	-5.831	0.455
2900	47.092	144.232	100.389	127.144	-354.314	6.642	-.501
3000	47.092	145.828	101.877	131.853	-353.020	19.064	-1.389

June 30, 1978

SODIUM SULFATE (Na_2SO_4) (V-IV-I-LIQUID) GFW = 142.03714

NA_2O_4S

0	to	458	K	Crystal, V
458	to	514	K	Crystal, IV
514	to	1157	K	Crystal, I
1157	to	2500	K	Liquid

Refer to the respective single phase tables for details.

NA_2O_4S

SODIUM SULFATE (NA_2SO_4) (IDEAL GAS) GFW=142.03714

NA_2O_4S

T, K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	0.000	0.000	INFINITE	-5.058	-243.812	-243.812	INFINITE
100	14.053	62.062	101.852	-3.979	-244.925	-241.415	527.605
200	20.382	73.777	85.038	-2.252	-246.157	-237.406	259.421
298	25.244	82.874	82.874	0.000	-247.040	-232.910	170.725
300	25.320	83.030	82.874	0.047	-247.053	-232.821	169.608
400	28.769	90.818	83.913	2.762	-249.546	-227.848	124.489
500	31.119	97.507	85.979	5.764	-250.427	-222.320	97.175
600	32.726	103.332	88.396	8.961	-251.038	-216.637	78.909
700	33.845	108.465	90.904	12.293	-251.474	-210.869	65.835
800	34.644	113.040	93.390	15.720	-264.793	-206.243	56.342
900	35.229	117.156	95.806	19.215	-264.745	-198.926	48.305
1000	35.668	120.891	98.131	22.760	-264.678	-191.615	41.877
1100	36.004	124.307	100.357	26.345	-264.610	-184.316	36.620
1200	36.267	127.452	102.486	29.959	-311.023	-176.104	32.072
1300	36.476	130.363	104.520	33.596	-310.547	-164.879	27.718
1400	36.644	133.073	106.464	37.253	-310.070	-153.693	23.992
1500	36.782	135.606	108.323	40.924	-309.595	-142.539	20.768
1600	36.896	137.983	110.103	44.608	-309.125	-131.418	17.951
1700	36.991	140.223	111.810	48.303	-308.655	-120.323	15.468
1800	37.071	142.340	113.447	52.006	-308.195	-109.259	13.266
1900	37.140	144.346	115.021	55.716	-307.742	-98.218	11.298
2000	37.198	146.252	116.536	59.433	-307.297	-87.203	9.529
2100	37.249	148.069	117.994	63.156	-306.859	-76.212	7.931
2200	37.293	149.802	119.401	66.883	-306.432	-65.237	6.481
2300	37.332	151.461	120.759	70.614	-306.014	-54.285	5.158
2400	37.366	153.051	122.072	74.349	-305.607	-43.346	3.947
2500	37.396	154.577	123.342	78.088	-305.208	-32.431	2.835
2600	37.423	156.044	124.571	81.829	-304.822	-21.525	1.809
2700	37.447	157.457	125.763	85.572	-304.448	-10.637	0.861
2800	37.469	158.819	126.920	89.318	-304.086	0.237	-0.018
2900	37.488	160.134	128.042	93.066	-303.736	11.103	-.837
3000	37.505	161.405	129.134	96.815	-303.402	21.951	-1.599
3100	37.521	162.635	130.194	100.567	-303.078	32.789	-2.312
3200	37.536	163.827	131.227	104.320	-302.768	43.621	-2.979
3300	37.549	164.982	132.232	108.074	-302.474	54.441	-3.605
3400	37.561	166.103	133.212	111.829	-302.196	65.250	-4.194
3500	37.572	167.192	134.168	115.586	-301.933	76.059	-4.749
3600	37.582	168.251	135.100	119.344	-301.688	86.853	-5.273
3700	37.591	169.281	136.010	123.102	-301.462	97.638	-5.767
3800	37.599	170.283	136.898	126.862	-301.253	108.426	-6.236
3900	37.607	171.260	137.767	130.622	-301.067	119.201	-6.680
4000	37.615	172.212	138.616	134.383	-300.901	129.978	-7.102
4100	37.621	173.141	139.447	138.145	-300.761	140.751	-7.503
4200	37.628	174.048	140.260	141.907	-300.646	151.515	-7.884
4300	37.634	174.933	141.056	145.670	-300.560	162.282	-8.248
4400	37.639	175.798	141.836	149.434	-300.504	173.041	-8.595
4500	37.644	176.644	142.600	153.198	-300.481	183.811	-8.927
4600	37.649	177.472	143.349	156.963	-300.496	194.566	-9.244
4700	37.654	178.282	144.084	160.728	-300.549	205.329	-9.548
4800	37.658	179.074	144.805	164.494	-300.647	216.092	-9.839
4900	37.662	179.851	145.512	168.260	-300.792	226.864	-10.118
5000	37.666	180.612	146.206	172.026	-300.990	237.633	-10.387
5100	37.669	181.358	146.888	175.793	-301.241	248.410	-10.645
5200	37.672	182.089	147.558	179.560	-301.554	259.188	-10.893
5300	37.676	182.807	148.217	183.327	-301.934	269.974	-11.132
5400	37.679	183.511	148.864	187.095	-302.384	280.770	-11.363
5500	37.681	184.202	149.500	190.863	-302.910	291.570	-11.586
5600	37.684	184.881	150.126	194.631	-303.517	302.384	-11.801
5700	37.687	185.548	150.741	198.400	-304.208	313.213	-12.009
5800	37.689	186.204	151.347	202.169	-304.993	324.049	-12.210
5900	37.691	186.848	151.943	205.938	-305.874	334.907	-12.406
6000	37.693	187.482	152.530	209.707	-306.855	345.775	-12.595

June 30, 1978

SODIUM SULFATE (Na_2SO_4) (IDEAL GAS) GFW = 142.03714

ΔHa_0° = 600.26 ± 6 kcal/mol
$S^\circ_{298.15}$ = [82.874 ± 4] cal/(mol K)
Ground State Quantum Weight = [1]

ΔHf_0° = -243.81 ± 6.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -247.04 ± 6.0 kcal/mol

NA_2O_4S

Vibrational Frequencies, Symmetry and Degeneracies

	ω, cm^{-1}		ω, cm^{-1}		ω, cm^{-1}
A_1	961 (1)	B_1	[460](1)	E	1101 (2)
	[510](1)	B_2	1131 (1)		610 (2)
	[160](1)		640 (1)		[333](2)
			[391](1)		[81](2)

Point Group [D_{2d}]
Bond Distances: S-O = [1.48] Å Na-O = [2.21] Å σ = [4]
Bond Angles: O-S-O = [109.47°] O-Na-O = [66.205°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [7.9153 x 10^{-113}] g^3 cm^6

Heat of Formation

The adopted value of the heat of formation, $\Delta Hf^\circ_{298}(Na_2SO_4,g)$ = -247.04±6.0 kcal/mol, is based on JANAF analyses of the vaporization data given below. Early studies of the vaporization of sodium sulfate failed to take dissociation into account. Thus many of the effusion and transpiration results in the literature are in error. The dissociation is retarded in the presence of SO_2, O_2 mixtures as in the study of Cubicciotti and Kenesha (1) or in the presence of air (O_2) as in the study of Fryxell et al. (4). We have "corrected" some of the original data by subtracting the calculated dissociation pressures (15) from the total pressure to give molecular vaporization pressures. These "corrected data sets" are explicitly noted. Mass spectrometric experiments (2, 3, 5, and 14) can lead to direct molecular vaporization data provided the $Na_2SO_4^+$ ion is directly measured. Results from the Knudsen effusion experiments (5, 14) are in reasonable agreement with the most reliable transpiration experiments (1, 4). The calculated 3rd law ΔHr°(298 K) may have an uncertainty of 4 kcal/mol since the JANAF free energy functions are partially based on the estimated molecular constants of Na_2SO_4(g). Vapor pressures from (1, 4, and 5) are in general agreement. Our adopted heat of formation is based on a weighted average of the second or third law results from (1, 4, 5, 14).

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] cal/(mol K)	ΔHr_{298}/(kcal/mol) 2nd law	ΔHr_{298}/(kcal/mol) 3rd law	$\Delta Hf^\circ_{298}(Na_2SO_4,g)$[c] kcal/mol
(1) Cubicciotti[d]	Transpiration (N_2)	A	1400-1624	8	9.24±2.8	90.36±4.2	76.31±2.0	-247.86±6
(1) Cubicciotti	Transpiration (SO_2+O_2)	A	1305-1663	12	4.69±1.2	84.26±1.8	77.06±1.1	-247.11±4
(4) Fryxell[d]	Transpiration(air)	A	1283-1477	20	0.23±1.1	78.51±1.5	78.20±0.6	-245.97±4
(4) Fryxell	Transpiration(air)	A	1339-1477	16	3.70±1.1	83.18±1.5	78.05±0.6	-246.12±3
(13)Jagannathan	Transpiration (SO_2+O_2)	A	1289-1412	6	5.60±1.4	81.39±1.8	73.81±0.6	-250.36±6
(13)Jagannathan[d]	Transpiration(N_2)	A	1301-1426	4	17.3±2.5	98.78±3.5	75.05±2.0	-249.12±6
(5) Kohl	Knudsen mass spec	A	1180-1370	2	----	75.76±4.0	----	-248.41±4
(5) Kohl	Knudsen mass spec	A	1196-1349	19	-1.89±0.7	76.36±0.9	78.76±0.4	-245.41±2
(14)Bonnell	Knudsen mass spec	A,B	1069-1281	?	----	74.93±2.5	----	-249.24±4
(14)Bonnell	Knudsen mass spec	A	1440-1540	?	----	77.41±4.0	----	-246.76±4

[a] Reactions: A) $Na_2SO_4(\ell) = Na_2SO_4(g)$
B) $Na_2SO_4(c) = Na_2SO_4(g)$

[b] $\delta S = \Delta Sr^\circ_{298}$(2nd) - ΔSr°_{298}(3rd law)

[c] 3rd law ΔHr°_{298} is used to derive $\Delta Hf^\circ_{298}(Na_2SO_4,g)$ if possible.

[d] data corrected for dissociation

Heat Capacity and Entropy

The adopted structure (D_{2d} symmetry) is based on the similar symmetry assigned to Cs_2SO_4(g) and to K_2SO_4(g) in the high temperature electron diffraction studies of Ugarov et al. (6) and Spiridonov and Lutoshkin (7). This symmetry is supported by the IR and Raman study of Atkins and Gingerich (9) on Na_2SO_4 and K_2SO_4. The molecule can be pictured as having a central sulfur atom surrounded at the corners of a tetrahedron by four oxygen atoms with bridging sodium atoms between two pairs of oxygens. The internuclear distance of 1.48 Å for S-O is taken from data on other sulphates (6, 7, 8) while Na-O = 2.21 Å is an estimate from (7). The principal moments of inertia are I_A = 15.518 x 10^{-39} and $I_B = I_C$ = 71.418 x 10^{-39} g cm^2.

Atkins and Gingerich (9) have observed the infrared and Raman spectra of Na_2SO_4 and K_2SO_4 isolated in oxygen and nitrogen matrices at 12 K. Five of the eleven fundamental frequencies were observed in this work. The two other sulphate-ion group fundamentals are estimates taken from Gurvich et al. (10). The four fundamentals involving the metal atoms are based on the Raman single-crystal study of Montero (11) and comparisons involving K_2SO_4, Cs_2SO_4 (10), LiO_2 and NaO_2 (12). Uncertainties in the estimates of the gas phase frequencies may contribute an uncertainty of 4 cal/(mol K) to S°_{298}.

NA_2O_4S

References

See $Na_2SO_4(\ell)$.

DISODIUM MONOSULFIDE (Na_2S) NA_2S
(CRYSTAL) GFW=78.03954

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	19.790	23.000	23.000	0.000	-87.500	-84.749	62.122
300	19.800	23.122	23.000	0.037	-87.497	-84.731	61.725
400	20.150	28.867	23.781	2.034	-89.287	-83.695	45.728
500	20.500	33.402	25.267	4.067	-89.674	-82.250	35.951
600	20.850	37.171	26.946	6.135	-89.905	-80.741	29.409
700	21.200	40.611	28.643	8.238	-90.014	-79.181	24.721
800	21.550	43.266	30.296	10.375	-103.092	-78.898	21.554
900	21.830	45.821	31.882	12.546	-102.739	-75.895	18.429
1000	22.190	48.140	33.393	14.747	-102.359	-72.931	15.939
1100	26.400	50.388	34.835	17.108	-101.833	-70.015	13.911
1200	38.120	53.124	36.240	20.261	-147.004	-66.256	12.067
1300	44.850	56.743	37.674	24.789	-143.915	-59.643	10.027
1400	32.780	59.544	39.143	28.562	-141.583	-53.257	8.314
1500	32.000	61.757	40.578	31.769	-139.818	-47.011	6.849
1600	32.000	63.822	41.967	34.969	-138.060	-40.879	5.584
1700	32.000	65.762	43.310	38.169	-136.301	-34.859	4.481
1800	32.000	67.591	44.608	41.369	-134.545	-28.943	3.514
1900	32.000	69.322	45.864	44.569	-132.789	-23.122	2.660
2000	32.000	70.963	47.078	47.769	-131.036	-17.398	1.901

Dec. 31, 1960; March 31, 1978

DISODIUM MONOSULFIDE (Na_2S) (CRYSTAL) GFW = 78.03954

NA_2S

$S^\circ_{298.15}$ = 23 ± 4 gibbs/mol
Tt = [1276 ± 20 K] (lambda transition)
Tm = 1445 ± 10 K

ΔHf°_0 = Unknown
$\Delta Hf^\circ_{298.15}$ = -87.5 ± 3 kcal/mol
ΔHt° = 0 kcal/mol
ΔHm° = [4.6 ± 1] kcal/mol

Heat of Formation

We adopt the average value, ΔHf°_{298} = -87.5±3 kcal/mol, derived from the experimental results summarized below.

Source	Reaction	ΔHf°_{298}, kcal/mol
Sabatier (1)	ΔHsoln $Na_2S(c)$ and Na(c), ΔHn NaOH(aq) + $H_2S(aq)$	-88.2
Rengade and Costeanu (2)		-89.7
Kraus and Ridderhof (3)	Na(in NH_3) + S(c) = $Na_2S(c)$	-87.0
Letoffe et al. (4)	$H_2SO_4(1100\ H_2O) + Na_2S(c) = Na_2SO_4(soln.) + H_2S(g)$	-85.1[a]

a. The authors' value of -84.35±0.9 kcal/mol is corrected for newer values for ΔHf°_{298} of Na_2SO_4(c,V) and $H_2S(g)$ (5, 11).

The adopted value is reasonably consistent with -86.6±1 kcal/mol calculated from the second law anaysis of Uusitalo's equilibrium data (10) described in the following section.

Heat Capacity and Entropy

The heat capacity is based on the drop calorimetry of May (6) (400-1500 K). The pre-melt S-shaped enthalpy curve is reinterpreted as incorporating a lambda transition in view of the enthalpy measurements on K_2S by Dworkin and Bredig (7) and the occurrence of lambda transitions in other materials having the fluorite or anti-fluorite type of structure (8). The adopted heat capacity shows the maximum of the lambda transition at 50.65 gibbs/mol and 1276 K. The heat capacity then falls to a constant value of 32 gibbs/mol at 1420 K. This interpretation along with the adopted melting point, heat of melting, and liquid heat capacity *(22 gibbs/mol, 9) leads to an enthalpy of the liquid consistent with May's measurement.*

May (6, 648,656 K) and Uusitalo (10, 462-763 K) have measured equilibrium pressures for the reaction Na_2SO_4(c) + 2 C (solid) = Na_2S(c) + 2 CO_2(g) and have derived $S^\circ_{298}(Na_2S,c)$ = 18.6 and 18.5 gibbs/mol. These derivations are open to question because of the uncertainty of the crystalline form of Na_2SO_4 used in the reaction (forward direction) or resulting from the reaction (reverse direction). Five crystalline forms of Na_2SO_4 have been identified (11, 12). S°_{298} for form V, stable at room temperature, has erroneously been used to derive $S^\circ_{298}(Na_2S,c)$ rather than S°_{298} for form I which is the form stable at the equilibrium measurement temperature. Furthermore, Uusitalo (10) used charcoal which probably deviates from graphite, the standard reference state. Our second law treatment of Uusitalo's data (10) with auxiliary data for Na_2SO_4(c,I) and C(graphite) (11), which is still questionable, leads to $S^\circ_{298}(Na_2S,c)$ = 23.2 gibbs/mol. The agreement of this derivation with the estimate below is almost surely fortuitous.

Kubaschewski et al. (13) have estimated the entropy as 23.5±2.5 gibbs/mol. Voronin's (14) estimate is 21.6 gibbs/mol. The summation of Kelley's additive entropy constants (15) gives 23.0 gibbs/mol. We adopt $S^\circ_{298}(Na_2S,c)$ = 23.0±4 gibbs/mol.

Melting Data

Tegman (16) has indicated that many of the early measurements of the melting point of Na_2S were made on impure brown material. Several measurements on white or light pink material are in reasonable agreement: in °C, ∿1200 (17), 1180±10 (18), 1180 (19), 1160±5 (20, 21), 1175±10 (22), and 1168±10 (23). We adopt a melting point of 1445±10 K (1172±10°C). This is consistant with May's (6) enthalpy measurements.

In an examination of May's (6) enthalpy data, Wagman (24) has used an entropy of fusion of 3.21 gibbs/mol--the entropy of fusion of K_2S is 3.16 gibbs/mol (7)--which leads to an enthalpy of fusion of 4.6 kcal/mol at the adopted melting point of 1445 K. *From the Na_2S-S phase diagram work of Rosen and Tegman (23), Wagman (24) calculates an average enthalpy of fusion of* 5.7 kcal/mol and recommends ΔHm° = 5±1 kcal/mol. We adopt ΔHm° = 4.6 kcal/mol to remain consistent with our incorporation of a lambda transition in the evaluation of May's (6) enthalpy measurements.

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NA_2S

DISODIUM MONOSULFIDE (Na_2S)
(LIQUID) GFW=78.03954

NA_2S

		gibbs/mol			kcal/mol		
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	19.790	30.511	30.511	0.000	-77.423	-76.911	56.377
300	19.800	30.633	30.511	0.037	-77.420	-76.907	56.026
400	20.150	36.378	31.292	2.034	-79.210	-76.622	41.864
500	20.500	40.912	32.778	4.067	-79.597	-75.928	33.188
600	20.850	44.681	34.457	6.135	-79.828	-75.170	27.380
700	21.200	47.922	36.154	8.238	-79.937	-74.362	23.217
800	21.550	50.776	37.807	10.375	-93.015	-74.830	20.442
900	21.830	53.332	39.392	12.546	-92.662	-72.577	17.624
1000	22.000	55.647	40.904	14.743	-92.286	-70.365	15.378
1100	22.000	57.744	42.341	16.943	-91.921	-68.195	13.549
1200	22.000	59.658	43.706	19.143	-138.045	-65.138	11.863
1300	22.000	61.419	45.001	21.343	-137.284	-59.092	9.934
1400	22.000	63.049	46.233	23.543	-136.525	-53.106	8.290
1500	22.000	64.567	47.405	25.743	-135.767	-47.176	6.873
1600	22.000	65.987	48.523	27.943	-135.009	-41.292	5.640
1700	22.000	67.321	49.590	30.143	-134.250	-35.457	4.558
1800	22.000	68.578	50.610	32.343	-133.494	-29.669	3.602
1900	22.000	69.768	51.587	34.543	-132.738	-23.919	2.751
2000	22.000	70.896	52.525	36.743	-131.985	-18.213	1.990
2100	22.000	71.969	53.425	38.943	-131.231	-12.546	1.304
2200	22.000	72.993	54.292	41.143	-130.479	-6.909	0.686
2300	22.000	73.971	55.126	43.343	-129.728	-1.312	0.125
2400	22.000	74.907	55.931	45.543	-128.979	4.259	-0.388
2500	22.000	75.805	56.708	47.743	-128.230	9.792	-0.856
2600	22.000	76.668	57.459	49.943	-127.486	15.301	-1.286
2700	22.000	77.498	58.186	52.143	-126.744	20.775	-1.682
2800	22.000	78.298	58.890	54.343	-126.007	26.222	-2.047
2900	22.000	79.070	59.573	56.543	-125.272	31.651	-2.385
3000	22.000	79.816	60.235	58.743	-124.544	37.050	-2.699

Dec. 31, 1960; March 31, 1978

DISODIUM MONOSULFIDE (Na_2S) (LIQUID) GFW = 78.03954

$S^\circ_{298.15}$ = [30.511] gibbs/mol
Tm = 1445 ± 10 K

$\Delta Hf^\circ_{298.15}$ = [-77.423] kcal/mol
ΔHm° = [4.6 ± 1] kcal/mol

NA_2S.

Heat of Formation

$\Delta Hf^\circ_{298}(Na_2S,\ell)$ is obtained from $\Delta Hf^\circ_{298}(Na_2S,c)$ by adding ΔHm° and the difference between $(H^\circ_{1445}-H^\circ_{298})$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity of 22 gibbs/mol is from the estimate of Barin et al. (1) and is assumed to be constant above the assumed glass transition at 970 K. Below the glass transition, the heat capacity is that of the crystal.

The entropy is obtained in a manner similar to that for the heat of formation.

References

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NA_2S

NEON, MONATOMIC (NE)

(REFERENCE STATE - IDEAL GAS) GFW=20.179

NE

	gibbs/mol			kcal/mol			
T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	0.000	0.000	0.000
100	4.968	29.520	39.364	-0.984	0.000	0.000	0.000
200	4.968	32.963	35.401	-0.488	0.000	0.000	0.000
298	4.968	34.947	34.947	0.000	0.000	0.000	0.000
300	4.968	34.978	34.947	0.009	0.000	0.000	0.000
400	4.968	36.407	35.142	0.506	0.000	0.000	0.000
500	4.968	37.515	35.510	1.003	0.000	0.000	0.000
600	4.968	38.421	35.922	1.500	0.000	0.000	0.000
700	4.968	39.187	36.335	1.996	0.000	0.000	0.000
800	4.968	39.850	36.734	2.493	0.000	0.000	0.000
900	4.968	40.436	37.113	2.990	0.000	0.000	0.000
1000	4.968	40.959	37.472	3.487	0.000	0.000	0.000
1100	4.968	41.433	37.811	3.984	0.000	0.000	0.000
1200	4.968	41.865	38.131	4.480	0.000	0.000	0.000
1300	4.968	42.262	38.434	4.977	0.000	0.000	0.000
1400	4.968	42.631	38.721	5.474	0.000	0.000	0.000
1500	4.968	42.973	38.993	5.971	0.000	0.000	0.000
1600	4.968	43.294	39.252	6.468	0.000	0.000	0.000
1700	4.968	43.595	39.498	6.964	0.000	0.000	0.000
1800	4.968	43.879	39.734	7.461	0.000	0.000	0.000
1900	4.968	44.148	39.959	7.958	0.000	0.000	0.000
2000	4.968	44.403	40.175	8.455	0.000	0.000	0.000
2100	4.968	44.645	40.382	8.952	0.000	0.000	0.000
2200	4.968	44.876	40.581	9.448	0.000	0.000	0.000
2300	4.968	45.097	40.773	9.945	0.000	0.000	0.000
2400	4.968	45.308	40.957	10.442	0.000	0.000	0.000
2500	4.968	45.511	41.136	10.939	0.000	0.000	0.000
2600	4.968	45.706	41.308	11.436	0.000	0.000	0.000
2700	4.968	45.893	41.474	11.932	0.000	0.000	0.000
2800	4.968	46.074	41.635	12.429	0.000	0.000	0.000
2900	4.968	46.248	41.791	12.926	0.000	0.000	0.000
3000	4.968	46.417	41.943	13.423	0.000	0.000	0.000
3100	4.968	46.580	42.090	13.920	0.000	0.000	0.000
3200	4.968	46.738	42.232	14.416	0.000	0.000	0.000
3300	4.968	46.890	42.371	14.913	0.000	0.000	0.000
3400	4.968	47.039	42.506	15.410	0.000	0.000	0.000
3500	4.968	47.183	42.638	15.907	0.000	0.000	0.000
3600	4.968	47.323	42.766	16.404	0.000	0.000	0.000
3700	4.968	47.459	42.891	16.900	0.000	0.000	0.000
3800	4.968	47.591	43.013	17.397	0.000	0.000	0.000
3900	4.968	47.720	43.132	17.894	0.000	0.000	0.000
4000	4.968	47.846	43.248	18.391	0.000	0.000	0.000
4100	4.968	47.969	43.362	18.888	0.000	0.000	0.000
4200	4.968	48.088	43.473	19.384	0.000	0.000	0.000
4300	4.968	48.205	43.582	19.881	0.000	0.000	0.000
4400	4.968	48.320	43.688	20.378	0.000	0.000	0.000
4500	4.968	48.431	43.792	20.875	0.000	0.000	0.000
4600	4.968	48.540	43.894	21.372	0.000	0.000	0.000
4700	4.968	48.647	43.994	21.868	0.000	0.000	0.000
4800	4.968	48.752	44.092	22.365	0.000	0.000	0.000
4900	4.968	48.854	44.189	22.862	0.000	0.000	0.000
5000	4.968	48.955	44.283	23.359	0.000	0.000	0.000
5100	4.968	45.053	44.375	23.855	0.000	0.000	0.000
5200	4.968	49.150	44.466	24.352	0.000	0.000	0.000
5300	4.968	49.244	44.556	24.849	0.000	0.000	0.000
5400	4.968	49.337	44.643	25.346	0.000	0.000	0.000
5500	4.968	49.428	44.729	25.843	0.000	0.000	0.000
5600	4.968	49.518	44.814	26.339	0.000	0.000	0.000
5700	4.968	49.606	44.897	26.836	0.000	0.000	0.000
5800	4.968	49.692	44.979	27.333	0.000	0.000	0.000
5900	4.968	49.777	45.060	27.830	0.000	0.000	0.000
6000	4.968	49.860	45.139	28.327	0.000	0.000	0.000

March 31, 1977

NEON, MONATOMIC (Ne) (REFERENCE STATE - IDEAL GAS) GFW = 20.179

NE

0 to 6000 K Ideal Gas

Ground State Configuration $^1S_0$
$S^\circ_{298.15}$ = 34.947 ± 0.004 gibbs/mol
T_{tr} = 24.553 K
T_b = 27.096 K

ΔHf°_0 = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Electronic Levels and Quantum Weights

state	ε_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore (1). All predicted levels have been observed for n=2 and 3 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (2) has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 134,000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of proper fill and cutoff procedures (2).

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations (3). The table agrees within the estimated uncertainty with those by Hultgren et al. (4) and McBride et al. (5). The estimated uncertainty is due to uncertainties in the gram formula weight and fundamental constants which are based on the 1971 scale (6) and the 1973 values (7), respectively.

Phase Data

The triple point (T_{tr}) and boiling point (T_b) are taken from Hultgren et al. (4). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values of T_{tr} and T_b the reference state for neon is chosen to be the ideal gas at all temperatures down to 0 K. This may differ from the choice of other authors. The tables of Hultgren et al. (4), among others, use appropriate condensed states of neon as reference states and will differ from the present work at low temperatures.

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NE

NEON UNIPOSITIVE ION (Ne^+) $\quad$ NE^+

(IDEAL GAS) GFW=20.17845

	gibbs/mol			kcal/mol			
T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0				-1.481	497.290		
100							
200							
298	5.287	37.810	37.810	0.000	498.797	496.456	-363.907
300	5.290	37.843	37.810	0.010	498.807	496.441	-361.652
400	5.413	39.384	38.020	0.546	499.343	495.572	-270.764
500	5.446	40.597	38.418	1.089	499.886	494.567	-216.172
600	5.430	41.589	38.866	1.633	500.430	493.452	-179.737
700	5.392	42.423	39.317	2.175	500.971	492.246	-153.684
800	5.349	43.141	39.751	2.712	501.509	490.963	-134.123
900	5.308	43.768	40.163	3.245	502.041	489.613	-118.893
1000	5.269	44.325	40.552	3.773	502.570	488.203	-106.695
1100	5.236	44.826	40.918	4.299	503.095	486.741	-96.705
1200	5.207	45.280	41.263	4.821	503.618	485.231	-88.371
1300	5.181	45.656	41.588	5.340	504.137	483.678	-81.313
1400	5.159	46.079	41.896	5.857	504.654	482.085	-75.256
1500	5.140	46.435	42.186	6.372	505.169	480.455	-70.001
1600	5.124	46.766	42.462	6.885	505.681	478.789	-65.399
1700	5.109	47.076	42.725	7.397	506.194	477.094	-61.334
1800	5.097	47.368	42.975	7.907	506.704	475.368	-57.717
1900	5.086	47.643	43.213	8.416	507.213	473.613	-54.477
2000	5.076	47.903	43.441	8.924	507.721	471.831	-51.559
2100	5.068	48.151	43.660	9.432	508.227	470.023	-48.915
2200	5.060	48.387	43.869	9.938	508.735	468.193	-46.510
2300	5.053	48.611	44.071	10.444	509.240	466.339	-44.312
2400	5.047	48.826	44.264	10.949	509.745	464.463	-42.295
2500	5.041	49.032	44.451	11.453	510.250	462.566	-40.437
2600	5.037	49.230	44.631	11.957	510.753	460.647	-38.720
2700	5.032	49.420	44.805	12.460	511.257	458.712	-37.130
2800	5.028	49.603	44.973	12.963	511.760	456.757	-35.651
2900	5.024	49.779	45.136	13.466	512.263	454.783	-34.273
3000	5.021	49.949	45.293	13.968	512.765	452.792	-32.985
3100	5.018	50.114	45.446	14.470	513.266	450.784	-31.780
3200	5.015	50.273	45.594	14.972	513.769	448.762	-30.649
3300	5.013	50.427	45.739	15.473	514.270	446.722	-29.585
3400	5.010	50.577	45.879	15.974	514.771	444.668	-28.583
3500	5.008	50.722	46.015	16.475	515.272	442.599	-27.637
3600	5.006	50.863	46.148	16.976	515.772	440.515	-26.743
3700	5.004	51.000	46.277	17.476	516.273	438.418	-25.896
3800	5.002	51.134	46.403	17.977	516.774	436.307	-25.093
3900	5.001	51.264	46.526	18.477	517.274	434.183	-24.331
4000	4.999	51.390	46.646	18.977	517.773	432.045	-23.606
4100	4.998	51.514	46.763	19.477	518.272	429.896	-22.915
4200	4.996	51.634	46.878	19.976	518.773	427.735	-22.257
4300	4.995	51.752	46.990	20.476	519.273	425.562	-21.629
4400	4.994	51.867	47.099	20.975	519.772	423.377	-21.029
4500	4.993	51.979	47.207	21.475	520.271	421.179	-20.455
4600	4.992	52.089	47.312	21.974	520.770	418.972	-19.905
4700	4.991	52.196	47.414	22.473	521.270	416.754	-19.379
4800	4.990	52.301	47.515	22.972	521.769	414.525	-18.874
4900	4.989	52.404	47.614	23.471	522.268	412.287	-18.389
5000	4.988	52.505	47.711	23.970	522.766	410.035	-17.922
5100	4.988	52.603	47.806	24.469	523.266	407.777	-17.474
5200	4.987	52.700	47.899	24.968	523.764	405.508	-17.043
5300	4.986	52.795	47.990	25.466	524.263	403.229	-16.627
5400	4.986	52.888	48.080	25.965	524.762	400.940	-16.227
5500	4.985	52.980	48.168	26.463	525.259	398.642	-15.840
5600	4.984	53.070	48.255	26.962	525.759	396.336	-15.468
5700	4.984	53.158	48.340	27.460	526.257	394.021	-15.107
5800	4.983	53.245	48.424	27.959	526.755	391.696	-14.759
5900	4.983	53.330	48.507	28.457	527.254	389.363	-14.423
6000	4.982	53.414	48.588	28.955	527.751	387.021	-14.097

March 31, 1977

NEON UNIPOSITIVE ION (Ne^+) (IDEAL GAS) GFW = 20.17845

Ground State Configuration $^2P_{3/2}$

$S^\circ_{298.15}$ = 37.810 ± 0.005 gibbs/mol

ΔHf°_0 = 497.290 ± 0.006 kcal/mol NE^+

$\Delta Hf^\circ_{298.15}$ = 498.797 ± 0.006 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	780.45	2

Heat of Formation

The ionization limit of neutral neon (173929.70 cm^{-1}) reported by Moore (1) is adopted as ΔHf°_0 for $Ne^+(g)$. The ionization limit is converted from cm^{-1} to kcal/mol using the factor, 1 cm^{-1} = 2.859144 x 10^{-3} kcal/mol, which is derived from the latest CODATA fundamental constants (2). The uncertainty in the ionization limit is estimated to be ±2 cm^{-1} which corresponds to an uncertainty of ±0.006 kcal/mol in the heat of formation. The value of ΔHf°_{298} is derived from ΔHf°_0 using auxiliary JANAF data (3).

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights by Moore (4) is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (5) has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 217,000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore (1). The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight, fundamental constants, and energy of the $^2P_{1/2}$ state. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (5).

The thermodynamic functions reported here agree with those by Green et al. (6) and Hilsenrath et al. (7) within the limits of the uncertainty.

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NE^+

NICKEL (Ni) (REFERENCE STATE) GFW = 58.71

N I

0 to 1728 K Crystal
1728 to 3159.45 K Liquid
3159.45 to 6000 K Ideal Monatomic Gas
631 K Curie Point

See crystal, liquid, and monatomic gas tables for details

N I

N I C K E L (N I) N I

(R E F E R E N C E S T A T E) G F W = 5 8 . 7 1

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	−1.144	0.000	0.000	0.000
100	3.258	1.778	12.008	−1.023	0.000	0.000	0.000
200	5.370	4.824	7.679	−0.571	0.000	0.000	0.000
298	6.211	7.140	7.140	0.000	0.000	0.000	0.000
300	6.220	7.178	7.140	0.011	0.000	0.000	0.000
400	6.810	9.050	7.391	0.664	0.000	0.000	0.000
500	7.420	10.630	7.885	1.373	0.000	0.000	0.000
600	8.330	12.056	8.463	2.156	0.000	0.000	0.000
700	7.360	13.284	9.069	2.950	0.000	0.000	0.000
800	7.410	14.269	9.659	3.688	0.000	0.000	0.000
900	7.550	15.149	10.221	4.436	0.000	0.000	0.000
1000	7.700	15.952	10.754	5.198	0.000	0.000	0.000
1100	7.870	16.694	11.261	5.977	0.000	0.000	0.000
1200	8.050	17.387	11.743	6.773	0.000	0.000	0.000
1300	8.250	18.039	12.202	7.587	0.000	0.000	0.000
1400	8.460	18.658	12.641	8.423	0.000	0.000	0.000
1500	8.680	19.249	13.062	9.280	0.000	0.000	0.000
1600	8.910	19.816	13.467	10.159	0.000	0.000	0.000
1700	9.150	20.364	13.857	11.063	0.000	0.000	0.000
1800	9.300	23.266	14.328	16.089	0.000	0.000	0.000
1900	9.300	23.769	14.812	17.019	0.000	0.000	0.000
2000	9.300	24.246	15.271	17.949	0.000	0.000	0.000
2100	9.300	24.700	15.710	18.879	0.000	0.000	0.000
2200	9.300	25.133	16.128	19.809	0.000	0.000	0.000
2300	9.300	25.546	16.529	20.739	0.000	0.000	0.000
2400	9.300	25.942	16.913	21.669	0.000	0.000	0.000
2500	9.300	26.321	17.282	22.599	0.000	0.000	0.000
2600	9.300	26.686	17.636	23.529	0.000	0.000	0.000
2700	9.300	27.037	17.978	24.459	0.000	0.000	0.000
2800	9.300	27.375	18.308	25.389	0.000	0.000	0.000
2900	9.300	27.702	18.626	26.319	0.000	0.000	0.000
3000	9.300	28.017	18.934	27.249	0.000	0.000	0.000
3100	9.300	28.322	19.232	28.179	0.000	0.000	0.000
3200	5.352	57.124	19.882	119.175	0.000	0.000	0.000
3300	5.348	57.289	21.013	119.710	0.000	0.000	0.000
3400	5.347	57.449	22.082	120.245	0.000	0.000	0.000
3500	5.348	57.604	23.095	120.780	0.000	0.000	0.000
3600	5.351	57.754	24.056	121.315	0.000	0.000	0.000
3700	5.357	57.901	24.969	121.850	0.000	0.000	0.000
3800	5.364	58.044	25.837	122.386	0.000	0.000	0.000
3900	5.374	58.183	26.665	122.923	0.000	0.000	0.000
4000	5.387	58.320	27.454	123.461	0.000	0.000	0.000
4100	5.402	58.453	28.209	124.000	0.000	0.000	0.000
4200	5.419	58.583	28.930	124.541	0.000	0.000	0.000
4300	5.439	58.711	29.622	125.084	0.000	0.000	0.000
4400	5.462	58.836	30.284	125.629	0.000	0.000	0.000
4500	5.488	58.959	30.920	126.177	0.000	0.000	0.000
4600	5.517	59.080	31.541	126.727	0.000	0.000	0.000
4700	5.550	59.199	32.118	127.281	0.000	0.000	0.000
4800	5.585	59.316	32.684	127.837	0.000	0.000	0.000
4900	5.624	59.432	33.228	128.398	0.000	0.000	0.000
5000	5.666	59.546	33.754	128.962	0.000	0.000	0.000
5100	5.711	59.659	34.260	129.531	0.000	0.000	0.000
5200	5.760	59.770	34.750	130.104	0.000	0.000	0.000
5300	5.813	59.880	35.223	130.683	0.000	0.000	0.000
5400	5.869	59.989	35.681	131.267	0.000	0.000	0.000
5500	5.929	60.098	36.124	131.857	0.000	0.000	0.000
5600	5.993	60.205	36.553	132.453	0.000	0.000	0.000
5700	6.061	60.312	36.969	133.056	0.000	0.000	0.000
5800	6.132	60.418	37.372	133.665	0.000	0.000	0.000
5900	6.207	60.523	37.763	134.282	0.000	0.000	0.000
6000	6.286	60.628	38.144	134.907	0.000	0.000	0.000

Dec. 31, 1976

NICKEL (NI) N I

(CRYSTAL) GFW=58.71

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.144	0.000	0.000	0.000
100	3.258	1.778	12.008	-1.023	0.000	0.000	0.000
200	5.370	4.824	7.679	-0.571	0.000	0.000	0.000
298	6.211	7.140	7.140	0.000	0.000	0.000	0.000
300	6.220	7.178	7.140	0.011	0.000	0.000	0.000
400	6.810	9.050	7.391	0.664	0.000	0.000	0.000
500	7.420	10.430	7.885	1.373	0.000	0.000	0.000
600	8.330	12.056	8.463	2.156	0.000	0.000	0.000
700	7.360	13.284	9.069	2.950	0.000	0.000	0.000
800	7.410	14.269	9.659	3.688	0.000	0.000	0.000
900	7.550	15.149	10.221	4.434	0.000	0.000	0.000
1000	7.700	15.952	10.754	5.198	0.000	0.000	0.000
1100	7.870	16.694	11.261	5.977	0.000	0.000	0.000
1200	8.050	17.387	11.743	6.773	0.000	0.000	0.000
1300	8.250	18.039	12.202	7.587	0.000	0.000	0.000
1400	8.460	18.658	12.641	8.423	0.000	0.000	0.000
1500	8.680	19.249	13.062	9.280	0.000	0.000	0.000
1600	8.910	19.816	13.467	10.159	0.000	0.000	0.000
1700	9.150	20.364	13.857	11.062	0.000	0.000	0.000
1800	9.400	20.891	14.233	11.985	-4.104	0.171	-0.021
1900	10.200	21.423	14.597	12.969	-4.050	0.408	-0.047
2000	10.470	21.953	14.952	14.003	-3.946	0.640	-0.070
2100	10.750	22.471	15.298	15.064	-3.815	0.866	-0.090
2200	11.040	22.978	15.635	16.153	-3.656	1.085	-0.108
2300	11.340	23.475	15.965	17.272	-3.467	1.297	-0.123
2400	11.640	23.964	16.288	18.421	-3.268	1.499	-0.137
2500	11.940	24.445	16.605	18.600	-2.999	1.692	-0.148

Dec. 31, 1976

NICKEL (Ni) (CRYSTAL) GFW = 58.71

N I

$S°_{298.15}$ = 7.14 ± 0.02 gibbs/mol
Tt = 631 ± 1 K
Tm = 1728 ± 4 K

$\Delta Hf°_0$ = 0 kcal/mol
$\Delta Hf°_{298.15}$ = 0 kcal/mol
ΔHt° = 0 kcal/mol
ΔHm° = 4.10 ± 0.1 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity values are based primarily on the studies by Keesom and Clark (1) and Busey and Giauque (2). The adopted values are actually those suggested by Busey and Giauque (2) with slight changes above 280 K so as to smoothly join the high temperature heat capacity data.

There are numerous heat capacity studies in the vicinity of the Curie point. The studies upon which our adopted values are based are as follows:

Source	Year	Range, K
Sykes and Wilkinson (3)	1938	343-1123
Krauss and Warncke (4)	1955	453-1437
Pawel and Stansbury (5)	1965	323- 883
Vollmer et al. (6)	1966	300-1728
Kraftmakher (7)	1966	571- 681
Kollie (8)	1970	333-1500
Connelly et al. (9)	1971	580- 680

The adoped value for the Curie point, T_t = 631 K, is from the study of Connelly et al. (9), using an ac calorimetric method to measure relative heat capacity values, and Vollmer et al. (6) using a high temperature adiabatic calorimeter.

Above 700 K, the adopted heat capacity values are those reported by Vollmer et al. (6). Below the Curie point, the above studies and that of Bronson and Wilson (203-383 K, 10) are used to construct a curve which joins smoothly with the low temperature values. The adopted table is identical (purposely) to that suggested by Mah and Pankatz (11).

Melting Data

See Ni(ℓ) table.

Sublimation Data

The heat of sublimation, $\Delta Hs°_{298}$, is calculated as the difference between $\Delta Hf°_{298}$ for Ni(g) and Ni(c).

References

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N I

NICKEL (NI)

(LIQUID) GFW=58.71

NI

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.246	9.916	9.916	0.000	4.178	3.350	-2.455
300	6.250	9.955	9.917	0.012	4.178	3.345	-2.437
400	6.450	11.781	10.164	0.647	4.160	3.068	-1.676
500	6.650	13.241	10.638	1.302	4.106	2.801	-1.224
600	6.850	14.471	11.177	1.977	3.998	2.549	-0.928
700	7.050	15.542	11.726	2.672	3.899	2.318	-0.724
800	7.250	16.497	12.264	3.387	3.876	2.094	-0.572
900	7.450	17.362	12.783	4.122	3.863	1.872	-0.454
1000	7.650	18.158	13.281	4.877	3.856	1.651	-0.361
1100	7.850	18.896	13.758	5.652	3.852	1.430	-0.284
1200	8.050	19.588	14.215	6.447	3.851	1.210	-0.220
1300	9.300	20.240	14.654	7.262	3.852	0.991	-0.167
1400	9.300	20.929	15.078	8.192	3.946	0.766	-0.120
1500	9.300	21.571	15.490	9.122	4.019	0.536	-0.078
1600	9.300	22.171	15.889	10.052	4.070	0.303	-0.041
1700	9.300	22.735	16.275	10.982	4.096	0.066	-0.008
1800	9.300	23.266	16.649	11.912	0.000	0.000	0.000
1900	9.300	23.769	17.010	12.842	0.000	0.000	0.000
2000	9.300	24.246	17.360	13.772	0.000	0.000	0.000
2100	9.300	24.700	17.699	14.702	0.000	0.000	0.000
2200	9.300	25.133	18.027	15.632	0.000	0.000	0.000
2300	9.300	25.546	18.345	16.562	0.000	0.000	0.000
2400	9.300	25.942	18.654	17.492	0.000	0.000	0.000
2500	9.300	26.321	18.953	18.422	0.000	0.000	0.000
2600	9.300	26.686	19.243	19.352	0.000	0.000	0.000
2700	9.300	27.037	19.525	20.282	0.000	0.000	0.000
2800	9.300	27.375	19.800	21.212	0.000	0.000	0.000
2900	9.300	27.702	20.067	22.142	0.000	0.000	0.000
3000	9.300	28.017	20.326	23.072	0.000	0.000	0.000
3100	9.300	28.322	20.579	24.002	0.000	0.000	0.000
3200	9.300	28.617	20.826	24.932	-90.066	1.157	-0.079
3300	9.300	28.903	21.067	25.862	-89.671	4.001	-0.265
3400	9.300	29.181	21.301	26.792	-89.276	6.834	-0.439
3500	9.300	29.451	21.530	27.722	-88.881	9.655	-0.603
3600	9.300	29.713	21.754	28.652	-88.486	12.464	-0.757
3700	9.300	29.967	21.972	29.582	-88.091	15.264	-0.902
3800	9.300	30.215	22.186	30.512	-87.697	18.052	-1.038
3900	9.300	30.457	22.395	31.442	-87.304	20.829	-1.167
4000	9.300	30.692	22.600	32.372	-86.912	23.597	-1.289

Dec. 31, 1976

NICKEL (Ni) (LIQUID) GFW = 58.71

$S^\circ_{298.15}$ = 9.916 kcal/mol
Tm = 1728 ± 4 K
Tb = 3159.45 K

$\Delta Hf^\circ_{298.15}$ = 4.178 kcal/mol
ΔHm° = 4.10 ± 0.1 kcal/mol
ΔHv° = 90.226 kcal/mol

NI

Heat of Formation

The heat of formation of Ni(ℓ) is calculated from that of the crystal by adding ΔHm° and the difference between (H°_{1728} − H°_{298}) for Ni(c) and Ni(ℓ).

Heat Capacity and Entropy

Vollmer et al. (1), using an adiabatic high temperature calorimeter with an inert gas atmosphere, measured the heat capacity of nickel in the liquid region (1728-1822 K) and reported Cp°(ℓ) = 9.32 gibbs/mol. Other studies yielding liquid phase heat capacity values are: 7.86 gibbs/mol by Wüst et al. (2), 9.2 gibbs/mol by Umino (3), 10.3 gibbs/mol by Geoffray et al. (4), and 2.58 gibbs/mol by Margrave (5). This latter value (5) is undoubtedly a misprint.

We adopt a constant value, Cp°(ℓ) = 9.3 gibbs/mol based on the heat capacity measurements of Vollmer et al. (1). The enthalpy study of Geoffray et al. (1393-2192 K, 4) leads to a reported heat capacity which is roughly 10% higher than our adopted value. The adopted value is identical to that chosen by Mah and Pankratz (6).

The entropy at 298.15 K is calculated in a manner analogous to that used for the heat of formation.

Melting Data

The adopted melting point, Tm = 1728±4 K (based on IPTS-68), is selected from the studies of Vollmer et al. (1727 K, 1), Geoffrey et al. (1728 K, 4), Oriani and Jones (1727 K, 7), and Kubachewski (1730 K, 8).

The adopted heat of melting, ΔHm° = 4.10±0.1 kcal/mol, is based on the calorimetric studies by Vollmer et al. (4.039± 0.060 kcal/mol, 1) and Geoffray et al. (4.176±0.054 kcal/mol). Other reported results are 3.31 kcal/mol by Wüst et al. (2), 4.21 kcal/mol by Umino (3), 3.32 kcal/mol by Margrave (5), and 4.4 kcal/mol by Lebedev et al. (9).

Vaporization Data

Tb is the temperature at which the Gibbs free energy change (ΔGr°) for the reaction Ni(ℓ) = Ni(g) is zero. The heat of vaporization, ΔHv°, is the difference between ΔHf°(Ni,g) and ΔHf°(Ni,ℓ) at Tb.

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NICKEL (Ni) N I
(IDEAL GAS) GFW=58.71

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.631	102.313	102.313	INFINITE
100	5.619	37.379	48.493	-1.111	102.712	99.151	-216.692
200	5.592	41.295	44.029	-0.547	102.824	95.530	-104.389
298	5.583	43.519	43.519	0.000	102.800	91.954	-67.403
300	5.585	43.554	43.519	0.010	102.799	91.887	-66.939
400	5.702	45.175	43.740	0.574	102.710	88.260	-48.222
500	5.826	46.462	44.160	1.151	102.578	84.662	-37.005
600	5.912	47.532	44.635	1.738	102.382	81.097	-29.539
700	5.957	48.447	45.114	2.332	102.182	77.567	-24.217
800	5.971	49.244	45.583	2.928	102.040	74.060	-20.232
900	5.961	49.947	46.030	3.525	101.889	70.572	-17.137
1000	5.937	50.574	46.453	4.120	101.722	67.101	-14.665
1100	5.904	51.138	46.854	4.712	101.535	63.647	-12.645
1200	5.865	51.650	47.233	5.301	101.328	60.212	-10.966
1300	5.823	52.118	47.591	5.885	101.098	56.796	-9.548
1400	5.781	52.548	47.930	6.465	100.842	53.396	-8.335
1500	5.739	52.945	48.251	7.041	100.561	50.017	-7.287
1600	5.698	53.314	48.556	7.613	100.256	46.658	-6.373
1700	5.659	53.659	48.846	8.181	99.918	43.317	-5.569
1800	5.622	53.981	49.123	8.745	95.456	40.170	-4.877
1900	5.588	54.284	49.386	9.306	95.087	37.108	-4.268
2000	5.556	54.570	49.638	9.863	94.714	34.066	-3.723
2100	5.526	54.840	49.880	10.417	94.338	31.043	-3.231
2200	5.499	55.097	50.111	10.968	93.959	28.038	-2.785
2300	5.474	55.340	50.333	11.517	93.578	25.050	-2.380
2400	5.452	55.573	50.547	12.063	93.194	22.079	-2.011
2500	5.432	55.795	50.752	12.607	92.808	19.124	-1.672
2600	5.414	56.008	50.950	13.149	92.420	16.184	-1.360
2700	5.398	56.212	51.141	13.690	92.031	13.259	-1.073
2800	5.385	56.408	51.326	14.229	91.640	10.349	-0.808
2900	5.373	56.597	51.505	14.767	91.248	7.453	-0.562
3000	5.364	56.779	51.677	15.304	90.855	4.570	-0.333
3100	5.357	56.954	51.845	15.840	90.461	1.700	-0.120
3200	5.352	57.124	52.007	16.375	0.000	0.000	0.000
3300	5.348	57.289	52.165	16.910	0.000	0.000	0.000
3400	5.347	57.449	52.318	17.445	0.000	0.000	0.000
3500	5.348	57.604	52.467	17.980	0.000	0.000	0.000
3600	5.351	57.754	52.611	18.515	0.000	0.000	0.000
3700	5.357	57.901	52.752	19.050	0.000	0.000	0.000
3800	5.364	58.044	52.890	19.586	0.000	0.000	0.000
3900	5.374	58.183	53.024	20.123	0.000	0.000	0.000
4000	5.387	58.320	53.154	20.661	0.000	0.000	0.000
4100	5.402	58.453	53.282	21.200	0.000	0.000	0.000
4200	5.419	58.583	53.407	21.741	0.000	0.000	0.000
4300	5.439	58.711	53.528	22.284	0.000	0.000	0.000
4400	5.462	58.836	53.648	22.829	0.000	0.000	0.000
4500	5.488	58.959	53.764	23.377	0.000	0.000	0.000
4600	5.517	59.080	53.879	23.927	0.000	0.000	0.000
4700	5.550	59.199	53.991	24.481	0.000	0.000	0.000
4800	5.585	59.316	54.100	25.037	0.000	0.000	0.000
4900	5.624	59.432	54.208	25.598	0.000	0.000	0.000
5000	5.666	59.546	54.314	26.162	0.000	0.000	0.000
5100	5.711	59.659	54.417	26.731	0.000	0.000	0.000
5200	5.760	59.770	54.519	27.304	0.000	0.000	0.000
5300	5.813	59.880	54.619	27.883	0.000	0.000	0.000
5400	5.869	59.989	54.718	28.467	0.000	0.000	0.000
5500	5.929	60.098	54.815	29.057	0.000	0.000	0.000
5600	5.993	60.205	54.910	29.653	0.000	0.000	0.000
5700	6.061	60.312	55.004	30.256	0.000	0.000	0.000
5800	6.132	60.418	55.096	30.865	0.000	0.000	0.000
5900	6.207	60.523	55.187	31.482	0.000	0.000	0.000
6000	6.286	60.628	55.277	32.107	0.000	0.000	0.000

Dec. 31, 1976

NICKEL, MONATOMIC (Ni) (IDEAL GAS) GFW = 58.71

Ground State Configuration $^3F_4$

$S°_{298.15}$ = 43.52 ± 0.02 gibbs/mol

$\Delta Hf°_0$ = 102.3 ± 2.0 kcal/mol

$\Delta Hf°_{298.15}$ = 102.8 ± 2.0 kcal/mol N I

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	9	22102.35	9	29013.23	5
204.79	7	25753.58	9	29084.48	9
879.81	5	26665.90	7	29832.81	7
1332.15	7	27260.89	13	29481.02	9
1713.08	3	27414.89	5	29320.78	7
2216.52	5	27580.41	11	29500.69	3
3409.92	5	27943.54	3	29668.92	7
13521.35	5	28068.09	9	29888.50	5
14728.85	1	28213.00	1	32518.38	252
15609.86	5	28542.11	11	43356.12	340
15734.02	3	28569.21	5	49036.61	435
16017.32	1	28578.05	7	53013.59	424
				57895.61	707

Heat of Formation

The heat of formation for Ni(g) is obtained by an anlysis of the vapor pressure data of Morris et al. (1). In this study a gas-transport method was used to measure vapor pressures (16 points) over liquid nickel in the range 1816-1895 K. For this vaporization process, we obtain $\Delta Hv°_{298}$ = 99.33±1.23 kcal/mol (2nd law) and 98.54±0.12 kcal/mol (3rd law). The entropy difference (2nd law-3rd law) is only -0.04±0.7 gibbs/mol which suggests good consistency between our adopted functions and the vapor pressure data. Using the 3rd law ΔHv° value and $\Delta Hf°_{298}$(Ni,ℓ) = 4.78 kcal/mol (2), we calculate and adopt $\Delta Hf°_{298}$(Ni,g) = 102.8 kcal/mol. [This is the same value chosen by Hultgren et al. (4) and *Mah and Pankratz* (5). *Thus we maintain closer* similarity with the most recent tabulations.]

Using mass spectrometric intensity data, Farber and Srivastava (3) obtained a 2nd law heat of sublimation of 99.4 kcal/mol at an average temperature of 1653K and a 2nd law heat of vaporization of 92.2 kcal/mol at an average temperature of 1863 K. Using auxiliary data (2), we calculate $\Delta Hf°_{298}$(Ni,g) = 102.1 kcal/mol and 99.8 kcal/mol respectively. Rutner and Haury (6) measured vapor pressures over Ni (28 points in the range 1277-1658 K), using the Langmuir technique. Their results yield a second law $\Delta Hf°_{298}$ value of 107.0±5.8 kcal/mol and a third law $\Delta Hf°_{298}$ value of 103.2±4.0 kcal/mol. The drift is -2.5±3.9 gibbs/mol. In addition Rutner and Haury (6) determined the best values of the heat of sublimation and vaporization and the parameters in a vapor pressure equation by statistically weighting nine sets of data. Although the results of this statistical treatment lead to heats of formation for Ni(g) consistent with the adopted value, the results are not consistent with the melting data. Other vapor pressure studies are discussed by Hultgren et al. (4).

Heat Capacity and Entropy

The electronic energy levels and quantum weights are obtained from Moore (7) and Roth (8). The levels above 30000 cm^{-1} and their respective quantum weights are average values calculated from those given by Moore (7) and Roth (8). The tabulated entropy values agree within 0.001 gibbs/mol with the recent tabulation by Hultgren et al. (4) and Mah and Pankratz (5). There are predicted levels which have not been observed and/or classified. It is not expected that $S°_{298}$ would be affected by these states, but that in the range 3000-6000K, an error of 0.2-0.3 gibbs/mol might result. In our present tabulation, the levels above 20000 cm^{-1} contribute 0.0005 gibbs/mol at 3000 K and 0.15 gibbs/mol at 6000 K to the entropy.

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NICKEL MONOSULFIDE (NiS) NiS
(CRYSTAL) GFW=90.77

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-2.023	-20.826	-20.826	INFINITE
100	5.542	3.073	21.481	-1.841	-20.929	-20.762	45.376
200	9.710	8.454	13.656	-1.040	-20.973	-20.575	22.483
298	11.260	12.665	12.665	0.000	-21.000	-20.372	14.933
300	11.280	12.735	12.666	0.021	-21.000	-20.368	14.838
400	12.070	16.093	13.118	1.190	-21.583	-20.131	10.999
500	12.680	18.853	13.997	2.428	-21.992	-19.719	8.619
600	13.220	21.214	15.008	3.724	-22.336	-19.231	7.005
700	13.030	23.599	16.205	6.575	-21.079	-18.779	5.863
800	13.710	27.383	17.493	7.912	-34.305	-19.706	5.383
900	14.390	29.037	18.485	9.317	-34.086	-17.894	4.345
1000	15.070	30.588	19.798	10.790	-33.816	-16.108	3.520
1100	15.750	32.057	20.846	12.331	-33.497	-14.354	2.852
1200	16.430	33.456	21.839	13.940	-33.128	-12.629	2.300
1300	17.110	34.798	22.785	15.617	-32.710	-10.935	1.838
1400	17.790	36.091	23.689	17.362	-32.248	-9.278	1.448
1500	18.470	37.342	24.558	19.175	-31.740	-7.657	1.116
1600	19.150	38.555	25.395	21.056	-31.186	-6.067	0.829
1700	19.830	39.737	26.204	23.005	-30.590	-4.516	0.581

Dec. 31, 1976

NICKEL MONOSULFIDE (NiS) (CRYSTAL) GFW = 90.77

$S^o_{298.15}$ = 12.67 ± 0.1 gibbs/mol
T_t = 652 ± 3 K
T_m = 1249 ± 3 K

ΔHf^o_0 = -20.8 ± 1.5 kcal/mol
$\Delta Hf^o_{298.15}$ = -21.0 ± 1.5 kcal/mol
ΔHt° = 1.54 ± 0.1 kcal/mol
ΔHm° = 7.20 ± 0.7 kcal/mol

NiS

Heat of Formation

Rosenqvist (1) studied the sulfur vapor pressure above solid nickel sulfides using the H_2/H_2S equilibrium. Combining his data for several equilibria we calculate second and third law values of ΔHf^o_{298} for NiS(c) to be -20.5±0.7 kcal/mol and -22.6±3.6 kcal/mol, respectively. The stoichiometry of NiS varies from at least $NiS_{.98}$ to $NiS_{1.06}$ and Ariya et al. (2) investigated ΔHf^o_{298} in this composition range by calorimetric methods. These authors found ΔHf^o_{298} = -20.3±0.6 kcal/mol for stoichiometric NiS with an ill-defined trend toward more exothermic values at higher sulfur content. DeRanter and Breckpot (3) obtained a value of -20.08 kcal/mol for amorphous $Ni_{.98}S$ from an enthalpometric titration. We calculate ΔHf^o_{298} = -21.3 kcal/mol for the same material based on a third law analysis of DeRanter and Breckpot's emf data (3).

In view of the rather large uncertainties and variations due to stoichiometry we choose to adopt the average of the five values above, ΔHf^o_{298} = -21.0±1.5 kcal/mol. This value is somewhat less negative than values of -22.1 and -22.5 kcal/mol adopted by Mah and Pankrantz (4) and Mills (5), respectively.

Heat Capacity and Entropy

The low temperature heat capacity data (52-296 K) are taken from Weller and Kelley (6). High temperature enthalpies of $NiS_{1.03}$ were measured by Conard et al. (7) via drop calorimetry. We have joined these values smoothly with the low temperature Cp° measurements of Weller and Kelley to derive the Cp° values from 298-652 K. Values of Cp° above the transition are also taken from our analysis of Conard's et al. enthalpy data, disregarding the points above 1000 K to avoid problems due to incongruent melting. Values above 1000 K are extrapolated.

Phase Data

Both the low (β) and high (α) temperature polymorphs of NiS dissolve excess sulfur to form solid solutions. The β phase shows a limited range of homogeneity but the α phase shows a broad limit extending to approximately $NiS_{1.10}$ (8). The α phase is normally designated $\alpha\text{-}Ni_{1-x}S$ to emphasize this feature. However the sulfur-poor limit of this phase has the stoichiometric composition to at least 873 K; at 1070 K the deviation from stoichiometry is less than 0.05 weight percent nickel (8). Above 1079 K the deviation of the sulfur-poor limit from stoichiometry increases more rapidly and a material of stoichiometry NiS will exist as an equilibrium mixture of liquid Ni_yS_z and solid $\alpha\text{-}Ni_{1-x}S$ (8). Thus, NiS melts incongruently.

Transition Data

We adopt 652±3 K as the transition temperature of stoichiometric NiS from rhombohedral (β) to hexagonal (α) form based on the phase diagram of Kullerud and Yund (8). The temperature of this transition is very dependent on the exact stoichiometry of the material (8). The transition heat has been measured via a DTA technique by Conard et al. (7) and we adopt their value of 1.54±0.1 kcal/mol. This is considerably higher than an older value of 0.63 kcal/mol measured by Biltz et al. (9, 5) but should be much more accurate due to the calibration technique used. Mah and Pankrantz (4) estimated 0.7 kcal/mol. This transition heat cannot be measured by drop calorimetry since the α form does not revert to the β form on cooling.

Melting Data

As stated above stoichiometric NiS will begin to form a liquid at 1079 K. The conversion to stoichiometric liquid NiS is complete at 1249 K (8). We adopt the latter as the melting point of NiS with an uncertainity estimated to be ±3 K. The adopted heat of melting, ΔHm° = 7.20±0.7 kcal/mol, is from our analysis of the high temperature enthalpy data of Conard et al. (7). This value compares favorably with estimated values of 7.4 and 7.0 kcal/mol due to Nagamori and Ingraham (10) and Mah and Pankrantz (4).

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NiS

NICKEL MONOSULFIDE (NiS) NiS

(LIQUID) GFW=90.77

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.260	17.314	17.314	0.000	-14.932	-15.690	11.501
300	11.280	17.383	17.314	0.021	-14.932	-15.694	11.433
400	12.070	20.741	17.746	1.190	-15.515	-15.922	8.699
500	12.680	23.501	18.645	2.428	-15.924	-15.975	6.983
600	13.220	25.862	19.656	3.724	-16.268	-15.952	5.810
700	13.030	30.247	20.854	6.575	-15.011	-15.964	4.984
800	13.710	32.031	22.141	7.912	-28.237	-17.356	4.741
900	18.350	33.872	23.337	9.481	-27.854	-16.013	3.888
1000	18.350	35.805	24.489	11.316	-27.222	-14.730	3.219
1100	18.350	37.554	25.598	13.151	-26.609	-13.513	2.685
1230	18.350	39.151	26.662	14.986	-26.014	-12.348	2.259
1300	18.350	40.619	27.680	16.821	-25.438	-11.231	1.888
1400	18.350	41.979	28.653	18.656	-24.886	-10.160	1.586
1500	18.350	43.265	29.584	20.491	-24.356	-9.128	1.330
1600	18.350	44.429	30.476	22.326	-23.848	-8.128	1.110
1700	18.350	45.542	31.330	24.161	-23.366	-7.161	0.921
1800	18.350	46.591	32.149	25.996	-27.007	-6.050	0.735
1900	18.350	47.583	32.935	27.831	-26.552	-4.897	0.563
2000	18.350	48.524	33.691	29.666	-26.098	-3.770	0.412
2100	18.350	49.419	34.419	31.501	-25.645	-2.666	0.277
2200	18.350	50.273	35.120	33.336	-25.192	-1.580	0.157
2300	18.350	51.089	35.797	35.171	-24.740	-0.518	0.049
2400	18.350	51.870	36.451	37.006	-24.288	0.526	-0.048
2500	18.350	52.619	37.082	38.841	-23.836	1.550	-0.136
2600	18.350	53.339	37.694	40.676	-23.385	2.557	-0.215
2700	18.350	54.031	38.286	42.511	-22.934	3.545	-0.287
2800	18.350	54.698	38.861	44.346	-22.484	4.516	-0.353
2900	18.350	55.342	39.418	46.181	-22.034	5.474	-0.412
3000	18.350	55.964	39.959	48.016	-21.585	6.416	-0.467
3100	18.350	56.566	40.485	49.851	-21.135	7.341	-0.518
3200	18.350	57.149	40.997	51.686	-110.753	9.409	-0.643
3300	18.350	57.713	41.495	53.521	-109.909	13.150	-0.871
3400	18.350	58.261	41.980	55.356	-109.066	16.868	-1.084

Dec. 31, 1976

NICKEL MONOSULFIDE (NiS) (LIQUID) GFW = 90.77

$S^\circ_{298.15}$ = 17.31 ± 0.3 gibbs/mol
T_m = 1249 ± 3 K
T_d = [2350 ± 200] K

$\Delta Hf^\circ_{298.15}$ = -14.9 ± 3 kcal/mol
ΔHm° = 7.20 ± 0.7 kcal/mol

NiS

Heat of Formation

The adopted value of ΔHf°_{298} is calculated from that of NiS(c) by adding ΔH°_m and the enthalpy difference (H°_{1249}-H°_{298}) between the crystal and liquid. Our second and third law analyses of Nagamori and Ingraham's (1) sulfur vapor pressure data yields ΔHf°_{298} = -14.4±0.4 and -16.7±0.4 kcal, respectively. These values agree with the adopted value within the estimated uncertainty. Meyer et al. (2) and Rosenqvist (3) conducted similar vapor pressure studies at higher and lower temperatures, respectively. Both studies qualitatively show good agreement with Nagamori at overlapping temperatures (2). However Meyer's data is presented graphically only and Rosenqvist's data covers only compositions near Ni_3S_2(ℓ) and is not of high enough quality to extrapolate to the proper composition.

Heat Capacity and Entropy

The heat capacity of liquid NiS above an assumed glass transition at 860 K is taken from our analysis of the enthalpy data of Conard et al. (4). This value has a fairly high uncertainty because of the limited temperature range of the data (35 K). It is in reasonable agreement with the estimated Cp° = 17 gibbs/mol of Mah and Pankrantz (5). The heat capacity below the glass transition is that of the crystal. The value of S°_{298} is calculated from that of NiS(c) by adding ΔHm°/Tm and the entropy difference (S°_{1249}-S°_{298}) between the crystal and liquid.

Melting Data

Refer to NiS(c) table.

Decomposition Data

The free energy data indicates that NiS(ℓ) will decompose to the elements, Ni(ℓ) + 1/2S_2(g), at a temperature of 2350±200 K. In view of the uncertainty in the free energy data, computation of the exact zero point does not seem justified. Since the free energy data for NiS(ℓ) and NiS(g) (6) intersect at 2990±200 K, it seems clear that decomposition will occur rather than boiling.

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NiS

NICKEL MONOSULFIDE (NiS) NiS
(IDEAL GAS) GFW=90.77

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.203	85.419	85.419	INFINITE
100	7.008	52.088	67.160	-1.507	85.830	81.095	-177.231
200	7.617	57.110	61.006	-0.779	85.713	76.380	-83.463
298	8.234	60.272	60.271	0.000	85.425	71.859	-52.673
300	8.244	60.322	60.272	0.015	85.419	71.776	-52.288
400	8.747	62.766	60.601	0.866	84.518	67.301	-36.771
500	9.153	64.763	61.240	1.761	83.767	63.084	-27.574
600	9.444	66.441	61.972	2.693	83.058	59.015	-21.496
700	9.685	67.937	62.721	3.651	82.422	55.086	-17.198
800	9.827	69.240	63.456	4.627	68.836	49.949	-13.645
900	9.910	70.403	64.164	5.615	68.637	47.600	-11.559
1000	9.948	71.450	64.842	6.608	68.427	45.274	-9.894
1100	9.956	72.398	65.486	7.603	68.201	42.968	-8.537
1200	9.945	73.264	66.099	8.599	67.954	40.685	-7.410
1300	9.920	74.059	66.681	9.592	67.690	38.425	-6.460
1400	9.889	74.793	67.234	10.582	67.398	36.184	-5.648
1500	9.855	75.475	67.761	11.570	67.080	33.963	-4.948
1600	9.820	76.109	68.264	12.553	66.737	31.769	-4.339
1700	9.786	76.704	68.743	13.534	66.364	29.593	-3.804
1800	9.753	77.262	69.201	14.511	61.865	27.61[illegible]	-3.353
1900	9.723	77.789	69.639	15.484	61.459	25.722	-2.959
2000	9.695	78.287	70.059	16.455	61.048	23.851	-2.606
2100	9.669	78.759	70.462	17.423	60.635	22.000	-2.290
2200	9.647	79.208	70.850	18.389	60.218	20.172	-2.004
2300	9.627	79.637	71.222	19.353	59.799	18.360	-1.745
2400	9.609	80.046	71.582	20.315	59.378	16.568	-1.509
2500	9.595	80.438	71.928	21.275	58.955	14.793	-1.293
2600	9.582	80.814	72.263	22.234	58.530	13.035	-1.096
2700	9.572	81.175	72.586	23.191	58.103	11.293	-0.914
2800	9.564	81.523	72.899	24.148	57.675	9.565	-0.747
2900	9.558	81.859	73.202	25.104	57.246	7.856	-0.592
3000	9.554	82.183	73.496	26.040	56.816	6.161	-0.449
3100	9.551	82.496	73.782	27.015	56.386	4.479	-0.316
3200	9.551	82.799	74.059	27.970	-34.112	3.968	-0.271
3300	9.552	83.093	74.328	28.925	-34.148	5.158	-0.342
3400	9.554	83.378	74.590	29.880	-34.184	6.351	-0.408
3500	9.558	83.655	74.845	30.836	-34.222	7.541	-0.471
3600	9.563	83.925	75.094	31.792	-34.258	8.736	-0.530
3700	9.569	84.187	75.336	32.749	-34.295	9.932	-0.587
3800	9.576	84.442	75.572	33.706	-34.332	11.127	-0.640
3900	9.584	84.691	75.803	34.664	-34.370	12.323	-0.691
4000	9.593	84.934	76.028	35.623	-34.408	13.524	-0.739
4100	9.603	85.171	76.248	36.583	-34.446	14.721	-0.785
4200	9.613	85.402	76.463	37.543	-34.487	15.922	-0.828
4300	9.624	85.629	76.674	38.505	-34.528	17.121	-0.870
4400	9.636	85.850	76.880	39.468	-34.571	18.323	-0.910
4500	9.648	86.067	77.082	40.432	-34.615	19.527	-0.948
4600	9.661	86.279	77.279	41.398	-34.661	20.729	-0.985
4700	9.674	86.487	77.473	42.345	-34.709	21.933	-1.020
4800	9.687	86.691	77.663	43.333	-34.759	23.138	-1.053
4900	9.701	86.890	77.849	44.302	-34.813	24.348	-1.086
5000	9.715	87.087	78.032	45.273	-34.869	25.553	-1.117
5100	9.729	87.279	78.211	46.245	-34.929	26.764	-1.147
5200	9.743	87.468	78.388	47.219	-34.991	27.975	-1.176
5300	9.757	87.654	78.561	48.194	-35.058	29.185	-1.203
5400	9.772	87.836	78.731	49.170	-35.130	30.400	-1.230
5500	9.786	88.016	78.898	50.148	-35.206	31.613	-1.256
5600	9.801	88.192	79.062	51.128	-35.287	32.830	-1.281
5700	9.815	88.366	79.224	52.108	-35.375	34.045	-1.305
5800	9.830	88.537	79.383	53.091	-35.466	35.265	-1.329
5900	9.844	88.705	79.540	54.074	-35.565	36.482	-1.351
6000	9.859	88.870	79.694	55.059	-35.670	37.708	-1.373

Dec. 31, 1976

NICKEL MONOSULFIDE (NiS) (IDEAL GAS) GFW = 90.77

D°_0 = 81.5 ± 3.5 kcal/mol
$S^\circ_{298.15}$ = [60.3 ± 2.0] gibbs/mol

ΔHf°_0 = 85.4 ± 4.0 kcal/mol NiS
$\Delta Hf^\circ_{298.15}$ = 85.4 ± 4.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
[0]	[9]
[1360.7]	[7]
[2269.6]	[5]
[16661.6]	[5]
[16977.8]	[3]
[17230.7]	[1]

ω_e = 544 cm^{-1} $\omega_e x_e$ = 2.6 cm^{-1} σ = 1
B_e = [0.191] cm^{-1} α_e = [0.0011] cm^{-1} r_e = [2.07] Å

Heat of Formation

Drowart et al. (1) used a modified Knudsen cell and a mass spectrometric technique to study the equilibrium NiS(g) + Mn(g) = MnS(g) + Ni(g). Since they report no data we adopt their value of D°_0 = 81.5±3.5 kcal/mol based on their third law analysis of this equilibrium. With auxiliary JANAF data (2) this yields ΔHf°_{298} = 85.4±4.0 kcal/mol. Trevedi (3) studied the absorption spectrum of NiS and determined D°_0 = 101.6 kcal/mol from the onset of continuous absorption due to photodissociation. This value is likely to be too high in view of the experimental difficulties in determining the exact position of the onset of continuous absorption. Complications arise because of background emission from the furnace. A Birge-Sponer extrapolation of the vibrational data to determine D°_0 is not meaningful since DeVore and Franzen (4) used the reverse procedure to arrive at the reported value of $\omega_e x_e$.

Heat Capacity and Entropy

No experimental information is available on the electronic structure of NiS. The electronic states are estimated to be identical to those of the Ni^{2+} ion (5) following the procedure of Brewer and Rosenblatt (6) for the transition metal oxides. As stated by Brewer and Rosenblatt (6), this procedure usually overestimates the contribution of electronic states. Nevertheless; it appears to be the best method available. The uncertainty assigned to S°_{298} is based mainly on the uncertainties in this approximation since the presence of the sulfide ion will undoubtedly alter the electronic structure of the nickel ion. Levels above 50,000 cm^{-1} are not included since they have a negligible effect on the thermodynamic properties. The vibrational constants are taken from a study of the matrix isolation spectrum by DeVore and Franzen (4). The rotational constants are estimated based on an oxide-sulfide correlation due to Barrow and Cousins (7), $r_{NiS} = 0.237 + 1.116\, r_{NiO}$. The value r_{NiO} = 1.64 Å is taken from Brewer and Chandraskharaiah (8). The value of α_e is estimated assuming a Morse potential function using the expression given by Herzberg (9).

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NICKEL DISULFIDE (NiS_2)
(CRYSTAL) GFW=122.83

NiS_2

* T, K	gibbs/mol Cp°	S°	-(G°-H°298)/T	kcal/mol H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	16.880	17.200	17.200	0.000	-31.400	-29.849	21.880
300	16.889	17.304	17.200	0.031	-31.400	-29.839	21.737
400	17.385	22.231	17.869	1.745	-32.537	-29.270	15.992
500	17.881	26.164	19.147	3.508	-33.359	-28.357	12.395
600	18.377	29.468	20.599	5.321	-34.043	-27.290	9.940
700	18.873	32.338	22.075	7.184	-34.574	-26.071	8.140
800	19.369	34.890	23.521	9.096	-61.050	-27.367	7.476
900	19.865	37.200	24.914	11.057	-60.713	-23.176	5.628
1000	20.361	39.319	26.250	13.069	-60.345	-19.024	4.158
1100	20.857	41.283	27.528	15.130	-59.949	-14.914	2.963
1200	21.353	43.119	28.752	17.240	-59.523	-10.837	1.974
1300	21.849	44.848	29.924	19.400	-59.067	-6.795	1.142
1400	22.345	46.485	31.049	21.610	-58.587	-2.793	0.436
1500	22.841	48.043	32.131	23.869	-58.081	1.171	-0.171
1600	23.337	49.533	33.172	26.178	-57.547	5.108	-0.698
1700	23.833	50.963	34.177	28.537	-56.990	9.005	-1.158
1800	24.329	52.339	35.148	30.945	-60.508	13.041	-1.583

March 31, 1977

NICKEL DISULFIDE (NiS_2) (CRYSTAL) GFW = 122.83

$S^o_{298.15}$ = [17.2 ± 2.0] gibbs/mol
T_m = 1280 ± 5 K

$\Delta Hf^o_{298.15}$ = -31.4 ± 4.0 kcal/mol
ΔHm° = [15.7 ± 2.0] kcal/mol

NiS_2

Heat of Formation

Our analysis of equilibrium data involving NiS_2 is summarized below.

Investigator(s)	Temp Range °K	Number of Data Points	$\Delta Hr^o_{298.15}$ kcal/mol 2nd Law	3rd Law	Drift gibbs/mol
Ariya et al. (1)[a]	298.15	1	calorimetric	-35.1	
Biltz et al. (2)[b]	923-1033	5	-46.3±0.4	-47.1±0.1	-0.8±0.4
Leegaard and Rosenqvist (3)[b]	673-873	equation	-49.2	-48.7	0.7
Delafosse and Barret (4)[c]	500-723	2	13.9	-5.1±9.9	-31.4
Rosenqvist (5)[c]	673-873	20	-2.9±0.2	-7.5±2.4	-14.1±0.3
DeRanter and Breckpot (6)[a]	298.15	1	emf(ΔG^o_{298} = -24.3)	-25.9	

[a] reaction is $Ni(c) + 2S(c) = NiS_2(c)$
[b] reaction is $2Ni_{1-x}S(c) + S_2(g) = 2NiS_2(c)$
[c] reaction is $Ni_{1-x}S(c) + H_2S(g) = NiS_2(c) + H_2(g)$

The studies due to Delafosse and Barret (4) and Rosenqvist (5) show poor agreement between second and third law values of ΔHr° as well as a large third law drift and are not considered further. Kullerud and Yund (7) mention that a coating of $NiS_2(c)$ often forms on $Ni_{1-x}S(c)$ and it seems possible that this may lead to a slow establishment of equilibrium in this system. DeRanter and Breckpot (6) state that their results may be biased for $NiS_2(c)$ since it is a semiconductor and this may interfere in emf measurements. Consequently their results are not considered further. Third law results of Biltz et al. (2) and Leegaard and Rosenquist (3) yield values of ΔHf^o_{298} = -29.1±1.6 and -29.8±1.7 kcal/mol respectively, when combined with auxiliary JANAF data (8). These values are averaged with the calorimetric value due to Ariya (1) of -35.1 kcal/mol to yield the adopted value of -31.4 kcal/mol. An uncertainty of ±4 kcal/mol is assigned due mainly to the variation in stoichiometry of one of the reactants, $Ni_{1-x}S$. The adopted value compares favorably with a value of -32.0 kcal/mol obtained by Mills (9) in a recent critical evaluation. It also compares favorably with a value of -31.3 kcal/mol calculated assuming the same contribution per gram-atom as in NiS and Ni_3S_2 (8).

Heat Capacity and Entropy

The only heat capacity measurements on NiS_2 are those of Winterberger and Bonnerot (10) at low temperature (5-10 K). Consequently the heat capacity is estimated via the following procedure. The value at 298.15 K is estimated assuming the same contribution per gram-atom as in NiS and Ni_3S_2 (8) yielding Cp^o_{298} = 16.88 gibbs/mol. The temperature dependence is estimated using method A of Kubaschewski et al. (11). This yields $Cp^o = 15.401 + 4.960 \times 10^{-3} T$.

Second law analyses of equilibrium data of Leegaard and Rosenqvist (3) and Biltz et al. (2) combined with auxiliary JANAF data (8) yield S^o_{298} = 16.89 and 17.60 gibbs/mol respectively. We adopt the average of these values, 17.2 gibbs/mol, with an uncertainty estimated to be ±2 gibbs/mol. Similar analyses of studies of Delafosse and Barret (4) and Rosenqvist (5) give values of 13.10 and 29.96 gibbs/mol respectively, but as mentioned above these studies do not appear to be reliable since equilibrium may not have been established. A value of 19.10 gibbs/mol is obtained assuming the same contribution per gram-atom as in NiS and Ni_3S_2 (8). This is somewhat higher than the adopted value but this may be reasonable since the crystal symmetry of NiS_2 is higher (cubic) than that of NiS and Ni_3S_2 (hexagonal) (7).

Melting Data

The melting point of $NiS_2(c)$ is taken from the phase study by Kullerud and Yund (7). The heat of melting of NiS_2 is unknown and is estimated as follows. Lewis and Randall (12) point out that the sum of the entropy of transition(s) plus the entropy of fusion is approximately constant, on a gram-atom basis, for compounds of similar structure. Using NiS and Ni_3S_2 (8) as base compounds we calculate the above sums to be 4.06 and 4.13 gibbs/gram-atom, respectively. Since NiS_2 has no known transition we use the average value of 4.10 gibbs/gram-atom to calculate $\Delta Sm^o(NiS_2)$ = 12.3 gibbs/mol which yields ΔHm° = 15.7 kcal/mol with an estimated uncertainty of ±2.0 kcal/mol.

NiS_2

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NICKEL DISULFIDE (NiS_2) NiS_2

(LIQUID) GFW=122.83

	gibbs/mol			kcal/mol			
T, K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0							
100							
200							
298	16.880	29.261	29.261	0.000	-15.910	-17.955	13.161
300	16.889	29.365	29.261	0.031	-15.910	-17.967	13.089
400	17.385	34.292	29.929	1.745	-17.047	-18.605	10.165
500	17.881	38.224	31.208	3.508	-17.869	-18.898	8.260
600	18.377	41.528	32.660	5.321	-18.553	-19.037	6.934
700	18.873	44.398	34.136	7.184	-19.084	-19.023	5.939
800	19.369	46.951	35.581	9.096	-45.560	-21.525	5.880
900	19.865	49.261	36.975	11.057	-45.223	-18.541	4.502
1000	21.750	51.440	38.312	13.128	-44.796	-15.596	3.408
1100	21.750	53.513	39.601	15.303	-44.286	-12.704	2.524
1200	21.750	55.406	40.841	17.478	-43.795	-9.853	1.794
1300	21.750	57.147	42.029	19.653	-43.324	-7.041	1.184
1400	21.750	58.759	43.167	21.828	-42.879	-4.268	0.666
1500	21.750	60.259	44.257	24.003	-42.457	-1.528	0.223
1600	21.750	61.663	45.301	26.178	-42.057	1.190	-0.163
1700	21.750	62.982	46.303	28.353	-41.684	3.880	-0.499
1800	21.750	64.225	47.265	30.528	-45.435	6.721	-0.816

March 31, 1977

NICKEL DISULFIDE (NiS_2) (LIQUID) GFW = 122.83

$S°_{298.15}$ = [29.261] gibbs/mol

T_m = 1280 ± 5 K

T_d = unknown

$\Delta Hf°_{298.15}$ = [-15.910] kcal/mol

$\Delta Hm°$ = [15.7 ± 2.0] kcal/mol

NiS_2

Heat of Formation

There are no experimental studies of the heat of formation of $NiS_2(\ell)$. Therefore $\Delta Hf°_{298}$ is calculated from that of $NiS_2(c)$ (1) by adding the heat of melting and the enthalpy difference ($H°_{1280}-H°_{298}$) for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to remain constant at 21.75 gibbs/mol (the value for $NiS_2(c)$ at the melting point) above an assumed glass transition point of 960 K. Below that temperature the crystal heat capacity (1) is assumed to be valid.

The entropy of $NiS_2(\ell)$ at 298.15 is calculated from that of $NiS_2(c)$ at the same temperature by adding the entropy of melting and the entropy difference ($S°_{1280}-S°_{298}$) for crystal and liquid.

Melting Data

See $NiS_2(c)$ table.

Decomposition Data

Under standard conditions (1 atm. pressure) the use of auxiliary JANAF data (1) indicates that $NiS_2(\ell)$ will decompose spontaneously to $NiS(\ell) + 1/2S_2(g)$ at all temperatures above the normal melting point. This appears to be at variance with the phase diagram of Kullerud and Yund (2) which indicates the presence of a liquid of variable composition in the Ni-S system from a stoichiometry less than Ni_3S_2 to just above NiS_2 at temperatures slightly above the melting point. However the authors point out that this diagram does not refer to a constant pressure system and give a short discussion of the loss of sulfur to the vapor from $NiS_2(c)$. From the sealed tube experiments of (2) it does appear that $NiS_2(\ell)$ will be stable under its own vapor pressure in a sealed tube.

References

1. JANAF Thermochemical Tables: $NiS_2(c)$, 3-31-77; $NiS(\ell)$, 12-31-76; $S_2(g)$, 12-31-65.
2. G. Kullerud and R. A. Yund, J. Petrology 3, 126 (1962).

TRINICKEL DISULFIDE (Ni_3S_2) Ni_3S_2
(CRYSTAL) GFW=240.25

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	0.000	0.000	INFINITE	-5.057	-51.219	-51.219	INFINITE
100	13.890	8.046	54.001	-4.595	-51.448	-51.127	111.736
200	24.256	21.491	34.470	-2.596	-51.591	-50.746	55.452
298	28.140	32.000	32.000	0.000	-51.700	-50.304	36.873
300	28.190	32.174	32.000	0.052	-51.701	-50.294	36.638
400	30.380	40.597	33.134	2.985	-52.925	-49.764	27.189
500	32.020	47.556	35.342	6.107	-53.806	-48.871	21.361
600	33.440	53.521	37.886	9.381	-54.595	-47.807	17.413
700	34.760	58.776	40.502	12.791	-55.167	-46.573	14.540
800	36.020	63.500	43.087	16.331	-61.491	-47.866	13.076
900	45.080	84.706	46.905	34.021	-66.921	-44.870	10.896
1000	45.080	89.456	50.926	38.529	-65.581	-42.491	9.286
1100	45.080	93.752	54.627	43.037	-64.296	-40.249	7.997
1200	45.080	97.675	58.054	47.545	-63.066	-38.117	6.942
1300	45.080	101.283	61.242	52.053	-61.888	-36.081	6.066
1400	45.080	104.624	64.223	56.561	-60.782	-34.140	5.329
1500	45.080	107.734	67.021	61.049	-59.741	-32.278	4.703
1600	45.080	110.643	69.658	65.577	-58.766	-30.475	4.163

Dec. 31, 1976

TRINICKEL DISULFIDE (Ni_3S_2) (CRYSTAL) GFW = 240.25

$S^\circ_{298.15}$ = 32.00 ± 0.1 gibbs/mol
T_t = 829 ± 3 K
T_m = 1062 ± 3 K

ΔHf°_0 = -51.2 ± 1.2 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -51.7 ± 1.2 kcal/mol
ΔHt° = 13.44 ± 0.1 kcal/mol
ΔHm° = 4.72 ± 0.1 kcal/mol

Ni_3S_2

Heat of Formation

Three sets of authors studied the phase equilibrium between Ni_3S_2(c) and Ni(c) by use of the H_2(g)/H_2S(g) method (1, 2, 3). Our third law analyses of the data due to Rosenqvist (1), Sudo (2) and Line and Laffitte (3) yield ΔHf°_{298} = -51.6±1.0, -50.1±1.6, and -53.4±1.8 kcal/mol, respectively. We adopt the average of these values, ΔHf°_{298} = -51.7±1.2 kcal/mol. Ariya et al. (4) and Vanyukov and Kiseleva (5) reported calorimetric values of -48.3±0.9 and -43.3 kcal/mol, respectively. Vanuykov's value is undoubtedly incorrect since Mills (6) determined that values for Fes and MnS from the same study are approximately 25% too low. A third law analysis of the emf value reported by DeRanter and Breckpot (7) yields ΔHf°_{298} = -38.7 kcal/mol. This value, however, refers to an amorphous material. At least part of the variation in values of the heat of formation apparently is a result of the very wide range of stoichiometry for the high temperature phase of Ni_3S_2 (8, 9).

Heat Capacity and Entropy

The low temperature heat capacities (52-296K) are from Weller and Kelley (10). The high temperature heat capacities are from our analysis of the high temperature enthalpy (298.15-1050 K) data of Conard et al. (11). Our analysis differs slightly from that of Conard et al. since we have forced the high and low temperature heat capacities to join smoothly at 298.15 K. Data above 1050 K are extrapolated assuming a constant heat capacity for the high temperature phase of Ni_3S_2. The thermodynamic functions show good agreement with those reported by Mah and Pankrantz (12).

The entropy at 298.15 is calculated based on an extrapolation of S°_{51} = 2.06 gibbs/mol by Weller and Kelley (10).

Phase Data

A phase transition is observed at 829 K for Ni_3S_2 (8). Below the transition Kullerud and Yund (8) reported the material to be stoichiometric within the limits of ±0.3 weight percent while Rau (9) reported the homogeneity range to extend over a smaller range and to the sulfur-rich side only. Above the phase transition a wide range of homogeneity exists for $Ni_{3\pm x}S_2$ from approximately $Ni_{2.5}S_2$ to $Ni_{3.7}S_2$ (1, 8, 9). The phase diagram indicates that upon heating stoichiometric Ni_3S_2, a two phase region [Ni_yS_z(ℓ)+$Ni_{3\pm x}S_2$(c)] will be encountered within a few degrees of the formation of stoichiometric liquid Ni_3S_2 (8, 9).

Transition Data

We adopt a value of 829±3 K for the phase transition from Ni_3S_2 to $Ni_{3\pm x}S_2$ based on the detailed study by Kullerud and Yund (8). This value is in fair agreement with values of 838 and 828±5 K reported by Rau (9) and Rosenqvist (1) respectively. The adopted heat of transition is from our analysis of the high temperature enthalpy data of Conard et al. (11). Mah and Pankrantz (12) reported the transition at 840 K with ΔHf° = 13.38 kcal/mol in excellent agreement with the adopted ΔHt°.

Melting Data

Kullerud and Yung (8) reported that stoichiometric Ni_3S_2 begins to melt at 1055 K with melting completed at 1062 K. The cooling curve yielded identical results. In view of the two-phase region in the phase diagram we adopt the latter temperature as the melting point with an estimated uncertainty of ±3 K. The adopted heat of melting is from our analysis of Conard's et al. high temperature enthalpy data (11) and is in good agreement with a value of 4.70 kcal/mol reported by Mah and Pankrantz (12).

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Ni_3S_2

TRINICKEL DISULFIDE (Ni_3S_2) Ni_3S_2
(LIQUID) GFW=240.25

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	28.140	51.608	51.608	0.000	-34.399	-38.850	28.477
300	28.190	51.783	51.609	0.052	-34.400	-38.875	28.320
400	30.380	60.206	52.742	2.985	-35.624	-40.307	22.022
500	32.020	67.165	54.951	6.107	-36.505	-41.376	18.084
600	33.440	73.130	57.495	9.381	-37.294	-42.272	15.397
700	34.760	78.385	60.111	12.792	-37.866	-42.998	13.424
800	45.840	83.625	62.709	16.733	-63.788	-46.263	12.638
900	45.840	89.025	65.338	21.317	-62.324	-44.160	10.723
1000	45.840	93.854	67.953	25.901	-60.908	-42.217	9.226
1100	45.840	98.223	70.509	30.485	-59.547	-40.419	8.030
1200	45.840	102.212	72.987	35.069	-58.239	-38.737	7.055
1300	45.840	105.881	75.378	39.653	-56.987	-37.157	6.247
1400	45.840	109.278	77.680	44.237	-55.805	-35.679	5.570
1500	45.840	112.441	79.893	48.821	-54.688	-34.285	4.995
1600	45.840	115.399	82.021	53.405	-53.637	-32.955	4.501
1700	45.840	118.178	84.067	57.989	-52.663	-31.696	4.075
1800	45.840	120.798	86.035	62.573	-64.057	-29.975	3.639
1900	45.840	123.277	87.931	67.157	-63.163	-28.103	3.233
2000	45.840	125.628	89.757	71.741	-62.271	-26.282	2.872
2100	45.840	127.865	91.519	76.325	-61.381	-24.507	2.550
2200	45.840	129.997	93.220	80.909	-60.491	-22.769	2.262
2300	45.840	132.035	94.864	85.493	-59.603	-21.076	2.003
2400	45.840	133.986	96.453	90.077	-58.715	-19.419	1.768
2500	45.840	135.857	97.992	94.661	-57.827	-17.800	1.556
2600	45.840	137.655	99.484	99.245	-56.941	-16.216	1.363
2700	45.840	139.385	100.930	103.829	-56.055	-14.668	1.187
2800	45.840	141.052	102.333	108.413	-55.171	-13.154	1.027
2900	45.840	142.661	103.696	112.997	-54.287	-11.668	0.879
3000	45.840	144.215	105.021	117.581	-53.405	-10.211	0.744
3100	45.840	145.718	106.309	122.165	-52.521	-8.786	0.619
3200	45.840	147.173	107.564	126.749	-321.839	-3.919	0.268
3300	45.840	148.584	108.786	131.333	-319.772	5.981	-0.396
3400	45.840	149.952	109.976	135.917	-317.707	15.825	-1.017
3500	45.840	151.281	111.138	140.501	-315.644	25.599	-1.598
3600	45.840	152.572	112.271	145.085	-313.579	35.321	-2.144
3700	45.840	153.828	113.377	149.669	-311.518	44.988	-2.657
3800	45.840	155.051	114.458	154.253	-309.458	54.594	-3.140

Dec. 31, 1976

TRINICKEL DISULFIDE (Ni_3S_2) (LIQUID) GFW = 240.25

$S^\circ_{298.15}$ = 51.61 ± 0.15 gibbs/mol
T_m = 1062 ± 3 K
T_d = [3240 ± 15] K

$\Delta Hf^\circ_{298.15}$ = -34.4 ± 1.5 kcal/mol
ΔHm° = 4.72 ± 0.1 kcal/mol Ni_3S_2

Heat of Formation

The adopted heat of formation is derived from that of Ni_3S_2(c) at 298.15 K by adding ΔHm° and the difference ($\Delta Hf^\circ_{1062} - \Delta Hf^\circ_{298}$) between crystal and liquid. Our second and third law analyses of Nagamori and Ingraham's equilibrium data (1) yield ΔHf°_{298} = -33.7±0.6 and -33.9±0.3 kcal/mol, respectively, in good agreement with the adopted value. Meyer et al. (2) and Rosenqvist (3) conducted silimar studies at higher and lower temperatures, respectively. Both studies qualitatively show good agreement with Nagamori and Ingraham at overlapping temperatures (2), but Meyer's data is only presented graphically so a re-analysis is not feasible. Rosenqvist's study included compositions near, but not exactly at, the Ni_3S_2 stoichiometry. Our extrapolation of his data to the proper stoichiometry leads to a higher value of K_p at 900 K than at 800 or 1000 K. We conclude that Rosenqvist's data is not of sufficient precision for the small number of points at each temperature (3 or 4) to yield meaningful results when extrapolated.

Heat Capacity and Entropy

The enthalpy of Ni_3S_2(ℓ) from the melting point to 1250 K was measured by Conard et al. (4). Our analysis of this data yields the adopted constant heat capacity of 45.84 gibbs/mol. Above 1250 K the heat capacity is assumed to remain constant. This value is in good agreement with a value of 45.20 gibbs/mol reported by Mah and Pankrantz (5).

The entropy at 298.15 K is calculated from that of Ni_3S_2(c) (6) by adding ΔHm°/Tm and the entropy difference ($S^\circ_{1062} - S^\circ_{298}$) between the liquid and crystal.

Melting Data

See the Ni_3S_2(c) table for details.

Decomposition Data

There is no evidence for the existence of Ni_3S_2(g). In the absence of such information we can only point out that Ni_3S_2(ℓ) will decompose to the gaseous elements at 3240±15 K according to the free energy of formation in this table. This seems to yield an excessively long liquid range for Ni_3S_2.

References

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4. B. R. Conard, R. Sridhar, and J. S. Warner, paper presented at the 106th AIME meeting, March, 1977.
5. A. D. Mah and L. B. Pankrantz, U.S. Bur. Mines Bull. 668, 1976.
6. JANAF Thermochemical Tables: Ni_3S_2(c), 12-31-76.

TRINICKEL TETRASULFIDE (Ni_3S_4) Ni_3S_4
(CRYSTAL) GFW=304.37

T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	39.390	44.570	44.570	0.000	-71.968	-69.770	51.143
300	39.454	44.814	44.571	0.073	-71.968	-69.754	50.816
400	42.887	56.634	46.159	4.190	-74.203	-68.921	37.656
500	46.321	66.573	49.272	8.650	-75.622	-67.431	29.474
600	49.754	75.322	52.898	13.454	-76.496	-65.702	23.932
700	53.188	83.249	56.676	18.601	-77.093	-63.748	19.903
800	56.622	90.576	60.461	24.092	-129.113	-66.921	18.282
900	60.055	97.443	64.192	29.926	-127.276	-59.254	14.389
1000	63.489	103.948	67.845	36.103	-125.151	-51.808	11.323
1100	66.922	110.160	71.412	42.623	-122.737	-44.592	8.860

March 31, 1977

TRINICKEL TETRASULFIDE (Ni_3S_4) (CRYSTAL) GFW = 304.37

$S^o_{298.15}$ = 44.6 ± 4.0 gibbs/mol
T_d = 629 ± 3 K

$\Delta Hf^o_{298.15}$ = -72.0 ± 6.0 kcal/mol

Ni_3S_4

Heat of Formation

The only measured value of ΔHf^o_{298} for Ni_3S_4 is based on the emf data of DeRanter and Breckpot (1). Our third law analysis of their data yields ΔHf^o_{298} = -71.0 kcal/mol. A value of -72.9 kcal/mol can be estimated assuming the same contribution per gram-atom as in NiS and Ni_3S_2 (2). The adopted value, ΔHf^o_{298} = -72.0±6.0 kcal/mol, lies approximately midway between the above values and is chosen so that ΔGr^o_{629} = 0 for the reaction $Ni_3S_4(c) = 2NiS(c) + NiS_2(c)$ (2). This temperature represents the decomposition point of $Ni_3S_4(c)$ (3,4).

Heat Capacity and Entropy

Since there are no measured values for the heat capacity of Ni_3S_4 it is estimated as follows. The value of Cp^o_{298} is estimated assuming the same contribution per gram-atom as in NiS and Ni_3S_2 (2), yielding a value of 39.39 gibbs/mol. The value at the melting point is estimated assuming a contribution of 7.25 gibbs/gram-atom and the heat capacity is assumed to be linear between these two points (5). This leads to Cp° = 29.153±0.03434 T.

The value of S^o_{298} *is estimated assuming the same contribution per gram atom as in* NiS and Ni_3S_2 (2). This estimate is subject to a rather large uncertainty since Ni_3S_4 has a spinel structure (6). Navrotsky and Kleppa (7) showed that the entropies of oxide spinels vary by ±3.7 gibbs/mol depending on the distribution of cations among the available octahedral and tetrahedral sites.

Decomposition Data

The decomposition temperature of Ni_3S_4 is 629±3 K (3,4). It decomposes according to $Ni_3S_4(c) = 2Ni_{1-x}S(c) + NiS_2(c)$. As mentioned above ΔHf^o_{298} for $Ni_3S_4(c)$ was chosen so that ΔGr^o_{629} for this reaction is zero. The value of ΔHr^o_{629} for this reaction, as calculated using auxiliary JANAF data (2), is -2.2 kcal/mol. Kullerud and Yund (4) calculate ΔHr^o_{629} = +7.0 kcal/mol for this reaction based on the volume change as calculated from cell dimensions for the three compounds.

Phase Data

The known crystal species in the Ni-S system include NiS, Ni_3S_2, NiS_2, Ni_3S_4, and Ni_7S_6 (3). The first four species occur naturally as minerals and we have prepared JANAF Thermochemical Tables for these species (2). The species Ni_7S_6 (sometimes reported as Ni_9S_8 or Ni_6S_5) does not occur as a mineral and we have not prepared a table since there is a lack of thermochemical data. It is interesting to note that Ni_2S_3 does not occur as a stable species even though stable M_2S_3 species have been observed for Cr, Fe, and Co (8). Estimates of ΔHf^o_{298} for Ni_2S_3 range from +225 to +484 kcal/mol (9). Although Moody and Thomas (9) acknowledge large uncertainties in their calculations, they are unlikely to be in error to the extent necessary to predict stability for $Ni_2S_3(c)$.

References

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Ni_3S_4

OXYGEN, MONATOMIC (O) 0

(IDEAL GAS) GFW=15.9994

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.607	58.984	58.984	INFINITE
100	5.665	32.466	43.265	-1.080	59.164	57.988	-126.730
200	5.433	36.339	38.952	-0.523	59.374	56.728	-61.988
298	5.237	38.468	38.468	0.000	59.554	55.390	-40.602
300	5.234	38.500	38.468	0.010	59.557	55.364	-40.332
400	5.134	39.991	38.672	0.528	59.720	53.942	-29.472
500	5.081	41.130	39.054	1.038	59.865	52.480	-22.939
600	5.049	42.053	39.479	1.544	59.994	50.991	-18.573
700	5.029	42.830	39.904	2.048	60.109	49.481	-15.448
800	5.015	43.501	40.313	2.550	60.212	47.955	-13.101
900	5.006	44.091	40.700	3.051	60.306	46.418	-11.272
1000	4.999	44.618	41.066	3.552	60.393	44.870	-9.806
1100	4.994	45.094	41.411	4.051	60.473	43.314	-8.606
1200	4.990	45.528	41.736	4.550	60.548	41.751	-7.604
1300	4.987	45.927	42.043	5.049	60.619	40.181	-6.755
1400	4.984	46.297	42.334	5.548	60.685	38.607	-6.027
1500	4.982	46.641	42.610	6.046	60.748	37.027	-5.395
1600	4.981	46.962	42.872	6.544	60.808	35.444	-4.841
1700	4.979	47.264	43.122	7.042	60.865	33.857	-4.353
1800	4.978	47.549	43.360	7.540	60.919	32.267	-3.918
1900	4.978	47.818	43.587	8.038	60.970	30.673	-3.528
2000	4.978	48.073	43.805	8.536	61.018	29.078	-3.177
2100	4.978	48.316	44.014	9.033	61.063	27.480	-2.860
2200	4.978	48.548	44.215	9.531	61.106	25.879	-2.571
2300	4.980	48.769	44.408	10.029	61.146	24.277	-2.307
2400	4.981	48.981	44.595	10.527	61.183	22.673	-2.065
2500	4.983	49.184	44.774	11.025	61.219	21.068	-1.842
2600	4.986	49.380	44.948	11.524	61.252	19.461	-1.636
2700	4.990	49.568	45.115	12.023	61.282	17.854	-1.445
2800	4.994	49.750	45.277	12.522	61.311	16.245	-1.268
2900	4.999	49.925	45.435	13.021	61.338	14.635	-1.103
3000	5.004	50.094	45.587	13.522	61.362	13.023	-0.949
3100	5.010	50.259	45.735	14.022	61.386	11.412	-0.805
3200	5.017	50.418	45.879	14.524	61.407	9.799	-0.669
3300	5.024	50.572	46.019	15.026	61.428	8.187	-0.542
3400	5.032	50.722	46.155	15.528	61.447	6.573	-0.422
3500	5.041	50.868	46.288	16.032	61.465	4.959	-0.310
3600	5.050	51.011	46.417	16.537	61.482	3.344	-0.203
3700	5.060	51.149	46.543	17.042	61.498	1.729	-0.102
3800	5.070	51.284	46.666	17.549	61.514	0.113	-0.006
3900	5.080	51.416	46.786	18.056	61.529	-1.503	0.084
4000	5.091	51.545	46.903	18.565	61.543	-3.119	0.170
4100	5.102	51.671	47.018	19.075	61.557	-4.736	0.252
4200	5.114	51.794	47.130	19.585	61.571	-6.353	0.331
4300	5.126	51.914	47.240	20.097	61.584	-7.971	0.405
4400	5.137	52.032	47.348	20.610	61.597	-9.588	0.476
4500	5.149	52.148	47.453	21.125	61.610	-11.206	0.544
4600	5.162	52.261	47.557	21.640	61.622	-12.825	0.609
4700	5.174	52.372	47.658	22.157	61.634	-14.443	0.672
4800	5.186	52.481	47.757	22.675	61.646	-16.062	0.731
4900	5.198	52.588	47.855	23.194	61.658	-17.681	0.789
5000	5.210	52.693	47.950	23.715	61.669	-19.300	0.844
5100	5.222	52.797	48.044	24.236	61.680	-20.919	0.896
5200	5.234	52.898	48.137	24.759	61.690	-22.539	0.947
5300	5.246	52.998	48.228	25.283	61.699	-24.159	0.996
5400	5.257	53.096	48.317	25.808	61.709	-25.779	1.043
5500	5.269	53.193	48.405	26.335	61.717	-27.399	1.089
5600	5.280	53.288	48.491	26.862	61.724	-29.020	1.133
5700	5.291	53.381	48.576	27.391	61.731	-30.640	1.175
5800	5.302	53.473	48.660	27.920	61.736	-32.261	1.216
5900	5.313	53.564	48.742	28.451	61.740	-33.882	1.255
6000	5.323	53.654	48.823	28.983	61.743	-35.502	1.293

June 30, 1962; June 30, 1974; March 31, 1977

OXYGEN, MONATOMIC (O) (IDEAL GAS) GFW = 15.9994

Ground State Configuration $^3P_2$

$S^\circ_{298.15}$ = 38.468 ± 0.005 gibbs/mol

ΔHf°_0 = 58.984 ± 0.024 kcal/mol 0

$\Delta Hf^\circ_{298.15}$ = 59.554 ± 0.024 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	158.265	3
$^3P_0$	226.977	1
$^1D_2$	15867.862	5
$^1S_0$	33792.583	1

Heat of Formation

ΔHf° is based on the D°_0 value for O_2(g) adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for ΔHf°_{298}(O, g) is derived using $D^\circ_0(O_2)$ = 41260±15 cm^{-1} (117.968±0.043 kcal/mol) from Brix and Herzberg (2). The products of dissociation were assumed to be O atoms in their ground states. The justification for this is discussed by Gaydon (3) and Krupenie (4).

Heat Capacity and Entropy

The electronic levels for O(g) are given in the compilation by Moore (5). Our calculations indicate that, except for the five states lying below 34000 cm^{-1}, the inclusion of levels up to n=12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 73768.20 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the lowest lying states (ε_i < 34000 cm^{-1}). The reported uncertainty in S°_{298} is due to uncertainties in the gram formula weight, the fundamental constants, and the position of the low lying electronic levels. The calculated value of S°_{298} is 0.001 gibbs/mol greater than that recommended by CODATA (1). The difference is due to our use of the current CODATA fundamental constants (6). Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (7).

References

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OXYGEN UNIPOSITIVE ION (O^+) O^+

(IDEAL GAS) GFW=15.99885

T, °K		gibbs/mol			kcal/mol		
	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0				-1.481	373.024		
100							
200							
298	4.968	37.010	37.010	0.000	374.949	369.733	-271.018
300	4.968	37.041	37.010	0.009	374.960	369.700	-269.323
400	4.968	38.470	37.205	0.506	375.599	367.850	-200.981
500	4.968	39.578	37.573	1.003	376.227	365.840	-159.907
600	4.968	40.484	37.985	1.500	376.844	363.705	-132.478
700	4.968	41.250	38.398	1.996	377.448	361.467	-112.853
800	4.968	41.913	38.797	2.493	378.042	359.143	-98.112
900	4.968	42.499	39.176	2.990	378.629	356.745	-86.628
1000	4.968	43.022	39.535	3.487	379.209	354.283	-77.427
1100	4.968	43.495	39.874	3.984	379.784	351.762	-69.888
1200	4.968	43.928	40.194	4.480	380.353	349.189	-63.595
1300	4.968	44.325	40.497	4.977	380.918	346.570	-58.263
1400	4.968	44.694	40.783	5.474	381.480	343.906	-53.685
1500	4.968	45.036	41.056	5.971	382.039	341.203	-49.713
1600	4.968	45.357	41.315	6.468	382.594	338.463	-46.231
1700	4.968	45.658	41.561	6.964	383.146	335.687	-43.155
1800	4.968	45.942	41.797	7.461	383.696	332.880	-40.417
1900	4.968	46.211	42.022	7.958	384.243	330.042	-37.963
2000	4.968	46.465	42.238	8.455	384.787	327.175	-35.752
2100	4.968	46.708	42.445	8.952	385.328	324.282	-33.748
2200	4.968	46.939	42.644	9.448	385.866	321.361	-31.924
2300	4.968	47.160	42.836	9.945	386.402	318.417	-30.256
2400	4.968	47.371	43.020	10.442	386.935	315.450	-28.725
2500	4.968	47.574	43.198	10.939	387.466	312.461	-27.315
2600	4.968	47.769	43.371	11.436	387.994	309.450	-26.011
2700	4.969	47.956	43.537	11.932	388.519	306.419	-24.803
2800	4.969	48.137	43.698	12.429	389.043	303.369	-23.679
2900	4.969	48.312	43.854	12.926	389.563	300.300	-22.631
3000	4.970	48.480	44.006	13.423	390.082	297.213	-21.652
3100	4.971	48.643	44.153	13.920	390.598	294.109	-20.734
3200	4.972	48.801	44.295	14.417	391.112	290.988	-19.873
3300	4.974	48.954	44.434	14.915	391.625	287.851	-19.063
3400	4.976	49.102	44.569	15.412	392.135	284.699	-18.300
3500	4.978	49.247	44.701	15.910	392.645	281.532	-17.579
3600	4.981	49.387	44.829	16.408	393.152	278.350	-16.898
3700	4.984	49.523	44.954	16.906	393.657	275.153	-16.252
3800	4.988	49.656	45.076	17.405	394.161	271.944	-15.640
3900	4.993	49.786	45.195	17.904	394.665	268.721	-15.059
4000	4.998	49.912	45.312	18.403	395.167	265.486	-14.505
4100	5.004	50.036	45.425	18.903	395.669	262.238	-13.978
4200	5.011	50.157	45.537	19.404	396.168	258.977	-13.476
4300	5.019	50.275	45.645	19.906	396.668	255.704	-12.996
4400	5.028	50.390	45.752	20.408	397.167	252.421	-12.538
4500	5.038	50.503	45.856	20.911	397.666	249.126	-12.099
4600	5.049	50.614	45.958	21.416	398.164	245.819	-11.679
4700	5.061	50.723	46.059	21.921	398.661	242.501	-11.276
4800	5.074	50.829	46.157	22.428	399.159	239.174	-10.890
4900	5.088	50.934	46.253	22.936	399.656	235.836	-10.519
5000	5.103	51.037	46.348	23.445	400.153	232.487	-10.162
5100	5.119	51.138	46.441	23.957	400.650	229.129	-9.819
5200	5.136	51.238	46.532	24.469	401.147	225.761	-9.488
5300	5.155	51.336	46.622	24.984	401.644	222.383	-9.170
5400	5.174	51.433	46.710	25.500	402.142	218.997	-8.863
5500	5.195	51.528	46.797	26.019	402.639	215.601	-8.567
5600	5.217	51.621	46.882	26.539	403.136	212.194	-8.281
5700	5.239	51.714	46.966	27.062	403.633	208.781	-8.005
5800	5.263	51.805	47.049	27.587	404.131	205.358	-7.738
5900	5.288	51.895	47.130	28.115	404.629	201.927	-7.480
6000	5.313	51.985	47.210	28.645	405.127	198.488	-7.230

March 31, 1977

OXYGEN UNIPOSITIVE ION (O^+) (IDEAL GAS) GFW = 15.99885

O^+

Ground State Configuration $^4S^o_{3/2}$

$S^o_{298.15}$ = 37.010 ± 0.005 gibbs/mol

ΔHf^o_0 = 373.024 ± 0.024 kcal/mol

$\Delta Hf^o_{298.15}$ = 374.949 ± 0.024 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^4S^o_{3/2}$	0.0	4
$^2D^o_{5/2}$	26810.7	6
$^2D^o_{3/2}$	26830.5	4
$^2P^o_{3/2}$	40466.9	4
$^2P^o_{1/2}$	40468.4	2

Heat of Formation

The heat of formation is calculated from the equation $O(g) = O^+(g) + e^-(g)$ with auxiliary data (1), using an ionization potential of IP = 109837.02±0.06 cm^{-1} (314.0398±0.0002 kcal/mol). This ionization potential, as reported by Moore (2) in units of cm^{-1}, is converted to units of kcal/mol using the current CODATA fundamental constants (3). The uncertainty lies mainly in the uncertainty of $D^o_0(O_2,g)$.

Heat Capacity and Entropy

The electronic levels for $O^+(g)$ are given in the compilation by Moore (4,5). Our calculations indicate that, except for the five states lying below 40500 cm^{-1}, the inclusion of levels up to n=12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 119837.7 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the lowest lying states (ε_i < 40500 cm^{-1}). The reported uncertainty in S^o_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (6).

References

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6. J. R. Downey, Dow Chemical Company, Thermal Research, to be published, 1977.

OXYGEN UNINEGATIVE ION (O^-) O^-

(IDEAL GAS) GFW=15.99995

	gibbs/mol			kcal/mol			
T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0				-1.571	25.270		
100							
200							
298	5.185	37.687	37.687	0.000	24.322	21.878	-16.037
300	5.183	37.719	37.687	0.010	24.316	21.863	-15.927
400	5.106	39.198	37.889	0.524	23.978	21.096	-11.526
500	5.063	40.332	38.269	1.032	23.624	20.416	-8.924
600	5.037	41.253	38.692	1.537	23.254	19.809	-7.215
700	5.020	42.028	39.114	2.040	22.872	19.266	-6.015
800	5.009	42.698	39.521	2.541	22.478	18.777	-5.129
900	5.001	43.287	39.908	3.042	22.074	18.338	-4.453
1000	4.995	43.814	40.272	3.541	21.663	17.945	-3.922
1100	4.991	44.290	40.616	4.041	21.246	17.593	-3.495
1200	4.987	44.724	40.941	4.540	20.825	17.280	-3.147
1300	4.984	45.123	41.247	5.038	20.399	17.002	-2.858
1400	4.982	45.492	41.538	5.536	19.968	16.756	-2.616
1500	4.980	45.836	41.813	6.035	19.534	16.542	-2.410
1600	4.979	46.157	42.074	6.533	19.097	16.356	-2.234
1700	4.978	46.459	42.323	7.030	18.657	16.199	-2.083
1800	4.977	46.744	42.561	7.528	18.214	16.067	-1.951
1900	4.976	47.013	42.788	8.026	17.768	15.960	-1.836
2000	4.975	47.268	43.006	8.523	17.319	15.876	-1.735
2100	4.974	47.511	43.215	9.021	16.867	15.815	-1.646
2200	4.974	47.742	43.415	9.518	16.413	15.776	-1.567
2300	4.973	47.963	43.608	10.016	15.956	15.757	-1.497
2400	4.973	48.175	43.794	10.513	15.495	15.758	-1.435
2500	4.973	48.378	43.974	11.010	15.033	15.778	-1.379
2600	4.972	48.573	44.147	11.507	14.567	15.817	-1.330
2700	4.972	48.760	44.314	12.005	14.101	15.875	-1.285
2800	4.972	48.941	44.476	12.502	13.630	15.949	-1.245
2900	4.971	49.116	44.633	12.999	13.157	16.041	-1.209
3000	4.971	49.284	44.785	13.496	12.682	16.148	-1.176
3100	4.971	49.447	44.933	13.993	12.205	16.271	-1.147
3200	4.971	49.605	45.077	14.490	11.726	16.410	-1.121
3300	4.971	49.758	45.216	14.987	11.245	16.564	-1.097
3400	4.971	49.906	45.352	15.484	10.761	16.732	-1.076
3500	4.970	50.050	45.484	15.981	10.276	16.915	-1.056
3600	4.970	50.190	45.613	16.478	9.788	17.111	-1.039
3700	4.970	50.327	45.739	16.975	9.300	17.322	-1.023
3800	4.970	50.459	45.861	17.472	8.809	17.545	-1.009
3900	4.970	50.588	45.981	17.969	8.316	17.781	-0.996
4000	4.970	50.714	46.097	18.466	7.822	18.030	-0.985
4100	4.970	50.837	46.211	18.963	7.326	18.291	-0.975
4200	4.970	50.957	46.323	19.460	6.830	18.566	-0.966
4300	4.970	51.073	46.432	19.957	6.331	18.851	-0.958
4400	4.969	51.188	46.539	20.454	5.831	19.148	-0.951
4500	4.969	51.299	46.643	20.951	5.329	19.456	-0.945
4600	4.969	51.409	46.746	21.448	4.826	19.774	-0.939
4700	4.969	51.515	46.846	21.945	4.322	20.106	-0.935
4800	4.969	51.620	46.945	22.442	3.816	20.447	-0.931
4900	4.969	51.723	47.041	22.939	3.309	20.799	-0.928
5000	4.969	51.823	47.136	23.436	2.799	21.160	-0.925
5100	4.969	51.921	47.229	23.933	2.289	21.533	-0.923
5200	4.969	52.018	47.320	24.430	1.777	21.916	-0.921
5300	4.969	52.112	47.409	24.927	1.262	22.307	-0.920
5400	4.969	52.205	47.497	25.424	0.746	22.709	-0.919
5500	4.969	52.297	47.584	25.920	0.228	23.121	-0.919
5600	4.969	52.386	47.669	26.417	-0.291	23.542	-0.919
5700	4.969	52.474	47.752	26.914	-0.813	23.972	-0.919
5800	4.969	52.560	47.834	27.411	-1.338	24.411	-0.920
5900	4.969	52.645	47.915	27.908	-1.864	24.859	-0.921
6000	4.969	52.729	47.995	28.405	-2.394	25.317	-0.922

June 30, 1965; March 31, 1977

OXYGEN UNINEGATIVE ION (O^-) (IDEAL GAS) GFW = 15.99995

Ground State Configuration $^2P^o_{3/2}$

$S^o_{298.15}$ = 37.687 ± 0.008 gibbs/mol

ΔHf^o_0 = 25.270 ± 0.09 kcal/mol O^-

$\Delta Hf^o_{298.15}$ = 24.322 ± 0.09 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2P^o_{3/2}$	0	4
$^2P^o_{1/2}$	181	2

Heat of Formation

The heat of formation is calculated from an adopted electron affinity of O(g) of EA=1.462±0.003 eV (33.714±0.069 kcal/mol). This value has been recommended in the critical compilations by Hotop and Lineberger (1) and Rosenstock et al. (2). The former (1) has an excellent discussion on the experimental and theoretical determinations of EA(O). Additional discussion is given by Massey (4).

Heat Capacity and Entropy

The ground state and the fine-structure separation (181±4 cm^{-1}) for O^-(g) has been experimentally determined; a thorough discussion of the relevant work is given by Hotop and Lineberger (1). Massey (4) listed the hyperfine splitting of the ground state as 226 cm^{-1} based on a quadratic isoelectronic extrapolation. Use of this value would decrease the entropy at 298.15 K by 0.04 gibbs/mol. The thermodynamic functions of the negative ion are calculated using the recent CODATA fundamental constants (3) and assuming that O^-(g) is an ideal monatomic gas.

A comparison of the isoelectronic sequence - O^-(g), F(g), Ne^+(g) - would suggest that stable electronic states may exist below EA(O), i.e. below 12000 cm^{-1}. These levels would greatly affect the entropy. However, lacking any experimental evidence as to the stability of these levels, we assume no stable excited states exist.

References

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SULFUR MONOXIDE (SO) OS

(IDEAL GAS) GFW=48.0594

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	−2.087	1.200	1.200	INFINITE
100	6.956	45.365	59.288	−1.392	1.384	−0.786	1.719
200	6.995	50.192	53.671	−0.696	1.339	−2.953	3.227
298	7.212	53.020	53.020	0.000	1.197	−5.030	3.687
300	7.217	53.064	53.020	0.013	1.194	−5.069	3.693
400	7.543	55.185	53.307	0.751	0.477	−7.109	3.884
500	7.846	56.901	53.859	1.521	−0.056	−8.943	3.909
600	8.087	58.354	54.490	2.318	−0.494	−10.677	3.889
700	8.273	59.615	55.134	3.137	−0.864	−12.321	3.847
800	8.414	60.730	55.765	3.971	−14.254	−15.203	4.153
900	8.526	61.727	56.373	4.819	−14.251	−15.321	3.720
1000	8.617	62.631	56.955	5.676	−14.249	−15.440	3.374
1100	8.695	63.456	57.509	6.541	−14.245	−15.561	3.092
1200	8.765	64.215	58.036	7.414	−14.240	−15.679	2.856
1300	8.830	64.919	58.539	8.294	−14.234	−15.798	2.656
1400	8.893	65.576	59.018	9.180	−14.226	−15.920	2.485
1500	8.955	66.192	59.476	10.073	−14.217	−16.042	2.337
1600	9.017	66.772	59.914	10.971	−14.205	−16.163	2.208
1700	9.077	67.320	60.334	11.876	−14.190	−16.286	2.094
1800	9.138	67.841	60.737	12.787	−14.173	−16.410	1.992
1900	9.197	68.336	61.124	13.704	−14.154	−16.534	1.902
2000	9.256	68.810	61.496	14.626	−14.131	−16.660	1.821
2100	9.313	69.263	61.855	15.555	−14.107	−16.789	1.747
2200	9.369	69.697	62.202	16.489	−14.080	−16.915	1.680
2300	9.423	70.115	62.537	17.429	−14.052	−17.046	1.620
2400	9.474	70.517	62.861	18.373	−14.020	−17.176	1.564
2500	9.524	70.905	63.175	19.323	−13.986	−17.308	1.513
2600	9.571	71.279	63.480	20.278	−13.951	−17.462	1.466
2700	9.615	71.641	63.775	21.237	−13.914	−17.577	1.423
2800	9.657	71.992	64.063	22.201	−13.876	−17.715	1.383
2900	9.696	72.331	64.342	23.169	−13.836	−17.852	1.345
3000	9.733	72.660	64.614	24.140	−13.796	−17.990	1.311
3100	9.767	72.980	64.878	25.115	−13.754	−18.131	1.278
3200	9.798	73.291	65.136	26.093	−13.712	−18.273	1.248
3300	9.828	73.593	65.388	27.075	−13.668	−18.417	1.220
3400	9.855	73.886	65.634	28.059	−13.625	−18.560	1.193
3500	9.880	74.172	65.874	29.046	−13.582	−18.708	1.168
3600	9.902	74.451	66.108	30.035	−13.537	−18.855	1.145
3700	9.923	74.723	66.337	31.026	−13.494	−19.002	1.122
3800	9.943	74.988	66.561	32.019	−13.450	−19.152	1.101
3900	9.961	75.246	66.781	33.015	−13.406	−19.304	1.082
4000	9.977	75.499	66.996	34.011	−13.362	−19.452	1.063
4100	9.993	75.745	67.206	35.010	−13.319	−19.607	1.045
4200	10.007	75.986	67.412	36.010	−13.276	−19.759	1.028
4300	10.021	76.222	67.614	37.011	−13.233	−19.916	1.012
4400	10.035	76.452	67.813	38.014	−13.192	−20.071	0.997
4500	10.048	76.678	68.007	39.018	−13.150	−20.226	0.982
4600	10.062	76.899	68.198	40.024	−13.109	−20.386	0.969
4700	10.076	77.115	68.385	41.031	−13.068	−20.545	0.955
4800	10.090	77.328	68.570	42.039	−13.027	−20.706	0.943
4900	10.106	77.536	68.750	43.049	−12.987	−20.862	0.930
5000	10.122	77.740	68.928	44.060	−12.948	−21.026	0.919
5100	10.141	77.941	69.103	45.073	−12.908	−21.187	0.908
5200	10.161	78.138	69.275	46.088	−12.869	−21.349	0.897
5300	10.183	78.332	69.444	47.106	−12.829	−21.514	0.887
5400	10.208	78.522	69.610	48.125	−12.790	−21.676	0.877
5500	10.236	78.710	69.774	49.147	−12.749	−21.842	0.868
5600	10.267	78.895	69.935	50.173	−12.709	−22.007	0.859
5700	10.302	79.077	70.094	51.201	−12.668	−22.174	0.850
5800	10.341	79.256	70.250	52.233	−12.625	−22.341	0.842
5900	10.383	79.433	70.405	53.269	−12.581	−22.512	0.834
6000	10.431	79.608	70.556	54.310	−12.535	−22.676	0.826

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965;
June 30, 1971; July 31, 1972 (NBS); June 30, 1977

SULFUR MONOXIDE (SO) (IDEAL GAS) GFW = 48.0594

0 S

D°_0 = 123.5 ± 0.3 kcal/mol
$S^\circ_{298.15}$ = 53.020 ± 0.01 gibbs/mol
Symmetry Number = 1

ΔHf°_0 = 1.2 ± 0.3 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 1.2 ± 0.3 kcal/mol

Electronic States and Molecular Constants

State	ε, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^3\Sigma^-$	0	3	1148.19	6.12	0.72082	0.00574	1.4811
$a^1\Delta$	6350	2	[1148.19]	[6.12]	0.7119	[0.00574]	1.494
$b^1\Sigma^+$	10510	1	1067.66	7.8	0.70261	0.00635	1.5005
$A^3\Pi_0$	38292	2	415.2	1.6	0.6067	0.0194	
$A^3\Pi_1$	38455	2	413.3	1.6	0.6107	0.0194	1.6094
$A^3\Pi_2$	38616	2	412.7	1.7	0.6164	0.0204	
$B^3\Sigma^-$	41629	3	630.4	4.8	0.502	0.0062	1.775
$C^3\Pi$	42200	6	170	[0]	[0.5]	[0]	2.2

Heat of Formation

The selection for ΔHf°_0 of SO(g), 1.2±0.3 kcal/mol, was derived from one of the two independent means, pointed out by Okabe (1), that employs principally spectroscopic data: $\Delta Hf^\circ_0(SO,g) = 1/2\ D^\circ_0(S_2) + 1/2\ D^\circ_0(O_2) - D^\circ_0(SO) + 1/2\ \Delta Hf^\circ_0(S_2,g)$. The data employed are as follows. Ricks and Barrow (2) give $D^\circ_0(S_2)$ = 100.69±0.01 kcal/mol. Brix and Herzberg (3) give $D^\circ_0(O_2)$ = 117.97±0.046 kcal/mol. On the basis of analysis of spectroscopic data to 1964, JANAF (4) gives $D^\circ_0(SO)$ = 123.5±0.3 kcal/mol. NBS (5) gives $\Delta Hf^\circ_0(S_2,g)$ = 30.65±0.2 kcal/mol. Assuming the dissociation products of SO are $S(^1D_2)$ and $O(^3P)$, Colin (6), concludes $D^\circ_0(SO)$ = 123.56±0.23 kcal/mol. A systematic error of 0.65 kcal/mol is incurred if the assumption is wrong. Support for this assumption is as follows: 1) Okabe (7) concludes that $D^\circ_0(OS-O)$ = 130.06±0.5 kcal/mol assuming the predissociation of SO_2 is to ground state products. Using $\Delta Hf^\circ_0(SO_2,g)$ = −70.336 kcal/mol from (5) and the relation: $\Delta Hf^\circ_0(SO,g) = D^\circ_0(OS-O) - 1/2\ D^\circ_0(O_2) + \Delta Hf^\circ_0(SO_2,g)$, one obtains $\Delta Hf^\circ_0(SO,g)$ = 0.7±0.7 kcal/mol; 2) Assuming the threshold energy for fluorescence of SO, 217.00±0.7 kcal/mol (see Okabe (8)), corresponds to the minimum energy for the reaction $OSCl_2 = SO(A^3\Pi_0) + 2\ Cl(^3P_{3/2})$ and using 108.43 kcal/mol for the difference in energy between the lowest vibrational levels of $SO(A^3\Pi_0)$ and $SO(X^3\Sigma^-)$ (Colin (6)) one obtains $\Delta Hf^\circ_0(SO,g)$ = 1.3±0.7 kcal/mol. This is based on $\Delta Hf^\circ_0(OSCl_2,g)$ = −50.07 kcal/mol (5) and $D^\circ_0(Cl_2)$ = 57.177±0.005 kcal/mol given by Douglas et al. (9); 3) Re-examination of the photoionization-yield curves of SO_2^+ and SO^+ obtained by Dibeler and Liston (10) suggests that their reported threshold for $SO \rightarrow SO^+ + O + e^-$ should be increased from 15.81±0.02 eV to 16.00 eV. Using the latter and the ionization energy of SO given by Jonathan et al. (11) of 10.34±0.02 eV and the relation $\Delta Hf^\circ_0(SO,g) = D^\circ_0(OS-O) - 1/2\ D^\circ_0(O_2) + \Delta Hf^\circ_0(SO_2,g)$, one obtains $\Delta Hf^\circ_0(SO,g)$ = 1.20±0.5 kcal/mol.

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen (12). The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2 \varepsilon_i/T)$. The National Bureau of Standards prepared this table (13) by critical analysis of data existing in 1972. Using molecular constants and ΔHf° selected by NBS (13), we recalculate the table in terms of 1973 fundamental constants (14), 1975 atomic weights (15), and current JANAF reference states for the elements.

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OXYGEN, DIATOMIC (O_2)
(REFERENCE STATE - IDEAL GAS) GFW=31.9988

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.075	0.000	0.000	0.000
100	6.956	41.395	55.206	-1.381	0.000	0.000	0.000
200	6.961	46.218	49.645	-0.685	0.000	0.000	0.000
298	7.021	49.005	49.005	0.000	0.000	0.000	0.000
300	7.023	49.049	49.005	0.013	0.000	0.000	0.000
400	7.196	51.090	49.283	0.723	0.000	0.000	0.000
500	7.431	52.721	49.812	1.454	0.000	0.000	0.000
600	7.670	54.097	50.415	2.209	0.000	0.000	0.000
700	7.883	55.296	51.028	2.987	0.000	0.000	0.000
800	8.062	56.360	51.629	3.785	0.000	0.000	0.000
900	8.211	57.319	52.209	4.599	0.000	0.000	0.000
1000	8.334	58.190	52.764	5.426	0.000	0.000	0.000
1100	8.437	58.990	53.294	6.265	0.000	0.000	0.000
1200	8.525	59.728	53.800	7.113	0.000	0.000	0.000
1300	8.601	60.413	54.283	7.969	0.000	0.000	0.000
1400	8.670	61.053	54.744	8.833	0.000	0.000	0.000
1500	8.734	61.653	55.185	9.703	0.000	0.000	0.000
1600	8.795	62.219	55.607	10.580	0.000	0.000	0.000
1700	8.853	62.754	56.012	11.462	0.000	0.000	0.000
1800	8.909	63.262	56.400	12.350	0.000	0.000	0.000
1900	8.965	63.745	56.774	13.244	0.000	0.000	0.000
2000	9.020	64.206	57.134	14.143	0.000	0.000	0.000
2100	9.075	64.648	57.482	15.048	0.000	0.000	0.000
2200	9.129	65.071	57.817	15.958	0.000	0.000	0.000
2300	9.182	65.478	58.141	16.874	0.000	0.000	0.000
2400	9.235	65.870	58.455	17.795	0.000	0.000	0.000
2500	9.287	66.248	58.760	18.721	0.000	0.000	0.000
2600	9.337	66.613	59.055	19.652	0.000	0.000	0.000
2700	9.387	66.966	59.341	20.588	0.000	0.000	0.000
2800	9.435	67.309	59.620	21.529	0.000	0.000	0.000
2900	9.482	67.641	59.891	22.475	0.000	0.000	0.000
3000	9.528	67.963	60.154	23.426	0.000	0.000	0.000
3100	9.572	68.276	60.411	24.381	0.000	0.000	0.000
3200	9.614	68.581	60.662	25.340	0.000	0.000	0.000
3300	9.655	68.877	60.906	26.303	0.000	0.000	0.000
3400	9.694	69.166	61.145	27.271	0.000	0.000	0.000
3500	9.731	69.447	61.378	28.242	0.000	0.000	0.000
3600	9.768	69.722	61.606	29.217	0.000	0.000	0.000
3700	9.802	69.990	61.829	30.196	0.000	0.000	0.000
3800	9.836	70.252	62.047	31.178	0.000	0.000	0.000
3900	9.868	70.508	62.261	32.163	0.000	0.000	0.000
4000	9.900	70.758	62.470	33.151	0.000	0.000	0.000
4100	9.930	71.003	62.675	34.143	0.000	0.000	0.000
4200	9.960	71.243	62.877	35.137	0.000	0.000	0.000
4300	9.990	71.477	63.074	36.135	0.000	0.000	0.000
4400	10.019	71.707	63.267	37.135	0.000	0.000	0.000
4500	10.048	71.933	63.458	38.138	0.000	0.000	0.000
4600	10.077	72.154	63.644	39.145	0.000	0.000	0.000
4700	10.107	72.371	63.828	40.154	0.000	0.000	0.000
4800	10.137	72.584	64.008	41.166	0.000	0.000	0.000
4900	10.168	72.793	64.185	42.181	0.000	0.000	0.000
5000	10.200	72.999	64.359	43.200	0.000	0.000	0.000
5100	10.232	73.201	64.531	44.221	0.000	0.000	0.000
5200	10.267	73.401	64.699	45.246	0.000	0.000	0.000
5300	10.302	73.596	64.865	46.275	0.000	0.000	0.000
5400	10.340	73.789	65.029	47.307	0.000	0.000	0.000
5500	10.379	73.979	65.190	48.343	0.000	0.000	0.000
5600	10.420	74.167	65.348	49.383	0.000	0.000	0.000
5700	10.464	74.352	65.505	50.427	0.000	0.000	0.000
5800	10.510	74.534	65.659	51.476	0.000	0.000	0.000
5900	10.558	74.714	65.811	52.529	0.000	0.000	0.000
6000	10.609	74.892	65.961	53.587	0.000	0.000	0.000

Dec. 31, 1960; March 31, 1961; Sept. 30, 1965;
March 31, 1977

OXYGEN, DIATOMIC (O_2) (REFERENCE STATE - IDEAL GAS) GFW = 31.9988

0 to 6000 K Ideal Gas

D_0^o = 117.968 ± 0.043 kcal/mol
$S^o_{298.15}$ = 49.005 ± 0.008 gibbs/mol
Symmetry Number = 2

ΔHf_0^o = 0 kcal/mol
$\Delta Hf^o_{298.15}$ = 0 kcal/mol

Electronic and Molecular Constants

State	g_i	T_o, cm^{-1}	ω_e, cm^{-1}	Vibrational Anharmonicity, cm^{-1}	B_e, cm^{-1}	α_i, cm^{-1}	D_e, cm^{-1}	β_i, cm^{-1}
X $^3\Sigma_g^-$	3	0	1580.1932	ω_ex_e 11.980804 ω_ey_e 0.047474736 ω_ez_e -1.272748×10^{-3}	1.445622	0.01593268 6.406456×10^{-5} -2.846158×10^{-6}		
a $^1\Delta_g$	2	7882.39	[1509.3]	ω_ex_e [12.9]	1.4263	0.0171	[4.97×10^{-6}]	
b $^1\Sigma_g^+$	1	13120.9085	1432.6661	ω_ex_e 13.9336 ω_ey_e -0.0143	1.4004796	0.018169303 -4.294192×10^{-5}	5.356×10^{-6}	0.077×10^{-6}
c $^1\Sigma_u^-$	1	32664.1	794.29	ω_ex_e 12.736 ω_ey_e -0.2444 ω_ez_e 0.00055	0.9155	0.01391 -0.000740	[10.5×10^{-6}]	
C $^3\Delta_{ui}$	6	34319	[750]	ω_ex_e [14]	[0.91]	[0.014]		
A $^3\Sigma_u^+$	3	35007.15	799.08	ω_ex_e 12.16 ω_ey_e -0.550	0.91053	0.02416 -0.00097	4.79×10^{-6}	-0.30×10^{-6} 0.10×10^{-6}
B $^3\Sigma_u^-$	3	49358.15	709.05770	ω_ex_e 10.614080 ω_ey_e -0.059212435 ω_ez_e -0.023974994	0.818975	0.0119225 -6.30472×10^{-4}		

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The thermal functions are calculated using the program of McBride and Gordon (1). The contributions of vibrational anharmonicity, rotation-vibration interaction, and centrifugal stretching are calculated via the procedures given by Pennington and Kobe (3). In this procedure the energy levels are calculated as follows: $\varepsilon_i = T_o + G(v) - G(o) + B_v J(J+1) - D_v J^2(J+1)^2$ where $G(v) = \omega_e(v+1/2) - \omega_ex_e(v+1/2)^2 + \omega_ey_e(v+1/2)^3 + \omega_ez_e(v+1/2)^4$ and $B_v = B_e - \alpha_1(v+1/2) + \alpha_2(v+1/2)^2 + \alpha_3(v+1/2)^3$ and $D_v = D_e + \Sigma_i\, \beta_i(v+1/2)^i$. Where a value of D_e is not available it is calculated to be $D_e = 4B_e^3/\omega_e^2$.

Molecular constant data in the table above is from Krupenie (2) with the exception of B_e and α_1 for the C $^3\Delta_{ui}$ state which we have estimated by analogy with neighboring states of the same electron configuration. Electronic levels above 50,000 cm^{-1} given by Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K.

The value of S^o_{298} agrees exactly with the CODATA recommended value (4). It also agrees with the values of McBride et al. (5) and Gurvich et al. (6) within the stated uncertainty. The uncertainty in S^o_{298} is due to uncertainties in fundamental constants (particularly the gas constant), the atomic weight, and the ground state molecular constants. At high temperatures, further uncertainties arise from excited state molecular constants and approximate procedures used to account for higher vibrational-rotational levels of all states. Despite these increased uncertainties our values of S° are within 0.016 (6000 K) and 0.035 (5000 K) gibbs/mol of those calculated by superior methods (5, 6) using older molecular constants.

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OXYGEN, DIATOMIC UNIPOSITIVE ION (O_2^+) O_2^+

(IDEAL GAS) GFW=31.99825

T, K	$C_p°$	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0				-2.073	278.370		
100							
200							
298	6.978	49.260	49.260	0.000	279.849	278.286	-203.986
300	6.979	49.304	49.261	0.013	279.858	278.276	-202.721
400	7.068	51.322	49.535	0.715	280.347	277.675	-151.713
500	7.230	52.915	50.057	1.429	280.827	276.952	-121.054
600	7.428	54.250	50.648	2.162	281.302	276.133	-100.580
700	7.628	55.411	51.247	2.915	281.773	275.233	-85.930
800	7.812	56.441	51.833	3.687	282.244	274.266	-74.925
900	7.974	57.371	52.397	4.476	282.717	273.240	-66.351
1000	8.113	58.219	52.938	5.281	283.191	272.163	-59.480
1100	8.231	58.998	53.454	6.098	283.666	271.037	-53.849
1200	8.332	59.718	53.946	6.927	284.143	269.867	-49.149
1300	8.417	60.389	54.416	7.764	284.621	268.659	-45.165
1400	8.490	61.015	54.866	8.609	285.100	267.413	-41.744
1500	8.553	61.603	55.295	9.462	285.579	266.133	-38.775
1600	8.607	62.157	55.707	10.320	286.057	264.821	-36.172
1700	8.654	62.680	56.102	11.183	286.534	263.479	-33.872
1800	8.696	63.176	56.481	12.050	287.011	262.109	-31.824
1900	8.733	63.647	56.846	12.922	287.485	260.712	-29.988
2000	8.765	64.096	57.197	13.797	287.958	259.291	-28.334
2100	8.795	64.524	57.536	14.675	288.428	257.847	-26.834
2200	8.821	64.934	57.863	15.556	288.895	256.379	-25.469
2300	8.845	65.327	58.179	16.439	289.359	254.890	-24.220
2400	8.867	65.704	58.485	17.325	289.821	253.382	-23.073
2500	8.888	66.066	58.781	18.212	290.280	251.854	-22.017
2600	8.906	66.415	59.068	19.102	290.735	250.308	-21.040
2700	8.923	66.751	59.346	19.994	291.187	248.744	-20.134
2800	8.940	67.076	59.617	20.887	291.636	247.165	-19.292
2900	8.955	67.390	59.879	21.781	292.082	245.569	-18.506
3000	8.969	67.694	60.135	22.678	292.524	243.957	-17.772
3100	8.983	67.988	60.383	23.575	292.963	242.331	-17.084
3200	8.996	68.274	60.626	24.474	293.399	240.690	-16.438
3300	9.008	68.551	60.862	25.374	293.834	239.037	-15.831
3400	9.020	68.820	61.092	26.276	294.264	237.370	-15.258
3500	9.032	69.081	61.316	27.178	294.693	235.690	-14.717
3600	9.044	69.336	61.535	28.082	295.118	233.999	-14.205
3700	9.055	69.584	61.750	28.987	295.540	232.294	-13.721
3800	9.067	69.826	61.959	29.893	295.961	230.579	-13.261
3900	9.079	70.061	62.164	30.800	296.381	228.853	-12.824
4000	9.091	70.291	62.364	31.709	296.798	227.117	-12.409
4100	9.103	70.516	62.560	32.619	297.213	225.370	-12.013
4200	9.116	70.735	62.752	33.530	297.626	223.612	-11.636
4300	9.130	70.950	62.940	34.442	298.037	221.845	-11.275
4400	9.144	71.160	63.125	35.355	298.448	220.069	-10.931
4500	9.159	71.366	63.306	36.271	298.857	218.284	-10.601
4600	9.175	71.567	63.483	37.187	299.264	216.488	-10.285
4700	9.193	71.765	63.657	38.106	299.669	214.683	-9.983
4800	9.211	71.959	63.828	39.026	300.074	212.871	-9.692
4900	9.231	72.149	63.996	39.948	300.478	211.051	-9.413
5000	9.252	72.335	64.161	40.872	300.880	209.221	-9.145
5100	9.275	72.519	64.323	41.798	301.282	207.384	-8.887
5200	9.300	72.699	64.482	42.727	301.682	205.539	-8.638
5300	9.326	72.877	64.639	43.658	302.082	203.686	-8.399
5400	9.354	73.051	64.793	44.592	302.481	201.826	-8.168
5500	9.385	73.223	64.945	45.529	302.879	199.959	-7.946
5600	9.417	73.392	65.094	46.469	303.275	198.082	-7.730
5700	9.451	73.559	65.241	47.413	303.671	196.202	-7.523
5800	9.488	73.724	65.386	48.360	304.066	194.312	-7.322
5900	9.527	73.887	65.529	49.311	304.461	192.417	-7.127
6000	9.569	74.047	65.670	50.265	304.855	190.516	-6.939

Sept. 30, 1977

OXYGEN DIATOMIC UNIPOSITIVE ION (O_2^+) (IDEAL GAS) GFW = 31.99825

Symmetry Number = 2

$S°_{298.15}$ = 49.26 ± 0.2 gibbs/mol

$\Delta Hf°_0$ = 278.37 ± 0.2 kcal/mol

$\Delta Hf°_{298.15}$ = [279.849] kcal/mol

O_2^+

Electronic and Molecular Constants

State	g_i	T_o, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_g$	4	0	1905.13	16.2818	1.68912	0.0195769	1.117123
$a^4\Pi_{ui}$	8	32524	1035.534	10.32194	1.104320	0.01545646	1.31816042
$A^2\Pi_u$	4	40070	898.17	13.568	1.06297	0.205830	1.408220
$b^4\Sigma_g^-$	4	49191	1196.913	17.13456	1.287297	0.02206747	1.2796516

Heat of Formation

The adopted value for the heat of formation of $O_2^+(g)$, $\Delta Hf°_0$ = 278.37±0.2 kcal/mol is that recommended in a critical review on the energetics of gaseous ions by Rosenstock et al. (1). This value is derived from ionization potentials determined in the photoelectron spectrum of O_2 by Edqvist et al. (2), the IP values are 12.071±0.005 ev for the $X^2\Pi_{3/2g}$ state and 12.095±0.005 ev for the $X^2\Pi_{1/2g}$ state. The $\Delta Hf°_0$ value is converted to a $\Delta Hf°_{298}$ value for $O_2^+(g)$ by including enthalpy differences ($H°_0 - H°_{298}$) for $O_2^+(g)$, $O_2(g)$ and $e^-(g)$. $\Delta Hf°_{298}$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (1). $\Delta Hf°_{298}$ should be changed by -1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic and molecular constants are from the critical review of Krupenie (3). Electronic levels above 50000 cm^{-1} given by Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$. Use of the program of McBride and Gordon (4) yields the same results.

The ground state is taken to be $^2\Pi_{3/2g}$ with a separation of the ground state doublet levels of ∿200 cm^{-1}. The hypothetical $^2\Pi$ state without spin-orbit splitting would be 100 cm^{-1} higher (3). Such a shift of the electronic energy levels does not significantly alter the thermal functions. The main source of error in the $S°_{298}$ value lies in the neglect of a more exact treatment of the splitting of the $X^2\Pi$ ground state.

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O_2^+

OXYGEN, DIATOMIC UNINEGATIVE ION (O_2^-) O_2^-

(IDEAL GAS) GFW=31.99935

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0				-2.092	-10.150		
100							
200							
298	7.279	50.064	50.064	0.000	-11.614	-10.443	7.655
300	7.285	50.109	50.064	0.013	-11.623	-10.435	7.602
400	7.639	52.254	50.354	0.760	-12.083	-9.970	5.447
500	7.950	53.993	50.913	1.540	-12.531	-9.389	4.104
600	8.191	55.465	51.552	2.347	-12.976	-8.719	3.176
700	8.373	56.742	52.204	3.176	-13.421	-7.974	2.490
800	8.511	57.869	52.843	4.020	-13.872	-7.166	1.958
900	8.617	58.878	53.459	4.877	-14.326	-6.300	1.530
1000	8.701	59.790	54.047	5.743	-14.784	-5.384	1.177
1100	8.769	60.623	54.608	6.617	-15.246	-4.422	0.879
1200	8.825	61.388	55.141	7.497	-15.711	-3.417	0.622
1300	8.873	62.097	55.649	8.382	-16.179	-2.373	0.399
1400	8.913	62.756	56.134	9.271	-16.650	-1.294	0.202
1500	8.949	63.372	56.596	10.164	-17.124	-0.181	0.026
1600	8.980	63.951	57.038	11.061	-17.602	0.964	-0.132
1700	9.008	64.496	57.461	11.960	-18.080	2.140	-0.275
1800	9.034	65.011	57.864	12.862	-18.563	3.343	-0.406
1900	9.058	65.501	58.255	13.767	-19.050	4.573	-0.526
2000	9.080	65.966	58.629	14.674	-19.539	5.829	-0.637
2100	9.100	66.409	58.989	15.583	-20.032	7.109	-0.740
2200	9.120	66.833	59.336	16.494	-20.527	8.414	-0.836
2300	9.139	67.239	59.671	17.407	-21.027	9.740	-0.926
2400	9.157	67.628	59.994	18.321	-21.530	11.088	-1.010
2500	9.175	68.002	60.307	19.238	-22.036	12.458	-1.089
2600	9.192	68.362	60.610	20.156	-22.546	13.847	-1.164
2700	9.209	68.710	60.904	21.074	-23.058	15.258	-1.235
2800	9.226	69.045	61.188	21.998	-23.574	16.686	-1.302
2900	9.243	69.369	61.465	22.921	-24.094	18.133	-1.367
3000	9.260	69.683	61.734	23.846	-24.617	19.597	-1.428
3100	9.277	69.986	61.995	24.773	-25.142	21.080	-1.486
3200	9.294	70.281	62.249	25.702	-25.668	22.580	-1.542
3300	9.312	70.568	62.497	26.632	-26.198	24.097	-1.596
3400	9.331	70.846	62.739	27.564	-26.731	25.628	-1.647
3500	9.350	71.117	62.974	28.498	-27.265	27.175	-1.697
3600	9.369	71.380	63.204	29.434	-27.801	28.739	-1.745
3700	9.389	71.637	63.428	30.372	-28.338	30.317	-1.791
3800	9.410	71.888	63.648	31.312	-28.877	31.909	-1.835
3900	9.432	72.133	63.862	32.254	-29.417	33.515	-1.878
4000	9.454	72.372	64.072	33.199	-29.958	35.136	-1.920
4100	9.477	72.605	64.277	34.145	-30.500	36.770	-1.960
4200	9.501	72.834	64.478	35.094	-31.041	38.418	-1.999
4300	9.526	73.058	64.675	36.045	-31.585	40.078	-2.037
4400	9.552	73.277	64.868	36.999	-32.128	41.751	-2.074
4500	9.578	73.492	65.058	37.956	-32.672	43.436	-2.110
4600	9.606	73.703	65.243	38.915	-33.216	45.132	-2.144
4700	9.634	73.910	65.425	39.877	-33.759	46.843	-2.178
4800	9.663	74.113	65.604	40.842	-34.304	48.564	-2.211
4900	9.693	74.313	65.780	41.809	-34.848	50.295	-2.243
5000	9.724	74.509	65.953	42.780	-35.393	52.038	-2.275
5100	9.755	74.701	66.122	43.754	-35.936	53.793	-2.305
5200	9.787	74.891	66.289	44.731	-36.481	55.558	-2.335
5300	9.820	75.078	66.453	45.712	-37.027	57.331	-2.364
5400	9.854	75.262	66.615	46.695	-37.572	59.127	-2.393
5500	9.889	75.443	66.773	47.682	-38.118	60.913	-2.420
5600	9.924	75.621	66.930	48.673	-38.663	62.719	-2.448
5700	9.959	75.797	67.084	49.667	-39.210	64.534	-2.474
5800	9.995	75.971	67.236	50.665	-39.758	66.358	-2.500
5900	10.032	76.142	67.385	51.666	-40.307	68.192	-2.526
6000	10.069	76.311	67.532	52.671	-40.857	70.036	-2.551

Sept. 30, 1966; Dec. 31, 1966; Sept. 30, 1977

OXYGEN, DIATOMIC UNINEGATIVE ION (O_2^-) (IDEAL GAS) GFW = 31.99935

D_0° = 94.4 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 50.064 ± 0.2 gibbs/mol

ΔH_0° = -10.15 ± 0.18 kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-11.614] kcal/mol

O_2^-

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^2\Pi_g$	0	4

ω_e = 1089 ± 40 cm^{-1}

B_e = 1.17 ± 0.02 cm^{-1}

$\omega_e x_e$ = 12.1 ± 1.6 cm^{-1}

α_e = [0.017] cm^{-1}

σ = 2

r_e = 1.341 ± 0.010 Å

Heat of Formation

The heat of formation at 0 K for $O_2^-(g)$ is based on the electron affinity (EA) value derived from a thorough analysis of the laser photodetachment measurements of Celotta et al. (1). This study led to EA(O_2) = 0.440±0.008 eV. Using auxiliary data (2), we calculate $\Delta Hf_0^\circ(O_2^-,g)$ = 10.15±0.18 kcal/mol and $D_0^\circ(O_2^-)$ = 94.4±0.3 kcal/mol; the latter value assumes dissociation into ground state O(g) and $O^-(g)$. The adopted EA(O_2) value is also recommended by Rosenstock et al. (3) and Massey (4). Both of these latter studies have reviewed and summarized earlier work from which EA values could be derived.

ΔHf_0° is converted to ΔHf°_{298} by use of JANAF (2) enthalpies ($H_0^\circ - H^\circ_{298}$) for $O_2(g)$, $O_2^-(g)$, and $e^-(g)$. ΔHf°_{298} should not be interpreted as a room-temperature electron affinity due to inclusion of these enthalpies and threshold effects discussed by Rosenstock et al. (3). ΔHf°_{298} should be changed by +1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The laser photodetachment study of Celotta et al. (1) which yielded a precise value for EA(O_2) also yielded precise values for r_e and B_e as well as values for ω_e and $\omega_e x_e$. We adopt these values and calculate α_e assuming a Morse function for the ground state. Support for these values comes from recent studies based on total scattering cross section (5) and differential elastic cross section (6, 7). Other (earlier) studies yielding vibrational information are discussed by Krupenie (8). The recent ab initio study by Das et al. (11) suggests slightly differant vibrational-rotational constants (ω_e = 1098, $\omega_e x_e$ = 9.04, B_e = 1.135, and α_e = 0.0151 cm^{-1}).

The ground and excited electronic states are discussed by Krupenie (8), Massey (4), and Das et al. (11). The approximate theoretical potential energy diagram given by Krupenie (8) suggests a $^2\Pi_g$ ground state with three rather low lying excited states: $^4\Sigma_u^-$ at ∿21000 cm^{-1}, $^2\Pi_u$ at ∿28500 cm^{-1}, and $^2\Sigma_u^-$ at ∿32300 cm^{-1}. The ab initio study by Das et al. (11) suggests the same ordering of the levels at 19833 cm^{-1}, 27213 cm^{-1}, and 30076 cm^{-1}. The fluorescence observed by Rolfe (9) was assigned as $^2\Pi_{ui} \rightarrow X^2\Pi_{gi}$, but an upper state assignment of $^2\Sigma_u^-$ cannot be ruled out (8). This study indicated that the presumed $^2\Pi_{ui}$ state lies at 29400 cm^{-1} (which we adopt), in good agreement with the calculated potential energy diagram. Hurst and Bortner (10) obtained evidence of excitation to an electronic state of O_2^- (presumably $^4\Sigma_u^-$) which lies approximately 1 eV above the ground state. The potential energy diagrams given by Krupenie (8) and Das et al. (11) suggest this level is significantly higher. The position of this level will not significantly affect the entropy values.

The three excited states are predicted to be quite shallow (binding energies ∿ 1 eV) as compared to the ground state. The inclusion in our calculation of such states, with the use of appropriate vibrational-rotational constants as given by Das et al. (11) would lead to erroneous heat capacity values above 3000 K. The proper inclusion of these three excited states would require a direct summation technique with rotational cutoff.

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O_2^-

SULFUR (S)

S

(REFERENCE STATE) GFW=32.06

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.054	0.000	0.000	0.000
100	3.052	2.992	11.888	-0.890	0.000	0.000	0.000
200	4.629	5.649	8.135	-0.497	0.000	0.000	0.000
298	5.425	7.661	7.661	0.000	0.000	0.000	0.000
300	5.436	7.695	7.661	0.010	0.000	0.000	0.000
400	7.687	10.709	7.933	1.110	0.000	0.000	0.000
500	9.079	12.797	8.700	2.049	0.000	0.000	0.000
600	8.200	14.361	9.519	2.905	0.000	0.000	0.000
700	7.811	15.595	10.302	3.705	0.000	0.000	0.000
800	4.378	31.363	9.533	17.465	0.000	0.000	0.000
900	4.417	31.881	11.988	17.904	0.000	0.000	0.000
1000	4.455	32.349	14.001	18.348	0.000	0.000	0.000
1100	4.491	32.775	15.688	18.795	0.000	0.000	0.000
1200	4.528	33.167	17.129	19.246	0.000	0.000	0.000
1300	4.566	33.531	18.377	19.701	0.000	0.000	0.000
1400	4.603	33.871	19.471	20.159	0.000	0.000	0.000
1500	4.639	34.190	20.442	20.621	0.000	0.000	0.000
1600	4.674	34.490	21.311	21.087	0.000	0.000	0.000
1700	4.708	34.775	22.095	21.556	0.000	0.000	0.000
1800	4.740	35.045	22.807	22.029	0.000	0.000	0.000
1900	4.769	35.302	23.457	22.504	0.000	0.000	0.000
2000	4.797	35.547	24.056	22.982	0.000	0.000	0.000
2100	4.822	35.782	24.609	23.463	0.000	0.000	0.000
2200	4.846	36.007	25.122	23.947	0.000	0.000	0.000
2300	4.867	36.223	25.600	24.432	0.000	0.000	0.000
2400	4.887	36.430	26.047	24.920	0.000	0.000	0.000
2500	4.906	36.630	26.466	25.410	0.000	0.000	0.000
2600	4.921	36.823	26.861	25.901	0.000	0.000	0.000
2700	4.935	37.009	27.233	26.394	0.000	0.000	0.000
2800	4.949	37.188	27.585	26.888	0.000	0.000	0.000
2900	4.962	37.362	27.920	27.384	0.000	0.000	0.000
3000	4.974	37.531	28.237	27.881	0.000	0.000	0.000
3100	4.985	37.694	28.540	28.379	0.000	0.000	0.000
3200	4.995	37.852	28.828	28.878	0.000	0.000	0.000
3300	5.005	38.006	29.104	29.378	0.000	0.000	0.000
3400	5.015	38.156	29.368	29.879	0.000	0.000	0.000
3500	5.025	38.301	29.621	30.381	0.000	0.000	0.000
3600	5.035	38.443	29.864	30.884	0.000	0.000	0.000
3700	5.045	38.581	30.098	31.388	0.000	0.000	0.000
3800	5.055	38.716	30.323	31.893	0.000	0.000	0.000
3900	5.065	38.847	30.540	32.399	0.000	0.000	0.000
4000	5.077	38.976	30.749	32.906	0.000	0.000	0.000
4100	5.088	39.101	30.951	33.414	0.000	0.000	0.000
4200	5.100	39.224	31.147	33.923	0.000	0.000	0.000
4300	5.112	39.344	31.336	34.434	0.000	0.000	0.000
4400	5.125	39.462	31.519	34.946	0.000	0.000	0.000
4500	5.138	39.577	31.697	35.459	0.000	0.000	0.000
4600	5.152	39.690	31.870	35.973	0.000	0.000	0.000
4700	5.167	39.801	32.037	36.489	0.000	0.000	0.000
4800	5.182	39.910	32.200	37.007	0.000	0.000	0.000
4900	5.197	40.017	32.359	37.526	0.000	0.000	0.000
5000	5.213	40.122	32.513	38.046	0.000	0.000	0.000
5100	5.229	40.226	32.663	38.568	0.000	0.000	0.000
5200	5.246	40.327	32.810	39.092	0.000	0.000	0.000
5300	5.263	40.427	32.952	39.617	0.000	0.000	0.000
5400	5.280	40.526	33.092	40.145	0.000	0.000	0.000
5500	5.297	40.623	33.228	40.673	0.000	0.000	0.000
5600	5.314	40.719	33.361	41.204	0.000	0.000	0.000
5700	5.332	40.813	33.491	41.736	0.000	0.000	0.000
5800	5.350	40.906	33.618	42.270	0.000	0.000	0.000
5900	5.368	40.997	33.742	42.806	0.000	0.000	0.000
6000	5.387	41.088	33.864	43.344	0.000	0.000	0.000

Dec. 31, 1960; Mar. 31, 1961
Dec. 31, 1965; Sept. 30, 1977

S

0	to 368.3 K	Crystal, orthorhombic
368.3	to 388.36 K	Crystal, monoclinic
388.36	to 717.824 K	Liquid
432.02 K		Lambda point
717.824	to 6000 K	Ideal gas, diatomic

The normal boiling point of sulfur, 717.824 K, is a secondary standard on the International Practical Temperature Scale of 1968. The vapor composition at this temperature is a mixture of eight distinct sulfur species, the predominant species being $S_8(g)$, $S_7(g)$, and $S_6(g)$. In our reference state for sulfur, we have adopted T_b = 717.824 K and we have arbitrarily chosen 0.5 $S_2(g)$ to be the gas phase species. This yields $\Delta Hf^\circ_T = \Delta Gf^\circ_T = 0$ for $S_2(g)$ at all $T \geq 717.824$ K. The partial pressure of $S_2(g)$ at T_b is 0.034 atm.

See crystal, liquid and diatomic gas tables for details.

S

SULFUR, ORTHORHOMBIC (S)
(CRYSTAL) GFW=32.06

S

	gibbs/mol			kcal/mol			
T, K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.054	0.000	0.000	0.000
100	3.052	2.992	11.888	-0.890	0.000	0.000	0.000
200	4.629	5.649	8.135	-0.497	0.000	0.000	0.000
298	5.425	7.661	7.661	0.000	0.000	0.000	0.000
300	5.436	7.695	7.661	0.010	0.000	0.000	0.000
400	5.950	9.331	7.881	0.580	-0.530	0.021	-0.012
500	6.440	10.712	8.312	1.200	-0.849	0.193	-0.084
600	6.930	11.929	8.815	1.868	-1.037	0.422	-0.154
700	7.420	13.034	9.340	2.586	-1.119	0.673	-0.210
800	7.910	14.057	9.867	3.352	-14.113	-0.268	0.073

Dec. 31, 1960; Dec. 31, 1965; Sept. 30, 1977

SULFUR, ORTHORHOMBIC (S) (CRYSTAL) GFW = 32.06

S

$S^\circ_{298.15}$ = 7.661 ± 0.012 gibbs/mol
T_t = 368.3 ± 0.3 K (α-β)

ΔHf°_0 = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol
ΔH°_t = 0.0957 ± 0.0007 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 15.35 ± 0.04 kcal/mol
Sublimation: S(c,α) = 0.5 S_2(g)

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Experimentally determined heat capacity values for orthorhombic (α) sulfur have been reported by Nernst (1, 23-202 K), Eastman and McGavock (2, 12.68-365.60 K), West (3, 298-368 K), Mal'tsev and Demidenko (4, 53-305 K), Finke (5, 12-432 K), Montgomery (6, 12.34-360.99 K), and Paukov (7). The thermochemical functions tabulated by Hultgren et al. (8) are based primarily on the work of Eastman and McGavock (2) and unpublished work of Finke (5), the latter presumably being the preliminary results of Montgomery (6). The tentative values reported by CODATA (9) for S°_{298} and ($H^\circ_{298.15}-H^\circ_0$) are based on Eastman and McGavock (2), Montgomery (6), and Paukov (7).

We adopt the heat capacity values tabulated (in 10 K increments) by Montgomery (6). Using S°_{10} = 0.036 cal/(mol K) and integrating the heat capacity values, we calculate S°_{298} = 7.661 cal/(mol K), in agreement with CODATA (9). The heat capacity values above T_t = 368.3 K are obtained by linear extrapolation of the tabulated values (6) above 340 K.

The various heat capacity studies are in reasonably good agreement. The values recommended by Eastman and McGavock (2), West (3), and Mal'tsev and Demidenko (4) agree with Montgomery (6) to within 0.5% except for the ranges 15-50 K (2) and 53-80 K (3). The smoothed value at 190 K reported by Mal'tsev and Demidenko (4) is undoubtedly a typographical error. The selected values of Hultgren et al. (8) agree within 0.5% with the data of Montgomery (6) except below 35 K.

Phase Data

The orthorhomic-monoclinic (α-β) phase change has been studied by many workers. An excellent review by Meyer (10) summarizes these studies. We adopt the results obtained by Montgomery (6) via adiabatic calorimetry: T_t = 368.3±0.3 K and ΔH°_t = 0.0957±0.0007 kcal/mol. The only other precise study reported in the literature is that of West (3) who obtained ΔH°_t = 0.0960±0.0005 kcal/mol by adiabatic calorimetry. Other drop calorimetric (11, 12) and vapor pressure (13, 14) studies are much less precise with an uncertainty of ±5 cal/mol or greater.

Sublimation Data

Since the reference state of sulfur involves 0.5 S_2(g) rather than S(g), we define the heat of sublimation (at 298.15 K) of orthorhombic sulfur as the process S(c,α) = 0.5 S_2(g). Thus the heat of sublimation of orthorhombic sulfur is one-half the heat of formation of S_2(g). Since the dominant gaseous sulfur species at room temperature is actually S_8(g), the heat of sublimation to the equilibrium gas is significantly smaller.

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SULFUR, MONOCLINIC (S) S

(CRYSTAL) GFW=32.06

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.081	0.059	0.059	INFINITE
100	3.077	3.098	12.241	-0.914	0.062	0.052	-0.113
200	4.817	5.836	8.378	-0.508	0.075	0.038	-0.041
298	5.551	7.893	7.893	0.000	0.086	0.017	-0.013
300	5.563	7.928	7.894	0.010	0.087	0.017	-0.012
400	6.070	9.601	8.118	0.593	-0.430	0.013	-0.007
500	6.540	11.006	8.559	1.224	-0.739	0.156	-0.068
600	7.010	12.240	9.072	1.901	-0.917	0.355	-0.129
700	7.480	13.356	9.605	2.626	-0.993	0.574	-0.179
800	7.950	14.386	10.139	3.397	-13.981	-0.399	0.109

Sept. 30, 1977

SULFUR, MONOCLINIC (S) (CRYSTAL) GFW = 32.06

$S^\circ_{298.15}$ = 7.893 gibbs/mol
Tt = 368.3 ± 0.3 K (α-β)
Tm = 388.36 ± 0.1 K (β-ℓ)

ΔHf°_0 = 0.059 kcal/mol S
$\Delta Hf^\circ_{298.15}$ = 0.087 kcal/mol
ΔHt° = 0.0957 ± 0.0007 kcal/mol
ΔHm° = 0.4128 ± 0.002 kcal/mol

Heat of Formation

The heat of formation of monoclinic sulfur at 298.15 K is calculated from that of orthorhombic sulfur by adding ΔHt° and the difference between ($H^\circ_{368.3}$ - $H^\circ_{298.15}$) for orthorhombic and monoclinic sulfur.

Heat Capacity and Entropy

Experimentally determined heat capacity values for monoclinic (β) sulfur have been reported by Eastman and McGavock (1, 64.83-376.16 K), West (2, 368-388 K), and Montgomery (3, 12.41-386.83 K). The thermochemical functions tabulated by Hultgren *et al. (4) are based on the work of Eastman and McGavock (1) and West (2).*

We adopt the heat capacity values tabulated (in 10 K increments) by Montgomery (3). The heat capacity values above Tm = 388.36 K are obtained by linear extrapolation of the tabulated heat capacity values (3) above 360 K. Using S°_{10} = 0.063 cal/(mol K) and integrating the heat capacity values, we calculate S°_{298} = 7.893 cal/(mol K). The S°_{10} value contains a contribution of 0.007 cal/(mol K) which is needed to make $S_{Tt}{}^\circ(\beta) = S_{Tt}{}^\circ(\alpha) + \Delta Ht^\circ/Tt$. Since both forms of sulfur are perfectly ordered crystals at 0 K (3), the S°_0 value should be zero, by definition. The contribution of 0.007 cal/(mol K) is arbitrarily added at 10 K although it could appear in any temperature region at or below 368.3 K. Part of this entropy may be in the region of the lambda anomaly at 198.3 K. This contribution is comparable to the uncertainty expected from this adiabatic calorimeter.

Phase Data

The α-β transition at 368.3 K is discussed on the orthorhombic sulfur table (5). The heat capacity data of Montgomery (3) did not support the transition at 374 K reported by West (2).

Montgomery (3) reported a lambda anomaly in the heat capacity of monoclinic sulfur with a peak at 198.3 K. The entropy change in the lambda anomaly was 0.052±0.005 cal/(mol K); this was interpreted as due to the disordering of the structure of monoclinic sulfur on heating (7).

Melting Data

The melting of sulfur has been studied by many workers. An excellent review by Meyer (6) summarizes these studies. *In addition, Hultgren et al. (4) tabulated numerous heat of melting determinations.* We adopt the results obtained by Montgomery (3) via adiabatic calorimetry: Tm = 388.36±0.02 K and ΔHm° = 0.4128±0.0006 kcal/mol. The only other precise study reported in the literature is that of West (2) who obtained ΔHm° = 0.41051±0.0005 kcal/mol by adiabatic calorimetry.

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S

SULFUR (S) S

(LIQUID) GFW=32.06

T, K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0							
100							
200							
298	5.385	8.805	8.805	0.000	0.444	0.103	-0.076
300	5.427	8.838	8.805	0.010	0.444	0.101	-0.074
400	7.687	10.709	9.045	0.666	0.000	0.000	0.000
500	9.079	12.797	9.588	1.604	0.000	0.000	0.000
600	8.200	14.361	10.260	2.461	0.000	0.000	0.000
700	7.811	15.595	10.937	3.261	0.000	0.000	0.000
800	7.576	16.620	11.585	4.028	-12.992	-1.198	0.327
900	7.568	17.512	12.195	4.785	-12.674	0.258	-0.063
1000	7.568	18.309	12.767	5.542	-12.362	1.678	-0.367
1100	7.568	19.030	13.304	6.299	-12.052	3.067	-0.609
1200	7.568	19.689	13.809	7.056	-11.746	4.428	-0.806
1300	7.568	20.295	14.285	7.812	-11.444	5.763	-0.969
1400	7.568	20.855	14.735	8.569	-11.145	7.076	-1.105
1500	7.568	21.378	15.160	9.326	-10.851	8.368	-1.219

Dec. 31, 1960; Dec. 31, 1965; Sept. 30, 1977

SULFUR (S) (LIQUID) GFW = 32.06

S

$S°_{298.15}$ = 8.805 gibbs/mol

Tt = 432.02 ± 0.2 K

Tm = 388.36 ± 0.2 K

Tb = 717.824 K

$\Delta Hf°_{298.15}$ = 0.444 kcal/mol

ΔHt° = 0.0

ΔHm° = 0.4128 ± 0.0006 kcal/mol

ΔHv° = [10.839] kcal/mol

Vaporization: $S(\ell) = 0.5\ S_2(g)$

Heat of Formation

The heat of formation of liquid sulfur at 298.15 K is calculated from that of monoclinic sulfur by adding ΔHm° and the difference between $(H°_{388.36} - H°_{298.15})$ for monoclinic and liquid sulfur.

Heat Capacity and Entropy

The adopted heat capacity values are based on the studies by Montgomery (1, 405.79-433.31 K) and West (2, 373-678 K). Liquid sulfur undergoes a second order transition with a maximum reported at 432.02±0.20 K (1) and 432.25±0.30 K (2); this has been attributed to the polymerization of S_8 molecules (3). We adopt the tabulated heat capacity values of Montgomery (1) up to 434 K and those of West (2) above 434 K. The heat capacity is assumed to be constant at 7.568 cal/(mol K) above 810 K. Below Tm = 388.36 K, the heat capacity values are obtained by linear extrapolation using the slope of the values in the region Tm to 420 K. The entropy is obtained in a manner similar to that used for the heat of formation.

Vaporization Data

The normal boiling point of sulfur, Tb = 717.824 K is a secondary reference on the International Practical Temperature Scale of 1968. At this temperature, equilibrium sulfur vapor contains monomeric and several polymeric sulfur species: $S_2(g)$ and S(g) predominate above 1000 K while $S_6(g)$, $S_7(g)$, and $S_8(g)$ dominate at Tb.

Since our reference state for sulfur is arbitrarily defined to involve 0.5 $S_2(g)$ as the vapor species we calculate ΔHv°(Tb) = [10.839] kcal/mol for the process $S(\ell) = 0.5\ S_2(g)$. The brackets are used to indicate the arbitrary nature of this value. This ΔHv° value contains a contribution RℓnP since the partial pressure of $S_2(g)$ at Tb is 0.034 atm.

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SULFUR, MONATOMIC (S)

(IDEAL GAS) GFW=32.06

S

	gibbs/mol			kcal/mol			
T, K	$C_p°$	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.591	65.663	65.663	INFINITE
100	5.104	34.126	45.046	-1.092	65.998	62.885	-137.432
200	5.590	37.831	40.603	-0.555	66.142	59.706	-65.243
298	5.658	40.086	40.086	0.000	66.200	56.533	-41.439
300	5.657	40.121	40.086	0.010	66.200	56.473	-41.140
400	5.553	41.735	40.307	0.571	65.661	53.251	-29.095
500	5.435	42.961	40.720	1.121	65.272	50.189	-21.937
600	5.339	43.943	41.178	1.659	64.954	47.205	-17.194
700	5.266	44.761	41.633	2.189	64.684	44.268	-13.821
800	5.210	45.460	42.069	2.713	51.448	40.171	-10.974
900	5.168	46.071	42.480	3.232	51.528	38.757	-9.411
1000	5.136	46.614	42.867	3.747	51.599	37.334	-8.159
1100	5.111	47.102	43.230	4.259	51.664	35.904	-7.133
1200	5.093	47.546	43.572	4.769	51.723	34.469	-6.278
1300	5.079	47.953	43.893	5.278	51.777	33.028	-5.553
1400	5.069	48.329	44.197	5.785	51.826	31.585	-4.931
1500	5.064	48.679	44.484	6.292	51.871	30.137	-4.391
1530	5.062	49.005	44.757	6.798	51.911	28.687	-3.918
1700	5.063	49.312	45.016	7.304	51.948	27.234	-3.501
1800	5.068	49.602	45.262	7.811	51.982	25.779	-3.130
1900	5.075	49.876	45.498	8.318	52.014	24.323	-2.798
2000	5.085	50.137	45.724	8.826	52.044	22.865	-2.499
2100	5.097	50.385	45.940	9.335	52.072	21.405	-2.228
2200	5.111	50.622	46.147	9.845	52.098	19.944	-1.981
2300	5.127	50.850	46.347	10.357	52.125	18.482	-1.756
2400	5.144	51.068	46.539	10.871	52.151	17.019	-1.550
2500	5.162	51.279	46.724	11.386	52.176	15.554	-1.360
2600	5.181	51.482	46.903	11.903	52.202	14.089	-1.184
2700	5.200	51.678	47.077	12.422	52.228	12.622	-1.022
2800	5.219	51.867	47.244	12.943	52.255	11.155	-0.871
2900	5.239	52.050	47.407	13.466	52.282	9.687	-0.730
3000	5.258	52.228	47.565	13.991	52.310	8.217	-0.599
3100	5.277	52.401	47.718	14.518	52.339	6.747	-0.476
3200	5.295	52.569	47.867	15.046	52.368	5.276	-0.360
3300	5.313	52.732	48.012	15.577	52.399	3.804	-0.252
3400	5.331	52.891	48.153	16.109	52.430	2.330	-0.150
3500	5.347	53.046	48.291	16.643	52.462	0.856	-0.053
3600	5.363	53.197	48.425	17.178	52.494	-0.619	0.038
3700	5.378	53.344	48.556	17.715	52.527	-2.094	0.124
3800	5.392	53.487	48.684	18.254	52.561	-3.571	0.205
3900	5.406	53.628	48.809	18.794	52.595	-5.049	0.283
4300	5.418	53.765	48.931	19.335	52.629	-6.527	0.357
4100	5.430	53.899	49.050	19.878	52.664	-8.006	0.427
4200	5.441	54.030	49.167	20.421	52.698	-9.486	0.494
4300	5.451	54.158	49.282	20.966	52.732	-10.967	0.557
4400	5.461	54.283	49.394	21.511	52.765	-12.449	0.618
4500	5.469	54.406	49.504	22.058	52.799	-13.931	0.677
4600	5.477	54.526	49.612	22.605	52.832	-15.414	0.732
4700	5.484	54.644	49.718	23.153	52.864	-16.898	0.786
4800	5.491	54.760	49.822	23.702	52.895	-18.383	0.837
4900	5.497	54.873	49.924	24.251	52.925	-19.869	0.886
5000	5.502	54.984	50.024	24.801	52.955	-21.354	0.933
5100	5.507	55.093	50.122	25.352	52.984	-22.841	0.979
5200	5.511	55.200	50.219	25.903	53.011	-24.328	1.022
5300	5.514	55.305	50.314	26.454	53.037	-25.815	1.064
5400	5.517	55.408	50.407	27.006	53.061	-27.304	1.105
5500	5.520	55.509	50.499	27.557	53.084	-28.791	1.144
5600	5.522	55.609	50.589	28.109	53.105	-30.280	1.182
5700	5.524	55.707	50.678	28.662	53.126	-31.769	1.218
5800	5.525	55.803	50.766	29.214	53.144	-33.259	1.253
5900	5.526	55.897	50.852	29.767	53.161	-34.749	1.287
6000	5.527	55.990	50.937	30.319	53.175	-36.239	1.320

Dec. 31, 1960; June 30, 1961
Dec. 31, 1965; June 30, 1971; Sept. 30, 1977

Ground State Configuration $^3P_2$
$S°_{298.15}$ = 40.086 ± 0.008 gibbs/mol

$\Delta Hf°_0$ = 65.65 ± 0.06 kcal/mol S
$\Delta Hf°_{298.15}$ = 66.20 ± 0.06 kcal/mol

Electronic Levels and Quantum Weight

State	ε_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	396.09	3
$^3P_0$	573.65	1
$^1D_2$	9238.58	5
$^1S_0$	22179.99	1

Heat of Formation

ΔHf° is based on the $D°_0$ value for $S_2(g)$ adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for $\Delta Hf°_{298}(S,g)$ is derived using $D°_0(S_2) = 35216.4\pm2.5$ cm^{-1} (100.689±0.021 kcal/mol) from the study of Ricks and Barrow (2).

The selected $D°_0$ value, obtained from precise spectroscopic measurements (2), is supported by additional studies on thermochemical cycles (3), photoionization (4, 5), and torsion-effusion measurements (6). Earlier measurements have been reviewed by Herzberg (7), Gaydon (8), Brewer (9), and Drowart and Goldfinger (3).

Heat Capacity and Entropy

The electronic levels for S(g) are given in the compilations by Moore (10, 11). Our calculations indicate that, except for the five levels lying below 23000 cm^{-1}, the inclusion of levels up to n = 10 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 52623.88 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the therodynamic functions (to 6000 K) we list only the lowest lying states (ε_i < 23000 cm^{-1}). The reported uncertainty in $S°_{298}$ is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (12). In fact, the inclusion of these higher excited states and consideration of various cutoff procedures leads to calculational differences in the free energy function of ∿0.1 cal/(mol K) or greater at temperatures in excess of 11500 K. The $S°_{298}$ value adopted by CODATA (1) is within 0.001 cal/(mol K) of the value reported here.

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SULFUR, MONATOMIC UNIPOSITIVE ION (S^+) S^+
(IDEAL GAS) GFW=32.059451

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	304.567		
100							
200							
298	4.968	39.082	39.082	0.000	306.475	295.620	-216.692
300	4.968	39.113	39.082	0.009	306.483	295.552	-215.307
400	4.968	40.542	39.277	0.506	306.377	291.865	-159.465
500	4.968	41.650	39.645	1.003	306.432	288.227	-125.982
600	4.968	42.556	40.057	1.500	306.570	284.576	-103.655
700	4.968	43.322	40.470	1.996	306.763	280.894	-87.698
800	4.968	43.985	40.869	2.493	293.996	275.986	-75.395
900	4.968	44.570	41.248	2.990	294.551	273.702	-66.463
1000	4.968	45.094	41.607	3.487	295.101	271.356	-59.304
1100	4.968	45.567	41.946	3.984	295.648	268.955	-53.436
1200	4.968	46.000	42.266	4.480	296.190	266.504	-48.536
1300	4.968	46.397	42.569	4.977	296.728	264.008	-44.383
1400	4.968	46.766	42.855	5.474	297.264	261.472	-40.817
1500	4.969	47.108	43.128	5.971	297.796	258.897	-37.721
1600	4.969	47.429	43.387	6.468	298.324	256.286	-35.007
1700	4.971	47.730	43.633	6.965	298.848	253.642	-32.607
1800	4.973	48.014	43.869	7.462	299.369	250.967	-30.471
1900	4.976	48.283	44.094	7.959	299.889	248.265	-28.557
2000	4.981	48.539	44.310	8.457	300.405	245.535	-26.830
2100	4.987	48.782	44.517	8.956	300.920	242.779	-25.266
2200	4.996	49.014	44.716	9.455	301.431	239.997	-23.841
2300	5.007	49.236	44.908	9.955	301.943	237.194	-22.538
2400	5.021	49.450	45.093	10.456	302.453	234.368	-21.342
2500	5.038	49.655	45.271	10.959	302.963	231.520	-20.239
2600	5.058	49.853	45.444	11.464	303.474	228.653	-19.220
2700	5.082	50.044	45.611	11.971	303.984	225.765	-18.274
2800	5.108	50.230	45.772	12.480	304.497	222.859	-17.395
2900	5.139	50.410	45.929	12.993	305.010	219.934	-16.574
3000	5.172	50.584	46.081	13.508	305.525	216.991	-15.808
3100	5.209	50.754	46.229	14.027	306.044	214.032	-15.089
3200	5.249	50.920	46.373	14.550	306.563	211.055	-14.414
3300	5.292	51.083	46.514	15.077	307.087	208.062	-13.779
3400	5.338	51.241	46.650	15.609	307.615	205.054	-13.181
3500	5.387	51.397	46.784	16.145	308.146	202.030	-12.615
3600	5.438	51.549	46.914	16.686	308.681	198.990	-12.080
3700	5.491	51.699	47.041	17.233	309.220	195.935	-11.573
3800	5.546	51.846	47.166	17.784	309.764	192.866	-11.092
3900	5.602	51.991	47.288	18.342	310.312	189.783	-10.635
4000	5.661	52.133	47.407	18.905	310.865	186.686	-10.200
4100	5.720	52.274	47.524	19.474	311.423	183.575	-9.785
4200	5.780	52.412	47.639	20.049	311.985	180.449	-9.390
4300	5.840	52.549	47.751	20.630	312.552	177.311	-9.012
4400	5.901	52.684	47.862	21.217	313.124	174.159	-8.650
4500	5.962	52.817	47.971	21.810	313.701	170.995	-8.305
4600	6.023	52.949	48.077	22.409	314.284	167.818	-7.973
4700	6.084	53.079	48.183	23.015	314.869	164.626	-7.655
4800	6.144	53.208	48.286	23.626	315.459	161.423	-7.350
4900	6.203	53.335	48.388	24.243	316.055	158.209	-7.056
5000	6.261	53.461	48.488	24.867	316.655	154.981	-6.774
5100	6.318	53.586	48.587	25.496	317.258	151.742	-6.502
5200	6.374	53.709	48.684	26.130	317.865	148.490	-6.241
5300	6.429	53.831	48.780	26.770	318.478	145.228	-5.989
5400	6.482	53.952	48.875	27.416	319.092	141.952	-5.745
5500	6.534	54.071	48.968	28.067	319.712	138.667	-5.510
5600	6.583	54.189	49.060	28.723	320.333	135.369	-5.283
5700	6.632	54.306	49.151	29.383	320.959	132.061	-5.063
5800	6.678	54.422	49.241	30.049	321.587	128.742	-4.851
5900	6.722	54.536	49.330	30.719	322.218	125.412	-4.645
6000	6.764	54.650	49.418	31.393	322.852	122.071	-4.446

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SULFUR UNIPOSITIVE ION (S^+) (IDEAL GAS) GFW = 32.059451

Ground State Configuration $^4S^o_{3/2}$

$S^o_{298.15}$ = 39.082 ± 0.008 gibbs/mol

ΔHf^o_0 = 304.57 ± 0.1 kcal/mol S^+

$\Delta Hf^o_{298.15}$ = [306.475] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^4S^o_{3/2}$	0	4
$^2D^o_{3/2}$	14853.0	4
$^2D^o_{5/2}$	14884.8	6
$^2P^o_{1/2}$	24524.9	2
$^2P^o_{3/2}$	24571.6	4

Heat of Formation

The heat of formation ΔHf^o_0 is calculated from the equation $S(g) = S^+(g) + e^-(g)$ with auxiliary data (1), using an ionization potential of IP = 83558.0 cm^{-1} (238.904 kcal/mol). This ionization potential, as reported by Moore (2) in units of cm^{-1}, is converted to units of kcal/mol using the current CODATA fundamental constants (3). The uncertainty in ΔHf^o_0 lies mainly in the uncertainty for $D^o_0(S_2,g)$.

As mentioned above, $\Delta Hf^o_{298}(S^+,g)$ is obtained from $\Delta Hf^o(S,g)$ by using IP(S) with JANAF (1) enthalpies ($H^o_0 - H^o_{298}$) for $S(g)$, $S^+(g)$, and $e^-(g)$. $\Delta Hr^o_{298}(S = S^+ + e^-)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (6). ΔHf^o_{298} should be changed by -1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic levels for $S^+(g)$ are given in the compilation by Moore (2, 4). Our calculations indicate that, except for the five states lying below 25000 cm^{-1}, the inclusion of levels up to n = 5 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 79394.8 cm^{-1} above the ground state. *Since the inclusion of these upper levels has no effect on the thermodynamic functions* (to 6000 K) we list only the lowest lying states (ϵ_i <25000 cm^{-1}). The reported uncertainty in S^o_{298} is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cutoff procedures (5).

References

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4. C. E. Moore, NSRDS-NBS 35, Vol. I, Reissued 1971.
5. J. R. Downey, The Dow Chemical Company, Thermal Research, AFOSR-TR-78-0960, March, 1978.
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S^+

SULFUR, MONATOMIC UNINEGATIVE ION (S^-) S^-

(IDEAL GAS) GFW=32.060549

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.545	17.762		
100							
200							
298	5.445	39.392	39.392	0.000	16.772	8.799	-6.450
300	5.446	39.425	39.392	0.010	16.763	8.750	-6.374
400	5.413	40.989	39.605	0.554	15.710	6.177	-3.375
500	5.345	42.190	40.007	1.092	14.812	3.894	-1.702
600	5.280	43.159	40.454	1.623	13.990	1.789	-0.652
700	5.226	43.969	40.900	2.148	13.219	-0.183	0.057
800	5.182	44.663	41.328	2.668	-0.517	-3.244	0.886
900	5.148	45.272	41.733	3.185	-0.937	-3.559	0.864
1000	5.121	45.813	42.114	3.698	-1.364	-3.829	0.837
1100	5.099	46.300	42.473	4.209	-1.797	-4.054	0.805
1200	5.082	46.743	42.811	4.718	-2.235	-4.239	0.772
1300	5.067	47.149	43.129	5.226	-2.680	-4.388	0.738
1400	5.055	47.524	43.430	5.732	-3.129	-4.503	0.703
1500	5.045	47.872	43.714	6.237	-3.583	-4.585	0.668
1600	5.037	48.198	43.985	6.741	-4.042	-4.638	0.633
1700	5.030	48.503	44.241	7.244	-4.504	-4.660	0.599
1800	5.024	48.790	44.486	7.747	-4.971	-4.657	0.565
1900	5.019	49.061	44.720	8.249	-5.441	-4.626	0.532
2000	5.014	49.319	44.944	8.750	-5.914	-4.571	0.499
2100	5.010	49.563	45.158	9.252	-6.391	-4.492	0.467
2200	5.007	49.796	45.363	9.753	-6.870	-4.390	0.436
2300	5.004	50.019	45.561	10.253	-7.352	-4.266	0.405
2400	5.001	50.232	45.751	10.753	-7.836	-4.122	0.375
2500	4.998	50.436	45.934	11.253	-8.323	-3.958	0.346
2600	4.996	50.632	46.111	11.753	-8.812	-3.773	0.317
2700	4.994	50.820	46.282	12.252	-9.301	-3.570	0.289
2800	4.993	51.002	46.448	12.752	-9.793	-3.348	0.261
2900	4.991	51.177	46.608	13.251	-10.287	-3.110	0.234
3000	4.990	51.346	46.763	13.750	-10.782	-2.855	0.208
3100	4.988	51.510	46.913	14.249	-11.278	-2.582	0.182
3200	4.987	51.668	47.060	14.748	-11.774	-2.293	0.157
3300	4.986	51.822	47.201	15.246	-12.272	-1.989	0.132
3400	4.985	51.970	47.340	15.745	-12.772	-1.671	0.107
3500	4.984	52.115	47.474	16.243	-13.272	-1.337	0.084
3600	4.983	52.255	47.605	16.742	-13.774	-0.989	0.060
3700	4.982	52.392	47.732	17.240	-14.276	-0.626	0.037
3800	4.982	52.525	47.857	17.738	-14.779	-0.251	0.014
3900	4.981	52.654	47.978	18.236	-15.284	0.138	-0.008
4000	4.980	52.780	48.097	18.734	-15.790	0.539	-0.029
4100	4.980	52.903	48.212	19.232	-16.297	0.954	-0.051
4200	4.979	53.023	48.325	19.730	-16.804	1.382	-0.072
4300	4.979	53.140	48.436	20.228	-17.314	1.821	-0.093
4400	4.978	53.255	48.544	20.726	-17.825	2.271	-0.113
4500	4.978	53.367	48.650	21.224	-18.338	2.733	-0.133
4600	4.977	53.476	48.754	21.722	-18.851	3.208	-0.152
4700	4.977	53.583	48.856	22.219	-19.365	3.694	-0.172
4800	4.977	53.688	48.955	22.717	-19.882	4.189	-0.191
4900	4.976	53.791	49.053	23.215	-20.401	4.696	-0.209
5000	4.976	53.891	49.149	23.712	-20.920	5.213	-0.228
5100	4.976	53.990	49.243	24.210	-21.441	5.742	-0.246
5200	4.975	54.086	49.335	24.708	-21.964	6.279	-0.264
5300	4.975	54.181	49.425	25.205	-22.488	6.828	-0.282
5400	4.975	54.274	49.514	25.703	-23.016	7.385	-0.299
5500	4.975	54.365	49.602	26.200	-23.543	7.954	-0.316
5600	4.974	54.455	49.687	26.698	-24.073	8.531	-0.333
5700	4.974	54.543	49.772	27.195	-24.605	9.118	-0.350
5800	4.974	54.629	49.855	27.692	-25.138	9.714	-0.366
5900	4.974	54.714	49.937	28.190	-25.674	10.319	-0.382
6000	4.974	54.798	50.017	28.687	-26.211	10.934	-0.398

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SULFUR UNINEGATIVE ION (S^-) (IDEAL GAS) GFW = 32.060549

Ground State Configuration $^2P_{3/2}$

$S^\circ_{298.15}$ = 39.392 ± 0.01 gibbs/mol

ΔHf°_0 = 17.76 ± 0.2 kcal/mol S^-

$\Delta Hf^\circ_{298.15}$ = [16.772] kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	482	2

Heat of Formation

The heat of formation ΔHf°_0 is calculated from an adopted electron affinity of S(g) of EA = 2.0772±0.0005 eV (47.901±0.012 kcal/mol). This value has been recommended in the critical compilations by Hotop and Lineberger (1) and Rosenstock et al. (2). The former (1) has an excellent discussion on the experimental and theoretical determinations of EA(s). Additional discussion is given by Massey (4). The ΔHf° value is converted to a ΔHf°_{298} value for $S^-(g)$ by including enthalpy differences ($H^\circ_0 - H^\circ_{298}$) for $S^-(g)$, S(g), and $e^-(g)$. ΔHr°_{298} ($S^- = S + e^-$) differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. (2). ΔHf°_{298} should be changed by +1.481 kcal/mol if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state and the fine-structure separation (482±2 cm^{-1}) for $S^-(g)$ has been experimentally determined; a discussion of the relevant work is given by Hotop and Lineberger (1) and Massey (4). The thermodynamic functions of the negative ion are calculated using the recent CODATA fundamental constants (3) and assuming that $S^-(g)$ is an ideal monatomic gas. Lacking any experimental evidence as to the stability of any excited states, we assume no stable excited states exist.

References

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S^-

STRONTIUM MONOSULFIDE (SrS) SSR

(CRYSTAL) GFW=119.68

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.345	-111.771	-111.771	INFINITE
100	7.650	5.371	25.966	-2.059	-111.969	-111.607	243.914
200	10.740	11.871	17.391	-1.104	-111.997	-111.241	121.557
298	11.640	16.350	16.350	0.000	-112.000	-110.864	81.264
300	11.646	16.422	16.351	0.022	-112.000	-110.857	80.758
400	12.000	19.820	16.811	1.203	-112.578	-110.449	60.345
500	12.400	22.543	17.694	2.424	-112.995	-109.872	48.024
600	12.710	24.832	18.698	3.680	-113.337	-109.213	39.780
700	12.930	26.808	19.719	4.963	-113.645	-108.502	33.875
800	13.120	28.548	20.716	6.266	-126.950	-108.944	29.762
900	13.270	30.101	21.674	7.585	-127.147	-106.675	25.904
1000	13.440	31.509	22.588	8.921	-127.155	-104.401	22.816
1100	13.570	32.796	23.458	10.271	-129.076	-102.014	20.268
1200	13.700	33.982	24.286	11.635	-129.003	-99.557	18.132
1300	13.831	35.084	25.075	13.011	-128.922	-97.107	16.325
1400	13.960	36.113	25.827	14.401	-128.830	-94.663	14.777
1500	14.086	37.081	26.545	15.803	-128.730	-92.226	13.437
1600	14.210	37.994	27.233	17.218	-128.621	-89.796	12.265
1700	14.329	38.859	27.891	18.645	-161.077	-86.468	11.116
1800	14.450	39.681	28.524	20.084	-160.609	-82.093	9.967
1900	14.575	40.466	29.132	21.535	-160.133	-77.743	8.942
2000	14.700	41.217	29.717	22.999	-159.649	-73.419	8.023
2100	14.825	41.937	30.282	24.475	-159.159	-69.120	7.193
2200	14.950	42.630	30.828	25.964	-158.663	-64.845	6.442
2300	15.075	43.297	31.356	27.465	-158.161	-60.591	5.757
2400	15.200	43.941	31.867	28.979	-157.656	-56.359	5.132
2500	15.325	44.564	32.362	30.505	-157.150	-52.150	4.559
2600	15.450	45.168	32.843	32.044	-156.642	-47.959	4.031
2700	15.575	45.753	33.310	33.595	-156.138	-43.789	3.544
2800	15.700	46.322	33.765	35.159	-155.637	-39.636	3.094
2900	15.825	46.875	34.208	36.735	-155.145	-35.503	2.676
3000	15.950	47.414	34.639	38.324	-154.661	-31.386	2.286

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STRONTIUM MONOSULFIDE (SrS) (CRYSTAL) GFW = 119.68

ΔHf°_0 = -111.8 ± 4 kcal/mol SSR

$S^\circ_{298.15}$ = 16.3 ± 0.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -112 ± 4 kcal/mol

Heat of Formation

Sabatier (1) measured the heat of solution of SrS in hydrochloric acid solution as $\Delta Hr_{283.6}$ = -26.9±1.0 kcal/mol for SrS (c) + 2HCl(100 H_2O,aq) → $SrCl_2$(100 H_2O,aq) + H_2S(aq). We derive ΔHf°_{298}(SrS,c) = -113.1±2.0 kcal/mol based on the following auxiliary data: ΔHf°_{298}(HCl·100 H_2O,aq) = -39.657 kcal/mol (3), ΔHf°_{298}(H_2S,aq) = -9.5 kcal/mol (2), and ΔHf°_{298}($SrCl_2$·200 H_2O,aq) = -209.78 kcal/mol (3). The uncertainty reflects the correction to 298.15 K and the ambiguity of the exact solution composition. Mourlot (4) also measured the heat of solution of SrS in hydrochloric acid solution as ΔHr = -27.1±1.0 kcal/mol from which we calculate ΔHf°_{298} (SrS,c) = -112.8±2.0 kcal/mol, using the same auxiliary data.

Cater and Johnson (5) determined that SrS sublimes congruently and derived partial pressures of the various gaseous species Sr(g), S(g), and SrS(g) in an effusion and mass-spectrometric study. We analyze their data and the equilibrium study of Schenck and Hammerschmidt (6) below. Other mass-spectrometric studies of Berkowitz and Marquart (7) and Colin et al. (8) are also listed. The calculated 3rd law $\Delta H\overset{\circ}{r}$(298 K) may have an uncertainty of 0.5 kcal/mol since the JANAF free energy functions are partially based on the estimated $\overset{\circ}{Cp}$ data (above 300 K).

The heat of solution studies (1, 4) show wide disagreement from the mass spectrometric studies (5, 7, 8). Our experience tends to indicate that mass spectrometric experiments provide very good data on gas phase species for homogeneous reactions, but are not as reliable for condensed phases in heterogeneous reactions. A weighted average of the equilibrium and heat of solution studies, ΔHf°_{298}(SrS,c) = -112.0±4 kcal/mol is adopted in the tabulation.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd law	3rd law	ΔHf°_{298} [c]
(5) Cater (1967)	Knudsen mass spec.	A	1825-2181	Equation	1.26	212.70	210.18±0.38	-104.70±2
(5) Cater (1967)	Knudsen mass spec.	B	1825-2181	Equation	0.23	131.75	131.29±0.08	-105.43±2
(6) Schenck (1933)	Equilibrium	C	1237-1383	3	8.8±1.8	-53.0±2.4	-64.55±1.3	-110.02±4
(7) Berkowitz (1963)	Mass spec.	B	1809	1			210.18±1.0	-104.7 ±2
(8) Colin et al. (1964)	Mass spec.	D	1857-2170	9	-12.6±2.8	-3.3±5.5	21.8 ±2.4	-119.8 ±16
(9) Nikonov (1961)	Vaporization	B	1400-1700	Equation	-3.3	102.6	107.7 ±0.9	-82 ±30

[a] Reactions:
A) SrS(c) = Sr(g) + S(g)
B) SrS(c) = SrS(g)
C) SrS(c) + $2SO_2$(g) = $SrSO_4$(c) + S_2(g)
D) SrS(c) + 3S(g) = Sr(g) + $2S_2$(g)

[b] $\delta S = \Delta S_{298}$ (2nd law) - ΔS_{298} (3rd law)

[c] 3rd law $\Delta H\overset{\circ}{r}_{298}$ is used to derive ΔHf°_{298} (SrS,c).

Heat Capacity and Entropy

King and Weller (10) measured the low temperature heat capacities from 53-296 K. Their smooth values are adopted in the tabulation. The entropy, $S^\circ_{298.15}$ = 16.3±0.2 gibbs/mol, is based on S°_{51} = 1.59 gibbs/mol as extrapolated by King and Weller using Debye and Einstein functions (θ_D = 208, θ_E = 311). The $\overset{\circ}{Cp}$ values above 300 K are estimated by graphical extrapolation combined with method B of Kubaschewski et al. (11).

Melting Data

Literature melting data for SrS(c) are not available. The value quoted by Mills (12) for the melting point ,2275 K, seems too low when compared to the alkaline earth oxide melting points (13).

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SSR

STRONTIUM MONOSULFIDE (SRS)

SSR

(IDEAL GAS) GFW=119.68

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.279	26.155	26.155	INFINITE
100	7.198	49.502	65.296	-1.579	26.371	22.320	-48.779
200	8.053	54.772	58.842	-0.814	26.153	18.328	-20.028
298	8.479	58.078	58.078	0.000	25.860	14.555	-10.669
300	8.485	58.130	58.078	0.016	25.854	14.485	-10.552
400	8.686	60.602	58.414	0.875	24.954	10.771	-5.885
500	8.794	62.553	59.053	1.750	24.191	7.309	-3.195
600	8.861	64.163	59.775	2.633	23.476	4.001	-1.457
700	8.906	65.532	60.502	3.521	22.773	0.810	-0.253
800	8.942	66.724	61.207	4.414	9.058	-3.477	0.950
900	8.981	67.779	61.879	5.310	8.438	-5.001	1.214
1000	9.037	68.728	62.518	6.211	7.995	-6.470	1.414
1100	9.126	69.593	63.122	7.118	5.631	-7.785	1.547
1200	9.267	70.393	63.695	8.038	5.260	-8.988	1.637
1300	9.474	71.143	64.239	8.974	4.901	-10.161	1.708
1400	9.758	71.855	64.758	9.935	4.564	-11.306	1.765
1500	10.124	72.540	65.254	10.928	4.255	-12.429	1.811
1600	10.567	73.207	65.730	11.962	3.983	-13.532	1.848
1700	11.077	73.863	66.190	13.044	-28.818	-13.715	1.763
1800	11.637	74.511	66.634	14.179	-28.654	-12.831	1.558
1900	12.226	75.156	67.065	15.372	-28.436	-11.957	1.375
2000	12.821	75.799	67.486	16.625	-28.163	-11.096	1.213
2100	13.397	76.438	67.897	17.936	-27.838	-10.251	1.067
2200	13.933	77.074	68.300	19.303	-27.464	-9.423	0.936
2300	14.412	77.704	68.695	20.721	-27.045	-8.611	0.818
2400	14.819	78.326	69.083	22.183	-26.592	-7.820	0.712
2500	15.146	78.938	69.465	23.682	-26.113	-7.048	0.616
2600	15.392	79.537	69.841	25.209	-25.617	-6.294	0.529
2700	15.556	80.121	70.211	26.757	-25.116	-5.561	0.450
2800	15.644	80.689	70.575	28.318	-24.618	-4.845	0.378
2900	15.664	81.239	70.934	29.884	-24.136	-4.149	0.313
3000	15.624	81.769	71.286	31.449	-23.676	-3.467	0.253
3100	15.533	82.280	71.633	33.007	-23.247	-2.800	0.197
3200	15.402	82.771	71.973	34.554	-22.857	-2.148	0.147
3300	15.239	83.243	72.307	36.086	-22.511	-1.506	0.100
3400	15.053	83.695	72.636	37.601	-22.215	-0.874	0.056
3500	14.851	84.128	72.958	39.096	-21.973	-0.250	0.016
3600	14.639	84.544	73.274	40.571	-21.788	0.367	-0.022
3700	14.421	84.942	73.584	42.024	-21.663	0.981	-0.058
3800	14.203	85.324	73.888	43.455	-21.601	1.593	-0.092
3900	13.988	85.690	74.186	44.865	-21.602	2.203	-0.123
4000	13.777	86.041	74.478	46.253	-21.668	2.814	-0.154
4100	13.574	86.379	74.764	47.621	-21.797	3.428	-0.183
4200	13.378	86.704	75.045	48.968	-21.991	4.045	-0.210
4300	13.192	87.016	75.319	50.296	-22.249	4.668	-0.237
4400	13.015	87.317	75.589	51.607	-22.567	5.298	-0.263
4500	12.848	87.608	75.853	52.900	-22.946	5.935	-0.288
4600	12.691	87.889	76.111	54.177	-23.383	6.582	-0.313
4700	12.543	88.160	76.365	55.438	-23.877	7.239	-0.337
4800	12.405	88.423	76.613	56.686	-24.424	7.906	-0.360
4900	12.276	88.677	76.857	57.920	-25.022	8.585	-0.383
5000	12.156	88.924	77.096	59.141	-25.667	9.278	-0.406
5100	12.044	89.164	77.330	60.351	-26.358	9.984	-0.428
5200	11.941	89.396	77.560	61.550	-27.091	10.703	-0.450
5300	11.844	89.623	77.785	62.739	-27.862	11.438	-0.472
5400	11.755	89.843	78.006	63.919	-28.670	12.186	-0.493
5500	11.672	90.058	78.224	65.091	-29.509	12.951	-0.515
5600	11.596	90.268	78.437	66.254	-30.379	13.731	-0.536
5700	11.525	90.473	78.646	67.410	-31.275	14.527	-0.557
5800	11.460	90.672	78.852	68.559	-32.195	15.338	-0.578
5900	11.400	90.868	79.054	69.702	-33.136	16.166	-0.599
6000	11.344	91.059	79.252	70.839	-34.096	17.009	-0.620

Sept. 30, 1977

STRONTIUM MONOSULFIDE (SrS) (IDEAL GAS) GFW = 119.68

SSR

D_0° = 78.8 ± 2.0 kcal/mol
$S_{298.15}^\circ$ = 58.078 ± 0.10 gibbs/mol
Symmetry Number = 1

ΔHf_0° = 26.15 ± 2.0 kcal/mol
$\Delta Hf_{298.15}^\circ$ = 25.86 ± 2.0 kcal/mol

Electronic and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(7)	$X^1\Sigma^+$	0.0	1	2.4405	0.12072	0.00044	388.38	1.310
(6)	$^3\Pi$	[7800.]	6	[2.76]	[0.0943]	[0.0005]	[270]	[1.1]
(6)	$^3\Sigma^+$	[8000.]	3	[2.51]	[0.114]	[0.0005]	[330]	[1.2]
(6)	$^1\Pi$	[8100.]	2	[2.76]	[0.0943]	[0.0005]	[270]	[1.1]
(6)	$^1\Sigma^+$	[11000.]	1	[2.51]	[0.114]	[0.0005]	[330]	[1.2]
(7, 8)	$B^1\Sigma^+$	26531.2	1	2.609	0.10566	0.00032	286.8	0.84

Heat of Formation

The adopted value for the heat of formation, ΔHf_{298}°(SrS,g) = 25.86±2.0 kcal/mol, is based on the Knudsen mass spectrometric studies analyzed below. The three independent studies are in very good agreement and we have chosen the average of the measurements. Our value is in very good agreement with ΔHf_{298}° = 26.0 kcal/mol adopted by NBS (4) and is slightly greater than ΔHf_{298}° = 24.1±4 kcal/mol obtained by Mills (5) (using different free energy functions) in a recent critical compilation. Using auxiliary JANAF data (6) and a recommended value for $D_0^\circ(S_2,g)$ = 100.69±0.01 kcal/mol (6), we calculate D_0°(SrS,g) = 78.8±2.0 kcal/mol.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] Gibbs/mol	ΔHr_{298}°/(kcal/mol) 2nd Law	3rd Law	ΔHf_{298}°[c] Kcal/mol	D_0°
(1) Colin (1964)	Mass Spec	A	2010-2170	4	-1.86±8.5	17.42±17.9	21.310±1.60	25.06±1.66	79.63±2.0
(2) Marquart (1963)	Mass spec	A	1809-1934	2	6.85	34.19	21.375±1.21	25.12±1.3	79.56±1.5
(3) Cater (1967)	Mass Spec	A	1825-2181	Equation	-1.16	20.85	23.07 ±0.34	26.82±0.6	77.87±1.0
(3) Cater (1967)	Mass Spec	B	1825-2181	Equation	-1.03	-80.95	-78.89 ±0.31	26.60±0.6	78.09±0.3

[a] Reactions: A) $Sr(g) + S_2(g) = SrS(g) + S(g)$
B) $Sr(g) + S(g) = SrS(g)$

[b] $\delta S = \Delta S_{298}(\text{2nd Law}) - \Delta Hr_{298}^\circ$

Heat Capacity and Entropy

Electronic levels (T_{oo}) and vibrational-rotational constants for the observed states are from the optical study of Barrow (7, 8). Other low-lying electronic states and their vibrational-rotational constants are estimated in isoconfigurational groups by analogy with SrO (6) and from trends observed in the known states of the other alkaline-earth oxides and sulfides (6). Uncertainty in the energy and constants for the estimated states may contribute as much as 2-3 gibbs/mol to S° at 3000 K. The molecular constants have been corrected to the natural isotopic abundances. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\varepsilon_i/T)$.

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5. K. C. Mills, "Thermodynamic Data for Inorganic Sulphides, Selenides, and Tellurides," Butterworths, London, 1974.
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SSR

SULFUR, DIATOMIC (S_2) (IDEAL GAS) GFW=64.12

S_2

	gibbs/mol			kcal/mol			
T, K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.182	30.636	30.636	INFINITE
100	7.019	46.596	61.084	-1.449	31.041	26.980	-58.964
200	7.278	51.508	55.201	-0.739	30.965	22.923	-25.049
298	7.765	54.506	54.506	0.000	30.710	19.027	-13.947
300	7.774	54.555	54.507	0.014	30.704	18.955	-13.808
400	8.148	56.845	54.816	0.812	29.302	15.131	-8.267
500	8.392	58.691	55.413	1.639	28.251	11.702	-5.115
600	8.553	60.236	56.091	2.487	27.387	8.479	-3.088
700	8.666	61.563	56.780	3.348	26.648	5.387	-1.682
800	8.756	62.727	57.452	4.219	0.000	0.000	0.000
900	8.835	63.762	58.097	5.099	0.000	0.000	0.000
1000	8.909	64.697	58.711	5.986	0.000	0.000	0.000
1100	8.983	65.550	59.295	6.881	0.000	0.000	0.000
1200	9.057	66.335	59.849	7.783	0.000	0.000	0.000
1300	9.131	67.062	60.376	8.692	0.000	0.000	0.000
1400	9.205	67.742	60.878	9.609	0.000	0.000	0.000
1500	9.278	68.379	61.357	10.533	0.000	0.000	0.000
1600	9.348	68.980	61.815	11.464	0.000	0.000	0.000
1700	9.415	69.549	62.254	12.403	0.000	0.000	0.000
1800	9.479	70.089	62.674	13.347	0.000	0.000	0.000
1900	9.539	70.603	63.078	14.298	0.000	0.000	0.000
2000	9.595	71.094	63.467	15.255	0.000	0.000	0.000
2100	9.644	71.563	63.841	16.217	0.000	0.000	0.000
2200	9.691	72.013	64.202	17.184	0.000	0.000	0.000
2300	9.734	72.445	64.551	18.155	0.000	0.000	0.000
2400	9.775	72.860	64.889	19.131	0.000	0.000	0.000
2500	9.812	73.260	65.216	20.110	0.000	0.000	0.000
2600	9.842	73.645	65.533	21.093	0.000	0.000	0.000
2700	9.871	74.017	65.840	22.078	0.000	0.000	0.000
2800	9.898	74.377	66.139	23.067	0.000	0.000	0.000
2900	9.924	74.725	66.429	24.058	0.000	0.000	0.000
3000	9.949	75.061	66.711	25.051	0.000	0.000	0.000
3100	9.969	75.388	66.986	26.047	0.000	0.000	0.000
3200	9.989	75.705	67.253	27.045	0.000	0.000	0.000
3300	10.010	76.012	67.514	28.045	0.000	0.000	0.000
3400	10.030	76.312	67.768	29.047	0.000	0.000	0.000
3500	10.050	76.603	68.017	30.051	0.000	0.000	0.000
3600	10.069	76.886	68.259	31.057	0.000	0.000	0.000
3700	10.089	77.162	68.496	32.065	0.000	0.000	0.000
3800	10.110	77.431	68.727	33.075	0.000	0.000	0.000
3900	10.131	77.694	68.954	34.087	0.000	0.000	0.000
4000	10.153	77.951	69.176	35.101	0.000	0.000	0.000
4100	10.176	78.202	69.393	36.118	0.000	0.000	0.000
4200	10.199	78.448	69.606	37.136	0.000	0.000	0.000
4300	10.224	78.688	69.814	38.158	0.000	0.000	0.000
4400	10.250	78.923	70.018	39.181	0.000	0.000	0.000
4500	10.277	79.154	70.219	40.208	0.000	0.000	0.000
4600	10.305	79.380	70.416	41.237	0.000	0.000	0.000
4700	10.334	79.602	70.609	42.269	0.000	0.000	0.000
4800	10.363	79.820	70.798	43.303	0.000	0.000	0.000
4900	10.394	80.034	70.985	44.341	0.000	0.000	0.000
5000	10.425	80.244	71.168	45.382	0.000	0.000	0.000
5100	10.458	80.451	71.348	46.426	0.000	0.000	0.000
5200	10.492	80.654	71.525	47.474	0.000	0.000	0.000
5300	10.525	80.854	71.699	48.525	0.000	0.000	0.000
5400	10.559	81.052	71.870	49.579	0.000	0.000	0.000
5500	10.594	81.246	72.039	50.637	0.000	0.000	0.000
5600	10.629	81.437	72.205	51.698	0.000	0.000	0.000
5700	10.664	81.625	72.369	52.762	0.000	0.000	0.000
5800	10.700	81.811	72.530	53.831	0.000	0.000	0.000
5900	10.737	81.994	72.689	54.903	0.000	0.000	0.000
6000	10.773	82.175	72.845	55.978	0.000	0.000	0.000

Dec. 31, 1960; Dec. 31, 1965; Sept. 30, 1977

SULFUR, DIATOMIC (S_2) (IDEAL GAS) GFW = 64.12

D_0° = 100.689 ± 0.021 kcal/mol

$S_{298.15}^\circ$ = 54.506 ± 0.012 cal/(mol K)

ΔHf_0° = 30.64 ± 0.07 kcal/mol

$\Delta Hf_{298.15}^\circ$ = 30.71 ± 0.07 kcal/mol

S_2

Electronic and Molecular Constants

State	g_i	ε_i, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	D_e, cm^{-1}	r_e, Å
$X^3\Sigma_g^-$	3	0	724.67	2.836	0.2946	0.00157	2.134×10^{-7}	1.889
$a^1\Delta_g$	2	4700	702.35	3.09	0.2923	0.0017	2.040×10^{-7}	1.889
$b^1\Sigma_g$	1	8500	700.87	3.47	[0.29]	[0.0016]	$[2.0 \times 10^{-7}]$	--
$A^3\Delta$	6	21855	488.6	2.63	0.2284	0.0014	1.996×10^{-7}	2.148

Heat of Formation

The adopted heat of formation is that selected by CODATA (1). The value was calculated from measurements of the equilibrium $H_2S(g) = H_2(g) + 0.5\ S_2(g)$ reported by Randall and Bichowsky (2), Preuner (3), and Preuner and Schupp (4), and from measurements of the partial pressure of $S_2(g)$ over sulfur reported by Drowart, Goldfinger, Detry, Rickert, and Keller (5).

The dissociation energy, D_0° = 35216.4±2.5 cm^{-1} (100.689±0.021 kcal/mol) is from the spectroscopic study by Ricks and Barrow (12).

Heat Capacity and Entropy

The thermal functions above 600 K are calculated using the program of McBride and Gordon (6). The contribution of vibrational anharmonicity, rotation-vibration interaction, and centrifugal stretching are calculated via the procedures given by Pennington and Kobe (7). The electronic and molecular constant data in the above table are that summarized by Rosen (8) and Suchard (9) with the exception that the position of the $a^1\Delta_g$ state at 4700±800 cm^{-1} is from the more recent absorption study by Carleer and Colin (10).

The thermal functions below 600 K are calculated by direct summation over vibrational-rotational energy levels of the ground state (including the proper treatment of the splitting of this level, i.e. $\alpha = -0.0066$ cm^{-1} and $\lambda = 11.84$ cm^{-1}) and three excited states. We performed the direct summation with a program written by W. H. Evans of the U.S. Bureau of Standards. The direct summation results are not extended to temperatures above 600 K since the energy levels derived from the reported vibrational-rotational constants do not converge to the dissociation energy. For these higher temperatures, the program of McBride and Gordon is used, as in the case of gaseous O_2 (11).

The value of S_{298}° agrees exactly with the CODATA recommended value (1). The uncertainty in S_{298}° is due to uncertainties in fundamental constants, the atomic weight, and the ground state molecular constants. The contributions of the excited states above 22000 cm^{-1} do not affect the thermal functions below 2000 K but do become significant at higher temperatures. However, these states are not included for two reasons. First, the electronic and molecular constants are not all well-defined. Second, many of these levels have a sufficiently shallow potential energy well, which would lead to unreasonably large heat capacity values at high temperatures.

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XENON, MONATOMIC (XE)

(REFERENCE STATE - IDEAL GAS) GFW=131.30

XE

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.481	0.000	0.000	0.000
100	4.968	35.102	44.946	-0.984	0.000	0.000	0.000
200	4.968	38.546	40.984	-0.488	0.000	0.000	0.000
298	4.968	40.530	40.529	0.000	0.000	0.000	0.000
300	4.968	40.560	40.530	0.009	0.000	0.000	0.000
400	4.968	41.989	40.724	0.506	0.000	0.000	0.000
500	4.968	43.098	41.092	1.003	0.000	0.000	0.000
600	4.968	44.004	41.504	1.500	0.000	0.000	0.000
700	4.968	44.770	41.918	1.996	0.000	0.000	0.000
800	4.968	45.433	42.316	2.493	0.000	0.000	0.000
900	4.968	46.018	42.696	2.990	0.000	0.000	0.000
1000	4.968	46.542	43.055	3.487	0.000	0.000	0.000
1100	4.968	47.015	43.394	3.984	0.000	0.000	0.000
1200	4.968	47.447	43.714	4.480	0.000	0.000	0.000
1300	4.968	47.845	44.016	4.977	0.000	0.000	0.000
1400	4.968	48.213	44.303	5.474	0.000	0.000	0.000
1500	4.968	48.556	44.575	5.971	0.000	0.000	0.000
1600	4.968	48.877	44.834	6.468	0.000	0.000	0.000
1700	4.968	49.178	45.081	6.964	0.000	0.000	0.000
1800	4.968	49.462	45.317	7.461	0.000	0.000	0.000
1900	4.968	49.730	45.542	7.958	0.000	0.000	0.000
2000	4.968	49.985	45.758	8.455	0.000	0.000	0.000
2100	4.968	50.227	45.965	8.952	0.000	0.000	0.000
2200	4.968	50.459	46.164	9.448	0.000	0.000	0.000
2300	4.968	50.679	46.355	9.945	0.000	0.000	0.000
2400	4.968	50.891	46.540	10.442	0.000	0.000	0.000
2500	4.968	51.094	46.718	10.939	0.000	0.000	0.000
2600	4.968	51.289	46.890	11.436	0.000	0.000	0.000
2700	4.968	51.476	47.057	11.932	0.000	0.000	0.000
2800	4.968	51.657	47.218	12.429	0.000	0.000	0.000
2900	4.968	51.831	47.374	12.926	0.000	0.000	0.000
3000	4.968	51.999	47.525	13.423	0.000	0.000	0.000
3100	4.968	52.162	47.672	13.920	0.000	0.000	0.000
3200	4.968	52.320	47.815	14.416	0.000	0.000	0.000
3300	4.968	52.473	47.954	14.913	0.000	0.000	0.000
3400	4.968	52.621	48.089	15.410	0.000	0.000	0.000
3500	4.968	52.765	48.220	15.907	0.000	0.000	0.000
3600	4.968	52.905	48.349	16.404	0.000	0.000	0.000
3700	4.968	53.041	48.474	16.900	0.000	0.000	0.000
3800	4.968	53.174	48.596	17.397	0.000	0.000	0.000
3900	4.968	53.303	48.715	17.894	0.000	0.000	0.000
4000	4.968	53.429	48.831	18.391	0.000	0.000	0.000
4100	4.968	53.551	48.945	18.888	0.000	0.000	0.000
4200	4.968	53.671	49.056	19.384	0.000	0.000	0.000
4300	4.968	53.788	49.164	19.881	0.000	0.000	0.000
4400	4.968	53.902	49.271	20.378	0.000	0.000	0.000
4500	4.968	54.014	49.375	20.875	0.000	0.000	0.000
4600	4.968	54.123	49.477	21.372	0.000	0.000	0.000
4700	4.968	54.230	49.577	21.868	0.000	0.000	0.000
4800	4.968	54.334	49.675	22.365	0.000	0.000	0.000
4900	4.968	54.437	49.771	22.862	0.000	0.000	0.000
5000	4.968	54.537	49.865	23.359	0.000	0.000	0.000
5100	4.968	54.636	49.958	23.855	0.000	0.000	0.000
5200	4.968	54.732	50.049	24.352	0.000	0.000	0.000
5300	4.968	54.827	50.138	24.849	0.000	0.000	0.000
5400	4.968	54.920	50.226	25.346	0.000	0.000	0.000
5500	4.968	55.011	50.312	25.843	0.000	0.000	0.000
5600	4.968	55.100	50.397	26.339	0.000	0.000	0.000
5700	4.968	55.188	50.480	26.836	0.000	0.000	0.000
5800	4.968	55.275	50.562	27.333	0.000	0.000	0.000
5900	4.968	55.359	50.643	27.830	0.000	0.000	0.000
6000	4.968	55.443	50.722	28.327	0.000	0.000	0.000

March 31, 1977

XENON, MONATOMIC (Xe) (REFERENCE STATE - IDEAL GAS) GFW = 131.30

0 to 6000 K Ideal Gas

XE

Ground State Configuration $^1S_0$

$S^\circ_{298.15}$ = 40.530 ± 0.005 gibbs/mol

T_{tr} = 161.36 K

T_b = 165.03 K

ΔHf°_0 = 0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Electronic Levels and Quantum Weights

state	ε_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore (1). Many of the theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (2) has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 67,000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of proper fill and cutoff procedures (2).

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations (3). The table agrees within the estimated uncertainty with those by Hultgren et al. (4) and Hilsenrath et al. (5). (Hultgren's table contains several typesetting errors; for C°_p and S° at 200 K and 298.15 K and for the free energy function at 700 K. We are in agreement with these exceptions.) The estimated uncertainty is due to uncertainties in the gram formula weight and fundamental constants which are based on the 1971 scale (6) and the 1973 values (7), respectively.

Phase Data

The triple point (T_{tr}) and boiling point (T_b) are taken from Hultgren et al. (4). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values of T_{tr} and T_b the reference state for xenon is chosen to be the ideal gas at all temperatures down to 0 K. This may differ from the choice of other authors. The tables of Hultgren et al. (4), among others, use appropriate condensed states of xenon as reference states and will differ from the present work at low temperatures.

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XE

XENON UNIPOSITIVE ION (XE$^+$) XE$^+$
(IDEAL GAS) GFW=131.29945

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-1.481	279.722		
100							
200							
298	4.968	43.284	43.284	0.000	281.203	278.894	-204.432
300	4.968	43.315	43.284	0.009	281.212	278.880	-203.161
400	4.968	44.744	43.479	0.506	281.709	278.027	-151.905
500	4.968	45.853	43.847	1.003	282.205	277.050	-121.097
600	4.968	46.759	44.259	1.500	282.702	275.972	-100.521
700	4.968	47.524	44.672	1.996	283.199	274.811	-85.799
800	4.968	48.188	45.071	2.493	283.696	273.578	-74.737
900	4.968	48.773	45.451	2.990	284.193	272.284	-66.119
1000	4.968	49.296	45.810	3.487	284.689	270.934	-59.212
1100	4.968	49.770	46.148	3.984	285.186	269.534	-53.551
1200	4.968	50.202	46.468	4.480	285.683	268.090	-48.825
1300	4.969	50.600	46.771	4.977	286.180	266.603	-44.819
1400	4.970	50.968	47.058	5.474	286.677	265.079	-41.380
1500	4.972	51.311	47.330	5.971	287.174	263.519	-38.394
1600	4.975	51.632	47.589	6.469	287.670	261.925	-35.777
1700	4.979	51.934	47.836	6.966	288.169	260.301	-33.464
1800	4.983	52.219	48.072	7.464	288.667	258.648	-31.404
1900	4.990	52.488	48.297	7.963	289.166	256.966	-29.557
2000	4.997	52.744	48.513	8.462	289.665	255.258	-27.893
2100	5.006	52.988	48.720	8.963	290.164	253.525	-26.384
2200	5.016	53.221	48.920	9.464	290.666	251.769	-25.011
2300	5.027	53.445	49.112	9.966	291.169	249.990	-23.754
2400	5.039	53.659	49.297	10.469	291.672	248.189	-22.600
2500	5.053	53.865	49.475	10.974	292.176	246.367	-21.537
2600	5.067	54.063	49.648	11.480	292.681	244.524	-20.554
2700	5.082	54.255	49.815	11.987	293.190	242.663	-19.642
2800	5.097	54.440	49.977	12.496	293.699	240.782	-18.794
2900	5.113	54.619	50.134	13.007	294.209	238.883	-18.002
3000	5.129	54.793	50.286	13.519	294.721	236.967	-17.263
3100	5.145	54.961	50.434	14.032	295.234	235.032	-16.570
3200	5.162	55.125	50.578	14.548	295.750	233.083	-15.919
3300	5.178	55.284	50.719	15.065	296.267	231.117	-15.306
3400	5.194	55.439	50.855	15.583	296.786	229.135	-14.728
3500	5.210	55.589	50.988	16.103	297.306	227.137	-14.183
3600	5.225	55.736	51.118	16.625	297.827	225.124	-13.667
3700	5.241	55.880	51.245	17.149	298.351	223.098	-13.178
3800	5.255	56.020	51.369	17.673	298.876	221.058	-12.714
3900	5.270	56.156	51.490	18.200	299.402	219.003	-12.272
4000	5.283	56.290	51.608	18.727	299.929	216.933	-11.853
4100	5.296	56.421	51.724	19.256	300.458	214.852	-11.453
4200	5.309	56.548	51.837	19.787	300.989	212.759	-11.071
4300	5.321	56.673	51.948	20.318	301.521	210.652	-10.706
4400	5.332	56.796	52.057	20.851	302.053	208.533	-10.358
4500	5.343	56.916	52.164	21.384	302.586	206.400	-10.024
4600	5.353	57.033	52.268	21.919	303.121	204.256	-9.704
4700	5.363	57.149	52.371	22.455	303.658	202.103	-9.398
4800	5.372	57.262	52.472	22.992	304.195	199.936	-9.103
4900	5.380	57.372	52.570	23.529	304.732	197.759	-8.820
5000	5.388	57.481	52.668	24.068	305.270	195.569	-8.548
5100	5.395	57.588	52.763	24.607	305.810	193.370	-8.286
5200	5.402	57.693	52.857	25.147	306.350	191.160	-8.034
5300	5.408	57.796	52.949	25.687	306.890	188.940	-7.791
5400	5.413	57.897	53.040	26.228	307.431	186.710	-7.556
5500	5.418	57.996	53.129	26.770	307.972	184.469	-7.330
5600	5.423	58.094	53.217	27.312	308.515	182.219	-7.111
5700	5.427	58.190	53.303	27.855	309.057	179.958	-6.900
5800	5.431	58.284	53.388	28.397	309.600	177.689	-6.695
5900	5.434	58.377	53.472	28.941	310.143	175.410	-6.498
6000	5.437	58.469	53.555	29.484	310.686	173.121	-6.306

March 31, 1977

XENON UNIPOSITIVE ION (Xe$^+$) (IDEAL GAS) GFW = 131.29945

Ground State Configuration $^2P_{3/2}$
$S^o_{298.15}$ = 43.284 ± 0.005 gibbs/mol

ΔHf^o_0 = 279.722 ± 0.006 kcal/mol
$\Delta Hf^o_{298.15}$ = 281.203 ± 0.006 kcal/mol

XE$^+$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	10537.01	2

Heat of Formation

The ionization limit of neutral xenon (97834.0 cm^{-1}) reported by Moore (1) is adopted as ΔHf^o_0 for Xe$^+$(g). The ionization limit is converted from cm^{-1} to kcal/mol using the factor, 1 cm^{-1} = 2.859144 x 10^{-3} kcal/mol, which is derived from the latest CODATA fundamental constants (2). The uncertainty in the ionization limit is estimated to be ±2 cm^{-1} which corresponds to an uncertainty of ±0.006 kcal/mol in the heat of formation. The value of ΔHf^o_{298} is derived from ΔHf^o_0 using auxiliary JANAF data (3).

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights by Moore (4) is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function (5) has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 90,000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore (1). The reported uncertainty in S^o_{298} is due to uncertainties in the gram formula weight and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures (5).

The thermodynamic functions reported here agree with those by Green et al. (6) and Hilsenrath et al. (7) within the limits of the uncertainty.

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