JANAF thermochemical tables, 1978 supplement

Cite as: Journal of Physical and Chemical Reference Data **7**, 793 (1978); https://doi.org/10.1063/1.555580

M. W. Chase, J. L. Curnutt, R. A. McDonald, and A. N. Syverud

Journal of Physical and Chemical Reference Data **7**, 793 (1978); https://doi.org/10.1063/1.555580

JANAF Thermochemical Tables, 1978 Supplement

M. W. Chase, Jr., J. L. Curnutt, R. A. McDonald, and A. N. Syverud

Thermal Research, The Dow Chemical Company, Midland, Michigan 48640

The thermodynamic tabulations previously published in NSRDS-NBS 37, the 1974 Supplement (J. Phys. Chem. Ref. Data 3, 311 (1974)), and the 1975 Supplement (J. Phys. Chem. Ref. Data 4, 1 (1975)) are extended by 131 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. 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 seven publications [1–7]. The four early publications [4–7] are superseded by three more recent publications [1, 2, 3]. NSRDS-NBS 37 [1] includes all work through June 30, 1970. Tables generated in the period June 30, 1970 to June 30, 1974 are included in the 1974 and 1975 Supplements [2, 3]. Tables generated in the period June 30, 1974 to June 30, 1976 are combined in this article to provide 131 additional tables which are to be used in conjunction with the three more recent publications [1, 2, 3].

As of June 30, 1976, there are 1322 tabulations involving 35 elements and their compounds. The 35 elements are H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Fe, Co, Cu, Br, Sr, Zr, Nb, Mo, I, 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 2nd and 3rd law results and often list values (in units of eu 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 3rd law heats of reaction. Our experience indicates that this method agrees closely, but not exactly, with the Σ-method.

In the tabulations the Gibbs free energy function and the enthalpy are referenced 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 maintaining the nomenclature within the tables while gradually coverting each new or revised table to the 1969 atomic weights and the IPTS-68 temperature scale. This is not an easy and unambiguous task, as the articles appearing in the literature do not always specify the standards used.

Finally, the JANAF Tables are presented in terms of the thermochemical calorie. The symbols cal mol^{-1} deg^{-1} and gibbs/mol are identical and refer to units of defined thermochemical calorie per kelvin-mole. These units can be converted to SI units of J mol^{-1} K^{-1} by multiplying the tabulated value by 4.184. Similarly, values in kcal mol^{-1} can be converted to kJ mol^{-1} by multiplying by the same factor.

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 appro-

0047-2689/78/3120-0793 $08.00

priate cross reference for the currently accepted Chemical Abstracts name is also included. The index in section 5 is the complete index for the JANAF Thermochemical Tables as of June 30, 1976. This complete index lists tables which are in NSRDS-NBS 37 [1], the 1974 Supplement [2], the 1975 Supplement [3], and tables which are in this article (the latter indicated by an "*"). It should be emphasized that the tables in this article may be new (in which case there is no corresponding entry in the previous three publications [1, 2, 3]) or revised (in which case the table in this article supersedes the corresponding table in one of the previous three publications [1, 2, 3]). The tables are arranged in this article in the same order as given in the complete index of section 5. The order is the same as that used by Chemical Abstracts in their formula index.

2. Acknowledgements

The JANAF Thermochemical Tables Project, as contained in this article, is sponsored solely by the Air Force Office of Scientific Research (Contract F44620-70-C-0104 and F44620-75-C-0048). The JANAF project has been monitored by Dr. Joseph F. Masi. His cooperation, direction, and encouragement are greatly appreciated. In Thermal Research 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 Alan N. Syverud, Jerry L. Curnutt, Richard A. McDonald, Joseph R. Downey, Jr., and Edward A. Valenzuela. We thank the staff of Computation Research Laboratory of The Dow Chemical Company for their assistance in the production of these tables, with special thanks to Barbara Boman, Shiela Knoerr, Patricia Grochowski, Lisa Ittner, and Dana Donley.

3. References

[1] JANAF Thermochemical Tables, 2nd Edition, NSRDS-NBS 37, Catalog Number C13.48:37, U.S. Government Printing Office, Washington, D.C., 1971.

[2] JANAF Thermochemical Tables, 1974 Supplement, J. Phys. Chem. Ref. Data 3, 311 (1974).

[3] JANAF Thermochemical Tables, 1975 Supplement, J. Phys. Chem. Ref. Data 4, 1 (1975).

[4] JANAF Thermochemical Tables, PB 168370, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1965.

[5] JANAF Thermochemical Tables, PB 168370-1, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1966.

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

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

4. List of Tables in 1978 Supplement

5. Complete List of JANAF Thermochemical Tables

FILING ORDER	TABLE TITLE
Al	Aluminum (ref st)
Al	Aluminum (c)
Al	Aluminum (ℓ)
Al	Aluminum, monatomic (g)
Al^+	Aluminum unipos ion (g)
$AlBO_2$	Aluminum monoborate (g)
AlBr	Aluminum monobromide (g)
$AlBr_3$	Aluminum tribromide (c)
$AlBr_3$	Aluminum tribromide (ℓ)
$AlBr_3$	Aluminum tribromide (g)
AlCl	Aluminum monochloride (g)
$AlCl^+$	*Aluminum monochloride unipos ion (g)
AlClF	*Aluminum chloride fluoride (g)
$AlClF^+$	*Aluminum chloride fluoride unipos (g)
$AlClF_2$	*Aluminum chloride difluoride (g)
AlClO	Aluminum oxychloride (c)
AlClO	Aluminum oxychloride (g)
$AlCl_2$	*Aluminum dichloride (g)
$AlCl_2^+$	*Aluminum dichloride unipos ion (g)
$AlCl_2^-$	*Aluminum dichloride unineg ion (g)
$AlCl_2F$	*Aluminum dichloride fluoride (g)
$AlCl_3$	Aluminum trichloride (c)
$AlCl_3$	Aluminum trichloride (ℓ)
$AlCl_3$	Aluminum trichloride (g)
$AlCl_4K$	Potassium tetrachloroaluminate (c)
$AlCl_4Na$	Sodium tetrachloroaluminate (c)
$AlCl_6K_3$	Tripotassium hexachloroaluminate (c)
$AlCl_6Na_3$	Trisodium hexachloroaluminate (c)
AlF	*Aluminum monofluoride (g)
AlF^+	*Aluminum monofluoride unipos ion (g)
AlFO	*Aluminum fluoride oxide (g)
AlF_2	*Aluminum difluoride (g)
AlF_2^+	*Aluminum difluoride unipos ion (g)
AlF_2^-	*Aluminum difluoride unineg ion (g)
AlF_2O	*Aluminum difluoride oxide (g)
AlF_2O^-	*Aluminum difluoride oxide neg ion (g)
AlF_3	Aluminum trifluoride (c)
AlF_3	Aluminum trifluoride (g)
AlF_4^-	*Tetrafluoroaluminate unineg ion (g)
AlF_4Li	Lithium fluoroaluminate (g)
AlF_4Na	Sodium tetrafluoroaluminate (g)
AlF_6K_3	Tripotassium hexafluoroaluminate (c)
AlF_6Li_3	Trilithium hexafluoroaluminate (c)
AlF_6Li_3	Trilithium aluminum hexafluoride (ℓ)
AlF_6Na_3	Cryolite (c)
AlF_6Na_3	Cryolite (ℓ)
AlH	Aluminum monohydride (g)
AlHO	Aluminum monoxyhydride (g)
AlHO	Aluminum monohydroxide (g)
$AlHO^+$	Aluminum hydroxide unipos ion (g)
$AlHO^-$	Aluminum hydroxide unineg ion (g)
$AlHO_2$	Aluminum dioxyhydride (g)
AlH_4Li	Lithium aluminum hydride (c)

FILING ORDER	TABLE TITLE
AlI	Aluminum monoiodide (g)
AlI_3	Aluminum triiodide (c)
AlI_3	Aluminum triiodide (ℓ)
AlI_3	Aluminum triiodide (g)
$AlLiO_2$	Lithium aluminate (c)
$AlLiO_2$	Lithium aluminate (ℓ)
AlN	Aluminum nitride (c)
AlN	Aluminum nitride (g)
$AlNaO_2$	Sodium aluminate (c)
AlO	*Aluminum monoxide (g)
AlO^+	*Aluminum monoxide unipos ion (g)
AlO^-	*Aluminum monoxide unineg ion (g)
AlO_2	*Aluminum dioxide (g)
AlO_2^-	*Aluminum dioxide unineg ion (g)
AlS	Aluminum sulfide (g)
Al_2BeO_4	Beryllium aluminate (c)
Al_2BeO_4	Beryllium aluminate (ℓ)
Al_2Br_6	Aluminum tribromide, dimeric (g)
Al_2Cl_6	Aluminum trichloride dimeric (g)
$Al_2Cl_9K_3$	Potassium monochloroaluminate (c)
Al_2F_6	Aluminum trifluoride, dimer (g)
Al_2I_6	Aluminum triiodide, dimeric (g)
Al_2MgO_4	Magnesium aluminate (c)
Al_2MgO_4	Magnesium aluminate (ℓ)
Al_2O	*Aluminum suboxide (g)
Al_2O^+	*Aluminum suboxide unipos ion (g)
Al_2O_2	*Aluminum monoxide, dimeric (g)
$Al_2O_2^+$	*Dialuminum dioxide unipos ion (g)
Al_2O_3	*Alpha aluminum oxide (c)
Al_2O_3	*Delta aluminum oxide (c)
Al_2O_3	*Gamma aluminum oxide (c)
Al_2O_3	*Kappa aluminum oxide (c)
Al_2O_3	*Aluminum oxide (ℓ)
Al_2O_5Si	Aluminum silicate, sillimanite (c)
Al_2O_5Si	Andalusite (c)
Al_2O_5Si	Kyanite (c)
Al_6BeO_{10}	Aluminum beryllium oxide (c)
Al_6BeO_{10}	Aluminum beryllium oxide (ℓ)
$Al_6O_{13}Si_2$	Mullite (c)
B	Boron (ref st)
B	Boron, beta-rhombohedral (c)
B	Boron (ℓ)
B	Boron, monatomic (g)
B^+	Boron unipos ion (g)
$BBeO_2$	Beryllium monoborate (g)
BBr	Boron monobromide (g)
BBrCl	Boron bromochloride (g)
$BBrCl_2$	Boron bromodichloride (g)
BBrF	Boron bromofluoride (g)
$BBrF_2$	Boron bromodifluoride (g)
BBrO	Boron oxybromide (g)
BBr_2	Boron dibromide (g)

FILING ORDER	TABLE TITLE
BBr_2Cl	Boron dibromochloride (g)
BBr_2F	Boron dibromofluoride (g)
BBr_2H	Dibromoborane (g)
BBr_3	Boron tribromide (ℓ)
BBr_3	Boron tribromide (g)
BCl	Boron monochloride (g)
BCl^+	Boron monochloride unipos ion (g)
$BClF$	Boron chlorofluoride (g)
$BClF_2$	Boron chlorodifluoride (g)
$BClO$	Boron oxychloride (g)
BCl_2	Boron dichloride (g)
BCl_2^+	Boron dichloride unipos ion (g)
BCl_2^-	Boron dichloride unineg ion (g)
BCl_2F	Boron dichlorofluoride (g)
BCl_2H	Dichloroborane (g)
BCl_3	Boron trichloride (g)
BF	Boron monofluoride (g)
BFO	Boron oxyfluoride (g)
BF_2	Boron difluoride (g)
BF_2^+	Boron difluoride unipos ion (g)
BF_2^-	Boron difluoride unineg ion (g)
BF_2H	Difluoroborane (g)
BF_2HO	Boron hydroxydifluoride (g)
BF_2O	Boron oxydifluoride (g)
BF_3	Boron trifluoride (g)
BF_4K	Potassium tetrafluoroborate (c)
BF_4K	Potassium tetrafluoroborate (ℓ)
BF_4K	Potassium tetrafluoroborate (g)
BH	Boron monohydride (g)
BHO	* Boron hydride oxide (g)
BHO^+	* Boron hydride oxide unipos ion (g)
BHO^-	* Boron hydride oxide unineg ion (g)
BHO_2	Metaboric acid (c)
BHO_2	Metaboric acid (g)
BHS	* Boron hydride sulfide (g)
BHS^+	* Boron hydride sulfide unipos ion (g)
BH_2	Boron dihydride (g)
BH_2O_2	Boron dihydroxide (g)
BH_3	Boron trihydride (g)
BH_3O_3	Boric acid (c)
BH_3O_3	Boric acid (g)
BH_4K	Potassium borohydride (c)
BH_4Li	Lithium borohydride (c)
BH_4Na	Sodium borohydride (c)
BI	Boron iodide (g)
BI_2	Boron diiodide (g)
BI_3	Boron triiodide (g)
BKO_2	Potassium metaborate (c)
BKO_2	Potassium metaborate (ℓ)
BKO_2	Potassium metaborate (g)
$BLiO_2$	Lithium metaborate (c)
$BLiO_2$	Lithium metaborate (ℓ)
$BLiO_2$	Lithium metaborate (g)
BN	Boron nitride (c)

FILING ORDER	TABLE TITLE
BN	Boron nitride (g)
$BNaO_2$	Sodium metaborate (c)
$BNaO_2$	Sodium metaborate (ℓ)
$BNaO_2$	Sodium borate (g)
BO	Boron monoxide (g)
BO_2	Boron dioxide (g)
BO_2^-	Boron dioxide unineg ion (g)
BS	Boron monosulfide (g)
BTi	Titanium monoboride (c)
B_2	Boron, diatomic (g)
B_2BeO_4	Beryllium diborate (g)
$B_2Be_3O_6$	Beryllium orthoborate (c)
B_2Cl_4	Boron dichloride, dimeric (g)
B_2F_4	Boron difluoride dimeric (g)
B_2F_4O	Diboron tetrafluoromonoxide (g)
$B_2H_4O_4$	Boron dihydroxide dimeric (c)
$B_2H_4O_4$	Boron dihydroxide dimeric (g)
B_2H_6	Diborane (g)
B_2Mg	Magnesium diboride (c)
B_2O	Diboron monoxide (g)
B_2O_2	Boron monoxide, dimeric (g)
B_2O_3	Boron oxide (c)
B_2O_3	Boron oxide (ℓ)
B_2O_3	Boron oxide (g)
B_2O_4Pb	Lead diborate (c)
B_2Ti	Titanium diboride (c)
B_2Ti	Titanium diboride (ℓ)
B_2Zr	Zirconium diboride (c)
B_2Zr	Zirconium diboride (ℓ)
$B_3Cl_3O_3$	Boron oxychloride, trimeric (g)
$B_3FH_2O_3$	Monofluoroboroxine (g)
$B_3F_2HO_3$	Difluoroboroxine (g)
$B_3F_3O_3$	Boron oxyfluoride, trimeric (c)
$B_3F_3O_3$	Boron oxyfluoride, trimeric (g)
$B_3H_3O_3$	Boroxine (g)
$B_3H_3O_3$	Boroxin (c)
$B_3H_3O_6$	Metaboric acid, trimeric (g)
$B_3H_6N_3$	Borazine (g)
$B_4K_2O_7$	Dipotassiumtetraboronheptaoxide (c)
$B_4K_2O_7$	Dipotassiumtetraboronheptaoxide (ℓ)
$B_4Li_2O_7$	Lithium tetraborate (c)
$B_4Li_2O_7$	Lithium tetraborate (ℓ)
B_4Mg	Magnesium tetraboride (c)
$B_4Na_2O_7$	Sodium tetraboron heptaoxide (c)
$B_4Na_2O_7$	Sodium tetraboron heptaoxide (ℓ)
B_4O_7Pb	Lead tetraborate (c)
B_5H_9	Pentaborane (ℓ)
B_5H_9	Pentaborane (g)
$B_6K_2O_{10}$	Dipotassium hexaboron decaoxide (c)
$B_6Li_2O_{10}$	Lithium hexaborate (c)
$B_6Na_2O_{10}$	Disodium hexaboron decaoxide (c)
$B_6O_{10}Pb$	Lead hexaborate (c)
$B_8K_2O_{13}$	Dipotassium octaborontridecaoxide (c)
$B_8K_2O_{13}$	Dipotassium octaborontridecaoxide (ℓ)

FILING ORDER	TABLE TITLE
$B_8Li_2O_{13}$	Lithium octaborate (c)
$B_{10}H_{14}$	Decaborane (g)
$B_{10}H_{14}$	Decaborane (c)
$B_{10}H_{14}$	Decaborane (ℓ)
$B_{10}O_{17}Pb_2$	Lead decaborate (c)
Ba	Barium (ref st)
Ba	Barium (c)
Ba	Barium (ℓ)
Ba	Barium monatomic (g)
BaBr	* Barium monobromide (g)
$BaBr_2$	* Barium dibromide (c)
$BaBr_2$	* Barium dibromide (ℓ)
$BaBr_2$	* Barium dibromide (g)
BaCl	Barium monochloride (g)
$BaCl_2$	Barium dichloride (c)
$BaCl_2$	Barium dichloride (ℓ)
$BaCl_2$	Barium dichloride (g)
BaF	Barium monofluoride (g)
BaF^+	Barium monofluoride unipos ion (g)
BaF_2	Barium difluoride (c)
BaF_2	Barium difluoride (ℓ)
BaF_2	Barium difluoride (g)
BaHO	* Barium monohydroxide (g)
$BaHO^+$	* Barium monohydroxide unipos ion (g)
BaH_2O_2	* Barium dihydroxide, alpha (c)
BaH_2O_2	* Barium dihydroxide (ℓ)
BaH_2O_2	* Barium dihydroxide (g)
BaI	Barium monoiodide (g)
BaI_2	Barium diiodide (c)
BaI_2	Barium diiodide (ℓ)
BaI_2	Barium diiodide (g)
BaO	Barium oxide (c)
BaO	Barium oxide (ℓ)
BaO	Barium oxide (g)
Be	Beryllium (ref st)
Be	Beryllium (c)
Be	Beryllium (ℓ)
Be	Beryllium, monatomic (g)
Be^+	Beryllium unipos ion (g)
BeBr	* Beryllium monobromide (g)
$BeBr_2$	* Beryllium dibromide (c)
$BeBr_2$	Beryllium dibromide (ℓ)
$BeBr_2$	* Beryllium dibromide (g)
BeCl	Beryllium monochloride (g)
$BeCl^+$	Beryllium monochloride unipos ion (g)
BeClF	Beryllium chlorofluoride (g)
$BeCl_2$	Beryllium dichloride, alpha (c)
$BeCl_2$	Beryllium dichloride, beta (c)
$BeCl_2$	Beryllium dichloride (ℓ)
$BeCl_2$	Beryllium dichloride (g)
BeF	Beryllium monofluoride (g)

FILING ORDER	TABLE TITLE
BeF_2	Beryllium difluoride (c)
BeF_2	Beryllium difluoride (ℓ)
BeF_2	Beryllium difluoride (g)
BeF_3Li	Lithium beryllium fluoride (g)
BeF_3Li	Lithium beryllium trifluoride (c)
BeF_3Li	Lithium beryllium trifluoride (ℓ)
BeF_4Li_2	Lithium beryllium tetrafluoride (c)
BeF_4Li_2	Lithium beryllium tetrafluoride (ℓ)
BeH	Beryllium monohydride (g)
BeH^+	Beryllium hydride unipos ion (g)
BeHO	* Beryllium monohydroxide (g)
$BeHO^+$	* Beryllium hydroxide unipos ion (g)
BeH_2	Beryllium dihydride (g)
BeH_2O_2	* Beryllium dihydroxide, alpha (c)
BeH_2O_2	* Beryllium dihydroxide, beta (c)
BeH_2O_2	* Beryllium dihydroxide (g)
BeI	* Beryllium monoidide (g)
BeI_2	* Beryllium diiodide (c)
BeI_2	* Beryllium diiodide (ℓ)
BeI_2	* Beryllium diiodide (g)
BeN	Beryllium nitride (g)
BeO	* Beryllium oxide, alpha (c)
BeO	* Beryllium oxide, beta (c)
BeO	* Beryllium oxide (ℓ)
BeO	* Beryllium oxide (g)
BeO_4S	Beryllium sulfate, alpha (c)
BeO_4S	Beryllium sulfate, beta (c)
BeO_4S	Beryllium sulfate, gamma (c)
BeO_4W	Beryllium tungstate (c)
Be_2Cl_4	Beryllium chloride, dimeric (g)
Be_2F_2O	Diberyllium oxide difluoride (g)
Be_2O	Diberyllium oxide (g)
Be_2O_2	Beryllium oxide, dimeric (g)
Be_2O_4Si	Beryllium silicate (c)
Be_3N_2	Beryllium nitride, alpha (c)
Be_3N_2	Beryllium nitride (ℓ)
Be_3O_3	Beryllium oxide, trimeric (g)
Be_4O_4	Beryllium oxide, tetrameric (g)
Be_5O_5	Beryllium oxide, pentameric (g)
Be_6O_6	Beryllium oxide, hexameric (g)
Br	Bromine, monatomic (g)
BrCa	* Calcium monobromide (g)
BrCl	Bromine monochloride (g)
BrF	Bromine monofluoride (g)
BrF_3	Bromine trifluoride (g)
BrF_5	Bromine pentafluoride (g)
BrH	Hydrogen bromide (g)
BrH_4N	Ammonium bromide (c)
BrHg	Mercury monobromide (g)
BrI	Bromine monoiodide (g)
BrK	Potassium bromide (c)
BrK	Potassium bromide (ℓ)

FILING ORDER	TABLE TITLE
BrK	Potassium bromide (g)
BrLi	Lithium bromide (c)
BrLi	Lithium bromide (ℓ)
BrLi	Lithium bromide (g)
BrMg	* Magnesium monobromide (g)
BrN	Nitrogen bromide (g)
BrNO	Nitrosyl bromide (g)
BrNa	Sodium bromide (c)
BrNa	Sodium bromide (ℓ)
BrNa	Sodium bromide (g)
BrP	Phosphorus monobromide (g)
BrPb	Lead monobromide (g)
BrSr	* Strontium monobromide (g)
BrTi	Titanium monobromide (g)
BrW	Tungsten monobromide (g)
BrZr	Zirconium monobromide (g)
Br_2	Bromine, diatomic (ref st)
Br_2	Bromine, diatomic (ℓ)
Br_2	Bromine, diatomic (g)
Br_2Ca	Calcium dibromide (c)
Br_2Ca	Calcium dibromide (ℓ)
Br_2Ca	Calcium dibromide (g)
Br_2Fe	Ferrous bromide (c)
Br_2Fe	Ferrous bromide (ℓ)
Br_2Fe	Ferrous bromide (g)
Br_2Hg	Mercury dibromide (c)
Br_2Hg	Mercury dibromide (ℓ)
Br_2Hg	Mercury dibromide (g)
Br_2Hg_2	Mercury monobromide, dimeric (c)
Br_2K_2	Potassium bromide, dimeric (g)
Br_2Li_2	Lithium bromide, dimeric (g)
Br_2Mg	Magnesium dibromide (c)
Br_2Mg	Magnesium dibromide (ℓ)
Br_2Mg	Magnesium dibromide (g)
Br_2Mg^+	Magnesium dibromide unipos (g)
Br_2Na_2	Sodium dibromide, dimeric (g)
Br_2Pb	Lead dibromide (c)
Br_2Pb	Lead dibromide (ℓ)
Br_2Pb	Lead dibromide (g)
Br_2Sr	Strontium dibromide (c)
Br_2Sr	Strontium dibromide (ℓ)
Br_2Sr	Strontium dibromide (g)
Br_2Ti	Titanium dibromide (c)
Br_2Ti	Titanium dibromide (g)
Br_2Zr	Zirconium dibromide (c)
Br_2Zr	Zirconium dibromide (ℓ)
Br_2Zr	Zirconium dibromide (g)
Br_3OP	Phosphoryl bromide (g)
Br_3P	Phosphorus tribromide (g)
Br_3PS	Thiophosphoryl bromide (g)
Br_3Ti	Titanium tribromide (c)
Br_3Ti	Titanium tribromide (g)
Br_3Zr	Zirconium tribromide (c)
Br_3Zr	Zirconium tribromide (g)

FILING ORDER	TABLE TITLE
Br_4Fe_2	Iron dibromide dimeric (g)
Br_4Mg_2	Magnesium dibromide, dimeric (g)
Br_4Pb	Lead tetrabromide (g)
Br_4Ti	Titanium tetrabromide (c)
Br_4Ti	Titanium tetrabromide (ℓ)
Br_4Ti	Titanium tetrabromide (g)
Br_4Zr	* Zirconium tetrabromide (c)
Br_4Zr	* Zirconium tetrabromide (g)
Br_5Nb	* Niobium pentabromide (c)
Br_5Nb	* Niobium pentabromide (ℓ)
Br_5Nb	* Niobium pentabromide (g)
Br_5W	Tungsten pentabromide (c)
Br_5W	Tungsten pentabromide (ℓ)
Br_5W	Tungsten pentabromide (g)
Br_6W	Tungsten hexabromide (c)
Br_6W	Tungsten hexabromide (g)
CNb	Niobium monocarbide $NbC_{0.98}$ (c)
C	Carbon (ref st)
C	Carbon, monatomic (g)
C^-	Carbon unineg ion (g)
CAl	Aluminum carbide (g)
CB	Boron carbide (c)
CB_4	Boron carbide (ℓ)
CB_4	Boron carbide (g)
CBe_2	Beryllium carbide (c)
CBe_2	Beryllium carbide (ℓ)
CBr	Carbon monobromide (g)
$CBrF_3$	Bromotrifluoromethane (g)
CBrN	Cyanogen bromide (g)
CBr_4	Carbon tetrabromide (g)
CCl	Carbon monochloride (g)
CClFO	Carbonyl chlorofluoride (g)
$CClF_3$	Carbon chlorotrifluoride (g)
CClN	Cyanogen chloride (g)
CClO	Carbonyl monochloride (g)
CCl_2	Carbon dichloride (g)
CCl_2F_2	Carbon dichlorodifluoride (g)
CCl_2O	Carbonyl chloride (g)
CCl_3	Carbon trichloride (g)
CCl_3F	Carbon trichlorofluoride (g)
CCl_4	Carbon tetrachloride (g)
CCuN	Cuprous cyanide (c)
CF	Carbon monofluoride (g)
CF^+	Carbon monofluoride unipos ion (g)
CFN	Cyanogen fluoride (g)
CFO	Carbonyl monofluoride (g)
CF_2	Carbon difluoride (g)
CF_2^+	Carbon difluoride unipos ion (g)
CF_2O	Carbonyl fluoride (g)
CF_3	Carbon trifluoride (g)
CF_3^+	Trifluoromethyl unipos ion (g)
CF_3I	Trifluoriodomethane (g)
CF_4	Carbon tetrafluoride (g)

FILING ORDER	TABLE TITLE
CF_4O	Trifluoromethyl hypofluorite (g)
CH	Methylidyne (g)
CH^+	Methylidene unipos ion (g)
$CHCl$	Monochloromethylene (g)
$CHClF_2$	Chlorodifluoromethane (g)
$CHCl_2F$	Dichlorofluoromethane (g)
$CHCl_3$	Trichloromethane (g)
CHF	Monofluoromethylene (g)
$CHFO$	Formyl fluoride (g)
CHF_3	Trifluoromethane (g)
CHN	Hydrogen cyanide (g)
$CHNO$	Hydrogen isocyanate (g)
CHO	Formyl (g)
CHO^+	Formyl unipos ion (g)
CHP	Methinophosphide (g)
CH_2	Methylene (g)
CH_2ClF	Chlorofluoromethane (g)
CH_2Cl_2	Dichloromethane (g)
CH_2F_2	Difluoromethane (g)
CH_2O	Formaldehyde (g)
CH_3	Methyl (g)
CH_3Cl	Chloromethane (g)
CH_3Cl_3Si	Trichloromethylsilane (g)
CH_3F	Fluoromethane (g)
CH_3F_3Si	Trifluoromethylsilane (g)
CH_4	Methane (g)
CIN	Cyanogen iodide (g)
CKN	Potassium cyanide (c)
CKN	Potassium cyanide (ℓ)
CKN	Potassium cyanide (g)
CK_2O_3	Potassium carbonate (c)
CK_2O_3	Potassium carbonate (ℓ)
CLi_2O_3	Lithium carbonate (c)
CLi_2O_3	Lithium carbonate (ℓ)
$CMgO_3$	Magnesium carbonate (c)
CN	Cyano (g)
CN^+	Cyano unipos ion (g)
CN^-	Cyano unineg ion (g)
$CNNa$	Sodium cyanide (c)
$CNNa$	Sodium cyanide (ℓ)
$CNNa$	Sodium cyanide (g)
CNO	NCO radical (g)
CN_2	CNN radical (g)
CN_2	NCN radical (g)
CNa_2O_3	Sodium carbonate (c)
CNa_2O_3	Sodium carbonate (ℓ)
CO	Carbon monoxide (g)
COS	Carbon oxysulfide (g)
CO_2	Carbon dioxide (g)
CO_2^-	Carbon dioxide unineg ion (g)
CP	Carbon phosphide (g)
CS	Carbon monosulfide (g)
CS_2	Carbon disulfide (g)

FILING ORDER	TABLE TITLE
CSi	Silicon carbide alpha (c)
CSi	Silicon carbide, beta (c)
CSi	Silicon carbide (ℓ)
CSi	Silicon carbide (g)
CSi_2	Disilicon carbide (g)
CTa	Tantalum carbide (c)
CTa	Tantalum carbide (ℓ)
CTi	Titanium carbide (c)
CTi	Titanium carbide (ℓ)
CZr	Zirconium carbide (c)
CZr	Zirconium carbide (ℓ)
C_2	Carbon, diatomic (g)
C_2^-	Carbon dimeric unineg ion (g)
C_2Be	Beryllium carbide (g)
C_2Cl_2	Dichloroacetylene (g)
C_2Cl_4	Tetrachloroethylene (g)
C_2Cl_6	Perchloroethane (g)
C_2Cr_3	Trichromium dicarbide (c)
C_2F_2	Difluoroacetylene (g)
C_2F_3N	Trifluoroacetonitrile (g)
C_2F_4	Tetrafluoroethylene (g)
C_2F_6	Hexafluoroethane (g)
C_2H	CCH radical (g)
C_2HCl	Chloroacetylene (g)
C_2HF	Monofluoroacetylene (g)
C_2H_2	Acetylene (g)
C_2H_4	Ethylene (g)
C_2H_4O	Ethylene oxide (g)
$C_2K_2N_2$	Potassium cyanide, dimeric (g)
C_2Li_2	Lithium carbide (c)
C_2Mg	Magnesium carbide (c)
C_2N	CNC radical (g)
C_2N_2	Cyanogen (g)
$C_2N_2Na_2$	Sodium cyanide dimeric (g)
C_2O	CCO radical (g)
C_2Si	Silicon dicarbide (g)
C_3	Carbon, triatomic (g)
C_3Al_4	Aluminum carbide (c)
C_3Cr_7	Heptachromium tricarbide (c)
C_3Mg_2	Magnesium carbide (c)
C_3O_2	Carbon suboxide (g)
C_4	Carbon, tetratomic (g)
$C_4H_{12}Si$	Tetramethylsilane (g)
C_4N_2	Carbon subnitride (g)
C_5	Carbon, pentatomic (g)
C_6Cr_{23}	Chromium carbide $Cr_{23}C_6$ (c)
Ca	Calcium (ref st)
Ca	Calcium, alpha (c)
Ca	Calcium, beta (c)
Ca	Calcium (ℓ)
Ca	Calcium (g)
Ca^+	Calcium unipos ion (g)

FILING ORDER		TABLE TITLE
$CaCl$		Calcium monochloride (g)
$CaCl_2$		Calcium chloride (c)
$CaCl_2$		Calcium chloride (ℓ)
$CaCl_2$		Calcium chloride (g)
CaF		Calcium monofluoride (g)
CaF_2		Calcium difluoride (c)
CaF_2		Calcium difluoride (ℓ)
CaF_2		Calcium difluoride (g)
$CaHO$	*	Calcium monohydroxide (g)
$CaHO^+$	*	Calcium monohydroxide unipos ion (g)
CaH_2O_2	*	Calcium dihydroxide (c)
CaH_2O_2	*	Calcium dihydroxide (g)
CaI		Calcium monoiodide (g)
CaI_2		Calcium diiodide (c)
CaI_2		Calcium diiodide (ℓ)
CaI_2		Calcium diiodide (g)
CaO		Calcium oxide (c)
CaO		Calcium oxide (ℓ)
CaO	*	Calcium oxide (g)
CaS		Calcium sulfide (c)
Ca_2	*	Dicalcium (g)
Cl		Chlorine, monatomic (g)
Cl^+		Chlorine unipos ion (g)
Cl^-		Chlorine unineg ion (g)
$ClCo$		Cobalt monochloride (g)
$ClCs$		Cesium monochloride (c)
$ClCs$		Cesium monochloride (ℓ)
$ClCs$		Cesium monochloride (g)
$ClCu$		Cuprous chloride (c)
$ClCu$		Copper monochloride (ℓ)
$ClCu$		Copper monochloride (g)
ClF		Chlorine fluoride (g)
$ClFLi_2$		Lithium chlorofluoride (g)
$ClFMg$		Magnesium chlorofluoride (g)
$ClFO_2S$		Sulfuryl chloride fluoride (g)
$ClFO_3$		Perchloryl fluoride (g)
ClF_2OP		Phosphoryl difluorochloride (g)
ClF_3		Chlorine trifluoride (g)
ClF_3Si		Chlorotrifluorosilane (g)
ClF_5		Chlorine pentafluoride (g)
$ClFe$		Iron monochloride (g)
ClH		Hydrogen chloride (g)
$ClHO$		Hydrogen oxychloride (g)
ClH_3Si		Chlorosilane (g)
ClH_4N		Ammonium chloride (c)
ClH_4NO_4		Ammonium perchlorate (c)
$ClHg$		Mercury monochloride (g)
ClI		Iodine chloride (c)
ClI		Iodine chloride (ℓ)
ClI		Iodine chloride (g)
ClK		Potassium chloride (c)
ClK		Potassium chloride (ℓ)
ClK		Potassium chloride (g)
$ClKO_4$		Potassium perchlorate (c)
$ClLI$		Lithium chloride (c)
$ClLi$		Lithium chloride (ℓ)
$ClLi$		Lithium chloride (g)
$ClLiO$		Lithium oxychloride (g)
$ClLiO_4$		Lithium perchlorate (c)
$ClLiO_4$		Lithium perchlorate (ℓ)
$ClMg$		Magnesium monochloride (g)
$ClMg^+$		Magnesium monochloride unipos ion (g)
$ClNO$		Nitrosyl chloride (g)
$ClNO_2$		Nitryl chloride (g)
$ClNa$		Sodium chloride (c)
$ClNa$		Sodium chloride (ℓ)
$ClNa$		Sodium chloride (g)
$ClNaO_4$		Sodium perchlorate (c)
ClO		Chlorine monoxide (g)
$ClOTi$		Titanium oxychloride (g)
ClO_2		Chlorine dioxide (g)
ClP		Phosphorus monochloride (g)
$ClPb$		Lead monochloride (g)
$ClPb^+$		Lead monochloride unipos ion (g)
$ClSi$		Silicon monochloride (g)
$ClSr$		Strontium monochloride (g)
$ClTi$		Titanium monochloride (g)
ClW		Tungsten monochloride (g)
$ClZr$		Zirconium monochloride (g)
Cl_2		Chlorine, diatomic (ref st)
Cl_2Co		Cobalt dichloride (c)
Cl_2Co		Cobalt dichloride (ℓ)
Cl_2Co	*	Cobalt dichloride (g)
Cl_2Cs_2		Cesium monochloride dimer (g)
Cl_2Cu		Copper dichloride (c)
Cl_2FOP		Phosphoryl fluorodichloride (g)
Cl_2Fe		Iron dichloride (c)
Cl_2Fe		Iron dichloride (ℓ)
Cl_2Fe		Iron dichloride (g)
Cl_2H_2Si		Dichlorosilane (g)
Cl_2Hg		Mercury dichloride (c)
Cl_2Hg		Mercury dichloride (ℓ)
Cl_2Hg		Mercury dichloride (g)
Cl_2Hg_2		Mercury chloride, dimeric (c)
Cl_2K_2		Potassium chloride, dimeric (g)
Cl_2Li_2		Lithium chloride, dimeric (g)
Cl_2Mg		Magnesium chloride (c)
Cl_2Mg		Magnesium chloride (ℓ)
Cl_2Mg		Magnesium chloride (g)
Cl_2MoO_2		Molybdenum dioxydichloride (g)
Cl_2Na_2		Sodium chloride dimeric (g)
Cl_2O		Chlorine monoxide (g)
Cl_2OTl		Titanium oxydichloride (g)
Cl_2O_2S		Sulfuryl chloride (g)
Cl_2O_2W		Tungsten dioxydichloride (c)
Cl_2O_2W		Tungsten dioxydichloride (g)
Cl_2Pb		Lead dichloride (c)
Cl_2Pb		Lead dichloride (ℓ)
Cl_2Pb		Lead dichloride (g)

FILING ORDER	TABLE TITLE
Cl_2Pb^+	Lead dichloride unipos ion (g)
Cl_2Si	Silicon dichloride (g)
Cl_2Sr	Strontium dichloride (c)
Cl_2Sr	Strontium dichloride (ℓ)
Cl_2Sr	Strontium dichloride (g)
Cl_2Ti	Titanium dichloride (c)
Cl_2Ti	Titanium dichloride (g)
Cl_2W	Tungsten dichloride (c)
Cl_2W	Tungsten dichloride (g)
Cl_2Zr	Zirconium dichloride (c)
Cl_2Zr	Zirconium dichloride (ℓ)
Cl_2Zr	Zirconium dichloride (g)
Cl_3Co	Cobalt trichloride (g)
Cl_3Cu_3	Copper monochloride, trimeric (g)
Cl_3FSi	Trichlorofluorosilane (g)
Cl_3Fe	Iron trichloride (c)
Cl_3Fe	Iron trichloride (ℓ)
Cl_3Fe	Iron trichloride (g)
Cl_3HSi	Trichlorosilane (g)
Cl_3Li_3	Lithium chloride, trimeric (g)
Cl_3OP	Phosphoryl chloride (g)
Cl_3P	Phosphorus trichloride (g)
Cl_3PS	Thiophosphoryl chloride (g)
Cl_3Si	Silicon trichloride (g)
Cl_3Ti	Titanium trichloride (c)
Cl_3Ti	Titanium trichloride (g)
Cl_3Zr	Zirconium trichloride (c)
Cl_3Zr	Zirconium trichloride (g)
Cl_4Co_2	Cobalt dichloride, dimeric (g)
Cl_4Fe_2	Iron dichloride, dimeric (g)
Cl_4Mg_2	Magnesium dichloride, dimeric (g)
Cl_4Mo	Molybdenum tetrachloride (c)
Cl_4Mo	Molybdenum tetrachloride (ℓ)
Cl_4Mo	Molybdenum tetrachloride (g)
Cl_4OW	Tungsten oxytetrachloride (c)
Cl_4OW	Tungsten oxytetrachloride (ℓ)
Cl_4OW	Tungsten oxytetrachloride (g)
Cl_4Pb	Lead tetrachloride (g)
Cl_4Si	Silicon tetrachloride (g)
Cl_4Ti	Titanium tetrachloride (c)
Cl_4Ti	Titanium tetrachloride (ℓ)
Cl_4Ti	Titanium tetrachloride (g)
Cl_4W	Tungsten tetrachloride (c)
Cl_4W	Tungsten tetrachloride (g)
Cl_4Zr	* Zirconium tetrachloride (c)
Cl_4Zr	* Zirconium Tetrachloride (g)
Cl_5Mo	Molybdenum pentachloride (c)
Cl_5Mo	Molybdenum pentachloride (ℓ)
Cl_5Mo	Molybdenum pentachloride (g)
Cl_5Nb	* Niobium pentachloride (c)
Cl_5Nb	* Niobium pentachloride (ℓ)
Cl_5Nb	* Niobium pentachloride (g)
Cl_5P	Phosphorus pentachloride (g)

FILING ORDER	TABLE TITLE
Cl_5Ta	* Tantalum pentachloride (c)
Cl_5Ta	* Tantalum pentachloride (ℓ)
Cl_5Ta	* Tantalum pentachloride (g)
Cl_5W	Tungsten pentachloride (c)
Cl_5W	Tungsten pentachloride (ℓ)
Cl_5W	Tungsten pentachloride (g)
Cl_6Fe_2	*Iron trichloride, dimeric (g)*
Cl_6Mo	Molybdenum hexachloride (c)
Cl_6Mo	Molybdenum hexachloride (g)
Cl_6W	Tungsten hexachloride, alpha (c)
Cl_6W	Tungsten hexachloride, beta (c)
Cl_6W	Tungsten hexachloride (ℓ)
Cl_6W	Tungsten hexachloride (g)
$Cl_{10}W_2$	Tungsten pentachloride, dimeric (g)
Co	Cobalt (ref st)
Co	Cobalt (c)
Co	Cobalt (ℓ)
Co	Cobalt, monatomic (g)
Co^+	*Cobalt unipos ion (g)*
CoF_2	Cobalt difluoride (c)
CoF_2	Cobalt difluoride (ℓ)
CoF_2	Cobalt difluoride (g)
CoF_3	Cobalt trifluoride (c)
CoO	Cobalt monoxide (c)
CoO_4S	Cobalt sulfate (c)
Co_3O_4	Tricobalt tetraoxide (c)
Cr	Chromium (ref st)
Cr	Chromium (c)
Cr	Chromium (ℓ)
Cr	Chromium, monatomic (g)
CrN	Chromium mononitride (c)
CrN	Chromium mononitride (g)
CrO	Chromium monoxide (g)
CrO_2	Chromium dioxide (g)
CrO_3	Chromium trioxide (g)
Cr_2N	Chromium subnitride (c)
Cr_2O_3	Dichromium trioxide (c)
Cr_2O_3	Dichromium trioxide (ℓ)
Cs	Cesium (ref st)
Cs	Cesium (c)
Cs	Cesium (ℓ)
Cs	Cesium, monatomic (g)
Cs^+	Cesium unipos ion (g)
CsF	Cesium monofluoride (c)
CsF	Cesium monofluoride (ℓ)
CsF	Cesium monofluoride (g)
CsHO	Cesium hydroxide (c)
CsHO	Cesium hydroxide (ℓ)
CsHO	Cesium hydroxide (g)
$CsHO^+$	Cesium hydroxide unipos ion (g)
CsO	Cesium monoxide (g)

FILING ORDER	TABLE TITLE
Cs_2	Cesium, diatomic (g)
Cs_2F_2	Cesium monofluoride, dimeric (g)
$Cs_2H_2O_2$	Cesium hydroxide, dimeric (g)
Cs_2O	Dicesium monoxide (g)
Cu	Copper (ref st)
Cu	Copper (c)
Cu	Copper (ℓ)
Cu	Copper, monatomic (g)
Cu^+	Copper unipos ion (g)
CuF	Copper monofluoride (c)
CuF	Copper monofluoride (g)
CuF_2	Copper difluoride (c)
CuF_2	Copper difluoride (ℓ)
CuF_2	Copper difluoride (g)
CuH_2O_2	Copper hydroxide (c)
CuO	Cupric oxide (c)
CuO	Copper monoxide (g)
CuO_4S	Copper sulfate (c)
Cu_2	Copper, diatomic (g)
Cu_2O	Cuprous oxide (c)
Cu_2O	Dicopper monoxide (ℓ)
Cu_2O_5S	Basic copper sulfate (c)
F	Fluorine, monatomic (g)
F^-	Fluorine unineg ion (g)
FFe	Iron monofluoride (g)
FH	Hydrogen fluoride (g)
FHO	Hypofluorous acid (g)
FHO_3S	Fluorosulfuric acid (g)
FH_3Si	* Fluorosilane (g)
FHg	Mercury monofluoride (g)
FI	Iodine fluoride (g)
FK	Potassium fluoride (c)
FK	Potassium fluoride (ℓ)
FK	Potassium fluoride (g)
FLi	Lithium fluoride (c)
FLi	Lithium fluoride (ℓ)
FLi	Lithium fluoride (g)
FLiO	Lithium oxyfluoride (g)
FMg	* Magnesium monofluoride (g)
FMg^+	* Magnesium monofluoride unipos ion (g)
FN	Nitrogen monofluoride (g)
FNO	Nitrosyl fluoride (g)
FNO_2	Nitryl fluoride (g)
FNO_3	Fluorine nitrate (g)
FNa	Sodium fluoride (c)
FNa	Sodium fluoride (ℓ)
FNa	Sodium fluoride (g)
FO	Fluorine oxide (g)
FOTi	Titanium oxyfluoride (g)
FO_2	Dioxygen fluoride (g)
FP	Phosphorus monofluoride (g)

FILING ORDER	TABLE TITLE
FPS	Phosphorus thiofluoride (g)
FPb	Lead monofluoride (g)
FS	* Sulfur monofluoride (g)
FS^+	* Sulfur monofluoride unipos ion (g)
FSi	Silicon monofluoride (g)
FSr	Strontium monofluoride (g)
FSr^+	Strontium monofluoride unipos ion (g)
FTi	Titanium monofluoride (g)
FW	Tungsten monofluoride (g)
FZr	Zirconium monofluoride (g)
F_2	Fluorine, diatomic (ref st)
F_2Fe	Iron difluoride (c)
F_2Fe	Iron difluoride (ℓ)
F_2Fe	Iron difluoride (g)
F_2HK	Potassium bifluoride (c)
F_2HK	Potassium bifluoride (ℓ)
F_2H_2Si	* Difluorosilane (g)
F_2Hg	Mercury difluoride (c)
F_2Hg	Mercury difluoride (ℓ)
F_2Mg	Mercury difluoride (g)
F_2Hg_2	Mercury monofluoride, dimeric (c)
F_2K^-	Potassium difluoride unineg ion (g)
F_2K_2	Potassium fluoride, dimeric (g)
F_2Li^-	Lithium difluoride unineg ion (g)
F_2Li_2	Lithium fluoride, dimeric (g)
F_2Mg	* Magnesium difluoride (c)
F_2Mg	* Magnesium difluoride (ℓ)
F_2Mg	* Magnesium difluoride (g)
F_2Mg^+	* Magnesium difluoride unipos ion (g)
F_2N	Nitrogen difluoride (g)
F_2N_2	Cis-difluorodiazirine (g)
F_2N_2	Trans-difluorodiazirine (g)
F_2Na^-	Sodium difluoride unineg ion (g)
F_2Na_2	Sodium fluoride, dimeric (g)
F_2O	Oxygen difluoride (g)
F_2OS	Thionyl fluoride (g)
F_2OSi	Silicon oxydifluoride (g)
F_2OTi	Titanium oxydifluoride (g)
F_2O_2S	Sulfuryl fluoride (g)
F_2P	Phosphorus difluoride (g)
F_2Pb	Lead difluoride, alpha (c)
F_2Pb	Lead difluoride, beta (c)
F_2Pb	Lead difluoride (ℓ)
F_2Pb	Lead difluoride (g)
F_2S	* Sulfur difluoride (g)
F_2S_2	* Difluorodisulfane (g)
F_2S_2	* Thiothionyl fluoride (g)
F_2Si	* Silicon difluoride (g)
F_2Sr	Strontium difluoride (c)
F_2Sr	Strontium difluoride (ℓ)
F_2Sr	Strontium difluoride (g)
F_2Ti	Titanium difluoride (g)
F_2Zr	Zirconium difluoride (c)

FILING ORDER	TABLE TITLE
F_2Zr	Zirconium difluoride (ℓ)
F_2Zr	Zirconium difluoride (g)
F_3Fe	Iron trifluoride (c)
F_3Fe	Iron trifluoride (g)
F_3HSi	* Trifluorosilane (g)
F_3Li_3	Lithium fluoride, trimeric (g)
F_3N	Nitrogen trifluoride (g)
F_3NO	Trifluoramine oxide (g)
F_3OP	Phosphoryl fluoride (g)
F_3P	Phosphorus trifluoride (g)
F_3PS	Thiophosphoryl fluoride (g)
F_3S	* Sulfur trifluoride (g)
F_3Si	* Silicon trifluoride (g)
F_3Ti	Titanium trifluoride (c)
F_3Ti	Titanium trifluoride (g)
F_3Zr	Zirconium trifluoride (c)
F_3Zr	Zirconium trifluoride (g)
F_4Mg_2	* Magnesium difluoride dimeric (g)
F_4MoO	Molybdenum oxytetrafluoride (g)
F_4N_2	Tetrafluorohydrazine (g)
F_4OW	Tungsten oxytetrafluoride (c)
F_4OW	Tungsten oxytetrafluoride (ℓ)
F_4OW	Tungsten oxytetrafluoride (g)
F_4Pb	Lead Tetrafluoride (g)
F_4S	* Sulfur tetrafluoride (g)
F_4Si	* Silicon tetrafluoride (g)
F_4Ti	Titanium tetrafluoride (c)
F_4Ti	Titanium tetrafluoride (g)
F_4Zr	* Zirconium tetrafluoride (c)
F_4Zr	* Zirconium tetrafluoride (g)
F_5I	Iodine pentafluoride (g)
F_5P	Phosphorus pentafluoride (g)
F_5S	* Sulfur pentafluoride (g)
F_6Mo	Molybdenum hexafluoride (ℓ)
F_6Mo	Molybdenum hexafluoride (g)
F_6S	* Sulfur hexafluoride (g)
F_6W	Tungsten hexafluoride (ℓ)
F_6W	Tungsten hexafluoride (g)
F_7I	Iodine heptafluoride (g)
Fe	Iron (ref st)
Fe	Iron (c)
Fe	Iron (ℓ)
Fe	Iron (g)
FeH_2O_2	Iron hydroxide (c)
FeH_2O_2	Iron dihydroxide (g)
FeH_3O_3	Iron Trihydroxide (c)
FeI_2	Iron diiodide (c)
FeI_2	Iron diiodide (ℓ)
FeI_2	Iron diiodide (g)
FeO	Wustite (c)
FeO	Iron oxide (c)
FeO	Iron oxide (ℓ)

FILING ORDER	TABLE TITLE
FeO	Iron oxide (g)
FeO_4S	Iron sulfate (c)
Fe_2I_4	Iron diiodide, dimeric (g)
Fe_2O_3	Hematite (c)
$Fe_2O_{12}S_3$	Diiron trisulfate (c)
Fe_3O_4	Magnetite (c)
H	Hydrogen, monatomic (g)
H^+	Proton gas (g)
H^-	Hydrogen unineg ion (g)
HHg	Mercury monohydride (g)
HI	Hydrogen iodide (g)
HK	Potassium hydride (c)
HK	Potassium hydride (g)
HKO	Potassium hydroxide (c)
HKO	Potassium hydroxide (ℓ)
HKO	Potassium hydroxide (g)
HKO^+	Potassium hydroxide unipos ion (g)
HLi	Lithium hydride (c)
HLi	Lithium hydride (ℓ)
HLi	Lithium hydride (g)
HLiO	Lithium hydroxide (c)
HLiO	Lithium hydroxide (ℓ)
HLiO	Lithium hydroxide (g)
$HLiO^+$	Lithium hydroxide unipos ion (g)
HMg	Magnesium monohydride (g)
HMgO	* Magnesium monohydroxide (g)
$HMgO^+$	* Magnesium hydroxide unipos ion (g)
HN	Imidogen (g)
HNO	Nitroxyl (g)
HNO_2	Nitrous acid, cis- (g)
HNO_2	Nitrous acid, trans- (g)
HNO_3	Nitric acid (g)
HNa	Sodium hydride (c)
HNa	Sodium hydride (g)
HNaO	Sodium hydroxide (ℓ)
HNaO	Sodium hydroxide (g)
$HNaO^+$	Sodium hydroxide unipos ion (g)
HO	Hydroxyl (g)
HO^+	Hydroxyl unipos ion (g)
HO^-	Hydroxyl unineg ion (g)
HOSr	* Strontium monohydroxide (g)
$HOSr^+$	* Strontium hydroxide unipos ion (g)
HO_2	Hydroperoxyl (g)
HP	Phosphorus monohydride (g)
HPb	Lead monohydride (g)
HS	Sulfur monohydride (g)
HSi	Silicon monohydride (g)
HSi^+	Silicon monohydride unipos ion (g)
HZr	Zirconium hydride (g)
H_2	Hydrogen, diatomic (ref st)
$H_2K_2O_2$	Potassium hydroxide, dimeric (g)
$H_2Li_2O_2$	Lithium hydroxide, dimeric (g)

FILING ORDER	TABLE TITLE
H_2Mg	Magnesium hydride (c)
H_2MgO_2	* Magnesium dihydroxide (c)
H_2MgO_2	* Magnesium dihydroxide (g)
H_2MoO_4	Molybdic acid (g)
H_2N	Amidogen (g)
H_2N_2	Di-imide (g)
$H_2Na_2O_2$	Sodium hydroxide, dimeric (g)
H_2O	Water (g)
H_2O_2	Hydrogen peroxide (g)
H_2O_2Sr	* Strontium dihydroxide (c)
H_2O_2Sr	* Strontium dihydroxide (ℓ)
H_2O_2Sr	* Strontium dihydroxide (g)
H_2O_4S	Sulfuric acid (ℓ)
H_2O_4S	Sulfuric acid (g)
H_2O_4W	Tungstic acid (c)
H_2O_4W	Tungstic acid (g)
H_2P	Phosphorous hydride (g)
H_2S	Hydrogen sulfide (g)
H_2Ti	Titanium hydride (c)
H_3N	Ammonia (g)
H_3O^+	Hydronium (g)
H_3O_4P	Phosphoric acid (c)
H_3O_4P	Phosphoric acid (ℓ)
H_3P	Phosphine (g)
H_4IN	Ammonium iodide (c)
H_4N_2	Hydrazine (ℓ)
H_4N_2	Hydrazine (g)
H_4Si	* Silane (g)
Hg	Mercury (ref st)
Hg	Mercury (ℓ)
Hg	Mercury (g)
HgI	Mercury monoiodide (g)
HgI_2	Mercury diiodide (c)
HgI_2	Mercury diiodide (ℓ)
HgI_2	Mercury diiodide (g)
HgO	Mercuric oxide (c)
HgO	Mercuric oxide (g)
Hg_2I_2	Mercury monoiodide, dimeric (c)
Hg_2I_2	Mercury monoiodide, dimeric (ℓ)
I	Iodine, monatomic (g)
IK	Potassium iodide (c)
IK	Potassium iodide (ℓ)
IK	Potassium iodide (g)
ILi	Lithium iodide (c)
ILi	Lithium iodide (ℓ)
ILi	Lithium iodide (g)
IMg	* Magnesium monoiodide (g)
INO	Nitrosyl iodide (g)
INa	Sodium iodide (c)
INa	Sodium iodide (ℓ)
IPb	Lead monoiodide (g)
ISr	Strontium monoiodide (g)
ITi	Titanium monoiodide (g)

FILING ORDER	TABLE TITLE
IZr	Zirconium monoiodide (g)
I_2	Iodine, diatomic (ref st)
I_2	Iodine, diatomic (ℓ)
I_2	Iodine, diatomic (g)
I_2K_2	Potassium iodide, dimeric (g)
I_2Li_2	Lithium iodide, dimeric (g)
I_2Mg	* Magnesium diiodide (c)
I_2Mg	* Magnesium diiodide (ℓ)
I_2Mg	* Magnesium diiodide (g)
I_2Pb	Lead diiodide (c)
I_2Pb	Lead diiodide (ℓ)
I_2Pb	Lead diiodide (g)
I_2Sr	Strontium diiodide (c)
I_2Sr	Strontium diiodide (ℓ)
I_2Sr	Strontium diiodide (g)
I_2Ti	Titanium diiodide (c)
I_2Ti	Titanium diiodide (g)
I_2Zr	Zirconium diiodide (c)
I_2Zr	Zirconium diiodide (ℓ)
I_2Zr	Zirconium diiodide (g)
I_3Ti	Titanium triiodide (c)
I_3Ti	Titanium triiodide (g)
I_3Zr	Zirconium triiodide (c)
I_3Zr	Zirconium triiodide (g)
I_4Pb	Lead tetraiodide (g)
I_4Si	* Silicon tetraiodide (c)
I_4Si	* Silicon tetraiodide (ℓ)
I_4Si	* Silicon tetraiodide (g)
I_4Ti	Titanium tetraiodide (c)
I_4Ti	Titanium tetraiodide (ℓ)
I_4Ti	Titanium tetraiodide (g)
I_4Zr	* Zirconium tetraiodide (c)
I_4Zr	* Zirconium tetraiodide (g)
K	Potassium (ref st)
K	Potassium (ℓ)
K	Potassium (g)
K^+	Potassium unipos ion (g)
KO	Potassium monoxide (g)
KO^-	Potassium monoxide unineg ion (g)
KO_2	Potassium superoxide (c)
K_2	Potassium, dimeric (g)
K_2O	Potassium oxide (c)
K_2O_2	Potassium peroxide (c)
K_2O_3Si	Potassium metasilicate (c)
K_2O_3Si	Potassium metasilicate (ℓ)
K_2O_4S	Potassium sulfate (c)
K_2O_4S	Potassium sulfate (ℓ)
Li	Lithium (ref st)
Li	Lithium (c)
Li	Lithium (ℓ)
Li	Lithium (g)
Li^+	Lithium unipos ion (g)

FILING ORDER	TABLE TITLE
LiN	Lithium nitride (g)
LiNO	Lithium oxynitride (g)
LiNaO	Lithium sodium oxide (g)
LiO	Lithium monoxide (g)
LiO^-	Lithium monoxide unineg ion (g)
Li_2	Lithium, diatomic (g)
Li_2O	Lithium oxide (c)
Li_2O	Lithium oxide (ℓ)
Li_2O	Lithium oxide (g)
Li_2O_2	Lithium peroxide (c)
Li_2O_2	Lithium monoxide dimeric (g)
Li_2O_3Si	Lithium metasilicate (c)
Li_2O_3Si	Lithium metasilicate (ℓ)
Li_2O_3Ti	Lithium metatitanate (c)
Li_2O_3Ti	Lithium metatitanate (ℓ)
$Li_2O_5Si_2$	Lithium disilicate (c)
$Li_2O_5Si_2$	Lithium disilicate (ℓ)
Li_3N	Lithium nitride (c)
Mg	Magnesium (ref st)
Mg	Magnesium (c)
Mg	Magnesium (ℓ)
Mg	Magnesium, monatomic (g)
Mg^+	Magnesium unipos ion (g)
MgN	Magnesium nitride (g)
MgO	* Magnesium oxide (c)
MgO	* Magnesium oxide (ℓ)
MgO	* Magnesium oxide (g)
MgO_3Si	Magnesium metasilicate (c)
MgO_3Si	Magnesium metasilicate (ℓ)
MgO_3Ti	Magnesium metatitanate (c)
MgO_3Ti	Magnesium metatitanate (ℓ)
MgO_4S	Magnesium sulfate (c)
MgO_4S	Magnesium sulfate (ℓ)
MgO_4W	Magnesium tungstate (c)
MgO_5Ti_2	Magnesium dititanate (c)
MgO_5Ti_2	Magnesium dititanate (ℓ)
MgS	Magnesium sulfide (c)
MgS	Magnesium sulfide (g)
Mg_2	* Dimagnesium (g)
Mg_2O_4Si	Magnesium orthosilicate (c)
Mg_2O_4Si	Magnesium orthosilicate (ℓ)
Mg_2O_4Ti	Magnesium orthosilicate (c)
Mg_2O_4Ti	Magnesium orthosilicate (ℓ)
Mg_2Si	Magnesium silicide (c)
Mg_2Si	Magnesium silicide (ℓ)
Mg_3N_2	Magnesium nitride (c)
$Mg_3O_8P_2$	Magnesium orthophosphate (c)
$Mg_3O_8P_2$	Magnesium orthophosphate (ℓ)
Mo	Molybdenum (ref st)
Mo	Molybdenum (c)
Mo	Molybdenum (ℓ)
Mo	Molybdenum monatomic (g)
Mo^+	Molybdenum unipos ion (g)
MoO	Molybdenum monoxide (g)
MoO_2	Molybdenum dioxide (c)
MoO_2	Molybdenum dioxide (g)
MoO_3	Molybdenum trioxide (c)
MoO_3	Molybdenum trioxide (ℓ)
MoO_3	Molybdenum trioxide (g)
N	Nitrogen, monatomic (g)
NO	Nitric oxide (g)
NO^+	Nitric oxide unipos ion (g)
NO_2	Nitrogen dioxide (g)
NO_2^-	Nitrogen dioxide unineg ion (g)
NO_3	Nitrogen trioxide (g)
NP	Phosphorus nitride (g)
NS	Sulfur nitride (g)
NSi	Silicon nitride (g)
NSi_2	Disilicon nitride (g)
NTi	Titanium nitride (c)
NTi	Titanium nitride (ℓ)
NV	Vanadium mononitride (c)
NV	Vanadium mononitride (g)
NV_2	Vanadium subnitride $VN_{0.465}$ (c)
NZr	Zirconium nitride (c)
NZr	Zirconium nitride (ℓ)
NZr	Zirconium nitride (g)
N_2	Nitrogen, diatomic (ref st)
N_2O	Nitrous oxide (g)
N_2O^+	Dinitrogen monoxide unipos ion (g)
N_2O_3	Nitrogen trioxide (g)
N_2O_4	Nitrogen tetroxide (g)
N_2O_4	Nitrogen tetroxide (c)
N_2O_4	Nitrogen tetroxide (ℓ)
N_2O_5	Nitrogen pentoxide (g)
N_3	Azide (g)
N_4Si_3	Silicon nitride, alpha (c)
N_5P_3	Triphosphorus pentanitride (c)
Na	Sodium (ref st)
Na	Sodium (c)
Na	Sodium (ℓ)
Na	Sodium, monatomic (g)
Na^+	Sodium unipos ion (g)
NaO	Sodium monoxide (g)
NaO^-	Sodium monoxide unineg ion (g)
NaO_2	Sodium superoxide (c)
Na_2	Sodium, diatomic (g)
Na_2O	Sodium oxide (c)
Na_2O	Sodium oxide (ℓ)
Na_2O_2	Sodium peroxide (c)
Na_2O_3Si	Sodium metasilicate (c)
Na_2O_3Si	Sodium metasilicate (ℓ)
Na_2O_4S	Sodium sulfate phase V (c)
Na_2O_4S	Sodium sulfate phase III (c)
Na_2O_4S	Sodium sulfate phase I (c)
Na_2O_4S	Sodium sulfate, delta (c)
Na_2O_4S	Sodium sulfate (ℓ)
Na_2O_4W	Sodium tungstate (c)

FILING ORDER	TABLE TITLE
$Na_2O_5Si_2$	Sodium disilicate (c)
$Na_2O_5Si_2$	Sodium disilicate (ℓ)
Na_2S	Sodium sulfide (c)
Na_2S	Sodium sulfide (ℓ)
Nb	Niobium (ref st)
Nb	Niobium (c)
Nb	Niobium (ℓ)
Nb	Niobium, monatomic (g)
NbO	Niobium monoxide (c)
NbO	Niobium monoxide (ℓ)
NbO	Niobium monoxide (g)
NbO_2	Niobium dioxide (c)
NbO_2	Niobium dioxide (ℓ)
NbO_2	Niobium dioxide (g)
Nb_2O_5	Diniobium pentoxide (c)
Nb_2O_5	Diniobium pentoxide (ℓ)
O	Oxygen, monatomic (g)
O^-	Oxygen unineg ion (g)
OP	Phosphorus monoxide (g)
OPb	Lead oxide, red (c)
OPb	Lead oxide, yellow (c)
OPb	Lead oxide (ℓ)
OPb	Lead oxide (g)
OS	Sulfur monoxide (g)
OS_2	Disulfur monoxide (g)
OSi	Silicon monoxide (g)
OSr	Strontium oxide (c)
OSr	Strontium oxide (ℓ)
OSr	Strontium oxide (g)
OTa	Tantalum monoxide (g)
OTi	Titanium monoxide, alpha (c)
OTi	Titanium monoxide, beta (c)
OTi	Titanium monoxide (ℓ)
OTi	Titanium monoxide (g)
OV	Vanadium monoxide (c)
OV	Vanadium monoxide (ℓ)
OV	Vanadium monoxide (g)
OW	Tungsten monoxide (g)
OZr	Zirconium monoxide (g)
O_2	Oxygen, diatomic (ref st)
O_2^-	Oxygen diatomic unineg ion (g)
O_2P	Phosphorus dioxide (g)
O_2PB	Lead dioxide (c)
O_2S	Sulfur dioxide (g)
O_2Si	Cristobalite, low (c)
O_2Si	Cristobalite, high (c)
O_2Si	Silicon dioxide (c)
O_2Si	Silicon dioxide (ℓ)
O_2Si	Silicon dioxide (g)
O_2Ta	Tantalum dioxide (g)
O_2Ti	Titanium dioxide, anatase (c)
O_2Ti	Titanium dioxide, rutile (c)

FILING ORDER	TABLE TITLE
O_2Ti	Titanium dioxide (ℓ)
O_2Ti	Titanium dioxide (g)
O_2V	Vandium dioxide (g)
O_2W	Tungsten dioxide (c)
O_2W	Tungsten dioxide (g)
O_2Zr	Zirconium dioxide (c)
O_2Zr	Zirconium dioxide (ℓ)
O_2Zr	Zirconium dioxide (g)
O_3	Ozone (g)
O_3PbSi	Lead metasilicate (c)
O_3S	Sulfur trioxide (g)
O_3Ti_2	Dititanium trioxide (c)
O_3Ti_2	Dititanium trioxide (ℓ)
O_3V_2	Divanadium trioxide (c)
O_3V_2	Divanadium trioxide (ℓ)
O_3W	Tungsten oxide $WO_{2.72}$ (c)
O_3W	Tungsten oxide $WO_{2.90}$ (c)
O_3W	Tungsten oxide $WO_{2.96}$ (c)
O_3W	Tungsten trioxide (c)
O_3W	Tungsten trioxide (ℓ)
O_3W	Tungsten trioxide (g)
O_4Pb_2Si	Lead orthosilicate (c)
O_4Pb_3	Lead orthoplumbate (c)
O_4SiZr	Zirconium silicate (c)
O_4V_2	Divanadium tetroxide (c)
O_4V_2	Divanadium tetroxide (ℓ)
O_5Ta_2	Ditantalum pentoxide (c)
O_5Ta_2	Ditantalum pentoxide (ℓ)
O_5Ti_3	Trititanium pentaoxide, alpha (c)
O_5Ti_3	Trititanium pentaoxide, beta (c)
O_5Ti_3	Trititanium pentaoxide (ℓ)
O_5V_2	Divanadium pentoxide (c)
O_5V_2	Divanadium pentoxide (ℓ)
O_6P_4	Phosphorus trioxide, dimeric (g)
O_6W_2	Tungsten trioxide dimeric (g)
O_7Ti_4	Tetratitanium heptoxide (c)
O_7Ti_4	Tetratitanium heptoxide (ℓ)
O_8W_3	Tritungsten octaoxide (g)
O_9W_3	Tungsten trioxide, trimeric (g)
$O_{10}P_4$	Phosphorus pentoxide, dimeric (c)
$O_{10}P_4$	Phosphorus pentoxide, dimeric (g)
$O_{12}W_4$	Tungsten trioxide, tetrameric (g)
P	Phosphorus (ref st)
P	Phosphorus, red, v (c)
P	Phosphorus, white (c)
P	Phosphorus (ℓ)
P	Phosphorus, monatomic (g)
PS	Phosphorus sulfide (g)
P_2	Phosphorus, diatomic (g)
P_4	Phosphorus, tetratomic (ℓ)
P_4S_3	Phosphorus sulfide (c)
P_4S_3	Phosphorus sulfide (ℓ)
P_4S_3	Phosphorus sulfide (g)

FILING ORDER	TABLE TITLE
Pb	Lead (ref st)
Pb	Lead (c)
Pb	Lead (ℓ)
Pb	Lead (g)
PbS	Lead sulfide (c)
PbS	Lead sulfide (ℓ)
PbS	Lead sulfide (g)
Pb_2	Lead, diatomic (g)
S	Sulfur (ref st)
S	Sulfur (c)
S	Sulfur (ℓ)
S	Sulfur, monatomic (g)
SSi	Silicon monosulfide (g)
S_2	Sulfur, diatomic (g)
S_2Si	Silicon disulfide (c)
S_2Si	Silicon disulfide (ℓ)
S_8	Sulfur octatomic (g)
Si	Silicon (ref st)
Si	Silicon (c)
Si	Silicon (ℓ)
Si	Silicon, monatomic (g)
Si^+	Silicon unipos ion (g)
Si_2	Silicon, diatomic (g)
Si_3	Silicon, triatomic (g)
Sr	Strontium (ref st)
Sr	Strontium (c)
Sr	Strontium (ℓ)
Sr	Strontium monatomic (g)
Ta	Tantalum (ref st)
Ta	Tantalum (c)
Ta	Tantalum (ℓ)
Ta	Tantalum monatomic (g)
Ti	Titanium (ref st)
Ti	Titanium alpha phase (c)
Ti	Titanium beta phase (c)
Ti	Titanium (ℓ)
Ti	Titanium, monatomic (g)
Ti^+	Titanium unipos ion (g)
V	Vanadium (ref st)
V	Vanadium (c)
V	Vanadium (ℓ)
V	Vanadium monatomic (g)
W	Tungsten (ref st)
W	Tungsten (c)
W	Tungsten (ℓ)
W	Tungsten (g)
W^+	Tungsten unipos ion (g)
Zr	Zirconium (ref st)
Zr	Zirconium, alpha (c)
Zr	Zirconium, beta (c)
Zr	Zirconium (ℓ)
Zr	Zirconium, monatomic (g)
Zr^+	Zirconium unipos ion (g)
e^-	Electron gas (ref st)

ALUMINUM MONOCHLORIDE UNIPOS. ION ($AlCl^+$) ALCL$^+$
(IDEAL GAS) GFW=62.4340

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.188	204.522		
100							
200							
298	8.077	55.467	55.467	0.000	206.000	197.937	-145.092
300	8.085	55.517	55.467	0.015	206.005	197.887	-144.160
400	8.404	57.891	55.789	0.841	206.314	195.135	-106.617
500	8.592	59.788	56.405	1.691	206.604	192.306	-84.057
600	8.708	61.366	57.104	2.557	206.873	189.420	-68.996
700	8.786	62.714	57.812	3.432	207.120	186.491	-58.225
800	8.841	63.891	58.500	4.313	207.339	183.529	-50.138
900	8.883	64.935	59.158	5.200	207.515	180.542	-43.842
1000	8.915	65.873	59.783	6.090	205.122	177.720	-38.841
1100	8.942	66.724	60.376	6.983	205.305	174.971	-34.764
1200	8.966	67.503	60.938	7.878	205.487	172.204	-31.363
1300	8.989	68.222	61.471	8.776	205.673	169.424	-28.483
1400	9.013	68.889	61.977	9.676	205.859	166.629	-26.012
1500	9.039	69.511	62.459	10.578	206.046	163.820	-23.869
1600	9.068	70.096	62.918	11.484	206.235	160.998	-21.991
1700	9.100	70.646	63.357	12.392	206.427	158.166	-20.334
1800	9.138	71.167	63.776	13.304	206.622	155.322	-18.859
1900	9.181	71.663	64.178	14.220	206.820	152.467	-17.538
2000	9.229	72.135	64.565	15.140	207.021	149.600	-16.348
2100	9.282	72.586	64.936	16.066	207.226	146.722	-15.270
2200	9.340	73.019	65.293	16.997	207.436	143.836	-14.289
2300	9.402	73.436	65.639	17.934	207.653	140.944	-13.393
2400	9.468	73.837	65.972	18.877	207.873	138.039	-12.570
2500	9.536	74.225	66.294	19.828	208.100	135.122	-11.812
2600	9.608	74.601	66.607	20.785	208.331	132.199	-11.112
2700	9.680	74.965	66.909	21.749	208.570	129.265	-10.463
2800	9.754	75.318	67.203	22.721	139.404	127.155	-9.925
2900	9.828	75.662	67.489	23.700	139.917	126.707	-9.549
3000	9.901	75.996	67.767	24.686	140.435	126.244	-9.197
3100	9.974	76.322	68.038	25.680	140.958	125.761	-8.866
3200	10.045	76.640	68.302	26.681	141.488	125.264	-8.555
3300	10.114	76.950	68.559	27.689	142.024	124.749	-8.262
3400	10.181	77.253	68.810	28.704	142.564	124.216	-7.985
3500	10.246	77.549	69.056	29.725	143.110	123.667	-7.722
3600	10.308	77.838	69.295	30.753	143.659	123.107	-7.474
3700	10.366	78.122	69.531	31.787	144.214	122.527	-7.237
3800	10.422	78.399	69.760	32.826	144.772	121.932	-7.013
3900	10.474	78.670	69.985	33.871	145.336	121.327	-6.799
4000	10.522	78.936	70.206	34.921	145.899	120.701	-6.595
4100	10.568	79.196	70.422	35.975	146.468	120.062	-6.400
4200	10.610	79.452	70.634	37.034	147.040	119.413	-6.214
4300	10.649	79.702	70.342	38.097	147.614	118.748	-6.035
4400	10.684	79.947	71.046	39.164	148.190	118.075	-5.865
4500	10.716	80.187	71.246	40.234	148.766	117.380	-5.701
4600	10.746	80.423	71.443	41.307	149.345	116.678	-5.543
4700	10.772	80.655	71.637	42.383	149.924	115.958	-5.392
4800	10.796	80.882	71.827	43.461	150.503	115.228	-5.246
4900	10.816	81.104	72.014	44.542	151.083	114.494	-5.107
5000	10.835	81.323	72.198	45.625	151.661	113.737	-4.971
5100	10.850	81.538	72.379	46.709	152.240	112.976	-4.841
5200	10.864	81.749	72.557	47.795	152.817	112.199	-4.716
5300	10.876	81.956	72.733	48.882	153.391	111.411	-4.594
5400	10.885	82.159	72.905	49.970	153.965	110.616	-4.477
5500	10.893	82.359	73.076	51.059	154.533	109.804	-4.363
5600	10.899	82.555	73.243	52.148	155.100	108.988	-4.253
5700	10.903	82.748	73.408	53.238	155.664	108.156	-4.147
5800	10.906	82.938	73.571	54.329	156.223	107.321	-4.044
5900	10.907	83.124	73.731	55.419	156.778	106.473	-3.944
6000	10.907	83.308	73.889	56.510	157.327	105.616	-3.847

June 30, 1968; June 30, 1970; June 30, 1976

ALUMINUM MONOCHLORIDE UNIPOSITIVE ION ($AlCl^+$) (IDEAL GAS) GFW = 62.4340

ALCL$^+$

Ground State Configuration $[^2\Sigma]$

$S^\circ_{298.15}$ = [55.47 ± 0.4] gibbs/mol

ΔHf°_0 = 204.5 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 206 ± 10 kcal/mol

Electronic Levels and Quantum Weights

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

ω_e = [570] cm^{-1} $\omega_e x_e$ = [2] cm^{-1} σ = 1

B_e = [0.2618] cm^{-1} α_e = [0.0015] cm^{-1} r_e = [2.05] Å

Heat of Formation

We adopt ΔHf°_0 = 204.5±10 kcal/mol based on that of AlCl(g) (1) combined with the ionization potential IP(AlCl) = 9.4±0.4 eV (216.8±9 kcal/mol). IP(AlCl) is assumed to be equal to the electron-impact appearance potential of $AlCl^+$ measured as 9.4±0.4 (2), 9.5±0.3(3) and 9.3±0.6 eV (4). Theoretical values include IP = 8.83 eV from an extended Hückel calculation (5) and from ab initio calculations (6, 7) either 8.4 eV (direct value) or 9.8 eV derived from $D(AlCl^+)$. Electron-impact formation of $AlCl^+$ from $AlCl_3$ (8) apparently yields fragment ions with excess energy; i.e., we derive the upper limit IP≤11.7 eV.

For the dissociation process $AlCl^+(X^2\Sigma) \rightarrow Al^+(^1S) + Cl(^2P)$, our adopted ΔHf° yields $D^\circ_0(AlCl^+)$ = 39±10 kcal/mol. This compares with ∿31 kcal/mol derived from the theoretical potential energy curve (6, 7) which, however, has a maximum of ∿8 kcal/mol arising from an avoided crossing with another $^2\Sigma$ state.

Heat Capacity and Entropy

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

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

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

References

1. JANAF Thermochemical Tables: AlCl(g), $AlCl_3$(g) 6-30-70; AlF^+(g) 12-31-76; AlF(g), MgF(g) 6-30-76.
2. D. L. Hildenbrand and L. P. Theard, J. Chem. Phys. 50, 5350 (1969).
3. D. L. Hildenbrand, J. Chem. Phys. 52, 5751 (1970).
4. N. D. Potter, Rept. AD-715567 (avail. NTIS), Appendix 6 (1970).
5. J. W. Hastie and J. L. Margrave, J. Phys. Chem. 73, 1105 (1969).
6. M. Attermeyer, G. Das and A. C. Wahl, Argonne National Laboratory, unpublished calculations cited in ref. (7).
7. J. Berkowitz and J. L. Dehmer, J. Chem. Phys. 57, 3194 (1972).
8. R. F. Porter and E. F. Zeller, J. Chem. Phys. 33, 858 (1960).
9. R. B. Caton and A. E. Douglas, Can. J. Phys. 48, 432 (1970).

ALUMINUM CHLORIDE FLUORIDE (AlClF) AlClF

(IDEAL GAS) GFW=81.4329

	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	-2.900	-116.654	-116.654	INFINITE
100	9.039	56.437	77.139	-2.070	-116.626	-117.812	257.478
200	10.509	63.160	68.019	-1.092	-116.802	-118.950	129.982
298	11.665	67.586	67.586	0.000	-117.000	-119.966	87.938
300	11.682	67.659	67.567	0.022	-117.004	-119.985	87.409
400	12.421	71.130	68.055	1.230	-117.195	-120.949	66.083
500	12.868	73.953	68.961	2.496	-117.389	-121.866	53.267
600	13.149	76.326	69.996	3.798	-117.597	-122.742	44.709
700	13.333	78.368	71.050	5.123	-117.822	-123.582	38.584
800	13.459	80.157	72.078	6.463	-118.075	-124.388	33.981
900	13.548	81.748	73.066	7.813	-118.369	-125.160	30.393
1000	13.614	83.179	74.007	9.172	-121.233	-125.714	27.475
1100	13.663	84.479	74.901	10.535	-121.523	-126.148	25.063
1200	13.702	85.669	75.749	11.904	-121.812	-126.556	23.049
1300	13.732	86.767	76.555	13.276	-122.101	-126.940	21.340
1400	13.756	87.786	77.321	14.650	-122.391	-127.300	19.872
1500	13.775	88.735	78.051	16.026	-122.682	-127.641	18.597
1600	13.791	89.625	78.747	17.405	-122.974	-127.963	17.479
1700	13.805	90.463	79.411	18.785	-123.267	-128.264	16.490
1800	13.816	91.251	80.048	20.166	-123.560	-128.550	15.608
1900	13.825	91.999	80.657	21.548	-123.855	-128.819	14.818
2000	13.834	92.707	81.242	22.931	-124.152	-129.073	14.104
2100	13.841	93.382	81.804	24.314	-124.450	-129.313	13.458
2200	13.847	94.026	82.345	25.699	-124.750	-129.538	12.868
2300	13.853	94.642	82.856	27.084	-125.050	-129.746	12.329
2400	13.859	95.232	83.370	28.470	-125.353	-129.944	11.833
2500	13.864	95.798	83.855	29.856	-125.658	-130.131	11.376
2600	13.869	96.342	84.325	31.242	-125.965	-130.303	10.953
2700	13.874	96.865	84.760	32.629	-126.273	-130.465	10.560
2800	13.879	97.370	85.221	34.017	-195.993	-129.784	10.130
2900	13.884	97.857	85.648	35.405	-196.044	-127.419	9.603
3000	13.890	98.328	86.063	36.794	-196.097	-125.052	9.110
3100	13.896	98.783	86.466	38.183	-196.151	-122.683	8.649
3200	13.903	99.224	86.858	39.573	-196.207	-120.311	8.217
3300	13.911	99.652	87.239	40.964	-196.266	-117.938	7.811
3400	13.919	100.068	87.610	42.355	-196.326	-115.565	7.426
3500	13.928	100.471	87.972	43.748	-196.388	-113.189	7.068
3600	13.938	100.864	88.325	45.141	-196.452	-110.808	6.727
3700	13.949	101.246	88.669	46.535	-196.518	-108.430	6.405
3800	13.961	101.618	89.005	47.931	-196.585	-106.048	6.099
3900	13.974	101.981	89.333	49.328	-196.653	-103.663	5.809
4000	13.988	102.335	89.653	50.726	-196.724	-101.280	5.534
4100	14.003	102.680	89.967	52.125	-196.796	-98.896	5.272
4200	14.019	103.018	90.274	53.526	-196.868	-96.505	5.022
4300	14.036	103.348	90.574	54.929	-196.942	-94.114	4.783
4400	14.054	103.671	90.868	56.334	-197.017	-91.718	4.556
4500	14.073	103.987	91.156	57.740	-197.094	-89.328	4.338
4600	14.093	104.297	91.436	59.148	-197.169	-86.931	4.130
4700	14.114	104.600	91.715	60.558	-197.249	-84.537	3.931
4800	14.135	104.897	91.987	61.971	-197.328	-82.138	3.740
4900	14.158	105.189	92.253	63.386	-197.407	-79.731	3.556
5000	14.181	105.475	92.515	64.802	-197.489	-77.332	3.380
5100	14.205	105.756	92.772	66.222	-197.571	-74.928	3.211
5200	14.230	106.032	93.024	67.644	-197.655	-72.522	3.048
5300	14.255	106.304	93.272	69.068	-197.742	-70.116	2.891
5400	14.281	106.570	93.516	70.495	-197.829	-67.707	2.740
5500	14.308	106.833	93.756	71.924	-197.919	-65.298	2.595
5600	14.335	107.091	93.991	73.356	-198.011	-62.884	2.454
5700	14.362	107.345	94.223	74.791	-198.104	-60.473	2.319
5800	14.390	107.595	94.452	76.229	-198.201	-58.054	2.188
5900	14.417	107.841	94.677	77.669	-198.302	-55.639	2.061
6000	14.445	108.083	94.898	79.112	-198.405	-53.219	1.939

Dec. 31, 1960; Sept. 30, 1964; June 30, 1976

ALUMINUM CHLORIDE FLUORIDE (AlClF) (IDEAL GAS) GFW = 81.4329

Point Group C_s
$S^\circ_{298.15}$ = [67.59 ± 1] gibbs/mol

ΔHf°_0 = [-116.7 ± 15] kcal/mol AlClF
$\Delta Hf^\circ_{298.15}$ = [-117 ± 15] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
[0]	2
[20000]	2
[25000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[750](1)
[200](1)
[550](1)

Bond Distance: Al-F = [1.65] Å Al-Cl = [2.10] Å σ = 1
Bond Angle: Cl-Al-F = [120°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [1.4406 x 10^{-114}] g^3 cm^6

Heat of Formation

We tentatively adopt ΔHf°_{298} = -117±15 kcal/mol and Ha°_0 = 241±15 kcal/mol based on our average bond energies for $AlF_2(g)$ and $AlCl_2(g)$ (1). Mass-spectrometric data (2,3) yield ΔHf°_{298} = -142.6 and ΔHa°_0 = 267 kcal/mol, corresponding to an enhancement of 26 kcal/mol in the stability of AlClF(g). The same study (2,3) indicated stability enhancements of 22 (or 13) kcal/mol for AlF_2, 19 kcal/mol for $AlClF_2$ and 22 kcal/mol for $AlCl_2F$. See the appropriate tables (1) for further details.

Farber et al. (2,3) used molecular flow effusion of vapors of AlF_3 and $AlCl_3$ over Al(ℓ) in Al_2O_3(c) to study the reaction AlCl(g)+AlF(g)=AlClF(g)+Al(g). They calculated Kp (5 points, 1338-1537 K) directly from mass-spectrometric ion intensities. Using JANAF auxiliary data (1), we derive [ΔSr°(2nd law)-ΔSr°(3rd law)] = 0.8±18 gibbs/mol, ΔHr°_{298} = 12±25 (2nd law) or 11.2±5 (3rd law) and ΔHf°_{298} = -142.6±5 kcal/mol. These results are internally consistent but, as in the case of AlF_2 (2,3), we suspect that common problems may cause a negative bias in ΔHf°. The ionizing energy is ambiguous: 20 eV (3) or AP+3 eV (2). The appearance potential AP($AlClF^+$) = 11±1 eV is biased by ~2 eV, raising several questions about interpretation of the data (see $AlCl_2^+$, 1). It is conceivable that $AlClF^+$ *arises from a process other than direct ionization of AlClF.*

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

Heat Capacity and Entropy

The electronic ground state, excited levels, bond distances and bond angle are assumed to be the same as in $AlCl_2$ and AlF_2 (1). Vibrational frequencies are estimated by comparison with $AlCl_2$ and AlF_2 (1). The principal moments of inertia are 2.342 x 10^{-39}, 23.660 x 10^{-39} and 26.002 x 10^{-39} g cm^2.

References

1. *JANAF Thermochemical Tables:* $AlCl_2(g)$, $AlCl_2^+(g)$, $AlF_2(g)$, $AlClF_2(g)$, $AlCl_2F(g)$ 6-30-76; AlF(g) 12-31-75; AlCl(g) 6-30-70; Al(g) 12-31-65; Cl(g) 6-30-72; F(g) 9-30-65.
2. M. Farber and S. P. Harris, High Temp. Sci 3, 231 (1971).
3. M. Farber, R. D. Srivastava and O. M. Uy, Space Sciences, Inc., Rept. No. AFRPL-TR-70-97, Contract F04611-69-C-0094, July, 1970.
4. R. D. Srivastava and M. Farber, Trans. Faraday Soc. 67, 2298 (1971).

ALUMINUM CHLORIDE FLUORIDE POS. ION ALCLF⁺
(IDEAL GAS) GFW=81.4324

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-3.020	64.745		
100							
200							
298	12.536	62.048	62.048	0.000	66.000	63.198	-46.325
300	12.553	62.126	62.048	0.023	66.007	63.180	-46.026
400	13.298	65.847	62.550	1.319	66.400	62.179	-33.973
500	13.763	68.868	63.521	2.673	66.791	61.078	-26.697
600	14.062	71.406	64.630	4.066	67.171	59.900	-21.819
700	14.261	73.590	65.757	5.483	67.534	58.659	-18.314
800	14.399	75.503	66.858	6.916	67.871	57.367	-15.672
900	14.497	77.205	67.915	8.361	68.168	56.037	-13.608
1000	14.570	78.737	68.922	9.814	65.896	54.857	-11.989
1100	14.625	80.128	69.879	11.274	66.200	53.738	-10.677
1200	14.668	81.403	70.787	12.739	66.503	52.591	-9.578
1300	14.702	82.578	71.649	14.208	66.808	51.420	-8.645
1400	14.729	83.669	72.469	15.679	67.112	50.226	-7.841
1500	14.751	84.686	73.250	17.153	67.416	49.009	-7.141
1600	14.769	85.638	73.995	18.629	67.717	47.771	-6.525
1700	14.784	86.534	74.706	20.107	68.019	46.516	-5.980
1800	14.797	87.379	75.387	21.586	68.321	45.243	-5.493
1900	14.807	88.180	76.039	23.066	68.621	43.953	-5.056
2000	14.817	88.939	76.666	24.547	68.919	42.647	-4.660
2100	14.825	89.663	77.267	26.030	69.216	41.323	-4.301
2200	14.832	90.352	77.847	27.512	69.511	39.988	-3.972
2300	14.838	91.012	78.405	28.996	69.807	38.643	-3.672
2400	14.843	91.643	78.943	30.480	70.099	37.282	-3.395
2500	14.848	92.249	79.464	31.964	70.389	35.906	-3.139
2600	14.852	92.832	79.967	33.449	70.677	34.521	-2.902
2700	14.856	93.392	80.454	34.935	70.964	33.124	-2.681
2800	14.859	93.933	80.925	36.421	1.839	32.549	-2.541
2900	14.862	94.454	81.383	37.907	2.384	33.635	-2.535
3000	14.865	94.958	81.827	39.393	2.925	34.703	-2.528
3100	14.867	95.446	82.259	40.880	3.465	35.753	-2.521
3200	14.869	95.918	82.678	42.366	4.002	36.787	-2.512
3300	14.871	96.375	83.086	43.853	4.537	37.804	-2.504
3400	14.873	96.819	83.484	45.341	5.069	38.803	-2.494
3500	14.875	97.250	83.871	46.828	5.599	39.787	-2.484
3600	14.877	97.669	84.248	48.316	6.126	40.760	-2.474
3700	14.878	98.077	84.617	49.803	6.650	41.712	-2.464
3800	14.879	98.474	84.976	51.291	7.172	42.653	-2.453
3900	14.881	98.860	85.327	52.779	7.692	43.582	-2.442
4000	14.882	99.237	85.670	54.267	8.207	44.493	-2.431
4100	14.883	99.605	86.006	55.756	8.722	45.391	-2.420
4200	14.884	99.963	86.334	57.244	9.233	46.281	-2.408
4300	14.885	100.313	86.655	58.732	9.742	47.158	-2.397
4400	14.886	100.656	86.969	60.221	10.248	48.026	-2.385
4500	14.886	100.990	87.277	61.710	10.750	48.875	-2.374
4600	14.887	101.317	87.579	63.198	11.252	49.718	-2.362
4700	14.888	101.638	87.874	64.687	11.748	50.545	-2.350
4800	14.888	101.951	88.164	66.176	12.242	51.366	-2.339
4900	14.889	102.258	88.449	67.665	12.734	52.183	-2.327
5000	14.890	102.559	88.728	69.154	13.220	52.978	-2.316
5100	14.890	102.854	89.002	70.643	13.705	53.770	-2.304
5200	14.891	103.143	89.271	72.132	14.185	54.551	-2.293
5300	14.891	103.426	89.536	73.621	14.660	55.322	-2.281
5400	14.892	103.705	89.796	75.110	15.132	56.085	-2.270
5500	14.892	103.978	90.051	76.599	15.598	56.836	-2.258
5600	14.892	104.246	90.302	78.088	16.060	57.585	-2.247
5700	14.893	104.510	90.549	79.578	16.518	58.319	-2.236
5800	14.893	104.769	90.792	81.067	16.970	59.052	-2.225
5900	14.894	105.024	91.031	82.556	17.416	59.772	-2.214
6000	14.894	105.274	91.266	84.046	17.855	60.486	-2.203

June 30, 1976

ALUMINUM CHLORIDE FLUORIDE UNIPOSITIVE ION ($AlClF^+$) (IDEAL GAS) GFW = 81.4324

Point Group [$C_{\infty v}$]
$S°_{298.15}$ = [62.05 ± 1.5] gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = 64.7 ± 30 kcal/mol ALCLF⁺
$\Delta Hf°_{298.15}$ = 66 ± 30 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[850] (1)
[170] (2)
[500] (1)

Bond Distances: Al-F = [1.60] Å Al-Cl = [2.05] Å
Bond Angle: F-Al-Cl = [180°] σ = 1
Rotational Constant: B_o = [0.09596] cm^{-1}

Heat of Formation

We adopt $\Delta Hf°_{298}$ = 66±30 kcal/mol based on ΔHf° of AlClF (1) combined with the ionization potential IP(AlClF) = 182±23 kcal/mol (7.9±1 eV). IP is estimated by comparison with IP($AlCl_2$) = 7.8±0.9 eV and IP(AlF_2) = 8.1±0.9 eV (1). Farber and Harris (2) reported an appearance potential of AP($AlClF^+$) = 11±1 eV which appears to be seriously biased. This is discussed on the tables for $AlCl_2^+$(g) and AlClF(g).

Heat Capacity and Entropy

We assume the electronic ground state to be linear $^1\Sigma^+$ and neglect excited states (1). Bond distances are estimated to be the same as in $AlCl_2^+$ and AlF_2^+ (1). Vibrational frequencies are estimated by comparison with AlClF, $AlCl_2^+$ and AlF_2^+ (1). The moment of inertia is 29.169 x 10^{-39} g cm^2.

Reference

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

ALUMINUM CHLORIDE DIFLUORIDE $AlClF_2$
(IDEAL GAS) GFW=100.4313

	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	-3.536	-238.035	-238.035	INFINITE
100	10.484	56.948	83.640	-2.669	-238.317	-237.520	519.099
200	13.678	65.305	72.531	-1.445	-238.598	-236.620	258.567
298	15.642	71.158	71.158	0.000	-238.800	-235.609	172.706
300	15.672	71.255	71.158	0.029	-238.804	-235.590	171.627
400	16.968	75.955	71.790	1.666	-238.951	-234.494	128.121
500	17.795	79.837	73.023	3.407	-239.074	-233.366	102.004
600	18.332	83.132	74.440	5.215	-239.191	-232.213	84.584
700	18.692	85.987	75.890	7.067	-239.314	-231.040	72.134
800	18.943	88.500	77.313	8.950	-239.458	-229.850	62.792
900	19.124	90.742	78.682	10.854	-239.637	-228.638	55.521
1000	19.257	92.764	79.991	12.773	-242.382	-227.222	49.659
1100	19.358	94.605	81.237	14.704	-242.551	-225.698	44.842
1200	19.437	96.293	82.422	16.644	-242.717	-224.159	40.825
1300	19.499	97.851	83.550	18.591	-242.882	-222.605	37.423
1400	19.549	99.298	84.624	20.543	-243.048	-221.039	34.506
1500	19.589	100.648	85.648	22.500	-243.214	-219.461	31.975
1600	19.622	101.913	86.625	24.461	-243.381	-217.873	29.760
1700	19.650	103.104	87.560	26.425	-243.549	-216.272	27.804
1800	19.674	104.228	88.455	28.391	-243.718	-214.663	26.064
1900	19.694	105.292	89.313	30.359	-243.889	-213.044	24.506
2000	19.711	106.302	90.138	32.330	-244.062	-211.416	23.102
2100	19.725	107.265	90.930	34.301	-244.237	-209.782	21.832
2200	19.738	108.182	91.694	36.275	-244.414	-208.137	20.677
2300	19.750	109.060	92.430	38.249	-244.593	-206.480	19.620
2400	19.759	109.901	93.141	40.224	-244.775	-204.820	18.651
2500	19.768	110.708	93.827	42.201	-244.960	-203.154	17.760
2600	19.776	111.483	94.492	44.178	-245.148	-201.477	16.936
2700	19.783	112.230	95.135	46.156	-245.338	-199.794	16.172
2800	19.789	112.949	95.758	48.135	-314.940	-197.274	15.398
2900	19.794	113.644	96.363	50.114	-314.875	-193.072	14.550
3000	19.799	114.315	96.950	52.093	-314.813	-188.875	13.760
3100	19.804	114.964	97.521	54.074	-314.753	-184.678	13.020
3200	19.808	115.593	98.076	56.054	-314.698	-180.481	12.326
3300	19.812	116.203	98.616	58.035	-314.645	-176.288	11.675
3400	19.815	116.794	99.142	60.017	-314.596	-172.097	11.062
3500	19.819	117.368	99.655	61.998	-314.551	-167.906	10.485
3600	19.821	117.927	100.154	63.980	-314.509	-163.713	9.939
3700	19.824	118.470	100.642	65.963	-314.470	-159.527	9.423
3800	19.827	118.999	101.118	67.945	-314.436	-155.340	8.934
3900	19.829	119.514	101.583	69.928	-314.405	-151.153	8.470
4000	19.831	120.016	102.038	71.911	-314.378	-146.968	8.030
4100	19.833	120.505	102.482	73.894	-314.354	-142.787	7.611
4200	19.835	120.983	102.917	75.877	-314.334	-138.601	7.212
4300	19.836	121.450	103.343	77.861	-314.317	-134.416	6.832
4400	19.838	121.906	103.760	79.845	-314.304	-130.229	6.469
4500	19.839	122.352	104.168	81.829	-314.296	-126.049	6.122
4600	19.841	122.788	104.568	83.813	-314.289	-121.865	5.790
4700	19.842	123.215	104.960	85.797	-314.290	-117.685	5.472
4800	19.843	123.633	105.345	87.781	-314.292	-113.501	5.168
4900	19.844	124.042	105.722	89.765	-314.300	-109.311	4.875
5000	19.846	124.443	106.093	91.750	-314.312	-105.132	4.595
5100	19.847	124.836	106.456	93.735	-314.327	-100.949	4.326
5200	19.848	125.221	106.813	95.719	-314.349	-96.762	4.067
5300	19.848	125.599	107.164	97.704	-314.375	-92.579	3.818
5400	19.849	125.970	107.509	99.689	-314.407	-88.396	3.578
5500	19.850	126.334	107.848	101.674	-314.445	-84.211	3.346
5600	19.851	126.692	108.181	103.659	-314.488	-80.021	3.123
5700	19.852	127.043	108.509	105.644	-314.537	-75.837	2.908
5800	19.852	127.389	108.832	107.629	-314.592	-71.645	2.700
5900	19.853	127.728	109.149	109.614	-314.655	-67.459	2.499
6000	19.854	128.062	109.462	111.600	-314.725	-63.268	2.305

Dec. 31, 1960; Sept. 30, 1964; June 30, 1976

ALUMINUM CHLORIDE DIFLUORIDE ($AlClF_2$) (IDEAL GAS) GFW = 100.4313

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [71.16 ± 1] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -238.0 ± 1.5 kcal/mol ALCLF2
$\Delta Hf^\circ_{298.15}$ = -238.8 ± 1.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[800] (1)	[910] (1)
[520] (1)	[210] (1)
[240] (1)	[260] (1)

Bond Distances: Al-F = [1.63] Å Al-Cl = [2.06] Å σ = 2
Bond Angles: Cl-Al-F = [120°] F-Al-F = [120°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [1.2809×10^{-113}] $g^3\ cm^6$

Heat of Formation

We adopt ΔHf°_{298} = -238.8±1.5 kcal/mol and ΔHa°_0 = 380.8±3 kcal/mol based on ΔHr°_{298} = 0.5±1 kcal/mol for 1/3 $AlCl_3$(g) + 2/3 AlF_3(g) = $AlClF_2$(g). Krause and Douglas (1) obtained this result by an entrainment method which measured enhanced volatility of AlF_3 in the presence of $AlCl_3$. Corrections were made for all the possible dimers which can form in this system. The entrainment data establish that aluminum fluoride-chloride exchange reactions are almost thermoneutral.

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

Source	Method	Reaction	Range	ΔHr°_T	ΔHr°_{298}	ΔHf°_{298}
			T/K	kcal/mol		
(1) Krause	Entrainment	1/3 $AlCl_3$(g)+2/3 AlF_3(g) = $AlClF_2$(g)	1196-1257	0.5±1	0.5±1	-238.8
(2) Farber	Mass Spec.	AlF_2(g)+$AlCl_2$(g) = AlCl(g)+$AlClF_2$(g)	1491	---	-19.2	-240[a] or -258[b]

[a] *Assuming ΔHf°_{298} = -166 (AlF_2) and -67 ($AlCl_2$) kcal/mol.*
[b] Assuming ΔHf°_{298} = -180 (AlF_2) and -71 ($AlCl_2$) kcal/mol.

Heat Capacity and Entropy

We adopt a C_{2v} structure with bond angles and bond distances assumed equal to those in AlF_3 and $AlCl_3$ (4). We assume a singlet electronic ground state and neglect excited states. Vibrational frequencies are estimated by comparison of AlF_3 and $AlCl_3$ with the series BF_3, $BClF_2$, BCl_2F and BCl_3 (6, 7). The principal moments of inertia are 12.572×10^{-39}, 26.246×10^{-39} and 38.818×10^{-39} g cm^2.

References

1. R. F. Krause and T. B. Douglas, J. Phys. Chem. 72, 3444 (1968).
2. M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).
3. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
4. JANAF Thermochemical Tables: AlF_2(g), $AlCl_2$(g), $AlCl_2F$(g) 6-30-76; AlF_3(g), $AlCl_3$(g) 6-30-70.
5. M. Farber, Space Sciences, Inc., Monrovia, Calif., personal commun., August 30, 1976.
6. D. F. Wolfe and G. L. Humphrey, J. Mol. Struct. 3, 293 (1969).
7. L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956).

ALCLF2

ALUMINUM DICHLORIDE ($ALCL_2$) (IDEAL GAS) GFW=97.8875

$ALCL_2$

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	-3.051	-66.763	-66.763	INFINITE
100	9.443	57.302	79.321	-2.202	-66.716	-67.766	148.103
200	11.249	64.428	70.244	-1.163	-66.845	-68.785	75.165
298	12.341	69.146	69.146	0.000	-67.000	-69.710	51.098
300	12.356	69.222	69.146	0.023	-67.003	-69.727	50.796
400	12.932	72.864	69.639	1.290	-67.165	-70.610	38.579
500	13.249	75.787	70.586	2.601	-67.338	-71.451	31.237
600	13.436	78.221	71.061	3.936	-67.531	-72.256	26.319
700	13.555	80.302	72.751	5.286	-67.744	-73.027	22.800
800	13.635	82.117	73.810	6.646	-67.987	-73.766	20.152
900	13.691	83.727	74.824	8.012	-68.273	-74.471	18.084
1000	13.731	85.171	75.788	9.383	-71.129	-74.960	16.383
1100	13.762	86.482	76.702	10.758	-71.410	-75.330	14.967
1200	13.785	87.680	77.567	12.135	-71.692	-75.675	13.782
1300	13.803	88.784	78.388	13.515	-71.972	-75.995	12.776
1400	13.818	89.808	79.168	14.896	-72.254	-76.293	11.910
1500	13.830	90.762	79.909	16.278	-72.537	-76.572	11.157
1600	13.839	91.654	80.616	17.662	-72.820	-76.832	10.495
1700	13.847	92.494	81.290	19.046	-73.104	-77.073	9.908
1800	13.854	93.285	81.935	20.431	-73.388	-77.298	9.385
1900	13.860	94.034	82.552	21.817	-73.673	-77.506	8.915
2000	13.865	94.746	83.144	23.203	-73.961	-77.702	8.491
2100	13.869	95.422	83.713	24.590	-74.248	-77.883	8.105
2200	13.873	96.067	84.260	25.977	-74.538	-78.050	7.754
2300	13.877	96.684	84.787	27.364	-74.828	-78.200	7.431
2400	13.880	97.275	85.295	28.752	-75.120	-78.340	7.134
2500	13.884	97.842	85.785	30.141	-75.414	-78.471	6.860
2600	13.887	98.386	86.260	31.529	-75.710	-78.586	6.606
2700	13.891	98.910	86.716	32.918	-76.008	-78.693	6.370
2800	13.895	99.416	87.163	34.307	-145.719	-77.955	6.085
2900	13.899	99.903	87.594	35.697	-145.759	-75.536	5.693
3000	13.904	100.375	88.012	37.087	-145.802	-73.113	5.326
3100	13.909	100.831	88.418	38.478	-145.847	-70.689	4.984
3200	13.916	101.272	88.813	39.869	-145.895	-68.264	4.662
3300	13.922	101.701	89.197	41.261	-145.945	-65.836	4.360
3400	13.930	102.116	89.571	42.654	-145.997	-63.409	4.076
3500	13.939	102.520	89.935	44.047	-146.052	-60.981	3.808
3600	13.948	102.913	90.290	45.441	-146.109	-58.546	3.554
3700	13.958	103.295	90.637	46.837	-146.167	-56.114	3.315
3800	13.970	103.668	90.975	48.233	-146.228	-53.681	3.087
3900	13.982	104.031	91.305	49.631	-146.289	-51.241	2.873
4000	13.996	104.385	91.627	51.029	-146.355	-48.806	2.667
4100	14.010	104.731	91.943	52.430	-146.419	-46.369	2.472
4200	14.026	105.068	92.251	53.832	-146.485	-43.927	2.286
4300	14.043	105.399	92.553	55.235	-146.553	-41.485	2.109
4400	14.060	105.722	92.849	56.640	-146.621	-39.035	1.939
4500	14.079	106.038	93.138	58.047	-146.691	-36.593	1.777
4600	14.099	106.348	93.422	59.456	-146.759	-34.144	1.622
4700	14.119	106.651	93.701	60.867	-146.830	-31.699	1.474
4800	14.141	106.948	93.973	62.280	-146.901	-29.250	1.332
4900	14.163	107.240	94.241	63.695	-146.972	-26.791	1.195
5000	14.186	107.527	94.504	65.113	-147.043	-24.341	1.064
5100	14.210	107.808	94.762	66.532	-147.115	-21.883	0.938
5200	14.235	108.084	95.016	67.955	-147.187	-19.428	0.817
5300	14.260	108.355	95.265	69.379	-147.262	-16.973	0.700
5400	14.286	108.622	95.510	70.807	-147.335	-14.512	0.587
5500	14.312	108.884	95.751	72.236	-147.412	-12.053	0.479
5600	14.339	109.143	95.987	73.669	-147.488	-9.591	0.374
5700	14.366	109.397	96.220	75.104	-147.566	-7.133	0.273
5800	14.393	109.647	96.450	76.542	-147.646	-4.662	0.176
5900	14.421	109.893	96.676	77.987	-147.728	-2.198	0.081
6000	14.449	110.136	96.698	79.426	-147.813	0.270	-0.010

June 30, 1961; Sept. 30, 1964; June 30, 1972; June 30, 1976

ALUMINUM DICHLORIDE ($AlCl_2$) (IDEAL GAS) GFW = 97.8875

$ALCL_2$

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [69.15 ± 0.6] gibbs/mol

ΔHf°_0 = -66.8 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -67 ± 5 kcal/mol

Electronic Levels and Quantum Weights

State	ε, cm^{-1}	g_i
$^2A_1$	[0]	2
$^2B_1$	[20000]	2
$^2B_2$	[25000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[430](1)
[160](1)
[570](1)

Bond Distance: Al-Cl = [2.10] Å

σ = 2

Bond Angle: Cl-Al-Cl = [120°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.9239×10^{-114}] g^3 cm^6

Heat of Formation

We adopt ΔHf°_{298} = -67±5 kcal/mol and ΔHa°_0 = 201.4±6 kcal/mol; i.e., the average bond energy $\Delta Ha^\circ_0/2$ = 101 kcal/mol is taken equal to that of $AlCl_3$ (1). ΔHf° is consistent with experimental results of -66±3 (2) and ≥-71±5 kcal/mol (3, 4), but there may be significant bias in these values.

Chai et al. (2) derived ΔHf°_{298} = -66±3 kcal/mol from study of reactions of Al(c,ℓ) with the vapor of $AlCl_3$ in an argon carrier gas. Weight-loss data (800-1000 K) for Al and $AlCl_3$ were analyzed assuming five vapor species (AlCl, $AlCl_2$, $AlCl_3$, Al_2Cl_4, Al_2Cl_6) in four simultaneous equilibrium reactions. Experimental data were combined with auxiliary data, including S°($AlCl_2$) and Kp for two reactions, to derive ΔHf°($AlCl_2$) and Kp for another reaction involving Al_2Cl_4. Despite minor changes in S°($AlCl_2$), ΔHf° = -66 is still appropriate for the $AlCl_2$ equilibrium (2). We suspect, however, that this equilibrium is strongly dependent on the other equilibria, particularly that involving Al_2Cl_4(g).

Farber and Harris (3, 4) reported Kp (5 points, 1150-1430 K) for the reaction AlCl(g) + $AlCl_3$(g) = 2 $AlCl_2$(g). We obtain [ΔSr°(2nd law)-ΔSr°(3rd law)] = -35±10 gibbs/mol, ΔHr°_{298} = -36±13(2nd law) or 10.5±9(3rd law) and $\Delta Hf^\circ_{298} \geq -70.7\pm5$ kcal/mol. We consider ΔHf° to be a negative limit due to possible bias arising from the ionizing energy. Energy of the ionizing electrons was variously reported as 20 eV (4) or as 3 eV above the appearance potentials (3). If 20 eV was used, we expect $AlCl_2^+$ to be enhanced due to fragmentation of $AlCl_3$. The alternative ionizing energy leads to another problem, since the authors (3, 4) used literature values for appearance potentials (AP) of $AlCl^+$ and $AlCl_3^+$ but their own value for $AlCl_2^+$. Their value has a bias of ∿3 eV which is discussed in detail on the table for $AlCl_2^+$(g) (1). We suspect that the mass spectrometer had a biased energy scale during the measurments (3, 4). This would induce negative bias in the ionizing energy used for $AlCl^+$ and $AlCl_3^+$, since the AP's were not based on the experimental energy scale. Again we expect $AlCl_2^+$ to be enhanced relative to $AlCl^+$ and $AlCl_3^+$. The large discrepancy in ΔSr° is symptomatic of a temperature-dependent error; we expect that bias in Kp is greatest at low T.

Average bond energies (BE) suggest that MX_n (M=Al, B and X=F, Cl) does not show the progression to multiple bonding of NO_3, NO_2 and NO. Although [BE(MX)-BE(MX_3)] = ∿20 kcal/mol, only the mass-spectrometric data of Farber et al. (3-6) yield BE(MX_2)>BE(MX_3). Other data (1,2,7) and theoretical calculations (8) suggest that BE(MX_2)≤BE(MX_3).

Source	Method	Species	Average Bond Energy (ΔHa°_0/n)/(kcal/mol)				
			$AlCl_n$	BCl_n	AlF_n	BF_n	NO_n
(1) JANAF	Review	MX	118.4	127.1	159.3	179.4	150.0
(1) JANAF	Review	MX_3	100.8	104.5	140.2	152.5	90.3
(1) JANAF	Review	MX_2	101	---	140	---	111.0
(3,4) Farber et al.	Mass spec.	MX_2	102.6	---	146.5, 151	---	---
(5,6) Srivastava et al.	Mass spec.	MX_2	---	104.0	147.0	155.0	---
(7) Dibeler et al.	*Photoionization*	MX_2	---	102.6	---	145.6	---
(2,1) Others	Various	MX_2	100.2(2)	103.5(1)	132.4(1)	---	---

Heat Capacity and Entropy

The electronic ground state and excited levels are assumed to be the same as in AlF_2 (1). Vibrational frequencies are calculated from the estimated force constants f_r = 2.2 and f_α/r^2 = 0.13 mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of $AlCl_2^+$, $AlCl_2$, $AlCl_2^-$ and the analogous boron species. We assume that frequency changes are qualitatively similar to those of NO_2^+, NO_2, and NO_2^-. Thus, in going from $AlCl_2^+$ to $AlCl_2$, we expect a large decrease in ν_3, an increase in ν_2 and a small increase in ν_1. By analogy with BF_2 (8), the odd electron of $AlCl_2$ should occupy an anti-bonding orbital which increases the bond length but decreases the bond angle and stretching force constant. We assume a bond length 0.05 Å longer than in $AlCl_2^+$ (1) and a bond angle equal to that in BF_2 (8). The principal moments of inertia are 3.5779×10^{-39}, 38.941×10^{-39} and 42.519×10^{-39} g cm^2.

References

1. JANAF Thermochemical Tables: $AlCl_2^+$(g), $AlCl_2^-$(g), AlF_2(g) 6-30-76; AlF(g) 12-31-75; $AlCl_3$(g), AlCl(g), AlF_3(g) 6-30-70; Al(g) 12-31-65; F(g) 9-30-65; BCl_2(g) 6-30-72; BCl_3(g), BCl(g), B(g) 12-31-64; BF_3(g) 6-30-69.
2. B. J. Chai, H. C. Ko, M. A. Greenbaum and M. Farber, J. Phys. Chem. 71, 3331 (1967).
3. M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).
4. M. Farber, R. D. Srivastava and O. M. Uy, Space Science, Inc., Rept. No. AFRPL-TR-70-97, Contract F04611-69-C-0094, July, 1970.
5. R. D. Srivastava and M. Farber, Trans. Faraday Soc. 67, 2298 (1971).
6. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
7. V. H. Dibeler and J. A. Walker, Inorg. Chem. 8, 50 (1969); 7, 1742 (1968).
8. C. Thomsom and D. A. Brotchie, Theoret. Chim. Acta 32, 101 (1973); Mol. Phys. 28, 301 (1974).

$ALCL_2$

ALUMINUM DICHLORIDE UNIPOS. ION ($ALCL_2^+$) $ALCL_2^+$

(IDEAL GAS) GFW= 97.8870

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0				-3.222	113.585		
100							
200							
298	13.160	64.089	64.089	0.000	115.000	112.311	-82.326
300	13.175	64.170	64.089	0.024	115.007	112.294	-81.806
400	13.778	68.051	64.614	1.375	115.426	111.327	-60.826
500	14.127	71.166	65.623	2.772	115.836	110.255	-48.192
600	14.340	73.762	66.769	4.196	116.229	109.101	-39.740
700	14.478	75.984	67.931	5.637	116.603	107.883	-33.683
800	14.572	77.924	69.061	7.090	116.950	106.613	-29.125
900	14.639	79.644	70.143	8.551	117.256	105.303	-25.571
1000	14.687	81.189	71.172	10.017	114.992	104.142	-22.760
1100	14.723	82.591	72.147	11.488	115.304	103.042	-20.473
1200	14.752	83.873	73.072	12.961	115.614	101.912	-18.561
1300	14.774	85.055	73.949	14.438	115.928	100.758	-16.939
1400	14.791	86.150	74.782	15.916	116.240	99.581	-15.545
1500	14.805	87.171	75.574	17.396	116.552	98.379	-14.334
1600	14.817	88.127	76.329	18.877	116.862	97.157	-13.271
1700	14.827	89.026	77.050	20.359	117.173	95.917	-12.331
1800	14.835	89.873	77.739	21.842	117.484	94.658	-11.493
1900	14.842	90.676	78.399	23.326	117.794	93.383	-10.742
2000	14.848	91.437	79.032	24.811	118.102	92.089	-10.063
2100	14.853	92.162	79.640	26.296	118.409	90.779	-9.447
2200	14.858	92.853	80.225	27.781	118.714	89.456	-8.887
2300	14.861	93.513	80.788	29.267	119.020	88.123	-8.374
2400	14.865	94.146	81.332	30.754	119.324	86.773	-7.902
2500	14.868	94.753	81.857	32.240	119.624	85.408	-7.466
2600	14.871	95.336	82.364	33.727	119.923	84.034	-7.064
2700	14.873	95.897	82.855	35.214	120.220	82.646	-6.690
2800	14.875	96.438	83.330	36.702	51.105	82.082	-6.407
2900	14.877	96.960	83.791	38.189	51.659	83.176	-6.268
3000	14.879	97.465	84.239	39.677	52.211	84.254	-6.138
3100	14.880	97.953	84.673	41.165	52.759	85.313	-6.015
3200	14.882	98.425	85.096	42.653	53.305	86.355	-5.898
3300	14.883	98.883	85.507	44.142	53.849	87.380	-5.787
3400	14.884	99.327	85.907	45.630	54.389	88.387	-5.681
3500	14.885	99.759	86.296	47.118	54.926	89.377	-5.581
3600	14.886	100.178	86.676	48.607	55.460	90.358	-5.485
3700	14.887	100.586	87.047	50.096	55.992	91.318	-5.394
3800	14.888	100.983	87.408	51.584	56.520	92.264	-5.306
3900	14.889	101.370	87.761	53.073	57.047	93.202	-5.223
4000	14.890	101.747	88.106	54.562	57.568	94.119	-5.142
4100	14.890	102.114	88.443	56.051	58.089	95.024	-5.065
4200	14.891	102.473	88.773	57.540	58.607	95.920	-4.991
4300	14.892	102.824	89.096	59.029	59.122	96.802	-4.920
4400	14.892	103.166	89.412	60.519	59.636	97.678	-4.852
4500	14.893	103.501	89.721	62.008	60.144	98.532	-4.785
4600	14.893	103.828	90.024	63.497	60.653	99.381	-4.722
4700	14.894	104.148	90.321	64.986	61.157	100.215	-4.660
4800	14.894	104.462	90.613	66.476	61.660	101.039	-4.600
4900	14.894	104.769	90.898	67.965	62.160	101.862	-4.543
5000	14.895	105.070	91.179	69.455	62.657	102.662	-4.487
5100	14.895	105.365	91.454	70.944	63.152	103.461	-4.434
5200	14.895	105.654	91.724	72.434	63.644	104.245	-4.381
5300	14.896	105.938	91.990	73.923	64.131	105.019	-4.331
5400	14.896	106.216	92.251	75.413	64.617	105.788	-4.281
5500	14.896	106.490	92.507	76.902	65.096	106.544	-4.234
5600	14.897	106.758	92.759	78.392	65.574	107.294	-4.187
5700	14.897	107.022	93.007	79.882	66.048	108.030	-4.142
5800	14.897	107.281	93.251	81.372	66.517	108.768	-4.099
5900	14.897	107.535	93.491	82.861	66.980	109.491	-4.056
6000	14.897	107.786	93.727	84.351	67.438	110.208	-4.014

June 30, 1968; June 30, 1972; June 30, 1976

ALUMINUM DICHLORIDE UNIPOSITIVE ION ($AlCl_2^+$) (IDEAL GAS) GFW = 97.8870

Point Group [$D_{\infty h}$]
$S^\circ_{298.15}$ = [64.09 ± 1] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = 113.6 ± 18 kcal/mol $ALCL_2^+$
$\Delta Hf^\circ_{298.15}$ = 115 ± 18 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[390](1)
[120](2)
[690](1)

Bond Distance: Al-Cl = [2.05] Å
Bond Angle: Cl-Al-Cl = [180°] $\sigma = 2$
Rotational Constant: B_0 = [0.056573] cm^{-1}

Heat of Formation

We adopt ΔHf°_{298} = 115±18 kcal/mol and an ionization potential IP($AlCl_2$) = 7.8±0.9 eV. Electron-impact studies gave 13.4±0.5 eV(1) and 13.4±0.7 eV (2) for the appearance potential (AP) of $AlCl_2^+$ from $AlCl_3$. The analogous process for onset of BCl_2^+ from BCl_3 has been studied by both photoionization (3) and electron impact (2). Comparison indicates that BCl_2^+ from electron impact (2) carried an excess energy (E*) of ∼0.9 eV. We estimate the excess energy for $AlCl_2^+$ as 1.2±0.6 eV. Thus, we take AP-E* = ΔHr°_0=12.2±0.8 eV (281.3±18 kcal/mol) for the reaction $AlCl_3(g) + e^-(g) = AlCl_2^+(g) + Cl(g) + 2e^-(g)$. With JANAF auxiliary data (4) this yields $\Delta Hf^\circ_0(AlCl_2^+)$ = 113.5±18, ΔHf°_{298} = 115±18 and IP($AlCl_2$) = 180±20 kcal/mol (7.8±0.9 eV).

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

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

Heat Capacity and Entropy

We assume the electronic ground state to be linear $^1\Sigma^+$ and neglect excited states by analogy with $MgCl_2$ (4, 11) and other triatomic species having sixteen valence electrons (12). We estimate the bond distance to be almost the same as in $AlCl_3$ and 0.05 Å shorter than in $AlCl_2$ (4). Likewise, we transfer the stretching force constant from $AlCl_3$ and the ratio f_r/f_α = 19 Å^{-2} from $MgCl_2$ (11). Thus, we calculate vibrational frequencies from the estimated force constants f_r = 2.9, f_{rr} = 0.2 and f_α/r^2 = 0.036 mdyn/Å. *The resulting values have been rounded upward. The moment of inertia is* 49.477 x 10^{-39} g cm^2.

References

1. R. F. Porter and E. F. Zeller, J. Chem. Phys. 33, 858 (1960).
2. N. D. Potter, Rept. AD-715567 (avail. NTIS), 160 pp. (1970).
3. V. H. Dibeler and J. A. Walker, Inorg. Chem. 8, 50 (1969).
4. *JANAF Thermochemical* Tables: $AlCl_2(g)$, $AlF_2^+(g)$ 6-30-76; Cl(g) 6-30-72; $AlCl_3(g)$ 6-30-70; $MgCl_2(g)$ 12-31-69.
5. M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).
6. M. Farber, R. D. Srivastava and O. M. Uy, Space Sciences, Inc., Rept. No. AFRPL-TR-70-97, Contract No. F04611-69-C-0094, July, 1970.
7. R. D. Srivastava and M. Farber, Trans. Faraday Soc. 67, 2298 (1971).
8. J. L. Franklin, J. G. Dilland, H. M. Rosenstock, J. T. Herron, K. Draxl and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, 1969.
9. R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N.J., pp. 166-173, 1965.
10. J. W. Hastie and J. L. Margrave, J. Phys. Chem. 73, 1105 (1969).
11. M. L. Lesiecki and J. W. Nibler, J. Chem. Phys. 64, 871 (1976).
12. J. W. Rabalais, J. M. McDonald, V. Scherr and S. P. McGlynn, Chem. Rev. 71, 73 (1971).

ALUMINUM DICHLORIDE UNINEG. ION ($AlCl_2^-$) $AlCl_2^-$

(IDEAL GAS) GFW=97.8881

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0				-3.100	-113.331		
100							
200							
298	12.584	68.275	68.275	0.000	-115.000	-115.963	85.003
300	12.597	68.353	68.276	0.023	-115.012	-115.969	84.483
400	13.106	72.055	68.777	1.311	-115.650	-116.192	63.484
500	13.374	75.012	69.738	2.637	-116.305	-116.252	50.813
600	13.529	77.465	70.827	3.982	-116.985	-116.178	42.318
700	13.626	79.558	71.929	5.341	-117.685	-115.988	36.213
800	13.691	81.382	72.999	6.707	-118.419	-115.696	31.607
900	13.736	82.997	74.022	8.078	-119.197	-115.309	28.007
1000	13.768	84.446	74.993	9.453	-122.546	-114.651	25.057
1100	13.792	85.760	75.913	10.831	-123.321	-113.825	22.615
1200	13.811	86.961	76.784	12.212	-124.095	-112.927	20.567
1300	13.826	88.067	77.610	13.593	-124.871	-111.965	18.823
1400	13.837	89.092	78.394	14.977	-125.647	-110.943	17.319
1500	13.846	90.047	79.140	16.361	-126.425	-109.866	16.008
1600	13.854	90.941	79.849	17.746	-127.203	-108.736	14.853
1700	13.860	91.781	80.527	19.132	-127.982	-107.557	13.827
1800	13.866	92.573	81.174	20.518	-128.762	-106.333	12.911
1900	13.870	93.323	81.794	21.905	-129.543	-105.065	12.085
2000	13.874	94.035	82.389	23.292	-130.327	-103.758	11.338
2100	13.878	94.712	82.959	24.680	-131.109	-102.411	10.658
2200	13.881	95.357	83.508	26.067	-131.896	-101.026	10.036
2300	13.884	95.974	84.037	27.456	-132.681	-99.602	9.464
2400	13.886	96.565	84.547	28.844	-133.470	-98.148	8.938
2500	13.889	97.132	85.039	30.233	-134.261	-96.662	8.450
2600	13.892	97.677	85.515	31.622	-135.052	-95.141	7.997
2700	13.895	98.201	85.975	33.011	-135.847	-93.592	7.576
2800	13.898	98.707	86.421	34.401	-206.054	-91.181	7.117
2900	13.902	99.194	86.853	35.791	-206.591	-87.072	6.562
3000	13.906	99.666	87.272	37.181	-207.131	-82.941	6.042
3100	13.911	100.122	87.679	38.572	-207.672	-78.791	5.555
3200	13.917	100.564	88.075	39.964	-208.216	-74.625	5.097
3300	13.924	100.992	88.460	41.356	-208.763	-70.441	4.665
3400	13.932	101.408	88.835	42.748	-209.313	-66.242	4.258
3500	13.941	101.812	89.200	44.142	-209.864	-62.029	3.873
3600	13.952	102.205	89.555	45.537	-210.416	-57.792	3.508
3700	13.964	102.587	89.903	46.933	-210.971	-53.547	3.163
3800	13.978	102.960	90.241	48.330	-211.528	-49.287	2.835
3900	13.993	103.323	90.572	49.728	-212.086	-45.006	2.522
4000	14.010	103.677	90.895	51.128	-212.646	-40.717	2.225
4100	14.029	104.024	91.211	52.530	-213.206	-36.415	1.941
4200	14.049	104.362	91.520	53.934	-213.767	-32.096	1.670
4300	14.071	104.693	91.823	55.340	-214.329	-27.764	1.411
4400	14.095	105.016	92.119	56.748	-214.891	-23.413	1.163
4500	14.121	105.334	92.409	58.159	-215.453	-19.058	0.926
4600	14.149	105.644	92.694	59.573	-216.013	-14.686	0.698
4700	14.178	105.949	92.972	60.989	-216.576	-10.307	0.479
4800	14.209	106.248	93.246	62.408	-217.138	-5.915	0.269
4900	14.242	106.541	93.514	63.831	-217.698	-1.501	0.067
5000	14.276	106.829	93.776	65.257	-218.257	2.914	-0.127
5100	14.312	107.112	94.036	66.686	-218.816	7.346	-0.315
5200	14.350	107.390	94.290	68.119	-219.375	11.785	-0.495
5300	14.389	107.664	94.540	69.556	-219.934	16.232	-0.669
5400	14.429	107.933	94.786	70.997	-220.491	20.696	-0.838
5500	14.471	108.198	95.027	72.442	-221.048	25.166	-1.000
5600	14.513	108.460	95.265	73.891	-221.605	29.648	-1.157
5700	14.557	108.717	95.498	75.345	-222.161	34.135	-1.309
5800	14.601	108.970	95.729	76.803	-222.718	38.642	-1.456
5900	14.647	109.220	95.955	78.265	-223.276	43.151	-1.598
6000	14.693	109.467	96.178	79.732	-223.833	47.673	-1.736

June 30, 1968; June 30, 1972; June 30, 1976

ALUMINUM DICHLORIDE UNINEGATIVE ION ($AlCl_2^-$) (Ideal Gas) GFW = 97.8881

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [68.28 ± 1] gibbs/mol

ΔHf°_0 = [-113.3 ± 25] kcal/mol $AlCl_2^-$
$\Delta Hf^\circ_{298.15}$ = [-115 ± 25] kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1A_1$	[0]	1
$^3B_1$	[23000]	3
$^1B_1$	[30000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[430](1)
[160](1)
[460](1)

Bond Distance: Al-Cl = [2.15] Å
Bond Angle: Cl-Al-Cl = [105°] $\sigma = 2$
Product of the Moments of Inertia: $I_AI_BI_C$ = [7.5817×10^{-114}] $g^3\ cm^6$

Heat of Formation

We adopt ΔHf°_{298} = -115±25 kcal/mol based on an estimated electron affinity of $EA(AlCl_2)$ = 46±23 kcal/mol (2.0±1 eV) and a chloride-ion affinity of IA(AlCl) = 46±25 kcal/mol. JANAF auxiliary data (1) are used in converting from one quantity to another. If AlX_2 radicals were analogous to X atoms (2, 3), then $EA(AlCl_2)$ should be approximately equal to $EA(AlF_2)$ = 2.2±0.4 eV (1). This analogy may not be justified, since the pertinent orbitals are quite different. An electron added to AlX_2 presumably occupies a molecular orbital centered mainly on the metal opposite the two halogens. We assume that the orbital energy is characteristic of the metal Al and is perturbed relatively little by substitution of Cl for F. This implies that $EA(AlCl_2) \approx EA(AlF_2)$.

The energy for the self-ionization process, $2\ AlF_2 = AlF_2^+ + AlF_2^-$, is $\Delta Hr^\circ_0 = [IP(AlF_2)-EA(AlF_2)]$ = 5.9±1 eV (1). *Assuming* $AlCl_2$ *is similar*, we estimate $EA(AlCl_2)$ = 1.9 eV. The energy difference between the reactions $AlF_2^- = AlF + F^-$ and $AlF_2 = AlF + F$ is $\Delta Hr^\circ_0 = [IA(AlF)-D^\circ_0(AlF_2)]$ = -29 kcal/mol (1). Assuming $AlCl_2^-$ is analogous, we estimate $EA(AlCl_2)$ = 2.3 eV. We adopt the intermediate value $EA(AlCl_2)$ = 2.0±1 eV but emphasize that all estimates depend on AlF_2^- (1).

Heat Capacity and Entropy

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

By analogy with BF_2 (4, 5), we expect that the odd electron in $AlCl_2$ occupies a molecular orbital centered mainly on the metal opposite the two chlorines. This orbital should be antibonding (4) in the sense that addition of an electron increases the bond length but decreases the bond angle and stretching force constant. We assume that the bond length is 0.05 Å longer and the bond angle is 15° smaller than in $AlCl_2$ (1). The principal moments of inertia are 5.5592×10^{-39}, 34.255×10^{-39} and 39.814×10^{-39} g cm^2.

References

1. JANAF Thermochemical Tables: $AlCl_2(g)$, $AlCl_2^+(g)$, $AlF_2(g)$, $AlF_2^+(g)$, $AlF_2^-(g)$ 6-30-76; $NO_2^-(g)$ 6-30-72; $SiCl_2(g)$ 12-31-70; AlCl(g) 6-30-70; $Cl^-(g)$ 6-30-65.
2. J. L. Franklin and P. W. Harland, Ann. Rev. Phys. Chem. 25, 485 (1974).
3. H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
4. C. Thomson and D. A. Brotchie, Theoret. Chim. Acta 32, 101 (1973).
5. W. Nelson and W. Gordy, J. Chem. Phys. 51, 4710 (1969).

ALUMINUM DICHLORIDE FLUORIDE $AlCl_2F$
(IDEAL GAS) GFW=116.8859

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	-3.763	-188.420	-188.420	INFINITE
100	11.445	59.182	87.678	-2.850	-188.656	-187.860	410.566
200	14.604	68.196	75.851	-1.531	-188.856	-186.995	204.338
298	16.444	74.400	74.400	0.000	-189.000	-186.054	136.381
300	16.471	74.502	74.400	0.030	-189.003	-186.036	135.527
400	17.592	79.407	75.061	1.738	-189.109	-185.029	101.095
500	18.271	83.412	76.343	3.534	-189.200	-183.999	80.426
600	18.698	86.784	77.810	5.384	-189.294	-182.950	66.640
700	18.979	89.689	79.304	7.269	-189.398	-181.884	56.787
800	19.173	92.236	80.765	9.177	-189.526	-180.804	49.393
900	19.311	94.503	82.168	11.102	-189.691	-179.703	43.638
1000	19.412	96.543	83.505	13.038	-192.424	-178.401	38.989
1100	19.489	98.397	84.776	14.983	-192.581	-176.991	35.165
1200	19.548	100.095	85.982	16.935	-192.737	-175.567	31.975
1300	19.594	101.662	87.129	18.892	-192.891	-174.130	29.274
1400	19.631	103.115	88.220	20.854	-193.046	-172.680	26.957
1500	19.662	104.471	89.258	22.819	-193.202	-171.221	24.947
1600	19.687	105.741	90.249	24.786	-193.359	-169.750	23.187
1700	19.707	106.935	91.196	26.756	-193.516	-168.268	21.632
1800	19.725	108.062	92.102	28.727	-193.675	-166.779	20.250
1900	19.740	109.129	92.970	30.701	-193.834	-165.279	19.011
2000	19.752	110.141	93.804	32.675	-193.997	-163.773	17.896
2100	19.763	111.105	94.605	34.651	-194.161	-162.260	16.887
2200	19.773	112.025	95.376	36.628	-194.327	-160.737	15.968
2300	19.781	112.904	96.119	38.606	-194.494	-159.203	15.128
2400	19.788	113.746	96.836	40.584	-194.664	-157.665	14.357
2500	19.795	114.554	97.529	42.563	-194.839	-156.123	13.648
2600	19.801	115.331	98.199	44.543	-195.015	-154.569	12.993
2700	19.806	116.078	98.847	46.523	-195.194	-153.011	12.385
2800	19.810	116.798	99.475	48.504	-264.786	-150.614	11.756
2900	19.815	117.494	100.085	50.485	-264.710	-146.540	11.044
3000	19.818	118.165	100.676	52.467	-264.638	-142.467	10.379
3100	19.822	118.815	101.251	54.449	-264.569	-138.395	9.757
3200	19.825	119.445	101.810	56.431	-264.504	-134.325	9.174
3300	19.827	120.055	102.353	58.414	-264.443	-130.257	8.627
3400	19.830	120.647	102.883	60.397	-264.386	-126.193	8.112
3500	19.832	121.222	103.399	62.380	-264.333	-122.131	7.626
3600	19.835	121.780	103.902	64.363	-264.283	-118.064	7.167
3700	19.836	122.324	104.392	66.347	-264.237	-114.005	6.734
3800	19.838	122.853	104.871	68.331	-264.195	-109.947	6.323
3900	19.840	123.368	105.339	70.314	-264.157	-105.885	5.934
4000	19.842	123.870	105.796	72.299	-264.124	-101.829	5.564
4100	19.843	124.360	106.243	74.283	-264.093	-97.776	5.212
4200	19.844	124.839	106.680	76.267	-264.066	-93.718	4.877
4300	19.846	125.305	107.107	78.252	-264.043	-89.663	4.557
4400	19.847	125.762	107.526	80.236	-264.023	-85.602	4.252
4500	19.848	126.208	107.936	82.221	-264.008	-81.552	3.961
4600	19.849	126.644	108.338	84.206	-263.994	-77.496	3.682
4700	19.850	127.071	108.732	86.191	-263.986	-73.445	3.415
4800	19.851	127.489	109.119	88.176	-263.980	-69.392	3.159
4900	19.852	127.898	109.498	90.161	-263.978	-65.330	2.914
5000	19.852	128.299	109.870	92.146	-263.980	-61.281	2.679
5100	19.853	128.692	110.235	94.131	-263.985	-57.224	2.452
5200	19.854	129.078	110.594	96.117	-263.994	-53.170	2.235
5300	19.854	129.456	110.946	98.102	-264.009	-49.118	2.025
5400	19.855	129.827	111.292	100.088	-264.027	-45.063	1.824
5500	19.856	130.191	111.633	102.073	-264.050	-41.009	1.630
5600	19.856	130.549	111.967	104.059	-264.078	-36.952	1.442
5700	19.857	130.901	112.296	106.044	-264.111	-32.900	1.261
5800	19.857	131.246	112.620	108.030	-264.149	-28.838	1.087
5900	19.858	131.586	112.939	110.016	-264.194	-24.784	0.918
6000	19.858	131.919	113.252	112.002	-264.245	-20.724	0.755

Dec. 31, 1960; Sept. 30, 1964; June 30, 1976

Point Group C_{2v}
$S^\circ_{298.15}$ = [74.40 ± 1] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -188.4 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -189.0 ± 1.5 kcal/mol

$AlCl_2F$

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[840] (1)	[640] (1)
[430] (1)	[190] (1)
[160] (1)	[220] (1)

Bond Distances: Al-F = [1.63] Å Al-Cl = [2.06] Å σ = 2
Bond Angles: Cl-Al-F = [120°] Cl-Al-Cl = [120°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [3.8405 x 10^{-113}] g^3cm^6

Heat of Formation

We adopt ΔHf°_{298} = -189.0±1.5 kcal/mol and ΔHa°_0 = 341.4±3 kcal/mol based on ΔHr°_{298} = 0.5±1 kcal/mol for 2/3 $AlCl_3$(g) + 1/3 AlF_3(g) = $AlCl_2F$(g). Krause and Douglas (1) obtained this result by an entrainment method which measured enhanced volatility of AlF_3 in the presence of $AlCl_3$. Corrections were made for all the possible dimers which can form in this system. The entrainment data establish that aluminum fluoride-chloride exchange reactions are almost thermoneutral.

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

Source	Method	Reaction	Range T/K	ΔHr°_T	ΔHr°_{298}	ΔHf°_{298}
				- - - - -kcal/mol- - - - - -		
(1) Krause	Entrainment	2/3 $AlCl_3$(g) + 1/3 AlF_3(g) = $AlCl_2F$(g)	1196-1257	0.5±1	0.5±1	-189.0
(2) Farber	Mass Spec.	AlF_2(g) + $AlCl_2$(g) = AlF(g) + $AlCl_2F$(g)	1491	---	-23.4	-194[a] or -211[b]

[a] Assuming ΔHf°_{298} = -166 (AlF_2) and -67 ($AlCl_2$) kcal/mol.
[b] Assuming ΔHf°_{298} = -180 (AlF_2) and -71 ($AlCl_2$) kcal/mol.

Heat Capacity and Entropy

We adopt a C_{2v} structure with bond angles and bond distances assumed equal to those in AlF_3 and $AlCl_3$ (4). We assume a singlet electronic ground state and neglect excited states. Vibrational frequencies are estimated by comparison of AlF_3 and $AlCl_3$ with the series BF_3, $BClF_2$, BCl_2F and BCl_3 (6, 7). The principal moments of inertia are 18.358x10^{-39}, 37.471x10^{39} and 55.830x10^{-39} g cm^2.

References

1. R. F. Krause and T. B. Douglas, J. Phys. Chem. 72, 3444 (1968).
2. M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).
3. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
4. JANAF Thermochemical Tables: AlF_2(g), $AlCl_2$(g), $AlCl_2F$(g) 6-30-76; AlF_3(g), $AlCl_3$(g) 6-30-70.
5. M. Farber, Space Sciences, Inc., Monrovia, Calif., personal commun., Aug. 30, 1976.
6. D. F. Wolfe and G. L. Humphrey, J. Mol. Struct. 3, 293 (1969).
7. L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956).

ALUMINUM MONOFLUORIDE (ALF) ALF
(IDEAL GAS) GFW=45.9799

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.125	-63.476	-63.476	INFINITE
100	6.960	43.580	57.879	-1.430	-63.234	-65.393	142.916
200	7.178	48.447	52.080	-.727	-63.323	-67.544	73.808
298	7.632	51.397	51.397	.000	-63.500	-69.583	51.006
300	7.640	51.444	51.397	.014	-63.504	-69.622	50.719
400	8.031	53.698	51.702	.799	-63.703	-71.630	39.137
500	8.302	55.522	52.289	1.616	-63.920	-73.588	32.165
600	8.485	57.052	52.959	2.456	-64.155	-75.500	27.501
700	8.613	58.371	53.640	3.311	-64.411	-77.370	24.156
800	8.705	59.527	54.305	4.178	-64.694	-79.203	21.637
900	8.774	60.556	54.943	5.052	-65.020	-80.997	19.669
1000	8.828	61.484	55.552	5.932	-67.916	-82.570	18.046
1100	8.871	62.327	56.130	6.817	-68.236	-84.020	16.693
1200	8.906	63.101	56.679	7.706	-68.554	-85.441	15.561
1300	8.936	63.815	57.201	8.598	-68.871	-86.835	14.598
1400	8.962	64.476	57.697	9.493	-69.189	-88.205	13.769
1500	8.985	65.097	58.170	10.390	-69.506	-89.552	13.048
1600	9.005	65.678	58.621	11.290	-69.823	-90.879	12.413
1700	9.024	66.224	59.053	12.191	-70.140	-92.165	11.851
1800	9.041	66.741	59.466	13.095	-70.455	-93.472	11.349
1900	9.057	67.230	59.862	14.000	-70.771	-94.742	10.898
2000	9.072	67.695	60.242	14.906	-71.087	-95.996	10.490
2100	9.086	68.138	60.607	15.814	-71.404	-97.235	10.119
2200	9.099	68.561	60.959	16.723	-71.720	-98.458	9.781
2300	9.113	68.965	61.299	17.634	-72.035	-99.663	9.470
2400	9.125	69.354	61.626	18.546	-72.351	-100.858	9.184
2500	9.137	69.726	61.943	19.459	-72.667	-102.042	8.920
2600	9.150	70.065	62.249	20.373	-72.963	-103.209	8.676
2700	9.161	70.430	62.546	21.289	-73.299	-104.367	8.448
2800	9.173	70.764	62.833	22.205	-143.025	-104.681	8.171
2900	9.185	71.086	63.112	23.123	-143.079	-103.311	7.786
3000	9.198	71.398	63.383	24.043	-143.133	-101.939	7.426
3100	9.210	71.699	63.647	24.963	-143.187	-100.565	7.090
3200	9.223	71.992	63.903	25.885	-143.241	-99.188	6.774
3300	9.236	72.276	64.152	26.808	-143.294	-97.810	6.478
3400	9.250	72.552	64.395	27.732	-143.349	-96.433	6.199
3500	9.265	72.820	64.632	28.658	-143.402	-95.052	5.935
3600	9.281	73.082	64.863	29.585	-143.455	-93.667	5.686
3700	9.298	73.336	65.089	30.514	-143.508	-92.285	5.451
3800	9.316	73.584	65.309	31.445	-143.561	-90.900	5.228
3900	9.335	73.826	65.525	32.377	-143.613	-89.512	5.016
4000	9.356	74.063	65.735	33.312	-143.666	-88.126	4.815
4100	9.379	74.294	65.941	34.248	-143.718	-86.739	4.624
4200	9.403	74.521	66.143	35.187	-143.768	-85.346	4.441
4300	9.429	74.742	66.340	36.129	-143.816	-83.955	4.267
4400	9.457	74.959	66.533	37.073	-143.868	-82.560	4.101
4500	9.486	75.172	66.723	38.020	-143.918	-81.168	3.942
4600	9.518	75.381	66.909	38.971	-143.965	-79.772	3.790
4700	9.552	75.586	67.091	39.924	-144.013	-78.380	3.645
4800	9.589	75.788	67.271	40.881	-144.060	-76.982	3.505
4900	9.627	75.986	67.446	41.842	-144.105	-75.579	3.371
5000	9.668	76.181	67.619	42.807	-144.150	-74.183	3.243
5100	9.711	76.372	67.789	43.776	-144.194	-72.783	3.119
5200	9.756	76.561	67.956	44.749	-144.238	-71.383	3.000
5300	9.803	76.748	68.120	45.727	-144.281	-69.981	2.886
5400	9.853	76.931	68.281	46.710	-144.323	-68.579	2.776
5500	9.905	77.113	68.440	47.697	-144.365	-67.179	2.669
5600	9.959	77.292	68.597	48.691	-144.406	-65.771	2.567
5700	10.016	77.468	68.751	49.689	-144.446	-64.369	2.468
5800	10.074	77.643	68.903	50.694	-144.487	-62.962	2.372
5900	10.134	77.816	69.052	51.704	-144.527	-61.556	2.280
6000	10.197	77.987	69.200	52.721	-144.567	-60.150	2.191

Dec. 31, 1960; Sept. 30, 1964; June 30, 1969;
Dec. 31, 1975

ALUMINUM MONOFLUORIDE (AlF) (IDEAL GAS) GFW = 45.9799

Symmetry Number = 1

$S^\circ_{298.15}$ = 51.397 ± 0.01 gibbs/mol

ΔHf°_0 = -63.48 ± 0.8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -63.5 ± 0.8 kcal/mol

Electronic Levels 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}
$X^1\Sigma^+$	0.0	1	1.6544	0.5525	0.00495	802.26	4.77
$a^3\Pi$	27254.	6	1.6476	0.5570	0.00453	827.8	3.93
$A^1\Pi$	43949.7	2	1.6485	0.55640	0.00534	803.94	5.99
$b^3\Sigma^+$	44804.5	3	1.6391	0.56280	0.00651	786.37	7.64
$B^1\Sigma^+$	54282.5	1	1.6151	0.57968	0.00560	866.60	7.45
$c^3\Sigma^+$	55023.4	3	1.6028	0.58861	0.00457	933.66	4.81
$C^1\Sigma^+$	57755.9	1	1.6010	0.58992	0.00458	938.22	5.09

Heat of Formation

We adopt ΔHf°_{298} = -63.5±0.8 kcal/mol and D°_0 = 159.3±1.5 kcal/mol based on equilibrium data analyzed below. Greatest weight is given to torsion effusion (2) and transport (5) data for the Al-AlF_3 system. The adopted value is bracketed by the results of other studies (1, 3, 4) and other reactions (7, 8). Equilibrium studies at a single temperature yield ΔHf°_{298} = -62.8 (9, Knudsen effusion, reaction A), -62.4 (10, capillary effusion, reaction B), and the approximate range -60.4 to -64.5 kcal/mol (11, microwave spectra, reaction A). Hildenbrand et al. (2) found that orifice area affected the torsion-effusion pressures of AlF from reaction A. They derived equilibrium pressures from a semiempirical correlation of data for the four cells listed below. Mass-spectrometric studies (9) of the Al-AlF_3 system near 950 K indicated that the vapor consists of AlF with a small amount of AlF_3. The JANAF Tables (12) predict P(AlF)/P(AlF_3) = 80(900K), 34(1000 K) and 3.5 (1400 K). The adopted D°_0 = 159.3±1.5 kcal/mol is consistent with D°_0>156.7 kcal/mol derived from the highest observed level in $A^1\Pi$ (13). The potential energy curve of this excited state may have a maximum (13, 14).

			Range	No. of	δS[b]	ΔHr°_{298}/(kcal/mol)		ΔHf°_{298}	D°_0
Source	Method	Reaction[a]	T/K	Points	gibbs/mol	2nd Law	3rd Law	kcal/mol	
(1)Blackburn(1965)	Microbal. eff.	A	828-919	7	2.5±2.6	58.2±2.3	56.02±0.5	-64.31±1	160.1
(2)Hildenbrand(1963)	Torsion eff.[c]								
Cell 7	P=1.30Pt	A	882-931	8	-2.7±2.1	54.1±2.0	56.60±0.2	-63.73±0.8	159.5
Cell 9	P=1.72Pt	A	856-932	8	0.4±1.5	57.3±1.4	56.91±0.2	-63.42±0.8	159.2
Cell 15X	P=2.07Pt	A	866-931	8	1.0±0.6	57.8±0.5	56.85±0.1	-63.48±0.8	159.3
Cell 16X	P=3.13Pt	A	867-929	7[d]	0.5±1.4	57.2±1.3	56.79±0.1	-63.54±0.8	159.3
(3)Witt (1959)	Torsion eff.	A	830-932	Line[e]	1.6	58.7	57.4	-63.0±1	158.7
(1)Blackburn(1965)	Microbal. eff.	B	948-1006	5	-8.4±4.9	46.4±4.7	54.58±0.6	-64.38±1	160.2
(4)Ono(1964)	DTA	B	1250-1330	Eqn.	-0.6	55.8	56.52	-62.44±1	158.2
(5)Semenkovich(1960)	Transport	B	1170-1373	5	-0.2±0.2	55.3±0.3	55.56±0.1	-63.40±0.8	159.2
(6)Baimakov(1957)	Weight loss	B	1287-1349	5	87±4	173±5	58.7±4.3	-60.2±4	156.0
(7)Ko(1965)	Transport	C	1199-1348	18	0.8±0.4	33.6±0.4	32.69±0.2	-62.27±1	158.0
(8)Hildenbrand(1965)	Torsion eff.	D	897-926	25	1.4±4.2	31.1±3.8	29.80±0.3	-65.33±1.5	161.1

[a] Reactions: A) 1/3 $AlF_3(c)$ + 2/3 Al(c) = AlF(g); B) 1/3 $AlF_3(c)$ + 2/3 Al(ℓ) = AlF(g); C) 1/3 $AlF_3(g)$ + 2/3 Al(ℓ) = AlF(g); D) 1/2 $BeF_2(g)$ + Al(c) = 1/2 Be(c) + AlF(g)

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

[c] P = equilibrium pressure and Pt = torsion pressure.

[d] One point rejected.

[e] Approximate values from graphical line.

Heat Capacity and Entropy

Electronic levels and molecular constants are based on the detailed analysis of electronic spectra published by Barrow, Kopp and Malmberg (15). Constants for the ground state are confirmed by microwave spectra (11, 16, 17). We omit electronic states between 60000 and 68000 cm^{-1}, including nine observed levels and one predicted level (15); these would have negligible effects on the thermodynamic functions. The analysis of Barrow et al. (15) is supported by theoretical calculations (18).

References

1. P. E. Blackburn (A. D. Little, Inc., Cambridge, Mass.), Rept. AD-618523 (Avail. NTIS), 65 pp. (1965).
2. D. L. Hildenbrand et al., Ford Motor Co., Aeronutronic Div., Rept. No. U-2055, Contract NOw 61-0905-c, March 15, 1963.
3. W. P. Witt and R. F. Barrow, Trans. Faraday Soc. 55, 730 (1959).
4. K. Ono, T. Matsushima and T. Ito, Light Metals 14(6), 363(1964).
5. S. A. Semenkovich, Trudy Vsesoyuz. Alyumin.-Magnievyi Inst. 1960, No. 44, 113 (1960).
6. A. Yu. Baimakov, Trudy Leningrad. Politekh. Inst., Elektromet. Tsvetnykh Metal. 1957, No. 188, 156 (1957).
7. H. C. Ko, M. A. Greenbaum, J. A. Blauer and M. Farber, J. Phys. Chem. 69, 2311 (1965).
8. D. L. Hildenbrand and L. P. Theard, J. Chem. Phys. 42, 3230 (1965).
9. R. F. Porter, J. Chem. Phys. 33, 951 (1960).
10. P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).
11. D. R. Lide, J. Chem. Phys. 42, 1013 (1965).
12. JANAF Thermochemical Tables: AlF_3(c, g) 6-30-70; AlF(g) 12-31-75.
13. R. F. Barrow, J. W. C. Johns and F. J. Smith, Trans. Faraday Soc. 52, 913 (1956).
14. E. Murad, D. L. Hildenbrand and R. P. Main, J. Chem. Phys. 45, 263 (1966).
15. R. F. Barrow, I. Kopp and C. Malmberg, Phys. Scripta 10, 86 (1974).
16. F. C. Wyse, W. Gordy and E. F. Pearson, J. Chem. Phys. 52, 3887 (1970).
17. J. Hoeft, F. J. Lovas, E. Tiemann and T. Torring, Z. Naturforsch. A25, 1029 (1970).
18. S. P. So and W. G. Richards, J. Phys. B 7, 1973 (1974).

ALUMINUM MONOFLUORIDE UNIPOS. ION (ALF^+) ALF^+
(IDEAL GAS) GFW=45.9794

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.106	163.962		
100							
200							
298	7.446	52.570	52.570	0.000	165.400	157.479	-115.435
300	7.454	52.616	52.570	0.014	165.405	157.430	-114.687
400	7.879	54.815	52.667	0.779	165.683	154.730	-84.541
500	8.133	56.597	53.440	1.578	165.945	151.961	-66.422
600	8.347	58.100	54.095	2.403	166.191	149.141	-54.324
700	8.508	59.399	54.762	3.246	166.420	146.280	-45.671
800	8.644	60.544	55.415	4.104	166.625	143.389	-39.172
900	8.773	61.570	56.043	4.975	166.793	140.474	-34.112
1000	8.905	62.501	56.643	5.858	164.398	137.726	-30.100
1100	9.046	63.356	57.215	6.756	164.587	135.049	-26.832
1200	9.196	64.150	57.760	7.668	164.788	132.354	-24.105
1300	9.351	64.892	58.280	8.595	165.003	129.643	-21.795
1400	9.509	65.591	58.778	9.538	165.230	126.916	-19.812
1500	9.664	66.252	59.254	10.497	165.471	124.170	-18.092
1600	9.812	66.881	59.711	11.471	165.725	121.408	-16.584
1700	9.951	67.480	60.151	12.459	165.992	118.630	-15.251
1800	10.078	68.052	60.574	13.461	166.272	115.837	-14.065
1900	10.192	68.600	60.982	14.474	166.561	113.027	-13.001
2000	10.292	69.126	61.376	15.499	166.860	110.202	-12.042
2100	10.377	69.630	61.757	16.532	167.166	107.359	-11.173
2200	10.448	70.114	62.126	17.574	167.479	104.504	-10.382
2300	10.506	70.580	62.484	18.621	167.798	101.638	-9.658
2400	10.552	71.028	62.830	19.674	168.120	98.754	-8.993
2500	10.587	71.460	63.167	20.731	168.444	95.855	-8.380
2600	10.612	71.875	63.494	21.791	168.770	92.945	-7.813
2700	10.629	72.276	63.612	22.853	169.097	90.022	-7.287
2800	10.638	72.663	64.121	23.917	100.015	87.918	-6.862
2900	10.641	73.036	64.422	24.981	100.604	87.475	-6.592
3000	10.638	73.397	64.715	26.045	101.192	87.013	-6.339
3100	10.632	73.746	65.001	27.108	101.777	86.530	-6.100
3200	10.621	74.083	65.280	28.171	102.362	86.030	-5.876
3300	10.609	74.410	65.551	29.233	102.944	85.511	-5.663
3400	10.594	74.726	65.817	30.293	103.522	84.972	-5.462
3500	10.577	75.033	66.076	31.351	104.099	84.419	-5.271
3600	10.559	75.331	66.329	32.408	104.671	83.851	-5.090
3700	10.541	75.620	66.576	33.463	105.241	83.263	-4.918
3800	10.523	75.901	66.817	34.516	105.807	82.662	-4.754
3900	10.504	76.174	67.054	35.568	106.371	82.046	-4.598
4000	10.486	76.440	67.285	36.617	106.930	81.413	-4.448
4100	10.469	76.698	67.512	37.665	107.486	80.766	-4.305
4200	10.451	76.950	67.733	38.711	108.039	80.111	-4.169
4300	10.435	77.196	67.951	39.755	108.589	79.440	-4.038
4400	10.420	77.436	68.163	40.798	109.134	78.758	-3.912
4500	10.405	77.670	68.372	41.839	109.675	78.058	-3.791
4600	10.391	77.898	68.577	42.879	110.214	77.351	-3.675
4700	10.379	78.122	68.777	43.917	110.749	76.627	-3.563
4800	10.367	78.340	68.974	44.955	111.279	75.896	-3.456
4900	10.356	78.554	69.168	45.991	111.806	75.159	-3.352
5000	10.347	78.763	69.358	47.026	112.327	74.403	-3.252
5100	10.338	78.968	69.544	48.060	112.845	73.639	-3.156
5200	10.331	79.168	69.727	49.094	113.359	72.865	-3.062
5300	10.324	79.365	69.907	50.127	113.868	72.082	-2.972
5400	10.319	79.558	70.084	51.159	114.372	71.289	-2.885
5500	10.314	79.747	70.258	52.190	114.870	70.483	-2.801
5600	10.310	79.933	70.429	53.222	115.364	69.675	-2.719
5700	10.308	80.116	70.598	54.252	115.853	68.853	-2.640
5800	10.306	80.295	70.763	55.283	116.336	68.026	-2.563
5900	10.304	80.471	70.926	56.314	116.813	67.189	-2.489
6000	10.304	80.644	71.087	57.344	117.282	66.343	-2.417

June 30, 1968; Dec. 31, 1975; June 30, 1976

Ground State Configuration $[^2\Sigma^+]$
$S^\circ_{298.15}$ = [52.57 ± 0.22] gibbs/mol

ΔHf°_0 = 164 ± 6 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 165.4 ± 6 kcal/mol

ALF^+

Electronic Levels and Quantum Weights

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

ω_e = [925] cm^{-1} $\omega_e x_e$ = [5.5] cm^{-1} σ = 1
B_e = [0.537] cm^{-1} α_e = [0.005] cm^{-1} r_e = [1.605] Å

Heat of Formation

We adopt ΔHf°_0 = 164±6 kcal/mol based on the ionization potential IP(AlF) = 9.86±0.25 eV (227.5±6 kcal/mol). Barrow, Kopp and Malmberg (1) used the observed data for BF to predict that, to a good approximation, IP(AlF) = T$_0$(AlF, 3d) + IP(Al, 3d). This gave IP(AlF) = 79335 cm^{-1} (9.84 eV) which the authors (1) rounded to 80000 cm^{-1} (9.92 eV). We adopt an intermediate value corresponding to ΔHf°_0 = 164 kcal/mol. This yields D°_0 = 70±6 kcal/mol for $AlF^+(g) \rightarrow Al^+(g) + F(g)$.

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

Heat Capacity and Entropy

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

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

References

1. R. F. Barrow, I. Kopp and C. Malmberg, Phys. Scripta 10, 86 (1974).
2. D. L. Hildenbrand and L. P. Theard, J. Chem. Phys. 42, 3230 (1965).
3. R. D. Srivastava and M. Farber, J. Phys. Chem. 75, 1760 (1971).
4. D. L. Hildenbrand and E. Murad, J. Chem. Phys. 44, 1524 (1966).
5. E. Murad, D. L. Hildenbrand and R. P. Main, J. Chem. Phys. 45, 263 (1966).
6. R. F. Porter, J. Chem. Phys. 33, 951 (1960).
7. T. C. Ehlert and J. L. Margrave, J. Amer. Chem. Soc. 86, 3901 (1964).
8. T. C. Ehlert, G. D. Blue, J. W. Green and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964).
9. R. B. Caton and A. E. Douglas, Can. J. Phys. 48, 432 (1970).
10. JANAF Thermochemical Tables: AlO(g) 6-30-75; AlF(g), MgF(g) 12-31-75; $AlCl^+$(g) 6-30-76.
11. J. Berkowitz and J. L. Dehmer, J. Chem. Phys. 57, 3194 (1972).

Aluminum Fluoride Oxide (OAlF) AlFO

(Ideal Gas) GFW=61.9793

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.578	-138.391	-138.391	INFINITE
100	7.445	46.744	65.479	-1.874	-138.488	-138.892	303.549
200	9.563	52.552	57.668	-1.023	-138.777	-139.197	152.107
298	11.187	56.693	56.693	.000	-139.000	-139.357	102.152
300	11.212	56.762	56.693	.021	-139.004	-139.360	101.524
400	12.307	60.149	57.147	1.201	-139.163	-139.452	76.193
500	13.021	62.977	58.038	2.469	-139.295	-139.509	60.979
600	13.495	65.396	59.068	3.797	-139.420	-139.541	50.828
700	13.817	67.502	60.126	5.163	-139.553	-139.550	43.569
800	14.045	69.363	61.166	6.557	-139.706	-139.540	38.121
900	14.209	71.027	62.171	7.970	-139.902	-139.508	33.877
1000	14.332	72.531	63.133	9.398	-142.663	-139.269	30.437
1100	14.425	73.901	64.051	10.836	-142.850	-138.921	27.601
1200	14.498	75.160	64.925	12.282	-143.035	-138.556	25.234
1300	14.555	76.322	65.757	13.735	-143.220	-138.174	23.229
1400	14.601	77.403	66.551	15.193	-143.407	-137.779	21.508
1500	14.639	78.411	67.308	16.655	-143.595	-137.371	20.015
1600	14.670	79.357	68.032	18.120	-143.784	-136.950	18.706
1700	14.696	80.247	68.725	19.588	-143.975	-136.516	17.550
1800	14.718	81.088	69.388	21.059	-144.168	-136.071	16.521
1900	14.737	81.884	70.025	22.532	-144.364	-135.617	15.599
2000	14.753	82.641	70.637	24.006	-144.562	-135.152	14.769
2100	14.766	83.361	71.226	25.482	-144.762	-134.677	14.016
2200	14.778	84.048	71.794	26.960	-144.966	-134.193	13.331
2300	14.789	84.705	72.341	28.438	-145.172	-133.696	12.704
2400	14.798	85.335	72.869	29.917	-145.381	-133.192	12.129
2500	14.806	85.939	73.380	31.398	-145.594	-132.683	11.595
2600	14.814	86.523	73.874	32.879	-145.810	-132.161	11.109
2700	14.820	87.079	74.353	34.360	-146.029	-131.632	10.655
2800	14.826	87.618	74.817	35.843	-215.600	-130.265	10.168
2900	14.831	88.138	75.268	37.325	-215.624	-127.215	9.587
3000	14.836	88.641	75.705	38.809	-215.590	-124.168	9.046
3100	14.840	89.128	76.130	40.293	-215.559	-121.120	8.539
3200	14.844	89.599	76.544	41.777	-215.531	-118.074	8.064
3300	14.848	90.056	76.946	43.261	-215.506	-115.029	7.616
3400	14.851	90.499	77.339	44.746	-215.485	-111.987	7.198
3500	14.854	90.930	77.721	46.231	-215.466	-108.943	6.803
3600	14.856	91.348	78.093	47.717	-215.450	-105.896	6.429
3700	14.859	91.755	78.457	49.203	-215.437	-102.855	6.075
3800	14.861	92.152	78.812	50.689	-215.428	-99.811	5.740
3900	14.863	92.538	79.159	52.175	-215.420	-96.769	5.423
4000	14.865	92.914	79.499	53.661	-215.417	-93.728	5.121
4100	14.867	93.281	79.830	55.148	-215.416	-90.688	4.834
4200	14.869	93.639	80.155	56.635	-215.417	-87.644	4.561
4300	14.871	93.989	80.473	58.122	-215.422	-84.600	4.300
4400	14.872	94.331	80.784	59.609	-215.430	-81.557	4.051
4500	14.873	94.665	81.088	61.096	-215.442	-78.516	3.813
4600	14.875	94.992	81.387	62.584	-215.456	-75.470	3.586
4700	14.876	95.312	81.680	64.071	-215.475	-72.432	3.366
4800	14.877	95.625	81.967	65.559	-215.497	-69.386	3.159
4900	14.878	95.932	82.249	67.047	-215.521	-66.339	2.959
5000	14.879	96.233	82.526	68.534	-215.551	-63.297	2.767
5100	14.880	96.527	82.798	70.022	-215.585	-60.251	2.582
5200	14.881	96.816	83.064	71.511	-215.622	-57.206	2.404
5300	14.882	97.100	83.326	72.999	-215.665	-54.157	2.233
5400	14.883	97.378	83.584	74.487	-215.712	-51.111	2.069
5500	14.883	97.651	83.837	75.975	-215.764	-48.064	1.910
5600	14.884	97.919	84.086	77.464	-215.822	-45.012	1.757
5700	14.885	98.183	84.331	78.952	-215.864	-41.964	1.609
5800	14.885	98.442	84.573	80.441	-215.953	-38.909	1.466
5900	14.886	98.696	84.810	81.929	-216.028	-35.857	1.328
6000	14.887	98.946	85.043	83.418	-216.109	-32.802	1.195

Dec. 31, 1960; March 31, 1964; Dec. 31, 1975

ALUMINUM FLUORIDE OXIDE (OAlF) (IDEAL GAS) GFW = 61.9793

Point Group $[C_{\infty v}]$

$S°_{298.15}$ = [56.69 ± 1 or 4] gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -138.4 ± 4 or 7 kcal/mol AlFO

$\Delta Hf°_{298.15}$ = -139 ± 4 or 7 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[675](1)	386 (2)	1022 (1)

Bond Distance: O-Al = [1.61] Å Al-F = [1.63] Å

Bond Angle: O-Al-F = [180°] σ = 1

Rotational Constant: B_o = [0.184212] cm^{-1}

Heat of Formation

We adopt $\Delta Hf°_{298}$ = -139±4 kcal/mol and $\Delta Ha°_0$ = 293.2±4 kcal/mol, derived from effusion data for reaction A (1). This reaction is analyzed below along with limited equilibrium data for three other reactions. The latter are in satisfactory agreement with reaction A. Dissociation energies calculated from our adopted values (5) are 13.9 kcal/mol larger than those of the corresponding diatomic molecules; i.e., $D°_0$(FAl-O) = 133.9±4, $D°_0$(OAl-F) = 173.2±4, or $\Delta Hr°_0$ = 13.9±5 kcal/mol for the reaction OAlF(g) + Al(g) = AlF(g) + AlO(g). These values suggest that O=Al-F has enhanced stability, consistent with the observation of this reaction (4) by mass-spectrometric sampling of flames containing aluminum species. We assign ΔHf° the alternative uncertainty of ±7 kcal/mol in case OAlF is nonlinear. Farber and Srivastava (4) emphasized that ΔHf° is much too negative to be compatible with the alternative arrangement Al-O-F.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	$\Delta Hr°_{298}$/(kcal/mol) 2nd law	$\Delta Hr°_{298}$/(kcal/mol) 3rd law	$\Delta Hf°_{298}$ kcal/mol
(1)Farber (1963)	Reaction effus.	A	2203-2228[c]	8	-22±26	43±25	91.0±1.6	-138.9±3
(2,3)Srivastava(1971)	Mass spec.[d]	B	1540-1923	8	-[d]	107.1±3.2	-[d]	-143.6±7
(4)Farber (1975)	Flame mass spec.	C	2250	1	-	-	-10.2	-135.3±6
	Flame mass spec.	D	2250	1	-	-	-11.7	-133.0±6

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

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

[c] T converted to IPTS-68 assuming published values to be IPTS-48.

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

Heat Capacity and Entropy

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

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

We adopt the linear structure O=Al-F with an O-Al distance slightly shorter than in AlO (5) and an Al-F distance equal to that in AlF_3 (5). We assume the ground-state configuration to be $^1\Sigma^+$ and neglect excited states which should be relatively unimportant (8). Vibrational frequencies are those assigned by Snelson (6) from a comparison of derived force constants for OAlF and OBX molecules. Values of ν_2 and ν_3 are from IR spectra in an argon matrix. Snelson (6) used a stretching force constant transferred from AlF_3 in order to estimate ν_1 = 675 cm^{-1}. Although a weak absorption was observed at 687 cm^{-1}, this band was not assigned (6) to ν_1 because it was not conclusively associated with ν_2 and ν_3. The moment of inertia is 15.195 x 10^{-39} g cm^2.

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

References

1. M. Farber and H. L. Petersen, Trans. Faraday Soc. 59, 836 (1963).
2. R. D. Srivastava and M. Farber, J. Phys. Chem. 75, 1760 (1971).
3. M. Farber, Space Sciences, Inc., Monrovia, Calif., personal commun., Dec. 5, 1975.
4. *M. Farber and R. D. Srivastava, submitted for publication* in Combust. Flame.
5. JANAF Thermochemical Tables: AlF(g) 12-31-75; AlO(g), $MgF_2(g)$ 6-30-75; $BeF_2(g)$, $AlF_3(g)$ 6-30-70.
6. A. Snelson, High Temp. Sci. 5, 77 (1973); 4, 141, 318 (1972).
7. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
8. J. W. Rabalais, J. M. McDonald, V. Scherr and S. P. McGlynn, Chem. Rev. 71, 73 (1971).
9. V. Calder, D. E. Mann, K. S. Seshadri, M. Allavena and D. White, J. Chem. Phys. 51, 2093 (1969).
10. M. Kaufman, J. Muenter and W. Klemperer, J. Chem. Phys. 47, 3365 (1967).

ALUMINUM DIFLUORIDE (AlF_2)

(IDEAL GAS) GFW=64.9783

	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	-2.750	-165.546	-165.546	INFINITE
100	8.551	52.661	72.063	-1.940	-165.537	-166.569	364.036
200	9.814	58.982	64.087	-1.021	-165.760	-167.533	183.072
298	10.960	63.120	63.120	0.000	-166.000	-168.357	123.409
300	10.979	63.188	63.121	0.020	-166.005	-168.372	122.659
400	11.844	66.473	63.563	1.164	-166.230	-169.125	92.406
500	12.420	69.183	64.424	2.379	-166.453	-169.824	74.230
600	12.801	71.483	65.413	3.642	-166.681	-170.477	62.096
700	13.058	73.477	66.426	4.936	-166.923	-171.090	53.417
800	13.239	75.233	67.419	6.251	-167.191	-171.669	46.898
900	13.369	76.800	68.376	7.582	-167.498	-172.210	41.818
1000	13.465	78.214	69.290	8.924	-170.374	-172.532	37.707
1100	13.538	79.501	70.161	10.274	-170.675	-172.734	34.319
1200	13.595	80.681	70.989	11.631	-170.974	-172.908	31.491
1300	13.640	81.771	71.777	12.992	-171.274	-173.056	29.093
1400	13.676	82.784	72.528	14.358	-171.574	-173.182	27.035
1500	13.705	83.728	73.243	15.727	-171.875	-173.286	25.248
1600	13.729	84.613	73.926	17.099	-172.177	-173.371	23.681
1700	13.750	85.446	74.580	18.473	-172.480	-173.436	22.297
1800	13.767	86.233	75.206	19.849	-172.784	-173.484	21.064
1900	13.781	86.978	75.806	21.226	-173.090	-173.514	19.959
2000	13.794	87.685	76.382	22.605	-173.397	-173.528	18.962
2100	13.804	88.358	76.937	23.985	-173.706	-173.530	18.059
2200	13.814	89.000	77.470	25.366	-174.017	-173.514	17.237
2300	13.823	89.615	77.985	26.748	-174.328	-173.481	16.484
2400	13.831	90.203	78.482	28.130	-174.643	-173.438	15.794
2500	13.838	90.766	78.962	29.514	-174.959	-173.384	15.157
2600	13.845	91.311	79.427	30.898	-175.277	-173.313	14.568
2700	13.851	91.833	79.877	32.283	-175.596	-173.232	14.022
2800	13.858	92.337	80.313	33.668	-245.327	-172.309	13.449
2900	13.865	92.824	80.736	35.054	-245.388	-169.699	12.789
3000	13.872	93.294	81.147	36.441	-245.451	-167.090	12.172
3100	13.879	93.749	81.546	37.829	-245.514	-164.476	11.596
3200	13.887	94.190	81.934	39.217	-245.580	-161.860	11.055
3300	13.896	94.617	82.312	40.606	-245.647	-159.243	10.546
3400	13.905	95.032	82.680	41.996	-245.716	-156.625	10.068
3500	13.915	95.435	83.039	43.387	-245.786	-154.002	9.616
3600	13.926	95.827	83.389	44.779	-245.857	-151.376	9.190
3700	13.937	96.209	83.730	46.173	-245.929	-148.753	8.786
3800	13.950	96.581	84.063	47.567	-246.004	-146.124	8.404
3900	13.963	96.943	84.389	48.963	-246.079	-143.495	8.041
4000	13.978	97.297	84.707	50.360	-246.156	-140.865	7.696
4100	13.993	97.642	85.018	51.758	-246.235	-138.234	7.369
4200	14.010	97.980	85.323	53.158	-246.314	-135.597	7.056
4300	14.027	98.310	85.621	54.560	-246.394	-132.959	6.758
4400	14.045	98.632	85.913	55.964	-246.476	-130.318	6.473
4500	14.065	98.948	86.200	57.369	-246.560	-127.680	6.201
4600	14.085	99.258	86.480	58.777	-246.643	-125.036	5.941
4700	14.106	99.561	86.755	60.186	-246.731	-122.396	5.691
4800	14.128	99.859	87.025	61.598	-246.818	-119.747	5.452
4900	14.151	100.149	87.290	63.012	-246.907	-117.094	5.223
5000	14.175	100.436	87.550	64.428	-246.999	-114.447	5.002
5100	14.199	100.717	87.805	65.847	-247.092	-111.797	4.791
5200	14.224	100.993	88.056	67.268	-247.188	-109.141	4.587
5300	14.250	101.264	88.303	68.692	-247.286	-106.485	4.391
5400	14.276	101.530	88.545	70.118	-247.387	-103.829	4.202
5500	14.302	101.792	88.784	71.547	-247.491	-101.172	4.020
5600	14.329	102.050	89.019	72.978	-247.599	-98.506	3.844
5700	14.357	102.304	89.249	74.413	-247.708	-95.845	3.675
5800	14.385	102.554	89.477	75.850	-247.822	-93.178	3.511
5900	14.413	102.800	89.700	77.290	-247.940	-90.513	3.353
6000	14.441	103.043	89.921	78.732	-248.063	-87.843	3.200

Dec. 31, 1960; Sept. 30, 1964, June 30, 1972; June 30, 1976

Point Group [C_{2v}]

$S°_{298.15}$ = [63.12 ± 0.5] gibbs/mol

$\Delta Hf°_0$ = -165.5 ± 10 kcal/mol

$\Delta Hf°_{298.15}$ = -166 ± 10 kcal/mol

Electronic Levels and Quantum Weights

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

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[730](1)
[280](1)
[880](1)

Bond Distance: Al-F = [1.65] Å

σ = 2

Bond Angle: F-Al-F = [120°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.3688×10^{-115}] g^3 cm^6

Heat of Formation

We tentatively adopt $\Delta Hf°_{298}$ = -166±10 kcal/mol which corresponds to an average bond energy, $\Delta Ha°_0/2$ = 140 kcal/mol, similar to that in $AlF_3(g)$ (1). ΔHf° is a compromise between discrepant results (-180 and -151 kcal/mol) from two mass-spectrometric equilibria analyzed below. In our opinion there is possible cause to suspect Kp for either reaction. The large entropy discrepancy (δS) for reaction B suggests a temperature-dependent bias in the mass-spectrometric Kp (5). If both AlF_2 and AlF_3 were determined from the intensity of AlF_2^+ at different ionizing energies, then we expect ΔHf° (5) to be a positive limit. Reaction A was studied twice by molecular flow effusion of $AlF_3(g)$ over the system Al(ℓ)-Al_2O_3(c). The earlier study (3,4) yields $\Delta Hf°_{298}$ = -188 or -179 kcal/mol, depending on the ionizing energy. Unfortunately, the ionizing energy in the first case is ambiguous. We conclude that ΔHf° is quite dependent on ionizing energy. In addition Kp and ΔHf° may be affected by bias in the ionizing energy scale or related problems. These are discussed in more detail on tables for AlF_2^+, $AlCl_2^+$ and $AlCl_2$ (1). We believe that ΔHf° (3,4) may be a negative limit.

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

Source	Reaction[a]	Ionizing Energy, eV	No. of Points	Range T/K	δS[b] gibbs/mol	$\Delta Hr°_{298}$/(kcal/mol) 2nd Law	3rd Law	$\Delta Hf°_{298}$	$\Delta Ha°_0/2$
								- - -kcal/mol- -	
(2) Uy (1972)	A	AP+(2 or 3)	7	1453-1675	4.0±1.7	31.0±2.6	24.6±0.9	-180.4	147.0
(3,4) Farber (1971)	A	AP+~2	1	1538	---	---	25.8	-179.2	146.5
(3,4) Farber (1971)	A	20(or AP+3)	5	1408-1633	3.6±0.6	22.5±0.9	17.0±0.8	-188.0	150.9
(5) Ehlert (1964)	B	?	4	1243-1301	-76±10	-47±13	50.2±3.7	<-151.2	>132.4

[a] Reactions: A) $2AlF(g) = Al(g) + AlF_2(g)$; B) $AlF_3(g) + AlF(g) = 2AlF_2(g)$. [b] δS = ΔSr°(2nd law)-ΔSr°(3rd law).

Heat Capacity and Entropy

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

Vibrational frequencies are calculated from the estimated force constants f_r = 4.25 and f_α/r^2 = 0.25 mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of AlF_2^+, AlF_2, AlF_2^- (1) and the analogous boron species. We assume that frequency changes are qualitatively similar to those of NO_2^+, NO_2 and NO_2^-. In going from AlF_2^+ to AlF_2, we expect a large decrease in ν_3, an increase in ν_2 and some increase in ν_1. By analogy with BF_2 (6), the odd electron in AlF_2 should occupy an antibonding orbital which increases the bond length but decreases the bond angle and stretching force constant. We assume a bond length 0.05 Å longer than in AlF_2^+ (1) and a bond angle equal to that in BF_2 (6). The principal moments of inertia are 1.783×10^{-39}, 12.882×10^{-39} and 14.665×10^{-39} g cm^2.

References

1. JANAF Thermochemical Tables: $AlCl_2(g)$, $AlF_2^+(g)$, $AlF_2^-(g)$, $AlF_4^-(g)$, $AlF_2O(g)$, AlClF(g), $AlClF_2(g)$, $AlCl_2F(g)$ 6-30-76; AlF(g) 12-31-75; $AlF_3(g)$ 6-30-70; Al(g) 12-31-65; F(g) 9-30-65.
2. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
3. M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).
4. M. Farber, R. D. Srivastava and O. M. Uy, Space Sciences, Inc., Rept. No. AFRPL-TR-70-97, Contract F04611-69-C-0094, July, 1970.
5. T. C. Ehlert and J. L. Margrave, J. Amer. Chem. Soc. 86, 3901 (1964); T. C. Ehlert, personal commun., Aug. 13, 1964.
6. C. Thomson and D. A. Brotchie, Theoret. Chim. Acta 32, 101 (1973); Mol. Phys. 28, 301 (1974).
7. J. W. Hastie and J. L. Margrave, J. Phys. Chem. 73, 1105 (1969).
8. R. A. Gangi and L. Burnelle, J. Chem. Phys. 55, 843 (1971); 49, 561 (1968).
9. G. D. Gillispie, A. U. Khan, A. C. Wahl, R. P. Hosteny and M. Krauss, J. Chem. Phys. 63, 3425 (1975).
10. P. W. Harland and J. L. Franklin, J. Chem. Phys. 61, 1621 (1974).
11. F. Petty, J. L. Wang, R. P. Steiger, P. W. Harland, J. L. Franklin and J. L. Margrave, High Temp. Sci. 5, 25 (1973).

ALUMINUM DIFLUORIDE UNIPOSITIVE ION (ALF_2^+) ALF_2^+

(IDEAL GAS) GFW=64.9778

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.804	20.919		
100							
200							
298	11.778	57.167	57.167	0.000	22.000	19.931	-14.610
300	11.798	57.240	57.167	0.022	22.006	19.918	-14.510
400	12.688	60.764	57.641	1.249	22.361	19.170	-10.474
500	13.286	63.664	58.564	2.550	22.721	18.330	-8.012
600	13.688	66.124	59.624	3.900	23.077	17.418	-6.345
700	13.964	68.256	60.709	5.283	23.420	16.448	-5.135
800	14.160	70.134	61.772	6.650	23.741	15.429	-4.215
900	14.302	71.810	62.796	8.113	24.023	14.373	-3.490
1000	14.407	73.323	63.774	9.549	21.738	13.470	-2.944
1100	14.488	74.700	64.706	10.994	22.029	12.629	-2.509
1200	14.551	75.964	65.592	12.446	22.321	11.761	-2.142
1300	14.601	77.130	66.435	13.904	22.615	10.870	-1.827
1400	14.641	78.214	67.238	15.366	22.908	9.956	-1.554
1500	14.674	79.225	68.004	16.832	23.201	9.021	-1.314
1600	14.701	80.173	68.735	18.300	23.491	8.065	-1.102
1700	14.723	81.065	69.435	19.772	23.783	7.093	-0.912
1800	14.742	81.907	70.104	21.245	24.073	6.102	-0.741
1900	14.758	82.705	70.747	22.720	24.362	5.096	-0.586
2000	14.772	83.462	71.364	24.197	24.650	4.075	-0.445
2100	14.784	84.183	71.957	25.674	24.934	3.037	-0.316
2200	14.795	84.871	72.529	27.153	25.218	1.987	-0.197
2300	14.804	85.529	73.080	28.633	25.502	0.928	-0.088
2400	14.812	86.159	73.612	30.114	25.783	-0.146	0.013
2500	14.819	86.764	74.126	31.596	26.062	-1.235	0.108
2600	14.825	87.345	74.623	33.078	26.338	-2.332	0.196
2700	14.831	87.905	75.105	34.561	26.614	-3.440	0.278
2800	14.836	88.444	75.571	36.044	-42.522	-3.728	0.291
2900	14.841	88.965	76.024	37.528	-41.988	-2.351	0.177
3000	14.845	89.468	76.464	39.012	-41.457	-0.995	0.072
3100	14.848	89.955	76.892	40.497	-40.927	0.345	-0.024
3200	14.852	90.427	77.307	41.982	-40.399	1.670	-0.114
3300	14.855	90.884	77.712	43.467	-39.873	2.976	-0.197
3400	14.858	91.327	78.106	44.953	-39.349	4.265	-0.274
3500	14.860	91.758	78.490	46.439	-38.827	5.542	-0.346
3600	14.863	92.176	78.864	47.925	-38.308	6.805	-0.413
3700	14.865	92.584	79.229	49.411	-37.791	8.049	-0.475
3800	14.867	92.980	79.586	50.898	-37.276	9.282	-0.534
3900	14.869	93.366	79.934	52.385	-36.763	10.500	-0.588
4000	14.870	93.743	80.275	53.871	-36.255	11.704	-0.639
4100	14.872	94.110	80.608	55.359	-35.747	12.894	-0.687
4200	14.873	94.468	80.934	56.846	-35.242	14.077	-0.733
4300	14.875	94.818	81.253	58.333	-34.740	15.247	-0.775
4400	14.876	95.160	81.565	59.821	-34.241	16.406	-0.815
4500	14.877	95.495	81.871	61.309	-33.746	17.547	-0.852
4600	14.878	95.822	82.170	62.796	-33.253	18.683	-0.888
4700	14.880	96.142	82.464	64.284	-32.765	19.803	-0.921
4800	14.881	96.455	82.752	65.772	-32.279	20.918	-0.952
4900	14.881	96.762	83.035	67.260	-31.797	22.027	-0.982
5000	14.882	97.063	83.313	68.749	-31.320	23.117	-1.010
5100	14.883	97.357	83.585	70.237	-30.847	24.199	-1.037
5200	14.884	97.646	83.853	71.725	-30.379	25.276	-1.062
5300	14.885	97.930	84.116	73.214	-29.915	26.342	-1.086
5400	14.885	98.208	84.374	74.702	-29.457	27.397	-1.109
5500	14.886	98.481	84.628	76.191	-29.005	28.444	-1.130
5600	14.887	98.749	84.878	77.679	-28.559	29.489	-1.151
5700	14.887	99.013	85.124	79.169	-28.117	30.519	-1.170
5800	14.888	99.272	85.365	80.657	-27.682	31.546	-1.189
5900	14.888	99.526	85.603	82.146	-27.254	32.562	-1.206
6000	14.889	99.777	85.837	83.634	-26.835	33.571	-1.223

June 30, 1968; June 30, 1972; June 30, 1976

ALUMINUM DIFLUORIDE UNIPOSITIVE ION (AlF_2^+) (IDEAL GAS) GFW = 64.9778

ALF_2^+

Point Group [$D_{\infty h}$]
$S^\circ_{298.15}$ = [57.17 ± 1] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = 20.9 ± 15 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 22 ± 15 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[570] (1)
[240] (2)
[1000] (1)

Bond Distance: Al-F = [1.60] Å σ = 2
Bond Angle: F-Al-F = [180°]
Rotational Constant: B_0 = [0.17330] cm^{-1}

Heat of Formation

We adopt ΔHf°_{298} = 22±15 kcal/mol and an ionization potential IP(AlF_2) = 8.1±0.9 eV. Electron-impact studies (1, 2) gave 15.2±0.3 eV for the appearance potential (AP) of AlF_2^+ from AlF_3. The analogous process for onset of BF_2^+ from BF_3 has been studied by both photoionization (3) and electron impact (4). Comparison indicates that BF_2^+ from electron impact (4) carried an excess energy (E*) of ∿0.4 to ∿0.9 eV. We estimate the excess energy for AlF_2^+ as 1.0±0.5 eV. Thus, we take AP−E* = ΔHr°_0 = 14.2±0.6 eV (327.5±14 kcal/mol) for the reaction $AlF_3(g) + e^-(g) = AlF_2^+(g) + F(g) + 2e^-(g)$. With JANAF auxiliary data (5) this yields $\Delta Hf^\circ_0(AlF_2^+)$ = 21±15, ΔHf°_{298} = 22±15 and IP(AlF_2) = 187±20 kcal/mol (8.1±0.9 eV).

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

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

Heat Capacity and Entropy

We assume the electronic ground state to be $^1\Sigma^+$ and neglect excited states. We expect the ground state to be linear by analogy with other triatomic species having sixteen valence electrons (10). Although conflicting data (5) suggest that isoelectronic MgF_2 is either linear or slightly nonlinear, recent Raman data (11) favor a linear structure. We estimate the bond distance to be slightly shorter than that in AlF_3 and 0.05 Å shorter than that estimated for AlF_2 (5). We transfer the stretching force constant from AlF_3 and the ratio f_r/f_α = ∿13 $Å^{-2}$ from MgF_2. This ratio is a compromise between very different values of ν_2 observed for MgF_2 in the gas (5) and matrix (11) phases. Thus, we calculate vibrational frequencies for AlF_2^+ from the force constants f_r = 4.9, f_{rr} = 0.2 and f_α/r^2 = 0.14 mdyn/Å. The resulting values have been rounded downward. The moment of inertia is 16.151 x 10^{-39} g cm^2.

References

1. T. C. Ehlert and J. L. Margrave, J. Amer. Chem. Soc. 86, 390 (1964).
2. T. C. Ehlert, G. D. Blue, J. W. Green and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964).
3. V. H. Dibeler and S. K. Liston, Inorg. Chem. 7, 1742 (1968).
4. J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, 1969.
5. JANAF Thermochemical Tables: $AlF_2(g)$, $AlCl_2^+(g)$ 6-30-76; AlFO(g) 12-31-75; $MgF_2(g)$ 6-30-75; $AlF_3(g)$ 6-30-70; F(g) 9-30-65.
6. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
7. M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).
8. C. Thomson and D. A. Brotchie, Theoret. Chim. Acta 32, 101 (1973).
9. J. W. Hastie and J. L. Margrave, J. Phys. Chem. 73, 1105 (1969).
10. J. W. Rabalais, J. M. McDonald, V. Scherr and S. P. McGlynn, Chem. Rev. 71, 73 (1971).
11. M. L. Lesiecki and J. W. Nibler, J. Chem. Phys. 64, 871 (1976).

ALUMINUM DIFLUORIDE UNINEG. ION (AlF_2^-) AlF_2^-
(IDEAL GAS) GFW=64.9789

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0				-2.766	-215.081		
100							
200							
298	11.116	62.125	62.125	0.000	-217.000	-217.573	159.485
300	11.136	62.194	62.126	0.021	-217.013	-217.576	158.504
400	12.000	65.525	62.574	1.180	-217.720	-217.656	118.922
500	12.552	68.267	63.446	2.410	-218.425	-217.560	95.095
600	12.908	70.589	64.448	3.684	-219.139	-217.321	79.159
700	13.146	72.598	65.472	4.986	-219.867	-216.959	67.738
800	13.310	74.365	66.476	6.311	-220.624	-216.493	59.143
900	13.428	75.940	67.441	7.648	-221.422	-215.929	52.435
1000	13.514	77.359	68.363	8.996	-224.789	-215.092	47.008
1100	13.580	78.650	69.241	10.351	-225.582	-214.084	42.535
1200	13.631	79.834	70.075	11.711	-226.374	-213.003	38.793
1300	13.671	80.927	70.868	13.076	-227.167	-211.856	35.616
1400	13.703	81.941	71.623	14.445	-227.961	-210.649	32.884
1500	13.729	82.888	72.343	15.817	-228.756	-209.385	30.501
1600	13.750	83.774	73.030	17.191	-229.552	-208.067	28.421
1700	13.768	84.608	73.687	18.567	-230.350	-206.699	26.573
1800	13.783	85.396	74.316	19.944	-231.150	-205.286	24.925
1900	13.796	86.141	74.919	21.323	-231.951	-203.827	23.445
2000	13.807	86.849	75.498	22.703	-232.754	-202.326	22.109
2100	13.817	87.523	76.054	24.085	-233.557	-200.786	20.896
2200	13.825	88.166	76.590	25.467	-234.364	-199.207	19.789
2300	13.832	88.781	77.107	26.850	-235.171	-197.588	18.775
2400	13.839	89.370	77.606	28.233	-235.982	-195.938	17.843
2500	13.844	89.935	78.088	29.617	-236.795	-194.255	16.982
2600	13.850	90.478	78.554	31.002	-237.608	-192.535	16.184
2700	13.854	91.001	79.005	32.387	-238.424	-190.787	15.443
2800	13.859	91.505	79.443	33.773	-308.651	-188.178	14.688
2900	13.863	91.991	79.867	35.159	-309.209	-183.865	13.856
3000	13.868	92.461	80.279	36.545	-309.770	-179.535	13.079
3100	13.872	92.916	80.679	37.932	-310.330	-175.183	12.350
3200	13.876	93.356	81.069	39.320	-310.893	-170.814	11.666
3300	13.881	93.783	81.448	40.708	-311.458	-166.428	11.022
3400	13.886	94.198	81.817	42.096	-312.026	-162.027	10.415
3500	13.892	94.600	82.176	43.485	-312.595	-157.605	9.841
3600	13.898	94.992	82.527	44.874	-313.165	-153.165	9.298
3700	13.905	95.373	82.869	46.265	-313.737	-148.715	8.784
3800	13.912	95.744	83.203	47.655	-314.313	-144.247	8.296
3900	13.920	96.105	83.529	49.047	-314.889	-139.764	7.832
4000	13.929	96.458	83.848	50.439	-315.467	-135.267	7.391
4100	13.940	96.802	84.160	51.833	-316.047	-130.758	6.970
4200	13.951	97.138	84.465	53.227	-316.629	-126.229	6.568
4300	13.963	97.466	84.763	54.623	-317.212	-121.688	6.185
4400	13.976	97.787	85.055	56.020	-317.798	-117.133	5.818
4500	13.991	98.102	85.342	57.418	-318.385	-112.567	5.467
4600	14.007	98.409	85.623	58.818	-318.973	-107.986	5.131
4700	14.023	98.711	85.898	60.220	-319.565	-103.398	4.808
4800	14.042	99.006	86.168	61.623	-320.158	-98.790	4.498
4900	14.061	99.296	86.433	63.028	-320.753	-94.167	4.200
5000	14.082	99.580	86.693	64.435	-321.350	-89.539	3.914
5100	14.104	99.859	86.948	65.844	-321.950	-84.900	3.638
5200	14.127	100.133	87.199	67.256	-322.552	-80.243	3.373
5300	14.151	100.403	87.446	68.670	-323.157	-75.578	3.117
5400	14.177	100.667	87.688	70.086	-323.765	-70.903	2.870
5500	14.204	100.928	87.927	71.505	-324.375	-66.216	2.631
5600	14.231	101.184	88.161	72.927	-324.989	-61.513	2.401
5700	14.260	101.436	88.392	74.352	-325.605	-56.804	2.178
5800	14.290	101.684	88.619	75.779	-326.226	-52.082	1.962
5900	14.321	101.929	88.842	77.210	-326.850	-47.352	1.754
6000	14.353	102.170	89.063	78.643	-327.478	-42.609	1.552

June 30, 1968; June 30, 1972; June 30, 1976

ALUMINUM DIFLUORIDE UNINEGATIVE ION (AlF_2^-) (IDEAL GAS) GFW = 64.9789

Point Group [C_{2v}]
$S°_{298.15}$ = [62.13 ± 0.8] gibbs/mol

$\Delta Hf°_0$ = -215.1 ± 20 kcal/mol AlF_2
$\Delta Hf°_{298.15}$ = -217 ± 20 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1A_1$	[0]	1
$^3B_1$	[26000]	3
$^1B_2$	[44000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[730](1)
[280](1)
[780](1)

Bond Distance: Al-F = [1.70] Å σ = 2
Bond Angle: F-Al-F = [105°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [4.5990×10^{-115}] g^3 cm^6

Heat of Formation

We adopt $\Delta Hf°_{298}$ = -217±20 kcal/mol which corresponds to an electron affinity of EA(AlF_2) = 50±8 kcal/mol (2.2±0.4 eV) and a fluoride-ion affinity of IA(AlF) = 92±20 kcal/mol. ΔHf° is based on Kp data for the reaction $AlF_2(g) + F^-(g) = F(g) + AlF_2^-(g)$ reported by Srivastava et al. (1). The authors measured Kp with a molecular-flow-effusion method using a mass spectrometer operating in both positive- and negative-ion modes. They give three points (1705-1900 K) obtained from study of the vapor species over the system $AlF_3(c)$-KF(c)-Al(ℓ). Our analysis gives [ΔSr°(2nd law)-ΔSr°(3rd law)] = -0.2±4.8 gibbs/mol and $\Delta Hr°_{298}$ = 28.4±8.8(2nd law) or 28.8±1(3rd law) kcal/mol. Reducing the third-law ΔHr° to absolute zero and combining with EA(F) = 78.38 kcal/mol (2), we derive EA(AlF_2) = 49.7±8 kcal/mol. The uncertainity of ±8 kcal/mol is our estimate of a reasonable bound for error in ΔHr°.

Depending on the value used for ΔHf°(AlF_2), the above reaction yields $\Delta Hf°_{298}(AlF_2^-)$ = -231 (3, 2), -217 (2) or -202 (4, 2) kcal/mol. In contrast, we derive $\Delta Hf°_{298}(AlF_2^-)$ = -181±25 kcal/mol, independent of ΔHf°(AlF_2), from $\Delta Hr°_0 \approx AP - E^*$ = 127 kcal (5) for the reaction $AlF_3(g) + e^-(g) = AlF_2^-(g) + F(g)$. Depending on ΔHf°($AlF_2$), this yields EA($AlF_2$) = 0±25 (3, 2), 14±25 (2) or 29±25 (4, 2) kcal/mol. Petty et al. (5) measured the appearance potential (AP) and excess translational energy of AlF_2^- in the dissociative electron-attachment reaction. E*, the excess vibrational-translational energy of the products at threshold, was estimated (5) from the measured translational energy via an approximate empirical correlation. We estimate ±25 kcal/mol as an approximate bound for error in E* (6). The resulting ΔHf°(AlF_2^-) = -181±25 kcal/mol is inconsistent with the two most likely values (-231 and -217) derived from AlF_2. Bias might exist in either experiment (5, 2). It is conceivable that AlF_2^- is formed (5) in an excited electronic state. Thus far, electronic excitation has been observed (7) in only one negative molecular ion, AsF_4^-. If it occurs for AlF_2^-, then ΔHf° = -181±25 refers to an excited electronic state. The electronic energy of this state would be ∿17000±9000 or ∿13000±9000 cm^{-1}, based on the two most likely values of ΔHf°(AlF_2^-). Such values are not unreasonable, so we cannot rule out electronic excitation (5). We conclude that additional data are needed to confirm ΔHf°(AlF_2^-).

Heat Capacity and Entropy

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

By analogy with BF_2 (8, 9), we expect that the odd electron in AlF_2 occupies a molecular orbital centered mainly on the metal opposite the two fluorines. This orbital should be antibonding (8) in the sense that addition of an electron increases the bond length but decreases the bond angle and stretching force constant. We assume that the bond length is 0.05 Å longer and the bond angle is 15° smaller than in AlF_2 (2). The principal moments of inertia are $I_A = 2.8058 \times 10^{-39}$, $I_B = 11.476 \times 10^{-39}$ and $I_C = 14.282 \times 10^{-39}$ g cm^2.

References

1. R. D. Srivastava, O. M. Uy and M. Farber, J. Chem. Soc., Faraday Trans. I 70, 1033 (1974); Rept. AD-731303, 50 pp. (1971).
2. JANAF Thermochemical Tables: AlF_2(g), SiF_2(g) 6-30-76; NO_2^-(g) 6-30-72; F^-(g) 12-31-71; F(g) 9-30-65.
3. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
4. T. C. Ehlert and J. L. Margrave, J. Amer. Chem. Soc. 86, 3901 (1964); T. C. Ehlert, personal commun., Aug. 13, 1964.
5. F. Petty, J. L. Wang, R. P. Steiger, P. W. Harland, J. L. Franklin and J. L. Margrave, High Temp. Sci. 5, 25 (1973).
6. J. L. Franklin, Science 193, 725 (1976).
7. J. L. Franklin, Rice University, Houston, Texas, personal commun., Sep., 1976.
8. C. Thomson and D. A. Brotchie, Theoret. Chim. Acta 32, 101 (1973).
9. W. Nelson and W. Gordy, J. Chem. Phys. 51, 4710 (1969).

AlF_2^-

ALUMINUM DIFLUORIDE OXIDE (ALF_2O) (IDEAL GAS) GFW=80.9777

ALF_2O

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	-3.424	-264.182	-264.182	INFINITE
100	10.102	56.244	81.964	-2.572	-264.479	-263.799	576.531
200	13.157	64.285	71.257	-1.395	-264.791	-263.003	287.396
298	15.150	69.931	69.931	0.000	-265.000	-262.082	192.111
300	15.182	70.025	69.931	0.028	-265.003	-262.064	190.914
400	16.576	74.597	70.545	1.621	-265.135	-261.062	142.638
500	17.493	78.402	71.747	3.327	-265.232	-260.033	113.660
600	18.098	81.648	73.133	5.109	-265.319	-258.985	94.335
700	18.509	84.471	74.556	6.941	-265.412	-257.921	80.527
800	18.796	86.962	75.954	8.807	-265.528	-256.845	70.167
900	19.004	89.189	77.303	10.697	-265.683	-255.750	62.105
1000	19.158	91.199	78.594	12.606	-268.406	-254.453	55.611
1100	19.276	93.031	79.824	14.528	-268.554	-253.051	50.277
1200	19.368	94.712	80.996	16.460	-268.702	-251.635	45.829
1300	19.441	96.266	82.111	18.401	-268.851	-250.206	42.063
1400	19.503	97.709	83.174	20.348	-269.002	-248.766	38.834
1500	19.555	99.056	84.189	22.301	-269.154	-247.316	36.034
1600	19.601	100.320	85.158	24.259	-269.309	-245.855	33.582
1700	19.644	101.509	86.085	26.221	-269.465	-244.384	31.418
1800	19.684	102.633	86.973	28.187	-269.623	-242.904	29.493
1900	19.723	103.698	87.826	30.158	-269.783	-241.416	27.769
2000	19.761	104.711	88.645	32.132	-269.945	-239.919	26.217
2100	19.800	105.676	89.433	34.110	-270.108	-238.415	24.812
2200	19.839	106.598	90.193	36.092	-270.274	-236.902	23.534
2300	19.879	107.481	90.925	38.078	-270.439	-235.379	22.366
2400	19.919	108.328	91.633	40.068	-270.607	-233.851	21.295
2500	19.961	109.142	92.317	42.062	-270.777	-232.319	20.309
2600	20.002	109.925	92.979	44.060	-270.947	-230.776	19.398
2700	20.044	110.681	93.621	46.062	-271.118	-229.227	18.555
2800	20.086	111.411	94.243	48.069	-340.699	-226.843	17.706
2900	20.129	112.116	94.648	50.079	-340.609	-222.777	16.789
3000	20.171	112.799	95.435	52.094	-340.521	-218.717	15.934
3100	20.213	113.462	96.006	54.114	-340.431	-214.658	15.133
3200	20.255	114.104	96.561	56.137	-340.342	-210.602	14.383
3300	20.297	114.728	97.102	58.165	-340.254	-206.549	13.679
3400	20.337	115.334	97.630	60.196	-340.167	-202.500	13.017
3500	20.377	115.925	98.144	62.232	-340.079	-198.451	12.392
3600	20.417	116.499	98.646	64.272	-339.991	-194.402	11.802
3700	20.455	117.059	99.136	66.315	-339.905	-190.362	11.244
3800	20.492	117.605	99.615	68.363	-339.819	-186.320	10.716
3900	20.529	118.138	100.083	70.414	-339.733	-182.283	10.215
4000	20.564	118.658	100.541	72.469	-339.648	-178.248	9.739
4100	20.599	119.166	100.989	74.527	-339.564	-174.216	9.287
4200	20.632	119.663	101.428	76.588	-339.480	-170.182	8.856
4300	20.664	120.149	101.857	78.653	-339.398	-166.150	8.445
4400	20.695	120.624	102.279	80.721	-339.317	-162.121	8.053
4500	20.724	121.090	102.691	82.792	-339.238	-158.098	7.678
4600	20.753	121.545	103.096	84.866	-339.158	-154.070	7.320
4700	20.780	121.992	103.494	86.942	-339.084	-150.052	6.977
4800	20.806	122.430	103.884	89.022	-339.009	-146.029	6.649
4900	20.831	122.859	104.267	91.103	-338.937	-142.006	6.334
5000	20.854	123.280	104.643	93.188	-338.868	-137.991	6.032
5100	20.877	123.693	105.012	95.274	-338.802	-133.975	5.741
5200	20.898	124.099	105.375	97.363	-338.739	-129.959	5.462
5300	20.919	124.497	105.732	99.454	-338.680	-125.941	5.193
5400	20.938	124.888	106.083	101.547	-338.624	-121.933	4.935
5500	20.956	125.273	106.429	103.641	-338.573	-117.920	4.686
5600	20.973	125.651	106.769	105.738	-338.528	-113.906	4.445
5700	20.988	126.022	107.103	107.836	-338.486	-109.898	4.214
5800	21.003	126.387	107.433	109.935	-338.450	-105.884	3.990
5900	21.017	126.746	107.757	112.036	-338.420	-101.878	3.774
6000	21.030	127.100	108.076	114.139	-338.396	-97.868	3.565

June 30, 1976

ALUMINUM DIFLUORIDE OXIDE (AlF_2O) (IDEAL GAS) GFW = 80.9777

ALF_2O

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [69.93 ± 3] gibbs/mol

ΔHf°_0 = -264.2 ± 7 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -265 ± 7 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$^2B_2$]	0	[2]
[$^2B_1$]	[10000]	[2]
[^2B]	[20000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[900](1)	[900](1)
[640](1)	[240](1)
[260](1)	[270](1)

Bond Distances: Al-F = [1.63] Å Al-O = [1.72] Å σ = [2]

Bond Angles: F-Al-F = [120°] F-Al-O = [120°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.7188×10^{-114}] g^3 cm^6

Heat of Formation

We adopt ΔHf°_{298} = -265±7 kcal/mol and ΔHa°_0 = 437±8 kcal/mol based on JANAF auxiliary data (1) combined with ΔHr°_{298} = 15.5±5 kcal/mol for the reaction AlF(g) + AlFO(g) = Al(g) + AlF_2O(g). ΔHr° is from our third-law analysis of Kp data reported by Uy, Srivastava and Farber (2). They calculated Kp directly from ion intensities observed at 1453-1675 K in a mass-spectrometric study of vapor species over the system *AlF_3(g)-Al(ℓ)-Al_2O_3(c). Second-law analysis gives ΔHr°_{298}* = 20.8±0.8 kcal/mol and the difference [ΔSr°(2nd law)-ΔSr°(3rd law)] = 3.4±0.5 gibbs/mol. Uy et al. (2) assigned ΔHr°(2nd law) an overall uncertainty (including contributions from T) of ±5 kcal/mol.

The adopted ΔHa°_0 = 437 kcal/mol implies that AlF_2O is surprisingly stable. Average bond energies from AlF_3 (140 kcal/mol) and AlO, AlO_2 and Al_2O (~120 kcal/mol) yield an estimate of $\Delta Ha^\circ_0(AlF_2O)$ = 400 kcal/mol. If we attribute all of the difference to the Al-O bond, then the AlF_2O data imply an Al-O bond energy of 157 kcal/mol. This enhancement of 37 kcal/mol contrasts with the near equality of Al-O bond energies in the oxides (1) and hydroxides (8). An analogous treatment of AlFO(g) (1) yields an Al-O bond energy of 153 kcal/mol, similar to that in AlF_2O. Existing data for BF_2O and BFO imply bond energies of ~166 and ~200 kcal/mol compared with values of ~130 (B-O) and ~190 (B=O) from the oxides. There are obvious differences between the Al and B systems which we are unable to rationalize via existing knowledge of electronic structure. We feel that confirmation of the oxyfluoride data is desirable.

Heat Capacity and Entropy

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

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

Vibrational frequencies of AlF_2O are estimated from those of BF_2O by comparison of AlF_3, AlFO, AlO and Al_2O (1) with the analogous boron species. Electronic levels are crude estimates based on calculations or data for the 24-valence-electron species BF_2O (4), BF_3^+ (5, 6) and NO_3 (5, 7). Bond angles are assumed to be 120°. Bond distances are assumed equal to those of AlF_3 and Al_2O (1). Principal moments of inertia are 12.026×10^{-39}, 12.572×10^{-39} and 24.598×10^{-39} g cm^2.

References

1. JANAF Thermochemial Tables: AlFO(g), AlO_2(g) 12-31-75; AlF(g), AlO(g), Al_2O(g) 6-30-75; AlF_3(g) 6-30-70; Al(g) 12-31-65.
2. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972); Rept. AD-731303 (avail. NTIS), 50 pp. (1971).
3. C. W. Mathews and K. K. Innes, J. Mol. Spectrosc. 15, 199 (1965); ibid. 19, 203 (1966).
4. R. Zahradnik and P. Carsky, Theoret. Chim. Acta 27, 121 (1972).
5. T. E. H. Walker and J. A. Horsley, Mol. Phys. 21, 939 (1971).
6. P. T. Bassett and D. R. Lloyd, J. Chem. Soc. A1971, 1551 (1971).
7. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
8. H. A. Skinner, Faraday Symposia of The Chemical Society, No. 8, 167 (1973).

ALUMINUM DIFLUORIDE OXIDE UNINEG. ION AlF_2O^-
(IDEAL GAS) GFW=80.9783

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-3.364	-310.642		
100							
200							
298	14.960	68.058	68.058	0.000	-313.000	-308.036	225.797
300	14.992	68.151	68.059	0.028	-313.013	-308.006	224.382
400	16.424	72.674	68.666	1.603	-313.659	-306.237	167.320
500	17.373	76.448	69.855	3.296	-314.266	-304.311	133.014
600	18.004	79.675	71.229	5.067	-314.861	-302.265	110.100
700	18.434	82.485	72.641	6.891	-315.458	-300.117	93.701
800	18.735	84.967	74.030	8.750	-316.078	-297.885	81.378
900	18.954	87.187	75.370	10.635	-316.735	-295.571	71.775
1000	19.116	89.193	76.654	12.539	-319.960	-293.000	64.035
1100	19.240	91.021	77.878	14.457	-320.609	-290.274	57.672
1200	19.336	92.699	79.044	16.386	-321.256	-287.486	52.358
1300	19.412	94.250	80.155	18.323	-321.905	-284.645	47.853
1400	19.473	95.691	81.214	20.268	-322.556	-281.755	43.984
1500	19.523	97.036	82.224	22.218	-323.208	-278.818	40.624
1600	19.564	98.297	83.190	24.172	-323.863	-275.837	37.678
1700	19.598	99.485	84.114	26.130	-324.519	-272.814	35.073
1800	19.627	100.606	84.999	28.091	-325.180	-269.755	32.753
1900	19.651	101.667	85.849	30.055	-325.843	-266.658	30.673
2000	19.673	102.676	86.665	32.022	-326.510	-263.526	28.797
2100	19.691	103.636	87.451	33.990	-327.179	-260.361	27.096
2200	19.707	104.553	88.207	35.960	-327.854	-257.164	25.547
2300	19.720	105.429	88.937	37.931	-328.531	-253.933	24.129
2400	19.733	106.268	89.642	39.904	-329.213	-250.675	22.827
2500	19.743	107.074	90.323	41.877	-329.901	-247.392	21.627
2600	19.753	107.849	90.982	43.852	-330.590	-244.075	20.516
2700	19.762	108.594	91.621	45.828	-331.284	-240.735	19.486
2800	19.769	109.313	92.240	47.805	-401.392	-236.539	18.463
2900	19.776	110.007	92.841	49.782	-401.833	-230.643	17.382
3000	19.782	110.678	93.424	51.760	-402.278	-224.734	16.372
3100	19.788	111.326	93.991	53.738	-402.725	-218.807	15.426
3200	19.793	111.955	94.543	55.717	-403.178	-212.867	14.538
3300	19.798	112.564	95.080	57.697	-403.635	-206.913	13.703
3400	19.802	113.155	95.603	59.677	-404.096	-200.947	12.917
3500	19.806	113.729	96.113	61.657	-404.561	-194.964	12.174
3600	19.809	114.287	96.610	63.638	-405.028	-188.964	11.472
3700	19.813	114.830	97.095	65.619	-405.501	-182.959	10.807
3800	19.816	115.358	97.569	67.601	-405.978	-176.937	10.176
3900	19.819	115.873	98.031	69.582	-406.458	-170.905	9.577
4000	19.821	116.375	98.484	71.564	-406.942	-164.859	9.007
4100	19.824	116.864	98.926	73.546	-407.432	-158.803	8.465
4200	19.826	117.342	99.359	75.529	-407.924	-152.732	7.947
4300	19.828	117.808	99.782	77.512	-408.420	-146.647	7.453
4400	19.830	118.264	100.197	79.495	-408.921	-140.554	6.981
4500	19.832	118.710	100.604	81.478	-409.426	-134.450	6.530
4600	19.833	119.146	101.002	83.461	-409.934	-128.331	6.097
4700	19.835	119.572	101.393	85.444	-410.450	-122.209	5.683
4800	19.837	119.990	101.776	87.428	-410.968	-116.069	5.285
4900	19.838	120.399	102.152	89.412	-411.490	-109.917	4.903
5000	19.839	120.800	102.521	91.395	-412.018	-103.759	4.535
5100	19.841	121.193	102.883	93.379	-412.552	-97.589	4.182
5200	19.842	121.578	103.239	95.364	-413.090	-91.408	3.842
5300	19.843	121.956	103.588	97.348	-413.635	-85.214	3.514
5400	19.844	122.327	103.932	99.332	-414.185	-79.017	3.198
5500	19.845	122.691	104.270	101.317	-414.740	-72.804	2.893
5600	19.846	123.049	104.602	103.301	-415.303	-66.580	2.598
5700	19.847	123.400	104.929	105.286	-415.872	-60.350	2.314
5800	19.848	123.745	105.250	107.271	-416.447	-54.104	2.039
5900	19.848	124.084	105.566	109.255	-417.031	-47.856	1.773
6000	19.849	124.418	105.878	111.240	-417.620	-41.592	1.515

June 30, 1976

ALUMINUM DIFLUORIDE OXIDE UNINEGATIVE ION (AlF_2O^-) (IDEAL GAS) GFW = 80.9783

AlF_2O^-

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [68.06 ± 3] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -310.6 ± 25 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -313 ± 25 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[950](1)	[900](1)
[650](1)	[270](1)
[260](1)	[300](1)

Bond Distances: Al-F = [1.63] Å Al-O = [1.66] Å σ = [2]
Bond Angles: F-Al-F = [120°] F-Al-O = [120°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [3.4674 x 10^{-114}] g^3 cm^6

Heat of Formation

We adopt ΔHf°_{298} = -313±25 kcal/mol which corresponds to the electron affinity EA(AlF_2O) = 46±25 kcal/mol (2.0±1.1 eV) and the fluoride-ion affinity IA(AlFO) = 112 kcal/mol. ΔHf° is derived from Kp for reaction A (see below) observed by Farber et al. (1) with a mass spectrometer operating in both positive- and negative-ion modes. Farber et al. (1) used a molecular-flow-effusion technique to study vapor species in the systems KF(g)-AlF_3(g)-Al_2O_3(c), KF(g)-AlF_3(g)-Al(ℓ)-Al_2O_3(c), and KCl(g)-AlF_3(g)-Al_2O_3(c). They considered the results to be limiting values; we presume this is due to very low intensities of AlF_2O^-.

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

	Reaction	No. of Points	Range T/K	ΔHr°_{298} kcal/mol	ΔHf°_{298} kcal/mol
A)	AlFO(g) + AlF_2^-(g) = AlF_2O^-(g) + AlF(g)	1	1793	≥-21.1	≥-313.6[a] or ≥-327.8[a]
B)	AlF_2O(g) + F^-(g) = AlF_2O^-(g) + F(g)	1	1753	≥0.1	≥-344.8
C)	AlF_2O(g) + Cl^-(g) = AlF_2O(g) + Cl(g)	2	1653-1793	≥0.8	≥-349.1

[a] Assuming ΔHf°_{298} (AlF_2^-) = -217 or -231.2 kcal/mol depending on choice of ΔHf°(AlF_2) (2).

Heat Capacity and Entropy

All molecular parameters are estimated via data for BF_2O^+ (or BF_2O) as discussed on the table for AlF_2O(g) (2). We assume a C_{2v} structure with equal bond angles. Formation of the negative ion is assumed to decrease the Al-O bond distance by 0.06 Å but leave the Al-F distance unchanged. By analogy with AlF_3 (2) we assume a singlet electronic ground state and neglect excited states. Formation of the negative ion is assumed to cause a significant increase in ν_1, ν_5, and ν_6. The principal moments of inertia are 11.471 x 10^{-39}, 12.572 x 10^{-39} and 24.043 x 10^{-39} g cm^2.

References

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

TETRAFLUOROALUMINATE UNINEG. ION (AlF_4^-) AlF_4^-
(IDEAL GAS) GFW=102.9757

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0				-4.058	-473.264		
100							
200							
298	19.636	70.419	70.419	0.000	-476.000	-464.601	340.562
300	19.684	70.543	70.419	0.036	-476.012	-464.531	338.410
400	21.719	76.507	71.219	2.115	-476.569	-460.615	251.668
500	22.950	81.497	72.790	4.354	-477.072	-456.570	199.567
600	23.724	85.755	74.604	6.690	-477.556	-452.424	164.795
700	24.232	89.452	76.467	9.090	-478.039	-448.195	139.933
800	24.580	92.712	78.298	11.531	-478.544	-443.900	121.268
900	24.828	95.622	80.064	14.002	-479.084	-439.537	106.734
1000	25.010	98.248	81.753	16.495	-482.191	-434.930	95.054
1100	25.147	100.638	83.303	19.003	-482.723	-430.179	85.469
1200	25.252	102.831	84.895	21.523	-483.252	-425.377	77.472
1300	25.337	104.856	86.354	24.053	-483.783	-420.532	70.698
1400	25.403	106.736	87.744	26.590	-484.316	-415.646	64.885
1500	25.458	108.491	89.069	29.133	-484.851	-410.722	59.842
1600	25.502	110.135	90.335	31.681	-485.388	-405.764	55.425
1700	25.539	111.682	91.545	34.233	-485.928	-400.769	51.522
1800	25.571	113.143	92.705	36.789	-486.471	-395.747	48.050
1900	25.597	114.526	93.817	39.347	-487.017	-390.691	44.940
2000	25.620	115.840	94.886	41.908	-487.566	-385.606	42.137
2100	25.639	117.090	95.914	44.471	-488.118	-380.497	39.599
2200	25.657	118.284	96.904	47.036	-488.675	-375.360	37.289
2300	25.671	119.424	97.858	49.602	-489.234	-370.193	35.176
2400	25.684	120.517	98.780	52.170	-489.798	-365.006	33.238
2500	25.696	121.566	99.670	54.739	-490.367	-359.798	31.454
2600	25.706	122.574	100.532	57.309	-490.938	-354.561	29.804
2700	25.715	123.544	101.366	59.880	-491.513	-349.305	28.274
2800	25.724	124.480	102.175	62.452	-561.501	-343.199	26.788
2900	25.731	125.383	102.960	65.025	-561.822	-335.394	25.276
3000	25.738	126.255	103.722	67.598	-562.149	-327.586	23.865
3100	25.744	127.099	104.463	70.172	-562.476	-319.760	22.543
3200	25.749	127.916	105.183	72.747	-562.809	-311.924	21.303
3300	25.754	128.709	105.884	75.322	-563.146	-304.079	20.138
3400	25.759	129.478	106.567	77.898	-563.487	-296.225	19.041
3500	25.763	130.225	107.232	80.474	-563.833	-288.356	18.006
3600	25.767	130.950	107.881	83.050	-564.181	-280.476	17.027
3700	25.770	131.656	108.514	85.627	-564.535	-272.594	16.101
3800	25.774	132.344	109.132	88.205	-564.893	-264.697	15.224
3900	25.777	133.013	109.736	90.782	-565.257	-256.796	14.390
4000	25.779	133.666	110.326	93.360	-565.623	-248.880	13.598
4100	25.782	134.302	110.903	95.938	-565.996	-240.961	12.844
4200	25.784	134.924	111.467	98.516	-566.373	-233.026	12.126
4300	25.787	135.530	112.020	101.095	-566.753	-225.082	11.440
4400	25.789	136.123	112.561	103.674	-567.141	-217.131	10.785
4500	25.791	136.703	113.091	106.252	-567.533	-209.176	10.159
4600	25.792	137.270	113.611	108.832	-567.928	-201.206	9.559
4700	25.794	137.824	114.120	111.411	-568.333	-193.234	8.985
4800	25.796	138.368	114.619	113.990	-568.741	-185.245	8.434
4900	25.797	138.899	115.110	116.570	-569.155	-177.246	7.906
5000	25.799	139.421	115.591	119.150	-569.575	-169.248	7.398
5100	25.800	139.932	116.063	121.730	-570.002	-161.242	6.910
5200	25.801	140.433	116.527	124.310	-570.436	-153.217	6.440
5300	25.802	140.924	116.982	126.890	-570.877	-145.188	5.987
5400	25.804	141.406	117.430	129.470	-571.325	-137.159	5.551
5500	25.805	141.880	117.871	132.051	-571.780	-129.114	5.130
5600	25.806	142.345	118.303	134.631	-572.245	-121.056	4.724
5700	25.807	142.802	118.729	137.212	-572.716	-112.996	4.333
5800	25.808	143.250	119.148	139.793	-573.195	-104.925	3.954
5900	25.808	143.692	119.560	142.373	-573.685	-96.853	3.598
6000	25.809	144.125	119.966	144.954	-574.182	-88.766	3.233

June 30, 1976

TETRAFLUOROALUMINATE UNINEGATIVE ION (AlF_4^-) (IDEAL GAS) GFW = 102.9757

AlF_4^-

Point Group T_d
$S°_{298.15}$ = 70.42 ± 0.5 gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -473.3 ± 25 kcal/mol
$\Delta Hf°_{298.15}$ = -476 ± 25 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
622(1)	760(3)
210(2)	322(3)

Bond Distance: Al-F = 1.69 Å
Bond Angle: F-Al-F = 109.4712°
σ = 12
Product of the Moments of Inertia: $I_AI_BI_C = 1.3869 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

We adopt $\Delta Hf°_{298}$ = -476±25 kcal/mol which corresponds to the fluoride-ion affinity $IA(AlF_3)$ = 125±25 kcal/mol for $AlF_4^-(g) = AlF_3(g) + F^-(g)$. ΔHf° is a compromise based mainly on Kp data (7 points, 1130-1485 K) for the reaction $2\ AlF_2(g) + AlF_2^-(g) = 2\ AlF(g) + AlF_4^-(g)$. Kp data were measured by Srivastava et al. (1) with a mass spectrometer operating in both positive- and negative-ion modes. The authors used a molecular-flow-effusion technique to react vapors from AlF_3 and K_3AlF_6 or KF with Al(ℓ). Analysis with JANAF auxiliary data (2) yields $\Delta Hr°_{298}$(3rd law) = -38.2±2.7 and $\Delta Hr°_{298}$(2nd law) = -33.9±6.3 kcal/mol with [ΔSr°(2nd law)-ΔSr°(3rd law)] = -3.3±4.8 gibbs/mol. The third-law ΔHr° yields $\Delta Hf°_{298}(AlF_4^-)$ = -460.4±25 or -502.4±14 kcal/mol, depending on the choice of $\Delta Hf°_{298}(AlF_2)$ = -166±10 (2) or -180±5 kcal/mol (2, 3).

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

By combining published data for $NaAlF_4(g)$ with a coulomb-energy calculation, Holm (4) estimated $IA(AlF_3)$ = 131 kcal/mol. This result has an unknown bias due to limitations of the calculational model and auxiliary data. Refined lattice energy calculations (5) yield halide-ion affinities IA = 87±7 ($AlCl_3$) and 80±7 ($AlBr_3$) kcal/mol. $\Delta Hf°(BF_4^-)$ = -421 kcal/mol (6) derived from lattice energy yields $IA(BF_3)$ = 90 compared to ≤101 kcal/mol from mass spectrometry. Comparison of stretching force constants (2, 7, 8) with average bond energies in AlX_3 and AlX_4^- suggests a slight, but not definitive, preference for $IA(AlF_3)$ = 109 kcal/mol. As a compromise, we adopt $IA(AlF_3)$ = 125±25 and $\Delta Hf°_{298}(AlF_4^-)$ = -476±25 kcal/mol.

Heat Capacity and Entropy

Vibrational frequencies are from Raman spectra of AlF_4^- observed in molten salt mixtures of AlF_3 with NaF or KF (8). Similar spectra were observed in mixtures of AlF_3 with LiF (9). The spectra (8) are consistent with T_d symmetry except for some asymmetry in ν_3 which was attributed to influence of the metal ion. By analogy with SiF_4 (2), we assume a singlet electronic ground state and neglect excited states. The bond distance is that derived from high-temperature electron diffraction (10) of $NaAlF_4(g)$. Within experimental uncertainty, the AlF_4 grouping was found to be tetrahedral (2, 10). The principal moment of inertia is $24.026 \times 10^{-39}\ g\ cm^2$.

References

1. R. D. Srivastava, O. M. Uy and M. Farber, J. Chem. Soc., Faraday Trans. I, 70, 1033 (1974); Rept. AD-731303 (avail. NTIS), 50 pp. (1971).
2. JANAF Thermochemical Tables: $AlF_2(g)$, $AlF_2^-(g)$, $AlF_2O^-(g)$, $SiF_4(g)$ 6-30-76; AlF(g) 6-30-75; $NaAlF_4(g)$ 6-30-70.
3. O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
4. J. L. Holm, Acta Chem. Scand. 27, 1410 (1973).
5. R. C. Gearhart, J. D. Beck and R. H. Wood, Inorg. Chem. 14, 2413 (1975).
6. F. Kutek, Sb. Vys. Sk. Chem.-Technol. Praze, Anorg. Chem. Technol. B14, 77 (1972); Chem. Abstr. 79, 35721 (1973).
7. V. G. Solomonik and K. S. Krasnov, Zh. Priklad. Spektrosk. 21, 360 (1974).
8. B. Gilbert, G. Mamantov and G. M. Begun, Inorg. Nucl. Chem. Lett. 10, 1123 (1974); J. Chem. Phys. 62, 950 (1975).
9. E. Rytter and S. K. Ratkje, Acta Chem. Scand. A29, 565 (1975).
10. V. P. Spiridonov and E. V. Erokhin, Dokl. Akad. Nauk 180 (1), 161 (1968); Proc. Acad. Sci. USSR (English Transl.) 180, 335 (1968).

ALUMINUM MONOXIDE (ALO)

(IDEAL GAS) GFW=42.9809

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.100	16.431	16.431	INFINITE
100	6.957	44.459	58.513	-1.405	16.673	14.462	-31.606
200	7.052	49.297	52.832	-.707	16.581	12.258	-13.395
298	7.381	52.169	52.169	.000	16.400	10.169	-7.454
300	7.388	52.214	52.169	.014	16.396	10.130	-7.380
400	7.765	54.392	52.463	.772	16.200	8.072	-4.410
500	8.066	56.159	53.031	1.564	15.996	6.063	-2.650
600	8.290	57.651	53.680	2.382	15.777	4.097	-1.492
700	8.460	58.942	54.341	3.220	15.541	2.169	-.677
800	8.604	60.081	54.989	4.074	15.279	.276	-.075
900	8.743	61.102	55.613	4.941	14.977	-1.582	.384
1000	8.892	62.031	56.209	5.823	12.112	-3.220	.704
1100	9.057	62.886	56.777	6.720	11.831	-4.740	.942
1200	9.241	63.682	57.320	7.635	11.563	-6.235	1.136
1300	9.440	64.430	57.838	8.568	11.310	-7.708	1.296
1400	9.650	65.137	58.335	9.523	11.073	-9.161	1.430
1500	9.863	65.810	58.811	10.499	10.855	-10.600	1.544
1600	10.073	66.453	59.268	11.495	10.654	-12.023	1.642
1700	10.275	67.070	59.709	12.513	10.471	-13.435	1.727
1800	10.463	67.663	60.135	13.550	10.306	-14.835	1.801
1900	10.633	68.233	60.546	14.605	10.154	-16.228	1.867
2000	10.783	68.782	60.944	15.676	10.016	-17.614	1.925
2100	10.913	69.312	61.330	16.761	9.890	-18.993	1.977
2200	11.022	69.822	61.705	17.858	9.772	-20.366	2.023
2300	11.110	70.314	62.066	18.964	9.662	-21.731	2.065
2400	11.178	70.788	62.422	20.079	9.557	-23.093	2.103
2500	11.229	71.246	62.766	21.200	9.455	-24.454	2.138
2600	11.264	71.687	63.100	22.324	9.354	-25.807	2.169
2700	11.284	72.112	63.426	23.452	9.254	-27.159	2.198
2800	11.293	72.523	63.744	24.581	-60.258	-27.675	2.160
2900	11.291	72.919	64.053	25.710	-60.100	-26.515	1.998
3000	11.280	73.302	64.355	26.839	-59.944	-25.358	1.847
3100	11.263	73.671	64.650	27.966	-59.793	-24.207	1.707
3200	11.239	74.028	64.937	29.091	-59.646	-23.061	1.575
3300	11.212	74.374	65.218	30.214	-59.503	-21.920	1.452
3400	11.182	74.708	65.492	31.333	-59.367	-20.786	1.336
3500	11.149	75.032	65.760	32.450	-59.234	-19.654	1.227
3600	11.115	75.345	66.022	33.563	-59.108	-18.521	1.124
3700	11.081	75.650	66.278	34.673	-58.987	-17.397	1.028
3800	11.047	75.945	66.529	35.779	-58.872	-16.274	.936
3900	11.014	76.231	66.774	36.882	-58.761	-15.154	.849
4000	10.982	76.510	67.014	37.982	-58.657	-14.039	.767
4100	10.952	76.780	67.249	39.079	-58.558	-12.926	.689
4200	10.923	77.044	67.479	40.173	-58.463	-11.813	.615
4300	10.897	77.301	67.704	41.264	-58.374	-10.702	.544
4400	10.873	77.551	67.925	42.352	-58.289	-9.593	.477
4500	10.852	77.795	68.142	43.438	-58.209	-8.489	.412
4600	10.834	78.033	68.354	44.523	-58.132	-7.382	.351
4700	10.818	78.266	68.563	45.605	-58.062	-6.285	.292
4800	10.805	78.494	68.767	46.686	-57.994	-5.183	.236
4900	10.795	78.716	68.968	47.766	-57.930	-4.081	.182
5000	10.788	78.934	69.165	48.845	-57.870	-2.985	.130
5100	10.784	79.148	69.359	49.924	-57.814	-1.885	.081
5200	10.783	79.357	69.549	51.002	-57.762	-.793	.033
5300	10.784	79.563	69.736	52.081	-57.713	.305	-.013
5400	10.789	79.764	69.920	53.159	-57.667	1.399	-.057
5500	10.796	79.962	70.101	54.239	-57.625	2.490	-.099
5600	10.806	80.157	70.279	55.319	-57.587	3.584	-.140
5700	10.819	80.348	70.454	56.400	-57.551	4.674	-.179
5800	10.834	80.537	70.626	57.483	-57.519	5.769	-.217
5900	10.852	80.722	70.796	58.567	-57.491	6.860	-.254
6000	10.872	80.905	70.962	59.653	-57.466	7.951	-.290

Dec. 31, 1960; Sept. 30, 1961; March 31, 1962;
Sept. 30, 1965; June 30, 1970; June 30, 1975

ALUMINUM MONOXIDE (AlO) (IDEAL GAS) GFW = 42.9809

Symmetry Number = 1

$S^\circ_{298.15}$ = 52.169 ± 0.02 gibbs/mol

ΔHf°_0 = 16.43 ± 2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 16.4 ± 2 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}
(1)	$X^2\Sigma^+$	0.0	2	1.6178	0.64136	0.0058	979.23	6.97
(2, 3)	$A^2\Pi i$	5282.	4	1.769	0.5364	[0.004]	728.5	4.15
(1)	$B^2\Sigma^+$	20635.2	2	1.6670	0.60408	0.00447	870.05	3.52
(3-5, 1)	$C^2\Pi r$	33050.	4	1.668	0.603	0.004	856.5	6.1
(4, 6)	$^4\Sigma^+$	[30200]	4	[1.724]	[0.565]	[0.004]	[820]	[5.0]
(4, 6)	$^4\Delta$	[31600]	8	[1.724]	[0.565]	[0.004]	[820]	[5.0]
(4, 6)	$^4\Sigma^-$	[33000]	4	[1.724]	[0.565]	[0.004]	[820]	[5.0]
(4, 6)	$^2\Delta$	[34700]	4	[1.724]	[0.565]	[0.004]	[820]	[5.0]
(4, 6)	$^2\Sigma^-$	[34900]	2	[1.724]	[0.565]	[0.004]	[820]	[5.0]
(2)	$D^2\Sigma^+$	40187	2	1.7234	0.56522	0.0046	817.5	4.8
(3, 6)	$E^2\Delta i$	45260	4	1.840	0.4960	[0.004]	[650]	[4.0]
(2, 4-6)	$F^2\Sigma^+$	47190	2	1.812	0.5113	[0.004]	[650]	[4.0]

Heat of Formation

We adopt D°_0 = 120±2 kcal/mol and ΔHf°_{298} = 16.4±2 kcal/mol as a compromise between the larger value of D°_0 = 121.5±1 kcal/mol proposed by Dagdigian, Cruse and Zare (7) and the somewhat smaller mass-spectrometric values (8-11) summarized below. Dagdigian et al. (7) interpreted laser-induced fluorescence to derive the lower limits $D^\circ_0 \geq 120.8$ or 121.8 kcal/mol. According to Dagdigian et al. (7), Drowart derived an upper limit of $D^\circ_0 \leq 122.1 \pm 0.6$ kcal/mol by reinterpreting the absorption edges observed by Tyte (12). These had previously been attributed to predissociation in the E-state of the A+E system (3), leading to $D^\circ_0 \leq 119.9$ kcal/mol. We lack sufficient information to judge the reinterpretation leading to $D^\circ_0 \leq 122.1 \pm 0.6$ *kcal/mol* (7). Interpretation depends on the shape of the potential energy curve of $E^2\Delta_i$, which Drowart considers to be nearly horizontal (7). Theoretical predictions (4) for the E-state yield a double minimum which may not occur in actuality.

Other reported values of D°_0 were summarized by Dagdigian et al. (7). Several flame-photometric values may be dismissed for reasons cited by Frank and Krauss (13). Their recent data gave D°_0 values ranging from 115.4 to 118.2 kcal/mol, depending on the reaction considered (13).

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd law	3rd law	ΔHf°_{298} kcal/mol	D°_0
(8) Hildenbrand (1973)	Mass spec.	A	2210-2240	3	-7±30	-14±67	0.1±1	18.5±3	117.8
		B	1965-2117	10	0.4±1.6	5.7±3.2	4.9±0.4	17.8±3	118.6
(9) Farber (1972)	Mass Spec.	C	2270	1	---	---	26.5	11.8±6	124.6
	Mass Spec.	D	1943-2093	7	16±4	-89±8	-121.1±1.9	16.4±3	119.9
(10) Burns (1966)	Mass Spec.	D	2327	1	---	---	-117.1	20.5±4	115.9
(11) Drowart (1960)	Mass Spec.	D	2188-2514	15[c]	-3.2±2.2	-122±5	-114.6±1.9	22.9±7	113.5
	Mass Spec.	D	2036-2466	15	0.4±3.1	-115±7	-116.0±2.6	21.5±7	114.8

[a] Reactions: A) $Al(g)+O_2(g)=AlO(g)+O(g)$; B) $Al(g)+SO(g)=AlO(g)+S(g)$; C) $Al(g)+VO(g)=AlO(g)+V(g)$; D) $Al(g)+O(g)=AlO(g)$.
[b] $\delta S = \Delta Sr^\circ$(2nd law) − ΔSr°(3rd law). [c] Two points rejected.

Heat Capacity and Entropy

Electronic levels (T_{oo}) and vibrational-rotational constants of the observed states are from recent studies (2-5) which supplement or revise the values of Rosen (1). Schamps (4) made extensive predictions of the unobserved levels of AlO and MgO. We adopt these estimates since additional data for MgO (6) and the F state of AlO (2) confirm that they are reasonably accurate. Estimated molecular constants are derived from isoconfigurational levels whenever possible. We omit levels predicted to lie above 40000 cm^{-1} since they will have a negligible effect. The thermodynamic functions are calculated using first-order anharmonic corrections to Q^i_r and Q^i_v in the partition function $Q=Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2 \varepsilon_i/T)$.

References

1. B. Rosen, *"Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press*, New York, 1970, pp 18-20.
2. M. Singh et al., J. Phys. B 6, 521 (1973); 2, 119 (1969); Proc. Indian Acad. Sci., Sect. A 77, 139 (1973); 71, 82 (1970).
3. J. K. McDonald, K. K. Innes et al., J. Mol. Spectrosc. 32, 501 and 511 (1969).
4. J. Schamps, Chem. Phys. 2, 352 (1973); J. Chem. Phys. 56, 573 (1972).
5. J. M. Mahieu and M. Becart, Can. Spectrosc. 13, 95 (1968); J. M. Mahieu, Thesis, Lille, France (1971).
6. JANAF Thermochemical Tables: AlO(g) 6-30-75; MgO(g) 12-31-74.
7. P. J. Dagdigian, H. W. Cruse and R. N. Zare, J. Chem. Phys. 62, 1824 (1975); 57, 5331 (1972); Ber. Bunsenges. Phys. Chem. 78, 153 (1974).
8. D. L. Hildenbrand, Chem. Phys. Lett. 20, 127 (1973).
9. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., *Faraday Trans.* I 68, 249 (1972); *J. Chem. Phys.* 56, 5312 (1972).
10. R. P. Burns, J. Chem. Phys. 44, 3307 (1966).
11. J. Drowart, G. DeMaria, R. P. Burns and M. G. Inghram, J. Chem. Phys. 32, 1366 (1960).
12. D. C. Tyte, Proc. Phys. Soc. (London) 92, 1137 (1967).
13. P. Frank and L. Krauss, Z. Naturforsch. A29, 742 (1974).

ALUMINUM MONOXIDE UNIPOSITIVE ION (AlO^+) AlO^+

(IDEAL GAS) GFW=42.9804

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	7.919	55.177	55.177	.000	237.700	229.085	- 167.924
300	7.927	55.226	55.177	.015	237.706	229.031	- 166.849
400	8.290	57.560	55.493	.827	238.061	226.087	- 123.528
500	8.549	59.439	56.100	1.669	238.404	223.053	- 97.496
600	8.743	61.015	56.792	2.534	238.729	219.952	- 80.117
700	8.892	62.375	57.494	3.416	239.033	216.798	- 67.687
800	9.007	63.570	58.181	4.312	239.310	213.602	- 58.353
900	9.095	64.636	58.840	5.217	239.543	210.375	- 51.086
1000	9.161	65.598	59.468	6.130	237.206	207.307	- 45.307
1100	9.211	66.474	60.066	7.049	237.444	204.305	- 40.592
1200	9.248	67.277	60.634	7.972	237.680	201.281	- 36.658
1300	9.276	68.018	61.174	8.898	237.916	198.238	- 33.327
1400	9.297	68.706	61.687	9.827	238.151	195.178	- 30.469
1500	9.313	69.348	62.177	10.757	238.384	192.100	- 27.989
1600	9.325	69.950	62.644	11.689	238.615	189.006	- 25.817
1700	9.335	70.516	63.091	12.622	238.845	185.899	- 23.899
1800	9.343	71.049	63.518	13.556	239.073	182.779	- 22.192
1900	9.350	71.555	63.928	14.491	239.298	179.645	- 20.664
2000	9.356	72.034	64.321	15.426	239.521	176.499	- 19.287
2100	9.363	72.491	64.700	16.362	239.742	173.341	- 18.040
2200	9.369	72.927	65.064	17.299	239.961	170.174	- 16.905
2300	9.376	73.343	65.415	18.236	240.179	166.999	- 15.869
2400	9.384	73.743	65.753	19.174	240.394	163.814	- 14.917
2500	9.392	74.126	66.081	20.113	240.607	160.616	- 14.041
2600	9.400	74.494	66.397	21.052	240.817	157.412	- 13.232
2700	9.409	74.849	66.704	21.993	241.027	154.199	- 12.482
2800	9.419	75.192	67.001	22.934	171.825	151.811	- 11.849
2900	9.429	75.522	67.289	23.876	172.293	151.087	- 11.386
3000	9.440	75.842	67.569	24.820	172.760	150.350	- 10.953
3100	9.452	76.152	67.841	25.764	173.225	149.595	- 10.546
3200	9.463	76.452	68.105	26.710	173.690	148.825	- 10.164
3300	9.476	76.744	68.363	27.657	174.154	148.041	- 9.804
3400	9.488	77.027	68.613	28.605	174.615	147.241	- 9.465
3500	9.501	77.302	68.858	29.555	175.078	146.428	- 9.143
3600	9.514	77.570	69.096	30.506	175.538	145.606	- 8.840
3700	9.527	77.831	69.328	31.458	175.998	144.767	- 8.551
3800	9.541	78.085	69.556	32.411	176.457	143.917	- 8.277
3900	9.554	78.333	69.777	33.366	176.916	143.056	- 8.017
4000	9.568	78.575	69.994	34.322	177.372	142.179	- 7.768
4100	9.582	78.811	70.207	35.279	177.829	141.292	- 7.532
4200	9.596	79.042	70.414	36.238	178.287	140.398	- 7.306
4300	9.609	79.268	70.617	37.199	178.742	139.491	- 7.090
4400	9.623	79.489	70.817	38.160	179.197	138.575	- 6.883
4500	9.637	79.706	71.012	39.123	179.650	137.645	- 6.685
4600	9.650	79.918	71.203	40.088	180.104	136.709	- 6.495
4700	9.664	80.125	71.391	41.053	180.554	135.756	- 6.313
4800	9.677	80.329	71.575	42.020	181.005	134.799	- 6.138
4900	9.691	80.529	71.755	42.989	181.455	133.835	- 5.969
5000	9.704	80.725	71.933	43.959	181.901	132.855	- 5.807
5100	9.717	80.917	72.107	44.930	182.347	131.872	- 5.651
5200	9.730	81.106	72.278	45.902	182.790	130.875	- 5.501
5300	9.743	81.291	72.447	46.876	183.231	129.874	- 5.355
5400	9.756	81.473	72.612	47.851	183.671	128.864	- 5.215
5500	9.768	81.653	72.775	48.827	184.105	127.842	- 5.080
5600	9.781	81.829	72.935	49.804	184.538	126.817	- 4.949
5700	9.793	82.002	73.093	50.783	184.968	125.780	- 4.823
5800	9.805	82.172	73.248	51.763	185.394	124.741	- 4.700
5900	9.817	82.340	73.400	52.744	185.816	123.692	- 4.582
6000	9.829	82.505	73.551	53.726	186.233	122.636	- 4.467

June 30, 1968; June 30, 1970; June 30, 1975

ALUMINUM MONOXIDE UNIPOSITIVE ION (AlO^+) (IDEAL GAS) GFW = 42.9804 AlO^+

Symmetry Number = 1

$S^\circ_{298.15}$ = [55.2±3] gibbs/mol

ΔHf°_0 = 236.2±5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 237.7±5 kcal/mol

Electronic Levels 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}
$^3\Pi$	[0]	6	[1.82]	[0.5066]	[0.004]	[710]	[4]
$^1\Pi$	[2000]	2	[1.82]	[0.5066]	[0.004]	[710]	[4]
$^1\Sigma$	[300]	1	[1.70]	[0.5806]	[0.005]	[820]	[5]
$^3\Sigma$	[12000]	3	[1.70]	[0.5806]	[0.005]	[870]	[5]
$^1\Sigma$	[20000]	1	[1.70]	[0.5806]	[0.005]	[870]	[5]

Heat of Formation

ΔHf°_0 is calculated from that of AlO (1) using Hildenbrand's appearance potential (2) of 9.53±0.15 eV (219.8±3.5 kcal/mol), assuming that it is identical with the ionization potential for $AlO(g) \rightarrow AlO^+(g) + e^-(g)$. Other reported values for the appearance potential include 9.5±0.5 (3), 9.5±1 and 10±1 eV (4). These values are consistent with, but less precise than, the adopted value.

Heat Capacity and Entropy

No spectroscopic data have been observed for AlO^+ but Schamps (5) recently predicted electronic levels and molecular constants from variational calculations with semiempirical estimates of correlation energy differences. Similar calculations were reasonably accurate for MgO (5). The predictions for AlO^+ yield almost equal energies for $^3\Pi$ and $^1\Sigma^+$; thus they do not distinquish which is the ground state. AlO^+ is isoelectronic with MgO and AlN. MgO has a $^1\Sigma^+$ ground state with the low-lying $^3\Pi$ level at 2600 cm^{-1} (6, 1). Triplet-triplet bands are observed for AlN (7, 8) and it is quite likely that the lower $^3\Pi$ level is the ground state (8). We conclude for AlO^+ that $^3\Pi$ is very low lying and probably the ground state; it will dominate the electronic partition function.

The adopted electronic levels are minor modifications of the predictions of Schamps (5). Molecular constants of the $^3\Pi$ state are estimated to be intermediate between those of MgO (1) and AlN (7). The r_e adopted for $^3\Pi$ is 0.1 Å longer than that of Al_2O (1). Values of r_e adopted for AlO^+ are also longer than those of their Π and Σ counterparts in AlO (1). Values of ω_e are based on force-constant comparisons. Other constants are based on comparisons with the observed and calculated values for MgO (1, 5).

The low-lying electronic levels cause an entropy uncertainty of perhaps 3 gibbs/mol at 298 K but <1 gibbs/mol at T >2000 K Uncertainty in the enthalpy is large (perhaps 4 kcal/mol) at high temperature. The enthalpy at absolute zero is -2.172 kcal/mol. The thermodynamic functions are calculated using first-order anharmonic corrections to Q^i_r and Q^i_v in the partition function $Q=Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2 \varepsilon_i/T)$.

References

1. JANAF Thermochemical Tables: AlO(g), Al_2O(g) 6-30-75; MgO(g) 12-31-74.
2. D. L. Hildenbrand, Chem. Phys. Lett. 20, 127 (1973).
3. R. P. Burns et al., J. Chem. Phys. 44, 3307 (1966); 32, 1366 (1960).
4. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., Faraday Trans. I 68, 249 (1972); J. Chem. Phys. 56, 5312 (1972).
5. J. Schamps, Chem. Phys. 2, 352 (1973); J. Chem. Phys. 56, 573 (1972).
6. G. A. Capelle, H. P. Broida and R. W. Field, J. Chem. Phys. 62, 3131 (1975).
7. J. D. Simmons and J. K. McDonald, J. Mol. Spectrosc. 41, 584 (1972).
8. T. M. Dunn, personal comm., Univ. Michigan, Ann Arbor, Aug., 1975.

ALUMINUM MONOXIDE UNINEGATIVE ION (ALO⁻)   ALO⁻

(IDEAL GAS) GFW=42.9814

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	7.481	50.835	50.835	.000	-64.000	-68.346	50.099
300	7.489	50.882	50.835	.014	-64.013	-68.373	49.809
400	7.878	53.091	51.134	.783	-64.695	-69.723	38.095
500	8.169	54.882	51.710	1.586	-65.385	-70.900	30.991
600	8.375	56.391	52.368	2.414	-66.091	-71.938	26.203
700	8.521	57.694	53.038	3.259	-66.816	-72.854	22.746
800	8.628	58.839	53.693	4.117	-67.571	-73.667	20.125
900	8.709	59.860	54.322	4.984	-68.370	-74.361	18.062
1000	8.771	60.781	54.923	5.858	-71.739	-74.821	16.352
1100	8.821	61.619	55.494	6.738	-72.535	-75.091	14.919
1200	8.862	62.369	56.037	7.622	-73.330	-75.288	13.712
1300	8.896	63.099	56.553	8.510	-74.126	-75.419	12.679
1400	8.924	63.760	57.045	9.401	-74.923	-75.468	11.784
1500	8.950	64.376	57.513	10.295	-75.720	-75.502	11.001
1600	8.972	64.954	57.960	11.191	-76.518	-75.460	10.307
1700	8.992	65.499	58.388	12.089	-77.317	-75.370	9.689
1800	9.010	66.014	58.797	12.989	-78.116	-75.231	9.134
1900	9.027	66.501	59.190	13.891	-78.918	-75.050	8.633
2000	9.043	66.965	59.567	14.794	-79.720	-74.827	8.177
2100	9.057	67.406	59.930	15.699	-80.523	-74.562	7.760
2200	9.071	67.828	60.280	16.606	-81.328	-74.260	7.377
2300	9.084	68.231	60.617	17.514	-82.133	-73.919	7.024
2400	9.097	68.618	60.942	18.423	-82.941	-73.544	6.697
2500	9.109	68.990	61.257	19.333	-83.751	-73.139	6.394
2600	9.121	69.347	61.561	20.244	-84.561	-72.696	6.111
2700	9.133	69.692	61.856	21.157	-85.373	-72.226	5.846
2800	9.145	70.024	62.142	22.071	-155.596	-70.894	5.533
2900	9.157	70.345	62.419	22.986	-156.149	-67.859	5.114
3000	9.169	70.656	62.688	23.902	-156.704	-64.804	4.721
3100	9.181	70.957	62.950	24.820	-157.258	-61.731	4.352
3200	9.194	71.248	63.205	25.739	-157.814	-58.640	4.005
3300	9.207	71.531	63.453	26.659	-158.371	-55.533	3.678
3400	9.221	71.807	63.695	27.580	-158.930	-52.411	3.369
3500	9.236	72.074	63.930	28.503	-159.488	-49.271	3.077
3600	9.252	72.334	64.160	29.427	-160.047	-46.110	2.799
3700	9.269	72.588	64.385	30.353	-160.607	-42.939	2.536
3800	9.288	72.836	64.604	31.281	-161.167	-39.751	2.286
3900	9.308	73.077	64.818	32.211	-161.726	-36.547	2.048
4000	9.329	73.313	65.027	33.143	-162.287	-33.332	1.821
4100	9.353	73.544	65.232	34.077	-162.847	-30.103	1.605
4200	9.378	73.769	65.433	35.013	-163.406	-26.858	1.396
4300	9.405	73.990	65.629	35.953	-163.966	-23.599	1.199
4400	9.434	74.207	65.822	36.894	-164.525	-20.327	1.010
4500	9.465	74.419	66.010	37.839	-165.082	-17.043	.828
4600	9.498	74.628	66.196	38.788	-165.638	-13.745	.653
4700	9.534	74.832	66.377	39.739	-166.196	-10.443	.486
4800	9.572	75.033	66.555	40.694	-166.751	-7.123	.324
4900	9.612	75.231	66.730	41.653	-167.305	-3.769	.169
5000	9.654	75.426	66.902	42.617	-167.857	-.447	.020
5100	9.699	75.617	67.071	43.584	-168.409	2.909	-.125
5200	9.746	75.806	67.238	44.557	-168.959	6.270	-.264
5300	9.795	75.992	67.401	45.534	-169.509	9.646	-.398
5400	9.846	76.176	67.562	46.516	-170.056	13.032	-.527
5500	9.900	76.357	67.720	47.503	-170.603	16.426	-.653
5600	9.955	76.536	67.876	48.496	-171.149	19.832	-.774
5700	10.012	76.713	68.029	49.494	-171.693	23.245	-.891
5800	10.072	76.887	68.181	50.498	-172.237	26.673	-1.005
5900	10.133	77.060	68.330	51.508	-172.780	30.107	-1.115
6000	10.196	77.231	68.477	52.525	-173.321	33.552	-1.222

Dec. 31, 1975

ALUMINUM MONOXIDE UNINEGATIVE ION (AlO⁻)   (IDEAL GAS)   GFW = 42.9814

ALO⁻

Ground State Configuration $[^1\Sigma^+]$

$S^\circ_{298.15}$ = [50.84 ± 0.4] gibbs/mol

ΔHf°_0 = -62.5 ± 4 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -64.0 ± 4 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma^+]$	0	[1]
$[^3\Pi]$	[27000]	[6]

ω_e = [900] cm^{-1}

B_e = [0.640] cm^{-1}

$\omega_e x_e$ = [5.4] cm^{-1}

α_e = [0.006] cm^{-1}

σ = 1

r_e = [1.62]Å

Heat of Formation

We adopt ΔHf°_{298} = -64.0±4 kcal/mol based on equilibrium data for $AlO(g) + Cl^-(g) = Cl(g) + AlO^-(g)$ obtained using effusion-mass spectrometry by Srivastava et al. (1, 2). Our analysis of the data is summarized below. For the process $AlO^-(g) \rightarrow Al(g) + O^-(g)$ we calculate a dissociation energy D°_0 = 165.2±4 kcal/mol; this is comparable to D°_0(AlF) = 159.3±1.5 kcal/mol (3) and much larger than D°_0(AlO) = 120±2 kcal/mol (3). The corresponding electron affinity, EA(AlO) = 78.9±4 kcal/mol (3.42 eV), is 4.4 kcal/mol less than EA(Cl) = 83.3 kcal/mol (3). Gaines and Page (4) used a semi-empirical method to predict EA(AlO) = 60 and EA(BO) = 49 kcal/mol, corresponding to a difference of 11 kcal/mol. Although this difference is comparable with the experimental difference of 9 kcal/mol, the values predicted for EA(AlO) and EA(BO) are ~20 kcal/mol lower than the experimental results (1, 2).

Source	Range T/K	No. of Points	δS^a gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	ΔHr°_{298}/(kcal/mol) 3rd Law	ΔHf°_{298} kcal/mol
(1, 2) Srivastava (1972)	2080-2222	5	-5.8±3.8	-8.1±8.3	4.48±1.1	-64.0±4

$^a\delta S = \Delta Sr^\circ$(2nd Law) − ΔSr°(3rd Law).

Heat Capacity and Entropy

All of the molecular constants are estimated by comparison with AlF and AlO (3). We estimate the electronic states and levels from the low-lying states of isoelectronic AlF. The bond distance is taken equal to that in AlO and slightly shorter than that in AlF. B_e is calculated from r_e. We derive ω_e = 900±100 cm^{-1} from k = 4.8 mdyn/Å estimated from k(AlF) = 4.23 and k(AlO) = 5.68. Similar comparisons of $\omega_e x_e/\omega_e$ and α_e/B_e are used to estimate $\omega_e x_e$ and α_e.

The enthalpy at absolute zero is -2.109 kcal/mol.

References

1. R. D. Srivastava, O. M. Uy and M. Farber, J. Chem. Soc., Faraday Trans. II 68, 1388 (1972); Trans. Faraday Soc. 67, 2941 (1971).
2. M. Farber, R. D. Srivastava and O. M. Uy (Space Sci. Inc., Monrovia, Calif.), Rept. AD-731303 (Avail. NTIS), 50 pp. (1971).
3. JANAF Thermochemical Tables: AlF(g) 12-31-75; AlO(g) 6-30-75; Cl⁻(g) 6-30-65.
4. A. F. Gaines and F. M. Page, Trans. Faraday Soc. 62, 3086 (1966).

ALUMINUM DIOXIDE (AlO_2) AlO_2

(IDEAL GAS) GFW=58.9803

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.712	- 44.443	- 44.443	INFINITE
100	7.982	47.987	67.919	- 1.993	- 44.524	- 45.018	98.388
200	10.187	54.242	59.632	- 1.078	- 44.747	- 45.437	49.652
298	11.684	58.608	58.608	.000	- 44.900	- 45.745	33.532
300	11.707	58.680	58.608	.022	- 44.902	- 45.751	33.329
400	12.701	62.195	59.080	1.246	- 44.988	- 46.019	25.143
500	13.332	65.102	60.002	2.550	- 45.046	- 46.269	20.224
600	13.740	67.571	61.063	3.905	- 45.105	- 46.509	16.941
700	14.014	69.711	62.149	5.293	- 45.180	- 46.737	14.592
800	14.204	71.596	63.215	6.705	- 45.283	- 46.953	12.827
900	14.340	73.277	64.241	8.132	- 45.432	- 47.153	11.450
1000	14.441	74.793	65.222	9.572	- 48.152	- 47.151	10.305
1100	14.517	76.173	66.155	11.020	- 48.302	- 47.044	9.347
1200	14.576	77.439	67.044	12.474	- 48.455	- 46.923	8.546
1300	14.623	78.608	67.889	13.934	- 48.610	- 46.789	7.866
1400	14.661	79.693	68.694	15.399	- 48.768	- 46.643	7.281
1500	14.691	80.705	69.461	16.866	- 48.931	- 46.486	6.773
1600	14.717	81.654	70.194	18.337	- 49.096	- 46.317	6.327
1700	14.738	82.547	70.894	19.810	- 49.264	- 46.138	5.931
1800	14.757	83.390	71.565	21.284	- 49.437	- 45.948	5.579
1900	14.773	84.188	72.209	22.761	- 49.614	- 45.750	5.262
2000	14.788	84.947	72.827	24.239	- 49.795	- 45.544	4.977
2100	14.801	85.668	73.422	25.716	- 49.980	- 45.327	4.717
2200	14.814	86.357	73.994	27.199	- 50.170	- 45.101	4.480
2300	14.827	87.016	74.546	28.681	- 50.362	- 44.865	4.263
2400	14.840	87.647	75.079	30.164	- 50.560	- 44.620	4.063
2500	14.854	88.253	75.594	31.649	- 50.762	- 44.373	3.879
2600	14.868	88.836	76.092	33.135	- 50.967	- 44.111	3.706
2700	14.882	89.398	76.574	34.623	- 51.176	- 43.845	3.549
2800	14.898	89.939	77.042	36.112	- 120.799	- 42.736	3.336
2900	14.915	90.462	77.496	37.602	- 120.754	- 39.951	3.011
3000	14.933	90.968	77.937	39.095	- 120.711	- 37.165	2.707
3100	14.952	91.458	78.365	40.589	- 120.671	- 34.380	2.424
3200	14.972	91.933	78.781	42.085	- 120.634	- 31.597	2.158
3300	14.994	92.394	79.187	43.583	- 120.599	- 28.816	1.906
3400	15.016	92.842	79.582	45.084	- 120.567	- 26.037	1.674
3500	15.040	93.278	79.967	46.587	- 120.535	- 23.259	1.452
3600	15.064	93.702	80.343	48.092	- 120.506	- 20.475	1.243
3700	15.090	94.115	80.709	49.600	- 120.478	- 17.699	1.045
3800	15.116	94.518	81.068	51.110	- 120.452	- 14.921	.858
3900	15.143	94.911	81.418	52.623	- 120.425	- 12.144	.681
4000	15.171	95.294	81.760	54.139	- 120.401	- 9.371	.512
4100	15.200	95.669	82.094	55.657	- 120.378	- 6.596	.352
4200	15.229	96.036	82.422	57.179	- 120.353	- 3.820	.199
4300	15.258	96.395	82.743	58.703	- 120.331	- 1.043	.053
4400	15.287	96.746	83.057	60.230	- 120.309	1.731	- .086
4500	15.317	97.090	83.365	61.760	- 120.288	4.504	- .219
4600	15.347	97.427	83.667	63.294	- 120.265	7.281	- .346
4700	15.377	97.757	83.963	64.830	- 120.246	10.048	- .467
4800	15.406	98.081	84.254	66.369	- 120.226	12.820	- .584
4900	15.436	98.399	84.540	67.911	- 120.206	15.593	- .695
5000	15.465	98.711	84.820	69.456	- 120.188	18.362	- .803
5100	15.494	99.018	85.095	71.004	- 120.171	21.137	- .906
5200	15.523	99.319	85.366	72.555	- 120.155	23.902	- 1.005
5300	15.551	99.615	85.632	74.109	- 120.140	26.676	- 1.100
5400	15.578	99.906	85.894	75.665	- 120.127	29.444	- 1.192
5500	15.605	100.192	86.151	77.224	- 120.116	32.214	- 1.280
5600	15.632	100.473	86.404	78.786	- 120.108	34.983	- 1.365
5700	15.657	100.750	86.653	80.350	- 120.101	37.749	- 1.447
5800	15.682	101.023	86.899	81.917	- 120.098	40.524	- 1.527
5900	15.707	101.291	87.141	83.487	- 120.097	43.292	- 1.604
6000	15.730	101.555	87.379	85.059	- 120.100	46.063	- 1.678

June 30, 1968; Dec. 31, 1968; Dec. 31, 1975

ALUMINUM DIOXIDE (AlO_2) (IDEAL GAS) GFW = 58.9803

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [58.6 ± 2] gibbs/mol

ΔHf°_0 = -44.4 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -44.9 ± 5 kcal/mol

AlO_2

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[15000]	[4]
[20000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[680](1)
[300](2)
[890](1)

Bond Distance: Al-O = [1.62] Å

Bond Angle: O-Al-O = [180°]

Rotational Constant: B_0=[0.20074] cm^{-1}

σ = 2

Heat of Formation

We adopt ΔHf°_{298} = -44.9±5 kcal/mol and ΔHa°_0 = 240±5 kcal/mol based on equilibrium data for Al(g) + AlO_2(g) = 2AlO(g) obtained using effusion-mass spectrometry by Farber et al. (1, 2). Analyses of the data are summarized below. Comparison of ΔHa°_0 = 240±5 kcal/mol with D°_0(AlO) = 120±2 (3) and $\Delta Ha^\circ_0(Al_2O)$ = 245±5 (3) suggests that the Al-O bond strengths are almost equal in AlO, AlO_2 and Al_2O. BO, BO_2 and B_2O_3 are very different in this respect.

The adopted ΔHf° is confirmed by a mass-spectrometric analysis of compositions in Al-containing flames. Farber et al. (4) reported ΔGr° = 7.4 kcal/mol for AlO(g) + H_2O(g) = AlO_2(g) + H_2(g) at 2250±100 K. Combining this with JANAF auxiliary data (3), we derive ΔHr°_{298} = -1.1 kcal/mol and ΔHf°_{298} = -42.5±5 kcal/mol for AlO_2(g). The uncertainty is that assigned by the authors (4).

Source	Range T/K	No. of Points	δS[a] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	3rd Law	ΔHf°_{298} kcal/mol
(1) Farber (1972)	1943-2093	7	-1.0±0.7	-2.5±1.4	-0.35±0.2	-44.85±5
(2) Farber (1971)	1663-1983	7	7.7±6.4	14 ±12	-0.25±3.6	-44.95±6
(1, 2) Combined	1663-2093	14	2.9±2.7	5.4±5.1	-0.30±2.5	-44.90±5

[a] δS = ΔSr°(2nd law) - ΔSr°(3rd law).

Heat Capacity and Entropy

Electronic ground and excited states are estimated by analogy with BO_2. We assume that the excited states have slightly lower values of T₀ than in BO_2 (5). We adopt the linear, symmetric structure and estimate the bond distance from that of the ground state of AlO (3). Vibrational frequencies are rounded values derived from the force constants f_r = 3.9, f_{rr} = 0.5 *and* f_α *= 0.2 mdyn/Å. Uncertainties in these estimated force constants suggest uncertainties in the frequencies of* 680±100, 300±90 and 890±150 cm^{-1}. The corresponding uncertainty is ±2 gibbs/mol in the entropy and Gibbs-energy function.

The adopted force constants are derived from FAlO and from OBO, BO and AlO. Values of (f_r+f_{rr}) = 4.46 and 4.39 mdyn/Å are estimated from FAlO (6) and from BO_2 (7, 8, 5) adjusted via the ratio k(AlO)/k(BO). We adopt (f_r+f_{rr}) = 4.4 mdyn/Å for AlO_2 and vary f_{rr} over a wide range to see the effect on ν_3. Values of f_α/f_r = 0.07 and 0.03 are obtained from FAlO (6) and BO_2 (7). We adopt an intermediate value of 0.05 for AlO_2.

The assumed linear structure is consistent with the predictions of Walsh (9) for AB_2 molecules having 15 valence electrons and with known data (10) for such molecules. Lynch (11) postulated a highly bent $Al^+ - O_2^-$ species from observation of a weak IR band at 1116 cm^{-1} in an Ar-O_2 matrix and 1096 cm^{-1} in N_2-O_2. In these experiments Al was codeposited with Al_2O using a matrix gas containing ~21% O_2. The weak IR band disappeared immediately during annealing of the matrix. The species $Al^+ - O_2^-$ was presumed to be different (11) from AlO_2 observed mass spectrometrically. A relatively strong band observed at 686 cm^{-1} first increased in intensity and then remained fairly constant during annealings. This band was assigned to the cyclic dimer of AlO, but it is also near our expected value for ν_1 of AlO_2. This mode should not be active in the infrared if AlO_2 is linear. The moment of inertia is 13.944 x 10^{-39} g cm^2.

References

1. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., Faraday Trans. I 68, 249 (1972).
2. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Phys. 55, 4142 (1971).
3. JANAF Thermochemical Tables: AlO(g), Al_2O(g) 6-30-75.
4. M. Farber, R. D. Srivastava, M. A. Frisch and S. P. Harris, Faraday Symposia of The Chemical Soc., No. 8, 121 (1973).
5. J. W. C. Johns, Can. J. Phys. 39, 1738 (1961).
6. A. Snelson, High Temp. Sci. 5, 77 (1973).
7. D. K. Russell, M. Kroll, D. A. Dows and R. A. Beaudet, Chem. Phys. Lett. 20, 153 (1973).
8. B. S. Snowden, Ph. D. Thesis, Vanderbilt Univ., 1963; Diss. Abstr. 24, 5030 (1964).
9. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
10. G. Herzberg, "Electronic Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York, 1966.
11. D. A. Lynch (Case Western Reserve Univ., Cleveland, Ohio), Rept. NASA-CR-133100 (N73-26102 Avail. NTIS), 138 pp. (1972).

ALUMINUM DIOXIDE UNINEGATIVE ION (AlO_2^-) AlO_2^-

(IDEAL GAS) GFW=58.9809

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	11.099	54.848	54.848	.000	- 140.900	- 139.137	101.990
300	11.125	54.917	54.848	.021	- 140.912	- 139.126	101.353
400	12.246	58.282	55.300	1.193	- 141.547	- 138.433	75.636
500	12.978	61.099	56.186	2.457	- 142.142	- 137.585	60.138
600	13.463	63.511	57.210	3.780	- 142.730	- 136.619	49.764
700	13.793	65.613	58.264	5.144	- 143.325	- 135.553	42.321
800	14.025	67.471	59.301	6.536	- 143.945	- 134.402	36.717
900	14.194	69.133	60.303	7.947	- 144.607	- 133.169	32.338
1000	14.319	70.635	61.262	9.373	- 147.838	- 131.677	28.778
1100	14.414	72.005	62.177	10.810	- 148.496	- 130.031	25.835
1200	14.489	73.262	63.049	12.255	- 149.154	- 128.323	23.371
1300	14.547	74.424	63.880	13.707	- 149.814	- 126.560	21.277
1400	14.595	75.504	64.672	15.164	- 150.477	- 124.746	19.474
1500	14.633	76.512	65.428	16.626	- 151.142	- 122.886	17.904
1600	14.665	77.458	66.151	18.091	- 151.809	- 120.979	16.525
1700	14.692	78.348	66.843	19.559	- 152.479	- 119.032	15.303
1800	14.714	79.188	67.505	21.029	- 153.153	- 117.044	14.211
1900	14.733	79.984	68.141	22.501	- 153.832	- 115.020	13.230
2000	14.749	80.740	68.753	23.976	- 154.513	- 112.962	12.344
2100	14.763	81.460	69.341	25.451	- 155.198	- 110.867	11.538
2200	14.776	82.147	69.907	26.928	- 155.889	- 108.740	10.802
2300	14.786	82.804	70.454	28.406	- 156.582	- 106.560	10.127
2400	14.796	83.434	70.982	29.885	- 157.281	- 104.390	9.506
2500	14.804	84.038	71.492	31.365	- 157.985	- 102.176	8.932
2600	14.812	84.619	71.986	32.846	- 158.691	- 99.927	8.400
2700	14.818	85.178	72.464	34.328	- 159.403	- 97.654	7.905
2800	14.824	85.717	72.928	35.810	- 229.530	- 94.524	7.378
2900	14.830	86.237	73.378	37.293	- 229.989	- 89.694	6.760
3000	14.834	86.740	73.815	38.776	- 230.453	- 84.647	6.181
3100	14.839	87.227	74.240	40.259	- 230.920	- 79.965	5.639
3200	14.843	87.698	74.653	41.743	- 231.392	- 75.109	5.130
3300	14.846	88.155	75.055	43.228	- 231.867	- 70.219	4.650
3400	14.850	88.598	75.447	44.713	- 232.348	- 65.315	4.196
3500	14.853	89.028	75.829	46.198	- 232.831	- 60.397	3.771
3600	14.855	89.447	76.201	47.683	- 233.318	- 55.459	3.367
3700	14.858	89.854	76.565	49.169	- 233.809	- 50.513	2.984
3800	14.860	90.250	76.920	50.655	- 234.304	- 45.552	2.620
3900	14.863	90.636	77.267	52.141	- 234.801	- 40.578	2.274
4000	14.865	91.013	77.606	53.627	- 235.303	- 35.594	1.945
4100	14.866	91.380	77.937	55.114	- 235.808	- 30.596	1.631
4200	14.868	91.738	78.261	56.601	- 236.315	- 25.584	1.331
4300	14.870	92.088	78.579	58.088	- 236.827	- 20.558	1.045
4400	14.871	92.430	78.890	59.575	- 237.342	- 15.523	.771
4500	14.873	92.764	79.194	61.062	- 237.860	- 10.475	.509
4600	14.874	93.091	79.493	62.549	- 238.381	- 5.413	.257
4700	14.875	93.411	79.786	64.037	- 238.907	- .349	.016
4800	14.877	93.724	80.073	65.524	- 239.436	4.733	- .216
4900	14.878	94.031	80.355	67.012	- 239.967	9.826	- .438
5000	14.879	94.331	80.631	68.500	- 240.502	14.928	- .652
5100	14.880	94.626	80.903	69.988	- 241.042	20.046	- .859
5200	14.881	94.915	81.169	71.476	- 241.586	25.165	- 1.058
5300	14.881	95.198	81.431	72.964	- 242.134	30.304	- 1.250
5400	14.882	95.476	81.689	74.452	- 242.686	35.447	- 1.435
5500	14.883	95.749	81.942	75.940	- 243.242	40.603	- 1.613
5600	14.884	96.018	82.191	77.429	- 243.804	45.769	- 1.786
5700	14.884	96.281	82.436	78.917	- 244.370	50.942	- 1.953
5800	14.885	96.540	82.677	80.405	- 244.943	56.133	- 2.115
5900	14.886	96.794	82.914	81.894	- 245.520	61.328	- 2.272
6000	14.886	97.045	83.147	83.383	- 246.102	66.536	- 2.424

June 30, 1968; Dec. 31, 1968; Dec. 31, 1975

ALUMINUM DIOXIDE UNINEGATIVE ION (AlO_2^-) (IDEAL GAS) GFW = 58.9809

Point Group [$D_{\infty h}$]
$S°_{298.15}$ = [54.85 ± 1.5] gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -138.8 ± 7 kcal/mol AlO_2^-
$\Delta Hf°_{298.15}$ = -140.9 ± 7 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[690] (1)
[400] (2)
[1020] (1)

Bond Distance: Al-O = [1.61] Å
Bond Angle: O-Al-O = [180°] σ = 2
Rotational Constant: B_0 = [0.20234] cm^{-1}

Heat of Formation

We adopt $\Delta Hf°_{298}$ = -140.9±7 kcal/mol based on equilibrium data for the reaction $AlO_2(g) + Cl^-(g) = AlO_2^-(g) + Cl(g)$ studied via effusion-mass spectrometry by Srivastava et al. (1, 2). Our analysis of the data is summarized below. For the reaction $AlO_2^-(g) = Al(g) + O(g) + O^-(g)$ we derive $\Delta Ha°_0$ = 300.5±7 kcal/mol; this is comparable with $\Delta Ha°_0$(OAlF) = 293.2±4 kcal/mol (3) and much larger than $\Delta Ha°_0$(OAlO) = 240±5 kcal/mol (3). The corresponding electron affinity, EA(AlO_2) = 94.2±5 kcal/mol (4.09±0.26 eV), is 10.9 kcal/mol greater than EA(Cl) = 83.3 kcal/mol (3).

Source	Range T/K	No. of Points	δS[a] gibbs/mol	$\Delta Hr°_{298}$/(kcal/mol) 2nd Law	3rd Law	$\Delta Hf°_{298}$ kcal/mol
(1,2)Srivastava(1972)	2080-2222	5	1.1±4.0	-8.8±8.6	-11.06±0.8[b]	-140.85±7

[a] δS = ΔSr°(2nd law) - ΔSr°(3rd law).

[b] Uncertainty derived from the scatter in ΔHr°. Estimation of reasonable bounds for bias in Gibbs-energy function and Kp yields an uncertainty of ~5 kcal/mol (or ~8 kcal/mol if the ion is nonlinear). Possible bias in the Gibbs-energy function is the dominant uncertainty.

Heat Capacity and Entropy

AlO_2^- is isoelectronic with OAlF and the related molecules SiO_2 and MgF_2. Pertinent structural information is reviewed on the tables (3) for OAlF and MgF_2. We conclude that OAlF is probably linear but cannot exclude the possibility of slight nonlinearity (bond angle of ~160°). This conclusion also applies to AlO_2^-. We adopt a linear, symmetric structure with a bond distance equal to that estimated for OAlF and slightly shorter than that observed for the ground state of AlO (3). We assume the ground state to be $^1\Sigma^+$ based on other triatomics with 16 valence electrons (4, 3). The moment of inertia is 13.772×10^{-39} g cm^2.

Vibrational frequencies are rounded values estimated from $f_r = 4.5$, $f_{rr} = 0.0$ and $f_\alpha = 0.338$ mdyn/Å. The Al-O stretching force constant and $f_\alpha/f_r = 0.075$ are transferred from OAlF (3). Raman spectra (5, 6) of alkaline aluminate solutions (pH>12.9) showed a single absorption at ~630 cm^{-1} assigned to ν_I of linear $OAlO^-$. Other information (5, 6) supports the existence of AlO_2^- in these highly alkaline solutions. The assigned ν_1, corresponding to (f_r+f_{rr}) = 3.74 mdyn/Å, agrees satisfactorily with our independent estimate for the gaseous phase.

References

1. R. D. Srivastava, O. M. Uy and M. Farber, J. Chem. Soc., Faraday Trans. II 68, 1388 (1972).
2. M. Farber, R. D. Srivasteva and O. M. Uy (Space Sci. Inc., Monrovia, Calif.), Rept. AD-731303 (Avail. NTIS), 50 pp. (1971).
3. JANAF Thermochemical Tables: AlFO(g), AlO_2(g) 12-31-75; Cl^-(g) 6-30-65; MgF_2(g), AlO(g) 6-30-75.
4. J. W. Rabalais, J. M. McDonald, V. Scherr and S. P. McGlynn, Chem. Rev. 71, 73 (1971).
5. L. A. Carreira, V. A. Maroni, J. W. Swaine and R. C. Plumb, J. Chem. Phys. 45, 2216 (1966); J. Phys. Chem. 68, 2057 (1964).
6. L. N. Pavlov, N. I. Eremin, T. Ya. Konenkova and V. E. Mironov, Sov. J. Non-Ferrous Metals 10(8), 60 (1969); 10(7), 56 (1969); English transl. of Tsvet. Metal. 42(8), 56 (1969); 42(7), 56 (1969).

AlO_2^-

ALUMINUM SUBOXIDE (AL_2O)

(IDEAL GAS) GFW=69.9624

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.129	-31.104	-31.104	INFINITE
100	10.198	49.064	71.875	-2.281	-30.815	-33.321	72.824
200	11.593	56.604	62.531	-1.185	-30.951	-35.821	39.143
298	12.513	61.414	61.414	.000	-31.200	-38.169	27.979
300	12.528	61.491	61.414	.023	-31.205	-38.213	27.838
400	13.190	65.192	61.914	1.311	-31.471	-40.507	22.132
500	13.643	68.187	62.879	2.654	-31.755	-42.734	18.679
600	13.952	70.704	63.979	4.035	-32.070	-44.902	16.356
700	14.166	72.871	65.098	5.441	-32.423	-47.012	14.678
800	14.318	74.773	66.191	6.866	-32.831	-49.070	13.405
900	14.429	76.466	67.240	8.304	-33.324	-51.071	12.402
1000	14.512	77.991	68.240	9.751	-38.957	-52.646	11.506
1100	14.575	79.377	69.191	11.205	-39.440	-53.992	10.727
1200	14.625	80.648	70.093	12.666	-39.921	-55.295	10.071
1300	14.664	81.820	70.951	14.130	-40.401	-56.556	9.508
1400	14.696	82.908	71.766	15.598	-40.883	-57.779	9.020
1500	14.722	83.923	72.543	17.069	-41.366	-58.971	8.592
1600	14.743	84.874	73.285	18.542	-41.849	-60.129	8.213
1700	14.761	85.768	73.993	20.017	-42.333	-61.256	7.875
1800	14.776	86.612	74.671	21.494	-42.817	-62.353	7.571
1900	14.789	87.411	75.320	22.973	-43.304	-63.426	7.296
2000	14.800	88.170	75.944	24.452	-43.792	-64.475	7.045
2100	14.809	88.893	76.544	25.932	-44.283	-65.498	6.816
2200	14.817	89.582	77.121	27.414	-44.775	-66.497	6.606
2300	14.825	90.240	77.677	28.896	-45.267	-67.469	6.411
2400	14.831	90.872	78.214	30.379	-45.763	-68.423	6.231
2500	14.837	91.477	78.732	31.862	-46.262	-69.362	6.064
2600	14.842	92.059	79.234	33.346	-46.762	-70.274	5.907
2700	14.846	92.619	79.719	34.830	-47.265	-71.171	5.761
2800	14.850	93.159	80.190	36.315	-186.589	-70.386	5.494
2900	14.854	93.680	80.646	37.800	-186.572	-66.238	4.992
3000	14.857	94.184	81.039	39.286	-186.557	-62.086	4.523
3100	14.860	94.671	81.519	40.772	-186.544	-57.936	4.085
3200	14.863	95.143	81.937	42.258	-186.533	-53.787	3.673
3300	14.865	95.600	82.345	43.744	-186.523	-49.639	3.287
3400	14.867	96.044	82.741	45.231	-186.518	-45.495	2.924
3500	14.869	96.475	83.127	46.718	-186.512	-41.349	2.582
3600	14.871	96.894	83.504	48.205	-186.510	-37.195	2.258
3700	14.873	97.302	83.871	49.692	-186.510	-33.051	1.952
3800	14.874	97.698	84.230	51.179	-186.513	-28.903	1.662
3900	14.876	98.085	84.580	52.667	-186.516	-24.752	1.387
4000	14.877	98.461	84.923	54.154	-186.524	-20.609	1.126
4100	14.879	98.829	85.257	55.642	-186.534	-16.464	.878
4200	14.880	99.187	85.585	57.130	-186.544	-12.312	.641
4300	14.881	99.537	85.905	58.618	-186.560	-8.163	.415
4400	14.882	99.880	86.219	60.106	-186.578	-4.011	.199
4500	14.883	100.214	86.526	61.594	-186.600	.137	-.007
4600	14.884	100.541	86.827	63.083	-186.623	4.291	-.204
4700	14.885	100.861	87.123	64.571	-186.654	8.431	-.392
4800	14.885	101.175	87.412	66.060	-186.687	12.583	-.573
4900	14.886	101.481	87.696	67.548	-186.723	16.743	-.747
5000	14.887	101.782	87.975	69.037	-186.766	20.891	-.913
5100	14.887	102.077	88.248	70.526	-186.813	25.048	-1.073
5200	14.888	102.366	88.517	72.014	-186.868	29.197	-1.227
5300	14.889	102.650	88.781	73.503	-186.928	33.355	-1.375
5400	14.889	102.928	89.041	74.992	-186.994	37.514	-1.518
5500	14.890	103.201	89.296	76.481	-187.069	41.666	-1.656
5600	14.890	103.470	89.546	77.970	-187.152	45.830	-1.789
5700	14.891	103.733	89.793	79.459	-187.241	49.987	-1.917
5800	14.891	103.992	90.035	80.948	-187.343	54.155	-2.041
5900	14.892	104.247	90.274	82.437	-187.453	58.320	-2.160
6000	14.892	104.497	90.509	83.927	-187.573	62.487	-2.276

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1965;

June 30, 1972; June 30, 1975

ALUMINUM SUBOXIDE (Al_2O) (IDEAL GAS)

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = 61.4±1.5 gibbs/mol

Ground State Quantum Weight = 1

GFW = 69.9624

ΔHf°_0 = -31.1±5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -31.2±5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[475] (1)	[118] (2)	994 (1)

Bond Distance: Al-O = 1.72 Å

Bond Angle: Al-O-Al = 180°±35°

$\sigma = 2$

Rotational Constant: B_0=0.105594 cm^{-1}

Heat of Formation

We adopt the heat of atomization ΔHa°_0=245±5 kcal/mol and ΔHf°_{298}=-31.2±5 kcal/mol. Four reactions analyzed below yield D°_0 values from 244.7 to 250.0 kcal/mol, excluding a mass-spectrometric study (3) which may be biased. Analysis of reactions A and B presumes D°_0(AlO)=120±2 kcal/mol (11). The alternative D°_0(AlO)=121.5±1(11) would change $\Delta Ha^\circ_0(Al_2O)$ by +3 (reaction A) or +1.5 kcal/mol (reaction B). Analysis using alternative reactions which are independent of AlO leads to lower values of $\Delta Ha^\circ_0(Al_2O)$: 242.7(1), 240.7(2), 242 and 244 (3), and 245.7 kcal/mol(4). ΔHa°_0=245±5 kcal/mol includes almost the whole range of values and also reproduces the approximate proportions of $Al_2O(g)$ and AlO(g) reported (2, 4) over α-Al_2O_3. Alternative thermodynamic functions are discussed below. These would increase $\Delta Ha^\circ_0(Al_2O)$ by approximately 1.7 to 2.8 kcal/mol, depending on the mean T of the data.

	Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd law	3rd law	ΔHf°_{298} kcal/mol	D°_0 kcal/mol
(1)	Hildenbrand (1973)	Mass spec.	A	2104-2256	9	-1.6±1.4	-10±3	-6.5±0.4	-33.2±5	247.0
(2)	Burns (1966)	Mass spec.	A	2327	1	---	---	-8.3	-35.0±6	248.8
(3)	Drowart (1960)	Mass spec.	A	2188-2594	16	-3.9±3.3	-24±8	-15.0±3.3	-41.8±7	255.6
		Mass spec.	A	2036-2466	11	-10±7	-36±15	-13.4±5.2	-40.2±7	254.0
(4)	Farber (1972)	Mass spec	B	1943-2093	7	-1.2±5.5	-129±11	-126.4±1.3	-32.0±5	245.8
(5)	Thompson (1973)	Mass spec.	C	1438-1580	17	-1.4±1.9	93±3	95.0±0.6	-35.7±5	249.5
(6)	Rao (1970)	Knudsen eff.	C	1556	1	---	---	99.8	-31.0±5	244.7
(7)	Kulifeev (1969)	Knudsen eff.	C	1472-1576	7	12±5	114±8	95.7±1.2	-35.1±5	248.8
(8)	Herstad (1966)	K.E.+P.C.c.	C	1585-2129	10	-1.1±1.0	97±2	99.3±1.2	-31.4±5	245.2
(9)	De Maria (1968)	Mass spec.	D	1313-1511	16	-2.2±0.7	-5.1±0.7	-2.0±0.4	-31.6±5	245.3
(10)	Brewer (1951)	Volatilization	D	1466-1725	12	3.9±2.7	-0.5±4.3	-6.8±1.3	-36.3±6	250.0

[a] Reactions: A) 2 AlO(g) = $Al_2O(g)$+O(g); B) Al(g)+AlO(g)=$Al_2O(g)$;
C) 4/3 Al(ℓ)+1/3 $Al_2O_3(c)$=$Al_2O(g)$; D) 4/3 Al(g)+1/3 $Al_2O_3(c)$ = $Al_2O(g)$.

[b] δS=ΔSr°(2nd law)-ΔSr°(3rd law) [c] Combined data from Knudsen effusion and pressure compensation.

Heat Capacity and Entropy

We tentatively adopt a linear structure with a low bending frequency. Recent studies indicate that ν_1 and ν_2 are unknown (12, 13) and that the bond angle is quite uncertain (14, 15). Electron diffraction data (14) yield a bond distance of 1.72 Å but, in the absence of ν_2, only a range of 144° to 180° for the bond angle. Linevsky et al. (16) derived angles of ~140° and ~150° from the oxygen-isotopic shift of ν_3 for Al_2O isolated in Kr and Ar matrices. A linear structure, however, is more consistent with the absence both of an IR absorption due to ν_1 (12, 13, 16-18) and of deflection by an inhomogeneous electric field (19). Theoretical calculations (15) which satisfactorily predict the geometry and frequencies of Li_2O predict that Al_2O also is quite ionic and linear with a low bending frequency. We estimate ν_2=118 cm^{-1} using f_α/f_r = 0.007 transferred from Li_2O as suggested by Snelson (18). We estimate ν_1=475±75 cm^{-1} from f_r=3.59 and f_{rr}=0.0±0.5 mdyn/Å. Theoretical predictions (15) are ν_1=527, ν_2=102 and ν_3=1057 cm^{-1}.

The more precise 2nd-law analyses of K suggest that S°_{2000} be changed by ~-1.2 gibbs/mol (see δS above). We feel that the data are not sufficiently accurate to justify this change. It could be accomplished in three ways: 1) using ν_2=160, 2) using an angle of 160° and ν_2=180, or 3) using an angle of 144° and ν_2=300 cm^{-1}.

References

1. D. L. Hildenbrand, Chem. Phys. Lett. 20, 127 (1973)
2. R. P. Burns, J. Chem. Phys. 44, 3307 (1966).
3. J. Drowart, G. De Maria, R. P. Burns and M. G. Inghram, J. Chem. Phys. 32, 1366 (1960).
4. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., Faraday Trans. I 68, 249 (1972).
5. K. R. Thompson, High Temp. Sci. 5, 62 (1973).
6. D. B. Rao and K. Motzfeldt, Acta. Chem. Scand. 24, 2796 (1970).
7. V. K. Kulifeev and G. A. Ukhlinov, Izv. Vyssh. Ucheb. Zaved., Tsvet. Met. 12(2), 72 (1969).
8. O. Herstad and K. Motzfeldt, Rev. Int. Hautes Temp. Refract. 3, 291 (1966).
9. G. A. De Maria, K. A. Gingerich and V. Piacente, J. Chem. Phys. 49, 4705 (1968).
10. L. Brewer and A. W. Searcy, J. Amer. Chem. Soc. 73, 5308 (1951).
11. JANAF Thermochemical Tables: AlO(g) 6-30-75.
12. D. A. Lynch, M. J. Zehe and K. D. Carlson, J. Phys. Chem. 78, 236 (1974); 75, 1963 (1971).
13. C. P. Marino and D. White, J. Phys. Chem. 78, 2929 (1973).
14. A. A. Ivanov, S. M. Tomalchev et al. J. Struct. Chem. 14, 854 (1973); High Temp. Sci. 5, 385 (1973).
15. E. L. Wagner, Theor. Chim. Acta 32, 295-310 (1974).
16. M. J. Linevsky, D. White and D. E. Mann, J. Chem. Phys. 41, 542 (1964).
17. A. A. Mal'tsev and V. F. Shevelkov, Teplofiz. Vysok. Temp., Akad. Nauk SSSR 2, 650 (1964).
18. A. Snelson, J. Phys. Chem. 74, 2574 (1970).
19. A. Buchler, J. L. Stauffer, W. Klemperer and L. Wharton, J. Chem. Phys. 39, 2299 (1963).

ALUMINUM SUBOXIDE UNIPOSITIVE ION (AL_2O^+) AL_2O^+

(IDEAL GAS) GFW=69.9619

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	12.714	63.573	63.573	.000	159.450	150.350	-110.209
300	12.729	63.652	63.573	.024	159.454	150.293	-109.488
400	13.378	67.409	64.081	1.331	159.705	147.203	-80.428
500	13.802	70.443	65.060	2.692	159.935	144.050	-62.964
600	14.082	72.986	66.174	4.087	160.132	140.853	-51.306
700	14.273	75.172	67.307	5.505	160.287	137.627	-42.969
800	14.406	77.087	68.413	6.939	160.385	134.382	-36.711
900	14.502	78.789	69.473	8.385	160.397	131.130	-31.843
1000	14.573	80.321	70.482	9.839	155.268	128.249	-28.029
1100	14.627	81.713	71.441	11.299	155.288	125.545	-24.943
1200	14.669	82.987	72.351	12.764	155.307	122.838	-22.372
1300	14.703	84.163	73.215	14.233	155.328	120.133	-20.196
1400	14.729	85.254	74.036	15.704	155.347	117.426	-18.331
1500	14.751	86.271	74.818	17.178	155.364	114.715	-16.714
1600	14.769	87.223	75.564	18.654	155.380	112.005	-15.299
1700	14.784	88.119	76.277	20.132	155.396	109.293	-14.051
1800	14.797	88.964	76.958	21.611	155.411	106.584	-12.941
1900	14.808	89.765	77.611	23.091	155.423	103.869	-11.948
2000	14.817	90.524	78.238	24.573	155.433	101.154	-11.054
2100	14.825	91.248	78.841	26.055	155.441	98.438	-10.245
2200	14.832	91.937	79.420	27.538	155.447	95.723	-9.509
2300	14.838	92.597	79.979	29.021	155.453	93.013	-8.838
2400	14.843	93.228	80.518	30.505	155.455	90.299	-8.223
2500	14.848	93.834	81.039	31.990	155.455	87.580	-7.656
2600	14.852	94.417	81.542	33.475	155.452	84.866	-7.134
2700	14.856	94.977	82.029	34.960	155.447	82.149	-6.649
2800	14.859	95.518	82.501	36.446	16.620	81.096	-6.330
2900	14.862	96.039	82.959	37.932	17.135	83.388	-6.284
3000	14.865	96.543	83.404	39.418	17.648	85.667	-6.241
3100	14.867	97.031	83.836	40.905	18.158	87.926	-6.199
3200	14.869	97.503	84.255	42.391	18.667	90.169	-6.158
3300	14.871	97.960	84.664	43.879	19.174	92.396	-6.119
3400	14.873	98.404	85.061	45.366	19.677	94.603	-6.081
3500	14.875	98.835	85.449	46.853	20.180	96.799	-6.044
3600	14.877	99.254	85.826	48.341	20.679	98.986	-6.009
3700	14.878	99.662	86.195	49.829	21.177	101.151	-5.975
3800	14.879	100.059	86.555	51.316	21.671	103.306	-5.941
3900	14.881	100.445	86.906	52.804	22.166	105.452	-5.909
4000	14.882	100.822	87.249	54.292	22.654	107.575	-5.878
4100	14.883	101.190	87.585	55.781	23.142	109.690	-5.847
4200	14.884	101.548	87.913	57.269	23.629	111.799	-5.818
4300	14.885	101.899	88.234	58.757	24.110	113.893	-5.789
4400	14.886	102.241	88.548	60.246	24.590	115.979	-5.761
4500	14.886	102.575	88.856	61.735	25.064	118.048	-5.733
4600	14.887	102.902	89.158	63.223	25.538	120.113	-5.707
4700	14.888	103.223	89.454	64.712	26.005	122.154	-5.680
4800	14.888	103.536	89.744	66.201	26.469	124.196	-5.655
4900	14.889	103.843	90.029	67.690	26.931	126.236	-5.630
5000	14.890	104.144	90.308	69.179	27.384	128.252	-5.606
5100	14.890	104.439	90.582	70.668	27.834	130.269	-5.582
5200	14.891	104.728	90.852	72.157	28.277	132.267	-5.559
5300	14.891	105.012	91.116	73.646	28.713	134.265	-5.537
5400	14.892	105.290	91.376	75.135	29.145	136.255	-5.515
5500	14.892	105.563	91.631	76.624	29.566	138.228	-5.493
5600	14.892	105.831	91.883	78.113	29.980	140.205	-5.472
5700	14.893	106.095	92.130	79.603	30.388	142.165	-5.451
5800	14.893	106.354	92.373	81.092	30.784	144.127	-5.431
5900	14.894	106.609	92.612	82.581	31.171	146.080	-5.411
6000	14.894	106.859	92.847	84.071	31.547	148.023	-5.392

June 30, 1968; June 30, 1972; June 30, 1975

ALUMINUM SUBOXIDE UNIPOSITIVE ION (Al_2O^+) (IDEAL GAS) GFW = 69.9619

ΔHf_0° = 158.0 ± 7 kcal/mol AL_2O^+

$\Delta Hf_{298.15}^\circ$ = 159.45±7 kcal/mol

Point Group [$D_{\infty h}$]

$S_{298.15}^\circ$ = [63.6±2] gibbs/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

[450]	(1)
[100]	(2)
[900]	(1)

Bond Distance: Al-O = [1.73] Å

Bond Angle: Al-O-Al = [180°]

Rotational Constant: B_0 = [0.104378] cm^{-1}

$\sigma = 2$

Heat of Formation

ΔHf_0° is calculated from that of Al_2O (1) using Hildenbrand's appearance potential (2) of 8.20±0.15 eV (189.1±3.5 kcal/mol). We assume that the appearance potential is identical with the ionization potential for $Al_2O(g) \rightarrow Al_2O^+(g) + e^-(g)$. Other values reported for the appearance potential include 7.7±0.5 (3, 4), 7.9±0.3 (5), 8.5±1 and 9±1 eV (6). These values are consistent with, but less precise than, the adopted value.

Heat Capacity and Entropy

Al_2O^+ is assumed to be linear as predicted by the correlation of Walsh (7). We assume that the bond distance is 0.01 Å longer than that in Al_2O, which we presume to be linear (1). Vibrational frequencies are estimated to be somewhat lower than those of Al_2O since the ion has one less bonding electron. The electronic ground state is doublet due to the odd number of electrons. The principal moment of inertia is 26.817x10^{-39} g cm^2.

The enthalpy at absolute zero is -3.195 kcal/mol.

References

1. JANAF Thermochemical Tables: $Al_2O(g)$ 6-30-75.
2. D. L. Hildenbrand, Chem. Phys. Lett. 20, 127 (1973).
3. K. R. Thompson, High Temp. Sci. 5, 62 (1973).
4. R. P. Burns et al., J. Chem. Phys. 44, 3307 (1966); 32, 1366 (1960).
5. G. DeMaria, K. A. Gingerich and V. Piacente, J. Chem. Phys. 49, 4705 (1968).
6. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., Faraday Trans. I 68, 249 (1972); J. Chem. Phys. 56, 5312 (1972).
7. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

ALUMINUM MONOXIDE, DIMERIC (AL_2O_2)

(IDEAL GAS) GFW=85.9618

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.330	-103.067	-103.067	INFINITE
100	9.370	52.849	77.861	-2.501	-103.144	-103.960	227.203
200	12.826	60.433	67.368	-1.387	-103.610	-104.624	114.328
298	15.250	66.043	66.043	.000	-104.000	-105.044	76.999
300	15.286	66.138	66.043	.028	-104.007	-105.051	76.529
400	16.786	70.759	66.663	1.638	-104.306	-105.350	57.561
500	17.699	74.610	67.878	3.366	-104.571	-105.581	46.149
600	18.276	77.892	69.281	5.167	-104.843	-105.759	38.523
700	18.657	80.740	70.719	7.015	-105.143	-105.887	33.059
800	18.919	83.249	72.131	8.894	-105.496	-105.971	28.950
900	19.107	85.489	73.493	10.796	-105.932	-106.005	25.741
1000	19.244	87.510	74.796	12.714	-111.507	-105.619	23.083
1100	19.349	89.349	76.036	14.644	-111.934	-105.011	20.864
1200	19.429	91.036	77.217	16.583	-112.361	-104.363	19.007
1300	19.493	92.594	78.341	18.529	-112.788	-103.678	17.430
1400	19.543	94.040	79.411	20.481	-113.218	-102.961	16.073
1500	19.585	95.390	80.432	22.437	-113.651	-102.215	14.893
1600	19.619	96.655	81.407	24.398	-114.085	-101.438	13.856
1700	19.647	97.845	82.339	26.361	-114.522	-100.634	12.937
1800	19.671	98.969	83.232	28.327	-114.961	-99.802	12.118
1900	19.691	100.033	84.088	30.295	-115.406	-98.948	11.382
2000	19.709	101.044	84.911	32.265	-115.854	-98.073	10.717
2100	19.724	102.006	85.702	34.237	-116.305	-97.173	10.113
2200	19.737	102.923	86.464	36.210	-116.762	-96.253	9.562
2300	19.748	103.801	87.199	38.184	-117.220	-95.306	9.056
2400	19.758	104.642	87.909	40.159	-117.685	-94.342	8.591
2500	19.767	105.448	88.594	42.135	-118.155	-93.366	8.162
2600	19.775	106.224	89.257	44.113	-118.627	-92.362	7.764
2700	19.782	106.970	89.900	46.090	-119.106	-91.345	7.394
2800	19.788	107.690	90.522	48.069	-258.408	-88.646	6.919
2900	19.794	108.384	91.126	50.048	-258.371	-82.586	6.224
3000	19.799	109.055	91.713	52.027	-258.339	-76.522	5.575
3100	19.803	109.705	92.283	54.008	-258.309	-70.461	4.967
3200	19.807	110.334	92.837	55.988	-258.285	-64.402	4.398
3300	19.811	110.943	93.377	57.969	-258.264	-58.343	3.864
3400	19.815	111.535	93.902	59.950	-258.250	-52.290	3.361
3500	19.818	112.109	94.414	61.932	-258.236	-46.234	2.887
3600	19.821	112.667	94.913	63.914	-258.228	-40.170	2.439
3700	19.824	113.210	95.401	65.896	-258.224	-34.116	2.015
3800	19.826	113.739	95.876	67.879	-258.224	-28.059	1.614
3900	19.828	114.254	96.341	69.861	-258.226	-21.999	1.233
4000	19.830	114.756	96.795	71.844	-258.235	-15.947	.871
4100	19.832	115.246	97.239	73.827	-258.247	-9.892	.527
4200	19.834	115.724	97.674	75.811	-258.260	-3.832	.199
4300	19.836	116.191	98.099	77.794	-258.281	2.228	-.113
4400	19.838	116.647	98.515	79.778	-258.304	8.290	-.412
4500	19.839	117.092	98.923	81.762	-258.333	14.347	-.697
4600	19.840	117.528	99.323	83.746	-258.364	20.412	-.970
4700	19.842	117.955	99.715	85.730	-258.404	26.462	-1.231
4800	19.843	118.373	100.099	87.714	-258.447	32.525	-1.481
4900	19.844	118.782	100.476	89.699	-258.493	38.593	-1.721
5000	19.845	119.183	100.846	91.683	-258.548	44.652	-1.952
5100	19.846	119.576	101.210	93.668	-258.608	50.722	-2.174
5200	19.847	119.961	101.567	95.652	-258.676	56.781	-2.386
5300	19.848	120.339	101.917	97.637	-258.750	62.852	-2.592
5400	19.849	120.710	102.262	99.622	-258.830	68.921	-2.789
5500	19.850	121.075	102.601	101.607	-258.920	74.987	-2.980
5600	19.851	121.432	102.934	103.592	-259.019	81.062	-3.164
5700	19.851	121.784	103.261	105.577	-259.124	87.130	-3.341
5800	19.852	122.129	103.584	107.562	-259.242	93.213	-3.512
5900	19.853	122.468	103.901	109.547	-259.369	99.291	-3.678
6000	19.853	122.802	104.213	111.533	-259.506	105.372	-3.838

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1961
Sept. 30, 1965; Dec. 31, 1975

ALUMINUM MONOXIDE, DIMERIC (Al_2O_2) (IDEAL GAS) GFW = 85.9618

Point Group [D_{2h}]
$S^\circ_{298.15}$ = [66.04 ± 4] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -103.1 ± 10 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -104 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[900](1)	[500](1)	496 (1)
[250](1)	[300](1)	686 (1)

Bond Distance: Al-O = [1.72] Å
Bond Angle: O-Al-O = [90°] Al-O-Al = [90°] σ = [4]
Product of the Moments of Inertia: $I_AI_BI_C$ = [2.1993×10^{-114}] g^3 cm^6

Heat of Formation

We adopt ΔHf°_{298} = -104±10 kcal/mol and ΔHa°_0 = 376±10 kcal/mol based on mass-spectrometric data of Farber et al. (1). They identified species effusing through an elongated orifice from an alumina cell. Their data are analyzed below along with an earlier study by Drowart et al. (2), who used tungsten and molybdenum Knudsen cells. The metal cells caused reduction of the vapor species (2, 1). This may not be a serious problem, but it probably contributes to variation in ΔHf° values derived from different reactions. Analysis of AlO via the atomization reaction (2) yields ΔHf° values which are biased by ∿6 kcal/mol (3). Similar analysis of Al_2O_2 (2) yields ΔHf° values which are 6 to 14 kcal/mol more positive than from alternative reactions A and C below. We exclude the atomization reaction because of this parallel. Instead we analyze both studies (1, 2) using isomolecular reaction A. We also include alternative reactions B and C. B is an isomolecular reaction derivable from the ion intensities of Farber et al. (2), while C is the association of monomeric AlO into dimer. Results based on JANAF auxiliary data (3) are summarized as ΔHf°_{298} and D°_0(d→2m), the dimer dissociation energy. Our uncertainty includes a large contribution from possible bias in the Gibbs-energy function of Al_2O_2.

ΔHf°_{298} = -104±10 kcal/mol is an average from reactions A and B of Farber et al. (1). It corresponds to D°_0(d→2m) = 136±10 kcal/mol. Results from Drowart et al. (2) are ∿6 kcal/mol lower. We would expect D°_0(d→2m) to be closer to D°_0(Al-Al) = ∿40 or D°_0(HO-OH) = 50 kcal/mol if the dimer structure were O=Al-Al=O or Al-O-O-Al. D°_0(d→2m) is similar to D°_0(AlO-Al) = 125 kcal/mol (3), so we cannot rule out the structure Al-O-Al=O. Since the planar cyclic structure involves four Al-O bonds, we would expect $\Delta Ha^\circ_0(Al_2O_2)/D^\circ_0(AlO)$ = 4 if the dimer and monomer had equal bond energies. Much lower ratios of ∿2.5 are found for the cyclic dimers of LiF and NaF (3). Dimeric AlO yields $\Delta Ha^\circ_0/D^\circ_0(AlO)$ = 3.1±0.1 which agrees with 3.1 (3) for the cyclic dimer (4) of LiO. This contrasts with 2.6 for dimeric BO (3) which probably has a non-cyclic structure.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	3rd Law	ΔHf°_{298} kcal/mol	D°_0(d→2m)[c] kcal/mol
(1)Farber(1972)	Eff. mass spec.	A	1943-2093	5	-4.2±1.0	-21.5±2.0	-12.9±8	-105.7±10	137.6
(2)Drowart(1960)	Eff. mass spec.	A[d]	2464-2594	5	34±23	79±57	-5.6±12	-98.4±14	130.3
		A[e]	2281-2466	7	-29±17	72±39	-2.4±12	-95.2±14	127.1
(1)Farber(1972)	Eff. mass spec.	B	1943-2093	5	62±32	118±66	-9.6±10	-102.0±12	133.9
(2)Drowart(1960)	Eff. mass spec.	C[d]	2464-2594	5	24±24	-72±59	-132.3±11	-99.5±12	131.4
		C[e]	2281-2466	8	-31±15	-203±34	-130.8±11	-98.0±12	129.9

[a] Reactions: A) $Al_2O(g) + AlO(g) = Al(g) + Al_2O_2(g)$; B) $Al_2O(g) + AlO_2(g) = AlO(g) + Al_2O_2(g)$; C) $2AlO(g) = Al_2O_2(g)$

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

[c] For dissociation of dimer into two monomers; i.e. the reverse of reaction C.

[d] Using a tungsten effusion cell.

[e] Using a molybdenum effusion cell.

Heat Capacity and Entropy

Proposed structures for Al_2O_2 include: 1) planar cyclic, 2) metaaluminate (MOMO), 3) peroxide (MOOM) and 4) metal-bonded (OMMO) models. Bond energy comparisons were used to favor the cyclic model (2). Later, the MOOM model was proposed (5) for all group III-A chalcogenides, M_2X_2, on the basis of the correlation of dimer dissociation energies with $D^\circ_0(X_2)$. New bond energy comparisons (6) for all four models led to the conclusion that MXMX is the most plausible structure for these chalcogenides. This structure has a precedent in metaborates such as Li-O-B=O (7). We find, however, that use of $\Delta Ha^\circ_0(M_2X_2)/D^\circ_0(MX)$ = 3.1 (see above) brings the cyclic structure into equally good agreement with experiment for all M_2X_2 except B_2O_2. Thermochemical evidence does not yield a definitive prediction of the structure.

We assume a planar cyclic structure with bond angles of 90° and bond distances equal to that observed for Al_2O (3). We assume the ground electronic state to be $^1\Sigma$ and neglect excited states. Infrared spectra of Al-O species in inert matrices include bands at 496 (8) and 686 cm^{-1} (9) which were tentatively assigned to Al_2O_2. We adopt these values and estimate the other frequencies by comparison with Li_2O_2 (4) and Li_2F_2 (10). Principal moments of inertia are 7.859×10^{-39}, 13.254×10^{-39} and 21.113×10^{-39} g cm^2.

We also estimate approximate parameters and calculate thermodynamic functions for the structures OMMO and MOMO. At 2000 K we obtain Gibbs-energy functions of 84.9 (cyclic), 85.4 (linear OMMO), 85.1 (linear MOMO) and 88.9 (bent MOMO, MOM angle = 120°) gibbs/mol. This is the basis of our estimated uncertainty of 4 gibbs/mol for entropy and Gibbs-energy function. Recently published thermodynamic functions (6) probably represent lower limits for non-linear Al-O-Al=O; this possible bias is suggested by new data for AlO, Al_2O and FAlO (3).

References

1. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., Faraday Trans. I 68, 249 (1972).
2. J. Drowart, G. DeMaria, R. P. Burns and M. G. Inghram, J. Chem. Phys. 32, 1366 (1960).
3. JANAF Thermochemical Tables: Al(g), 12-31-65; AlO(g), $Al_2O(g)$ 6-30-75; $AlO_2(g)$, AlFO(g) 12-31-75; LiF(g), $Li_2F_2(g)$, NaF(g), $Na_2F_2(g)$ 12-31-68; LiO(g), $Li_2O_2(g)$ 3-31-64.
4. K. S. Seshadri, D. White and D. E. Mann, J. Chem. Phys. 45, 4697 (1966).
5. O. M. Uy and J. Drowart, Trans. Faraday Soc. 67, 1293 (1971).
6. K. M. Maloney, S. K. Gupta and D. A. Lynch, J. Inorg. Nucl. Chem. 38, 49 (1976).
7. K. S. Seshadri, L. A. Nimon and D. White, J. Mol. Spectrosc. 30, 128 (1969).
8. C. P. Marino and D. White, J. Phys. Chem. 77, 2929 (1973).
9. D. A. Lynch (Case Western Reserve Univ., Cleveland, Ohio), Rept. NASA-CR-133100 (N73-26102 Avail. NTIS), 138 pp. (1972).
10. A. Snelson, J. Phys. Chem. 73, 1925 (1969).

DIALUMINUM DIOXIDE UNIPOSITIVE ION ($AL_2O_2^+$) $AL_2O_2^+$

(IDEAL GAS) GFW=85.9613

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	15.645	68.066	68.066	.000	126.000	122.866	-90.063
300	15.679	68.163	68.066	.029	126.003	122.845	-89.493
400	17.096	72.886	68.701	1.674	126.236	121.761	-66.527
500	17.936	76.799	69.940	3.429	126.495	120.612	-52.720
600	18.459	80.119	71.367	5.251	126.741	119.412	-43.496
700	18.801	82.991	72.827	7.115	126.953	118.173	-36.895
800	19.034	85.518	74.259	9.007	127.110	116.906	-31.937
900	19.200	87.770	75.637	10.920	127.182	115.626	-28.078
1000	19.322	89.800	76.954	12.846	122.112	114.710	-25.070
1100	19.414	91.646	78.207	14.783	122.189	113.964	-22.643
1200	19.485	93.338	79.398	16.728	122.264	113.212	-20.619
1300	19.540	94.900	80.531	18.679	122.339	112.455	-18.905
1400	19.585	96.350	81.610	20.636	122.411	111.694	-17.436
1500	19.621	97.702	82.638	22.596	122.479	110.924	-16.162
1600	19.651	98.970	83.620	24.560	122.544	110.152	-15.046
1700	19.676	100.162	84.558	26.526	122.607	109.375	-14.061
1800	19.697	101.287	85.457	28.495	122.668	108.598	-13.186
1900	19.714	102.352	86.318	30.465	122.722	107.814	-12.401
2000	19.729	103.364	87.145	32.438	122.774	107.025	-11.695
2100	19.743	104.327	87.941	34.411	122.820	106.236	-11.056
2200	19.754	105.246	88.707	36.386	122.862	105.444	-10.475
2300	19.764	106.124	89.445	38.362	122.903	104.656	-9.945
2400	19.773	106.965	90.157	40.339	122.937	103.864	-9.458
2500	19.780	107.773	90.846	42.316	122.965	103.062	-9.010
2600	19.787	108.549	91.512	44.295	122.990	102.268	-8.596
2700	19.793	109.295	92.157	46.274	123.010	101.468	-8.213
2800	19.799	110.015	92.782	48.253	-15.795	102.332	-7.987
2900	19.804	110.710	93.388	50.233	-15.260	106.540	-8.029
3000	19.808	111.382	93.977	52.214	-14.729	110.734	-8.067
3100	19.812	112.031	94.549	54.195	-14.203	114.907	-8.101
3200	19.816	112.660	95.105	56.176	-13.681	119.064	-8.132
3300	19.819	113.270	95.646	58.158	-13.162	123.204	-8.159
3400	19.822	113.862	96.173	60.140	-12.650	127.325	-8.184
3500	19.825	114.436	96.687	62.123	-12.138	131.433	-8.207
3600	19.827	114.995	97.188	64.105	-11.634	135.534	-8.228
3700	19.830	115.538	97.677	66.088	-11.132	139.612	-8.247
3800	19.832	116.067	98.154	68.071	-10.635	143.680	-8.263
3900	19.834	116.582	98.620	70.054	-10.139	147.737	-8.279
4000	19.836	117.084	99.075	72.038	-9.651	151.773	-8.292
4100	19.838	117.574	99.520	74.022	-9.165	155.800	-8.305
4200	19.839	118.052	99.956	76.005	-8.682	159.822	-8.316
4300	19.841	118.519	100.382	77.989	-8.205	163.830	-8.327
4400	19.842	118.975	100.799	79.974	-7.730	167.828	-8.336
4500	19.843	119.421	101.208	81.958	-7.263	171.810	-8.344
4600	19.845	119.857	101.609	83.942	-6.797	175.790	-8.352
4700	19.846	120.284	102.002	85.927	-6.339	179.744	-8.358
4800	19.847	120.702	102.387	87.911	-5.885	183.700	-8.364
4900	19.848	121.111	102.765	89.896	-5.434	187.651	-8.370
5000	19.849	121.512	103.136	91.881	-4.992	191.581	-8.374
5100	19.850	121.905	103.500	93.866	-4.555	195.514	-8.378
5200	19.850	122.291	103.858	95.851	-4.125	199.425	-8.382
5300	19.851	122.669	104.209	97.836	-3.702	203.340	-8.385
5400	19.852	123.040	104.555	99.821	-3.285	207.243	-8.388
5500	19.853	123.404	104.894	101.806	-2.879	211.133	-8.390
5600	19.853	123.762	105.228	103.792	-2.480	215.024	-8.392
5700	19.854	124.113	105.556	105.777	-2.088	218.899	-8.393
5800	19.855	124.459	105.879	107.762	-1.709	222.780	-8.395
5900	19.855	124.798	106.197	109.748	-1.338	226.647	-8.396
6000	19.856	125.132	106.509	111.733	-.980	230.509	-8.396

June 30, 1968; Dec. 31, 1975

DIALUMINUM DIOXIDE UNIPOSITIVE ION ($Al_2O_2^+$) (IDEAL GAS) GFW = 85.9613

Point Group [D_{2h}]
$S^\circ_{298.15}$ = [68.07 ± 4] gibbs/mol
Ground State Quantum Weight = [2]

ΔHf°_0 = 125.4 ± 16 kcal/mol $AL_2O_2^+$
$\Delta Hf^\circ_{298.15}$ = 126 ± 16 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[840](1)	[470](1)	[460](1)
[230](1)	[280](1)	[640](1)

Bond Distance: Al-O = [1.75] Å
Bond Angle: O-Al-O = [90°] Al-O-Al = [90°] σ = [4]
Product of the Moments of Inertia: [2.4397×10^{-114}] g^3 cm^6

Heat of Formation

We adopt ΔHf°_{298} = 126±16 kcal/mol derived from the ionization potential 9.9±0.5 eV (228.3±12 kcal/mol) for $Al_2O_2(g) \rightarrow Al_2O_2^+(g) + e^-(g)$. We assume that the ionization potential is equal to the appearance potential measured by Drowart et al. (1). Their value is confirmed by Farber et al. (2) who found AP = 10±1 eV. ΔHf° is based on JANAF auxiliary data (3) for $Al_2O_2(g)$ and includes the uncertainties inherent in the properties of this species.

The adopted ΔHf° *corresponds to* D°_0 = *128±16 kcal/mol for the dissociation* $Al_2O_2^+(g) \rightarrow AlO^+(g) + AlO(g)$; *this is* comparable to D°_0 = 136±10 kcal/mol (3) for $Al_2O_2(g) \rightarrow 2\ AlO(g)$. Likewise, we obtain D°_0 = 46±16 kcal/mol for $Al_2O_2^+(g) \rightarrow Al^+(g) + AlO_2(g)$; this is comparable to D°_0 = 38±5 kcal/mol (3) for $AlO^+(g) \rightarrow Al^+(g) + O(g)$. ΔHa°_0 = 286±16 kcal/mol for $Al_2O_2^+(g) \rightarrow Al^+(g) + Al(g) + 2\ O(g)$ is considerably less than $\Delta Ha^\circ_0(Al_2O_2)$ = 376±10 kcal/mol (3).

Heat Capacity and Entropy

Uncertainty about the structure of $Al_2O_2(g)$ carries over into the positive ion. We assume that both have the planar cyclic form with bond angles of 90°, although other structures (3, Al_2O_2, g) cannot be ruled out. The bond distance in the ion is taken to be 0.03Å longer than that assumed for the neutral molecule (3). This presumes that the overall bonding in the ion is weaker than in the neutral molecule. Vibrational frequencies are estimated to be somewhat lower than in Al_2O_2 (3). We assume the ground electronic state to be doublet, due to the odd number of electrons, and neglect excited states.

The enthalpy at absolute zero is -3.418 kcal/mol. The principal moments of inertia are 8.136×10^{-39}, 13.72×10^{-39} and 21.86×10^{-39} g cm^2.

References

1. J. Drowart, G. DeMaria, R. P. Burns and M. G. Inghram, J. Chem. Phys. 32, 1366 (1960).
2. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., Faraday Trans. I 68, 249 (1972).
3. JANAF Thermochemical Tables: $Al_2O_2(g)$, $AlO_2(g)$ 12-31-75; AlO(g), $AlO^+(g)$ 6-30-75; Al(g) 12-31-65; $Al^+(g)$ 6-30-65.

$AL_2O_2^+$

ALUMINUM OXIDE, ALPHA (α-AL_2O_3) AL_2O_3

(CRYSTAL) GFW=101.9612

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.395	- 397.594	- 397.594	INFINITE
100	3.071	1.024	24.190	- 2.317	- 398.769	- 392.332	857.441
200	12.220	5.945	13.711	- 1.553	- 399.934	- 385.429	421.177
298	18.685	12.175	12.175	.000	- 400.500	- 378.178	277.212
300	18.981	12.292	12.175	.035	- 400.506	- 378.040	275.402
400	22.965	18.348	12.974	2.150	- 400.656	- 370.519	202.442
500	25.366	23.752	14.600	4.576	- 400.589	- 362.989	158.662
600	26.899	28.522	16.531	7.194	- 400.421	- 355.485	129.485
700	27.946	32.751	18.552	9.939	- 400.213	- 348.011	108.654
800	28.713	36.535	20.568	12.774	- 400.009	- 340.569	93.039
900	29.317	39.953	22.535	15.677	- 399.851	- 333.148	80.899
1000	29.821	43.069	24.435	18.634	- 404.800	- 325.375	71.111
1100	30.260	45.932	26.261	21.638	- 404.573	- 317.445	63.071
1200	30.653	48.582	28.012	24.684	- 404.317	- 309.537	56.374
1300	31.008	51.050	29.690	27.768	- 404.035	- 301.649	50.712
1400	31.329	53.360	31.299	30.885	- 403.732	- 293.783	45.862
1500	31.618	55.531	32.843	34.032	- 403.409	- 285.942	41.662
1600	31.874	57.580	34.326	37.207	- 403.067	- 278.122	37.990
1700	32.100	59.520	35.751	40.406	- 402.709	- 270.323	34.752
1800	32.300	61.360	37.123	43.626	- 402.339	- 262.544	31.877
1900	32.480	63.111	38.445	46.865	- 401.960	- 254.789	29.307
2000	32.650	64.782	39.721	50.122	- 401.572	- 247.057	26.997
2100	32.820	66.379	40.952	53.395	- 401.174	- 239.341	24.908
2200	32.990	67.909	42.143	56.686	- 400.769	- 231.645	23.012
2300	33.160	69.380	43.296	59.993	- 400.352	- 223.963	21.281
2400	33.330	70.795	44.412	63.318	- 399.928	- 216.300	19.697
2500	33.510	72.159	45.495	66.660	- 399.496	- 208.665	18.242
2600	33.690	73.477	46.546	70.020	- 399.052	- 201.037	16.899
2700	33.880	74.752	47.567	73.398	- 398.599	- 193.432	15.657
2800	34.080	75.987	48.560	76.796	- 536.953	- 184.181	14.376
2900	34.300	77.187	49.527	80.215	- 535.950	- 171.600	12.932
3000	34.530	78.354	50.468	83.656	- 534.933	- 159.051	11.587

Dec. 31, 1960; Sept. 30, 1961; March 31, 1964;
June 30, 1972; June 30, 1975

ALUMINUM OXIDE, ALPHA (α-Al_2O_3) (CRYSTAL) GFW = 101.9612 AL_2O_3

$S^\circ_{298.15}$ = 12.175 ± 0.02 gibbs/mol
Tm = 2327 ± 6 K

ΔHf°_0 = -397.6 ± 0.3 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -400.5 ± 0.3 kcal/mol
ΔHm° = 26.55 ± 1.0 kcal/mol

Heat of Formation

The adopted ΔHf° is from calorimetric heats of combustion measured by Mah (1) and Holley and Huber (2). Early measurements of the heat of combustion of Al were seriously biased (3), but the sources of bias were minimized in later studies. These studies yield ΔHf° values of -400.5 ± 0.25 (1), -400.5 ± 0.3 (2), -399.2 ± 0.3 (3), and -402 ± 2 or -400.6 ± 1.4 (4) kcal/mol after conversion to the present atomic weight of Al.

ΔHf° may be compared with values of -401.8 ± 1.5 kcal/mol and -405.2 ± 1.5 kcal/mol derived from equilibrium data involving gaseous $AlCl_3$ (5) and crystalline AlF_3(6), respectively. Third-law analyses of the data give ΔHr°(298.15 K) = 81.4 ± 1.0 kcal/mol (entropy discrepancy of 5.0 ± 1.2 gibbs/mol) for $Al_2O_3(c) + 6HCl(g) \rightarrow 2AlCl_3(g) + 3H_2O(g)$ and ΔHr°(298.15 K) = 99.3 ± 0.6 kcal/mol (entropy discrepancy of -0.6 ± 0.6 gibbs/mol) for $2AlF_3(c) + 3H_2O(g) \rightarrow Al_2O_3(c) + 6HF(g)$. The value from the latter reaction may be biased by the formation of aluminum oxyfluorides (7).

Heat Capacity and Entropy

Cp° is from Ditmars and Douglas (8) who tabulated functions from 0 to 1200 K. These functions were derived from Cp° data (13-380 K) measured earlier (9) on the Calorimetry Conference Sample and new enthalpies (323-1173 K) measured (8) on NBS Standard Reference Material 720. Entropy and enthalpy were obtained from Cp° based on S°_{13} = 0.0016 gibbs/mol.

Ditmars and Douglas (8) derived an enthalpy equation for the range up to 2257 K by inclusion of high-temperature enthalpy data (1173-2257 K) from West and Ishihara (10). We adopt Cp° as calculated from this equation but modify the curve slightly above 1700 K in order to make the extrapolation above Tm more suitable. The literature contains many other measurements of Cp° or H° above room temperature; the thorough comparison of Ditmars and Douglas (8) included some twenty of these studies.

The adopted functions are confirmed by more recent studies, for example, enthalpy data up to 1300 K (11, 12) and up to Tm (13-15). The new liquid study (15) included crystal enthalpies which deviate by ± 0.5% (2071-2203 K) and +0.9±0.5% (2221-2304 K).

Melting Data and Sublimation Data

See $Al_2O_3(\ell)$.

References

1. A. D. Mah, J. Phys. Chem. 61, 1572 (1957).
2. C. E. Holley and E. J. Huber, J. Amer. Chem. Soc. 73, 5577 (1951).
3. P. E. Snyder and H. Seltz, J. Amer. Chem. Soc. 67, 683 (1945).
4. A. Schneider and G. Gattow, Z. Anorg. Allgem. Chem. 277, 40 (1954).
5. W. Fischer and R. Gewehr, Z. Anorg. Allgem. Chem. 209, 17 (1932).
6. V. P. Mashovets and B. F. Yudin, Izv. Vyssch. Ucheb. Zaved., Tsvet. Met. 5 (4), 95 (1962).
7. B. Siegel, Inorg. Chim. Acta, Rev. 2, 137 (1968).
8. D. A. Ditmars and T. B. Douglas, J. Res. Natl. Bur. Std. 75A, 401 (1971).
9. G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Res. Natl. Bur. Std. 57, 67 (1956).
10. E. D. West and S. Ishihara, U. S. Natl. Bur. Std. Rept. 9028, 71, Jan., 1966; Certificate for SRM-720, α-Alumina, Aug. 26, 1970.
11. D. R. Fredrickson and M. G. Chasonov, J. Chem. Thermodynamics 2, 623 (1970).
12. F. Gronvold, Acta Chem. Scand. 26, 2216 (1972).
13. E. N. Fomichev, V. P. Bondarenko and V. V. Kandyba, High Temp. - High Pressures 5, 1 (1973).
14. V. D. Tarasov and V. Ya. Chekhovskoi, Russ. J. Phys. Chem. 48, 1601 (1974).
15. E. E. Shpil'rain, D. N. Kagan and L. S. Barkhatov, High Temp. - High Pressures 4, 605 (1972).

ALUMINUM OXIDE, DELTA (δ-AL_2O_3) AL_2O_3

(CRYSTAL) GFW=101.9612

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	19.452	12.100	12.100	.000	− 398.300	− 375.955	275.583
300	19.550	12.221	12.100	.036	− 398.305	− 375.817	273.783
400	23.654	18.459	12.923	2.214	− 398.392	− 368.298	201.229
500	26.127	24.024	14.598	4.713	− 398.251	− 360.788	157.700
600	27.706	28.937	16.587	7.410	− 398.005	− 353.318	128.696
700	28.784	33.294	18.669	10.238	− 397.714	− 345.892	107.992
800	29.574	37.191	20.745	13.157	− 397.426	− 338.510	92.477
900	30.197	40.712	22.771	16.147	− 397.181	− 331.160	80.417
1000	30.716	43.921	24.728	19.193	− 402.041	− 323.468	70.694
1100	31.168	46.870	26.608	22.288	− 401.723	− 315.628	62.709
1200	31.573	49.599	28.412	25.425	− 401.376	− 307.817	56.061
1300	31.938	52.141	30.141	28.601	− 401.002	− 300.034	50.440
1400	32.269	54.520	31.798	31.811	− 400.605	− 292.281	45.627
1500	32.567	56.757	33.388	35.053	− 400.188	− 284.560	41.460
1600	32.830	58.867	34.915	38.324	− 399.751	− 276.865	37.818
1700	33.063	60.865	36.383	41.618	− 399.297	− 269.198	34.608
1800	33.269	62.761	37.797	44.935	− 398.830	− 261.557	31.757
1900	33.454	64.564	39.158	48.271	− 398.354	− 253.944	29.210
2000	33.629	66.285	40.472	51.626	− 397.868	− 246.359	26.921
2100	33.805	67.930	41.741	54.997	− 397.372	− 238.796	24.852
2200	33.980	69.507	42.967	58.387	− 396.868	− 231.258	22.973
2300	34.155	71.021	44.154	61.793	− 396.352	− 223.737	21.260
2400	34.330	72.478	45.304	65.217	− 395.829	− 216.241	19.691
2500	34.515	73.883	46.419	68.660	− 395.296	− 208.777	18.251
2600	34.701	75.241	47.502	72.120	− 394.752	− 201.323	16.923
2700	34.896	76.554	48.554	75.600	− 394.197	− 193.897	15.695
2800	35.102	77.827	49.577	79.100	− 532.449	− 184.827	14.426
2900	35.329	79.062	50.572	82.621	− 531.344	− 172.432	12.995
3000	35.566	80.264	51.542	86.166	− 530.223	− 160.072	11.661

June 30, 1975

ALUMINUM OXIDE, DELTA (δ-Al_2O_3) (CRYSTAL) GFW = 101.9612 AL_2O_3

$S^{\circ}_{298.15}$ = [12.1±1] gibbs/mol
Tm = [2308] K

ΔHf°_0 = [-395.4±1] kcal/mol
$\Delta Hf^{\circ}_{298.15}$ = -398.3±1 kcal/mol
ΔHm° = [22.3] kcal/mol

Heat of Formation

ΔHf° is calculated from that of α-Al_2O_3 (1) using ΔHr°_{978} = -2.7±0.4 kcal/mol for the irreversible process $\delta \rightarrow \alpha$. This yields ΔHr°_{298} = -2.2 kcal/mol based on our adopted functions. Yokokawa and Kleppa (2) determined ΔHr° for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. DTA studies by Gani and McPherson (3) gave ΔHr° = -2.8±0.5 kcal/mol. Assuming T = ∿1400 K, we derive ΔHr°_{298} = -1.9 kcal/mol. This confirms the calorimetric result. Both samples of δ-Al_2O_3 had been obtained by rapid quenching from high temperature, one (2) from combustion of Al_4C_3 and the other (3) by a plasma method.

Heat Capacity and Entropy

Cp° is assumed to be 3% larger than that of α-Al_2O_3(1) by comparison with the observed values for κ-Al_2O_3(1) and the adopted values for γ-Al_2O_3(1). S° is selected such that $\Delta Gr^{\circ}(\kappa \rightarrow \delta) < 0$ below Tm and $\Delta Gr^{\circ}(\delta \rightarrow \alpha) < 0$ at T $\leq$2400 K.

Marchidan et al. (4) measured enthalpy data (573-1177 K) for a sample designated only as TA-600 alumina. They attributed a transition at ∿993 K (720°C) to the irreversible process $\eta \rightarrow \delta$. This temperature corresponds roughly to processes designated as either $(\gamma \text{ or } \eta) \rightarrow \theta$ or $\gamma \rightarrow \delta$ by Lippens and Steggerda (5). DTA data of Alevra et al. (6) showed an endotherm near 750°C subsequent to the dehydration of hydroxide samples; however, TGA data indicated that the resulting alumina still retained considerable water at this temperature. The enthalpy data (4, 1003-1177 K) are 4.7±0.3% larger than those of α-Al_2O_3(1) and presumably correspond to an alumina containing a significant amount of water. The δ-Al_2O_3 used in ΔHf° studies was presumably essentially anhydrous. Thus, we omit the enthalpy data (4) on the presumption that they are larger than those of our standard state which is anhydrous δ-Al_2O_3.

Phase Data

The stable crystalline form is corundum (α-alumina). Delta-alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied (5) due to their importance in adsorbents and catalysts. Lippens and Steggerda (5) summarized the classifications of metastable forms, their crystal structures and conditions of formation by dehydration. Mixtures of the closely related δ- and θ-aluminas are also formed by rapid cooling of droplets of molten alumina following their passage through a flame (7). There is some controversy (5) over the X-ray data and unit-cell dimensions of δ-Al_2O_3 formed by the two methods. Recent data (8) for θ-Al_2O_3(5) suggest a similar controversy. Delta-alumina belongs to the "nearly anhydrous", high-temperature classification (5) based on the temperature of 600° to 900° at which it forms during dehydration. The irreversible transitions $\delta \rightarrow \theta (+\alpha) \rightarrow \alpha$ are thermally activated at temperatures of 800°-1050°C for the first step (5, 6) and ∿1200°C for the final step (5).

Melting Data

The hypothetical melting point of metastable δ-phase is calculated as the temperature at which $\Delta Gr^{\circ}(\delta \rightarrow \ell) = 0$. ΔHm° is the corresponding difference in ΔHf°.

References

1. JANAF Thermochemical Tables: Al_2O_3(c, α), Al_2O_3(c, κ), Al_2O_3(c, γ) 6-30-75.
2. T. Yokokawa and O. J. Kleppa, J. Phys. Chem. 68, 3246 (1964); J. Amer. Chem. Soc. 68, 3246 (1964).
3. M. S. J. Gani and R. McPherson, Thermochim. Acta 7, 251 (1973).
4. D. I. Marchidan, L. Pandele and A. Nicolescu, Rev. Roum. Chim. 17, 1493 (1972).
5. B. C. Lippens and J. J. Steggerda in "Physical and Chemical Aspects of Adsorbents and Catalysts," B. G. Linsen, Ed., Academic Press, New York, 1970, pp. 171-211.
6. V. Alevra, D. Ciomirtan and M. Ionescu, Rev. Roum. Chim. 17, 1379 (1972).
7. M. Plummer, J. Appl. Chem. 8, 35 (1958).
8. G. Yamaguchi, I. Yasui and W.-C. Chiu, Bull. Chem. Soc. Japan 43, 2487 (1970).

ALUMINUM OXIDE, GAMMA (γ-AL_2O_3) (CRYSTAL) GFW=101.9612

AL_2O_3

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	19.773	12.500	12.500	.000	- 396.000	- 373.775	273.984
300	19.873	12.623	12.500	.037	- 396.005	- 373.637	272.195
400	24.044	18.964	13.337	2.251	- 396.055	- 366.164	200.062
500	26.558	24.621	15.039	4.791	- 395.874	- 358.709	156.791
600	28.163	29.615	17.061	7.532	- 395.583	- 351.303	127.962
700	29.259	34.043	19.177	10.407	- 395.245	- 343.948	107.385
800	30.063	38.005	21.287	13.374	- 394.909	- 336.644	91.967
900	30.695	41.584	23.347	16.413	- 394.615	- 329.379	79.984
1000	31.223	44.846	25.336	19.510	- 399.425	- 321.777	70.324
1100	31.682	47.844	27.248	22.655	- 399.056	- 314.031	62.392
1200	32.094	50.618	29.081	25.845	- 398.656	- 306.320	55.788
1300	32.465	53.202	30.838	29.073	- 398.230	- 298.641	50.206
1400	32.801	55.621	32.523	32.336	- 397.780	- 290.996	45.427
1500	33.104	57.894	34.139	35.632	- 397.309	- 283.387	41.289
1600	33.372	60.039	35.692	38.956	- 396.818	- 275.808	37.674
1700	33.609	62.070	37.184	42.305	- 396.310	- 268.260	34.487
1800	33.818	63.997	38.621	45.677	- 395.788	- 260.740	31.658
1900	34.007	65.830	40.005	49.068	- 395.257	- 253.253	29.131
2000	34.185	67.579	41.340	52.478	- 394.716	- 245.796	26.859
2100	34.363	69.251	42.630	55.905	- 394.164	- 238.363	24.807
2200	34.541	70.854	43.877	59.350	- 393.605	- 230.959	22.944
2300	34.719	72.393	45.083	62.813	- 393.032	- 223.574	21.244
2400	34.897	73.875	46.252	66.294	- 392.452	- 216.217	19.689
2500	35.085	75.303	47.386	69.793	- 391.863	- 208.893	18.261
2600	35.273	76.683	48.486	73.311	- 391.261	- 201.583	16.945
2700	35.472	78.018	49.555	76.848	- 390.649	- 194.301	15.728
2800	35.682	79.311	50.595	80.406	- 528.844	- 185.379	14.469
2900	35.912	80.568	51.607	83.985	- 527.680	- 173.134	13.048
3000	36.153	81.789	52.593	37.588	- 526.501	- 160.925	11.723

Dec. 31, 1965; June 30, 1972; June 30, 1975

ALUMINUM OXIDE, GAMMA (γ-Al_2O_3). (CRYSTAL)

GFW = 101.9612
ΔHf_0° = [-393.1±1.5] kcal/mol
$\Delta Hf_{298.15}^\circ$ = -396.0±1.5 kcal/mol
ΔHm° = [18.77] kcal/mol

AL_2O_3

$S_{298.15}^\circ$ = [12.5±2] gibbs/mol
Tm = [2290] K

Heat of Formation

ΔHf° is calculated from that of α-Al_2O_3 (1) using ΔHr_{978}° = -5.3 kcal/mol for the irreversible process γ→α. Yokokawa and Kleppa (2) determined ΔHr° for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. This yields ΔHr_{298}° = -4.5 kcal/mol based on our adopted functions. DTA studies by Gani and McPherson (3) gave ΔHr°(γ→α) = -5.8±1.6 kcal/mol. Assuming T = ~1400 K, we derive ΔHr_{298}° = -4.4 kcal/mol which confirms the calorimetric result (2). Yamada et al. (4) used dynamic, adiabatic calorimetry to measure ΔHr_{773}° = 12.6±1.1 kcal/mol for $Al_2O_3 \cdot H_2O$ (c, boehmite) → Al_2O_3(γ) + H_2O(g). Using enthalpies from (4, 1) and ΔHf_{298}° (boehmite) = -472.0 kcal/mol (5), we derive ΔHr_{298}° = 17.54±1.3 kcal/mol and ΔHf_{298}° (γ-Al_2O_3) = -396.7±2 kcal/mol. This gives independent confirmation of ΔHf°.

We adopt ΔHf_{298}°(γ-Al_2O_3) = -396.0±1.5 kcal/mol and ΔHr_{298}°(γ→α) = -4.5 kcal/mol. These values derive (2) from the highest ignition temperature prior to the appearance of a more stable phase (κ- or α-Al_2O_3) in the sample. This standard state should involve maximum attainable crystal development and minimum residual water. γ-alumina shows much variability depending on its thermal history. Lower ignition temperatures gave values of ΔHr°(γ→α) more negative by as much as 2.5 kcal/mol (2). Other reported values of ΔHr°(γ→α), including -4.5 to -7.5 (3), -7.7 (6), -11.0 (7) and -7.8 (8) kcal/mol, tend to be skewed toward *more negative values. These values correspond to less stable samples, presumably with more residual water and less well* developed crystal structure. This is consistent with ΔHr_{298}° = -388±2 kcal/mol observed (4) for ρ'-Al_2O_3 which is nearly amorphous.

Heat Capacity and Entropy

Cp° is assumed to be 4.7% larger than that of α-Al_2O_3(1). Structural and related characteristics (9) suggest that Cp°(γ)>Cp°(κ) which in turn is ~2.2% larger (1, 4) than Cp°(α). Our estimate is derived from Marchidan et al. (10) who measured enthalpies (1003-1177 K) which are 4.7±0.3% larger than those of α-Al_2O_3. S° is estimated such that ΔGr°(γ→α)<0 at T≤2400 K. This is consistent with observed stability relationships (9, 2).

Marchidan et al. (10) measured enthalpy data (573-1177 K) for a sample designated only as TA-600 alumina. They attributed a transition at ~993 K to the irreversible process η→δ. Contemporary studies (11) from the same institution lead us to presume that the TA-600 sample retained a significant amount of water even above the transition. The "low-temperature" forms γ and η are difficult to distinguish (9); they retain more water (9, 11) than the "high-temperature" forms. This may explain the unusual enthalpy data attributed (10) to η-Al_2O_3; these deviate from α-Al_2O_3 by +12.4% at 573 to 620 K and then decrease linearly to +3.8% at 991 K. These data do not seem suitable for standard-state γ-Al_2O_3 having minimum water content and maximum crystal development. We adopt instead the constant deviation of +4.7% found at higher temperature.

The adopted entropy of 12.5±2 may be compared with the value ΔS°(α→γ) = 1.56 gibbs/mol estimated by Borer and Gunthard (12) for the "defect" spinel structure of γ-Al_2O_3. This yields S_{298}°(γ) = 13.7 or 14.3 gibbs/mol assuming Cp°(γ)/Cp°(α) = 1.00 or 1.047, respectively. The authors' assumption (12) concerning the structure of γ-Al_2O_3(9) is overly simplified.

Phase Data

The stable crystalline form is corundum (α-alumina). Gamma-alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied (9) due to their importance in adsorbents and catalysts. Lippens and Steggerda (9) summarized the classifications of metastable forms, their crystal structures and conditions of formation by dehydration. "Low-temperature" forms γ and η have similar X-ray diffraction patterns. Their nomenclature is confused in the literature. The term γ-Al_2O_3 has been applied to either form and as a generic term for all low temperature forms. γ and η are often poorly crystallized and difficult to distinguish (9). They retain various amounts of water (9, 11) depending on their thermal history. The low-temperature forms are obtained by dehydrating temperatures not exceeding 600°C and change irreversibly to "high-temperature" forms (δ, θ or κ) at 600° to 900°C (9, 11, 2).

Melting Data

The hypothetical melting point of metastable γ-phase is calculated as the temperature at which ΔGr°(γ→ℓ) = 0. ΔHm° is the corresponding difference in ΔHf°.

References

1. JANAF Thermochemical Tables: Al_2O_3(c, α), Al_2O_3(c, δ), Al_2O_3(c, κ) 6-30-75; H_2O(g) 3-31-61.
2. T. Yokokawa and O. J. Kleppa, J. Phys. Chem. 68, 3246 (1964).
3. M. S. J. Gani and R. McPherson, Thermochim. Acta 7, 251 (1973).
4. K. Yamada, T. Fukunaga, Y. Takahashi and T. Mukaibo, Denki Kagaku 41, 290 and 287 (1973).
5. U.S. Natl. Bur. Std. Tech. Note 270-3, 1968.
6. P. Gross, C. Hayman and R. H. Lewin, Fulmer Res. Inst. Rept. R.163/32/September 1968.
7. V. Kostomaroff and M. Rey, Silicates Ind. 28, 9 (1963).
8. W. A. Roth, Angew. Chem. 49, 198 (1936).
9. B. C. Lippens and J. J. Steggerda in "Physical and Chemical Aspects of Adsorbents and Catalysts," B. G. Linsen, Ed., Academic Press, New York, 1970, pp. 171-211.
10. D. I. *Marchidan, L. Pandele and A. Nicolescu, Rev. Roum. Chim.* 17, 1493 (1972).
11. V. Alevra, D. Ciomirtan and M. Ionescu, Rev. Roum. Chim. 17, 1379 (1972).
12. W. J. Borer and H. H. Gunthard, Helv. Chim. Acta 53, 1043 (1970).

ALUMINUM OXIDE, KAPPA (κ-Al_2O_3) Al_2O_3

(CRYSTAL) GFW=101.9612

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	19.300	12.800	12.800	.000	- 397.300	- 375.164	275.003
300	19.399	12.920	12.800	.036	- 397.306	- 375.027	273.207
400	23.470	19.109	13.617	2.197	- 397.409	- 367.576	200.834
500	25.924	24.632	15.279	4.676	- 397.288	- 360.128	157.412
600	27.491	29.506	17.252	7.353	- 397.062	- 352.717	128.477
700	28.561	33.829	19.317	10.158	- 396.794	- 345.346	107.822
800	29.345	37.696	21.377	13.055	- 396.528	- 338.017	92.342
900	29.962	41.189	23.388	16.021	- 396.307	- 330.716	80.309
1000	30.477	44.374	25.330	19.044	- 401.191	- 323.070	70.607
1100	30.926	47.300	27.196	22.114	- 400.897	- 315.274	62.639
1200	31.327	50.008	28.985	25.227	- 400.574	- 307.505	56.004
1300	31.690	52.530	30.700	28.379	- 400.224	- 299.762	50.395
1400	32.018	54.891	32.345	31.564	- 399.852	- 292.047	45.591
1500	32.314	57.110	33.923	34.781	- 399.460	- 284.362	41.432
1600	32.575	59.204	35.438	38.026	- 399.049	- 276.702	37.796
1700	32.806	61.186	36.895	41.295	- 398.620	- 269.068	34.591
1800	33.011	63.067	38.297	44.586	- 398.179	- 261.457	31.745
1900	33.195	64.857	39.648	47.897	- 397.729	- 253.875	29.202
2000	33.368	66.564	40.952	51.225	- 397.269	- 246.319	26.916
2100	33.542	68.196	42.210	54.570	- 396.799	- 238.783	24.850
2200	33.716	69.761	43.427	57.933	- 396.322	- 231.270	22.975
2300	33.890	71.263	44.605	61.313	- 395.832	- 223.775	21.263
2400	34.063	72.709	45.746	64.711	- 395.335	- 216.303	19.697
2500	34.247	74.103	46.853	68.126	- 394.830	- 208.860	18.259
2600	34.431	75.450	47.927	71.560	- 394.312	- 201.428	16.932
2700	34.625	76.753	48.971	75.013	- 393.784	- 194.022	15.705
2800	34.830	78.016	49.985	78.486	- 532.064	- 184.972	14.438
2900	35.055	79.242	50.973	81.980	- 530.986	- 172.596	13.007
3000	35.290	80.435	51.936	85.497	- 529.892	- 160.253	11.674

June 30, 1965

ALUMINUM OXIDE, KAPPA (*κ*-Al_2O_3) (*CRYSTAL*) Al_2O_3

GFW = 101.9612
$\Delta Hf°_0$ = [-394.4±1] kcal/mol
$\Delta Hf°_{298.15}$ = -397.3±1 kcal/mol
ΔHm° = [21.8] kcal/mol

$S°_{298.15}$ = [12.8±1] gibbs/mol
Tm = [2312] K

Heat of Formation

ΔHf° is calculated from that of α-Al_2O_3(1) using $\Delta Hr°_{978}$ = -3.6 kcal/mol for the irreversible process κ→α. This yields $\Delta Hr°_{298}$ = -3.2 kcal/mol based on our adopted functions. Yokokawa and Kleppa (2) determined ΔHr° for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. Yamada et al. (3) derived $\Delta Hf°_{298}$ = -397±1 kcal/mol from the same data.

Heat Capacity and Entropy

Cp° (380 to 1110 K) was measured by Takahashi et al. (4) using a dynamic, adiabatic calorimeter with an open-type container for the sample. Reproducibility of the data was reported to be within ±1.5% up to 1100 K. We represent the observed data by a Cp° curve which is 2.2% larger than that of α-Al_2O_3 (1). Deviations from the adopted curve exceed 1.0% for only 3 of the 39 points (4): i.e., -1.6% (400 K), +1.4% (993.8 K) and +1.3% (1070.8 K). Takahashi et al. (4) prepared their κ-Al_2O_3 by dehydration of tohdite ($Al_2O_3 \cdot 1/5H_2O$) at 840°C under a vacuum of 10^{-5} torr.

S° is selected arbitrarily so that ΔGr°(κ→α) = 0 near 2400 K. This is consistent with the view that κ-phase is unstable with respect to α-phase at all temperatures below Tm.

Phase Data

The stable crystalline form is corundum (α-alumina). Kappa-alumina is one of several structurally related, metastable forms. *These occur in "active alumina" and are much studied* (5) *due to their importance in adsorbents and catalysts. Lippens* and Steggerda (5) summarized the classifications of metastable forms, their crystal structures and conditions of formation by dehydration. Okumiya et al. (6) recently published an extensive study on the formation and structural relations of κ-Al_2O_3 and its precursors κ'-Al_2O_3 and tohdite. Kappa-alumina belongs to the "nearly anhydrous", high-temperature classification (5) based on its formation temperature of 900° to 1000°C (somewhat lower in vacuo). The irreversible transition κ→α is *thermally activated at* ∿1200°C (2, 5). *Thermochemical studies cited in this table presume that the samples of* κ-Al_2O_3 *were* essentially anhydrous.

Melting Data

The hypothetical melting point of metastable κ-phase is calculated as the temperature at which ΔGr°(κ→ℓ)=0. ΔHm° is the *corresponding difference in ΔHf°*.

References

1. JANAF Thermochemcal Tables: Al_2O_3(α) 6-30-75.
2. T. Yokokawa and O. J. Kleppa, J. Phys. Chem. 68, 3246 (1964).
3. K. Yamada, T. Fukunaga, Y. Takahashi and T. Mukaibo, Denki Kagaku 41, 290 (1973).
4. Y. Takahashi, K. Yamada, T. Fukunaga and T. Mukaibo, Denki Kagaku 41, 287 (1973).
5. B. C. Lippens and J. J. Steggerda in "Physical and Chemical Aspects of Adsorbents and Catalysts", B. G. Linsen, Ed., Academic Press, New York, 1970, pp. 171-211.
6. M. Okumiya, G. Yamaguchi, O. Yamada and S. Ono, Bull. Chem. Soc. Japan 44, 418 and 1567 (1971).

ALUMINUM OXIDE (AL_2O_3) AL_2O_3

(LIQUID) GFW=101.9612

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	18.885	18.541	18.541	.000	- 383.710	- 363.286	266.295
300	18.981	18.658	18.541	.035	- 383.716	- 363.159	264.561
400	22.965	24.714	19.340	2.150	- 383.866	- 356.275	194.659
500	25.366	30.118	20.966	4.576	- 383.799	- 349.382	152.715
600	26.899	34.887	22.897	7.194	- 383.631	- 342.514	124.761
700	27.946	39.117	24.918	9.939	- 383.422	- 335.676	104.803
800	28.713	42.901	26.933	12.774	- 383.219	- 328.871	89.843
900	29.317	46.319	28.901	15.677	- 383.061	- 322.087	78.213
1000	29.821	49.435	30.801	18.634	- 388.010	- 314.951	68.832
1100	30.260	52.298	32.626	21.638	- 387.782	- 307.658	61.126
1200	30.653	54.948	34.377	24.684	- 387.526	- 300.385	54.708
1300	31.008	57.416	36.056	27.768	- 387.245	- 293.134	49.280
1400	31.329	59.726	37.665	30.885	- 386.941	- 285.905	44.632
1500	31.618	61.897	39.209	34.032	- 386.618	- 278.701	40.607
1600	31.874	63.946	40.691	37.207	- 386.277	- 271.517	37.087
1700	46.000	66.735	42.142	41.807	- 384.518	- 264.398	33.991
1800	46.000	69.364	43.582	46.407	- 382.768	- 257.380	31.250
1900	46.000	71.851	45.005	51.007	- 381.028	- 250.463	28.810
2000	46.000	74.211	46.407	55.607	- 379.296	- 243.639	26.624
2100	46.000	76.455	47.785	60.207	- 377.572	- 236.898	24.654
2200	46.000	78.595	49.137	64.807	- 375.858	- 230.241	22.872
2300	46.000	80.640	50.462	69.407	- 374.148	- 223.656	21.252
2400	46.000	82.597	51.761	74.007	- 372.449	- 217.148	19.774
2500	46.000	84.475	53.032	78.607	- 370.759	- 210.719	18.421
2600	46.000	86.279	54.276	83.207	- 369.075	- 204.347	17.177
2700	46.000	88.015	55.494	87.807	- 367.400	- 198.046	16.031
2800	46.000	89.688	56.686	92.407	- 504.552	- 190.142	14.841
2900	46.000	91.302	57.852	97.007	- 502.368	- 178.953	13.486
3000	46.000	92.862	58.993	101.607	- 500.192	- 167.835	12.227
3100	46.000	94.370	60.110	106.207	- 498.021	- 156.791	11.054
3200	46.000	95.831	61.203	110.807	- 495.858	- 145.819	9.959
3300	46.000	97.246	62.274	115.407	- 493.701	- 134.914	8.935
3400	46.000	98.619	63.323	120.007	- 491.554	- 124.078	7.976
3500	46.000	99.953	64.351	124.607	- 489.409	- 113.303	7.075
3600	46.000	101.249	65.358	129.207	- 487.272	- 102.580	6.227
3700	46.000	102.509	66.345	133.807	- 485.141	- 91.927	5.430
3800	46.000	103.736	67.313	138.407	- 483.016	- 81.327	4.677
3900	46.000	104.931	68.262	143.007	- 480.894	- 70.782	3.967
4000	46.000	106.095	69.193	147.607	- 478.782	- 60.299	3.295

Dec. 31, 1960; Sept. 30, 1961; March 31, 1964;
June 30, 1972; June 30, 1975

ALUMINUM OXIDE (Al_2O_3) (LIQUID) GFW = 101.9612

$S°_{298.15}$ = 18.541 gibbs/mol
Tm = 2327 ± 6 K

$\Delta Hf°_{298.15}$ = -383.710 kcal/mol AL_2O_3
ΔHm° = 26.55 ± 1.0 kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by adding ΔHm° and the difference in $(H°_{2327}-H°_{298.15})$ for crystal and liquid.

Heat Capacity and Entropy

Enthalpy data for the liquid include those of Shpil'rain et al. (1, 2, 2326 to 3104 K), Sheindlin et al. (3, 2350-2800 K), Kantor et al. (4, 5, 2337 to 2480 K), and approximate values of West and Ishihara (6, 2345 to 2495 K). The latest study (1, 2) is the most extensive. It satisfactorily resolves the discrepancy in Cp° which was reported earlier to be 47.7 (3) or 34.6 (4) gibbs/mol. The new data (1, 2) yield 46.0 gibbs/mol, assuming Cp° is independent of temperature. Although Shpil'rain et al. (1, 2) derived a Cp° which decreases linearly with increasing temperature, this does not significantly improve the fit of the enthalpy data. The apparent value of the temperature coefficient of Cp° is very data dependent; it changes sign on omission of the point at 2326 K (2323 K, IPTS-48).

We adopt Cp° = 46.0 gibbs/mol. Compared to our adopted functions, the enthalpy data deviate by <±1.0% (1, 2), -0.9 to -0.1% (3, equation), +2.4 to +0.2% (4, 5) and +2 to +5% (6). We assume a glass transition at 1600 K, below which Cp° is taken to be the same as for Al_2O_3(c, α). The entropy is calculated in a manner analogous with ΔHf°.

Melting Data

Tm = 2054±6°C was recommended by Schneider (7) as the result of a cooperative measurement of the melting point by nine groups in seven countries. We adopt this value. It is confirmed by several recent studies (e.g. 8-10); however, Nelson et al. (11) suggested the possibility that Tm may be somewhat different in an oxygen atmosphere than in inert gases or vacuum.

ΔHm° is the difference at Tm between the adopted enthalpy fits of Al_2O_3(ℓ) and Al_2O_3(α). Reported calorimetric values of ΔHm° include 25.7±1.3 (1, 2), 25.9 (3), and 28.3±0.6 (4, 5) kcal/mol.

Sublimation and Vaporization Data

Vaporization of Al_2O_3(α) and Al_2O_3(ℓ) has been studied by several methods (12-18). Additional references are cited by Farber et al. (14) and Burns (16). Vaporization is considered to be congruent but the vapor composition is complex (14, 16). Atomic species predominate below Tm, but molecular species (e.g., AlO and Al_2O) become increasingly important at higher temperatures. For the crystal the average vaporization coefficient is α ≤ 0.3 (12, 14-16).

References

1. E. E. Shpil'rain, D. N. Kagan and L. S. Barkhatov, High Temp.-High Pressures 4, 605 (1972).
2. L. S. Barkhatov, D. N. Kagan, A. F. Tsytsarkin, E. E. Shpil'rain and K. A. Yakimovich, High Temperature (USSR) 11, 1063 (1973).
3. A. E. Sheindlin, V. Ya. Chekhovskoi and V. A. Petrov, Inzh-Fiz. Zh., Akad. Nauk Belorussk. SSR 7 (5), 63(1964); High Temp.-High Pressures 2, 1 (1970).
4. P. B. Kantor, L. S. Lazareva, V. V. Kandyba and E. N. Fomichev, Ukr. Fiz. Zh. 7, 205 (1962).
5. E. N. Fomichev, V. P. Bondarenko and V. V. Kandyba, High Temp.-High Pressures 5, 1 (1973).
6. E. D. West and S. Ishihara, U. S. Natl. Bur. Std. Rept. 9028, 71, Jan., 1966.
7. S. J. Schneider, Pure Appl. Chem. 21, 115 (1970).
8. E. N. Fomichev, P. B. Kantor and V. V. Kandyba, Heat Transfer-Sov. Res. 5 (3), 176 (1973).
9. E. E. Shpil'rain, K. A. Yakimovich and A. F. Tsytsarkin, High Temp.-High Pressures 5, 191 (1973).
10. T. Sata and T. Takahashi, Yogyo Kyokai Shi 79, 70 (1971).
11. L. S. Nelson, N. L. Richardson, K. Keil and S. R. Skaggs, High Temp. Sci. 5, 138 (1973).
12. M. Peleg and C. B. Alcock, High Temp. Sci. 6, 52 (1974); Trans Brit. Ceram. Soc. 66, 217 (1967); Bull. Soc. Fr. Ceram., No. 72, 25 (1966).
13. E. M. Akulenok, Yu. K. Danileiko et al., Kristallografiya 18, 1044 (1973).
14. M. Farber, R. D. Srivastava and O. M. Uy, J. Chem. Soc., Faraday Trans. I 68, 249 (1972); Proc. Symp. Thermophys. Prop., 5th, 483 (1970).
15. T. Sasamoto and T. Sata, Kogyo Kagaku Zasshi 74, 832 (1971).
16. R. P. Burns et al., J. Chem. Phys. 44, 3307 (1966); 40, 2739 (1964); 32, 1366 (1960).
17. W. Kroenert and A. Boehm, Glas-Email-Keramo-Tech. 23, 319 (1972).
18. H. von Wartenberg, Z. Anorg. Allgem. Chem. 269, 76 (1952); 270, 328 (1952).

BORON HYDRIDE OXIDE (HBO) BHO

(IDEAL GAS) GFW=27.8174

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.188	- 47.247	- 47.247	INFINITE
100	6.964	40.309	55.249	- 1.494	- 47.285	- 48.019	104.945
200	7.469	45.240	49.139	- .780	- 47.300	- 48.757	53.279
298	8.427	48.400	48.400	.000	- 47.400	- 49.454	36.251
300	8.445	48.452	48.400	.016	- 47.402	- 49.468	36.037
400	9.303	51.003	48.742	.905	- 47.538	- 50.136	27.395
500	10.003	53.157	49.415	1.871	- 47.700	- 50.767	22.190
600	10.598	55.034	50.198	2.902	- 47.871	- 51.365	18.710
700	11.116	56.708	51.011	3.988	- 48.041	- 51.933	16.214
800	11.570	58.223	51.819	5.123	- 48.203	- 52.479	14.337
900	11.965	59.609	52.609	6.300	- 48.355	- 53.004	12.871
1000	12.307	60.887	53.373	7.514	- 48.499	- 53.512	11.695
1100	12.603	62.075	54.111	8.760	- 48.639	- 54.007	10.730
1200	12.859	63.183	54.821	10.033	- 48.776	- 54.488	9.924
1300	13.079	64.221	55.505	11.330	- 48.913	- 54.960	9.240
1400	13.269	65.197	56.163	12.648	- 49.051	- 55.419	8.651
1500	13.434	66.118	56.796	13.983	- 49.196	- 55.869	8.140
1600	13.577	66.990	57.406	15.334	- 49.345	- 56.309	7.691
1700	13.701	67.817	57.994	16.698	- 49.501	- 56.739	7.294
1800	13.810	68.603	58.562	18.074	- 49.663	- 57.161	6.940
1900	13.906	69.353	59.110	19.460	- 49.831	- 57.573	6.622
2000	13.990	70.068	59.641	20.855	- 50.002	- 57.976	6.335
2100	14.064	70.752	60.154	22.257	- 50.179	- 58.370	6.075
2200	14.130	71.408	60.650	23.667	- 50.361	- 58.756	5.837
2300	14.189	72.038	61.132	25.083	- 50.548	- 59.134	5.619
2400	14.242	72.643	61.599	26.505	- 50.741	- 59.501	5.418
2500	14.289	73.225	62.052	27.931	- 56.327	- 59.755	5.224
2600	14.332	73.786	62.493	29.363	- 56.521	- 59.888	5.034
2700	14.370	74.328	62.921	30.798	- 56.719	- 60.012	4.858
2800	14.405	74.851	63.338	32.236	- 56.918	- 60.133	4.694
2900	14.437	75.357	63.744	33.679	- 57.119	- 60.240	4.540
3000	14.466	75.847	64.139	35.124	- 57.322	- 60.347	4.396
3100	14.492	76.322	64.525	36.572	- 57.527	- 60.445	4.261
3200	14.517	76.782	64.900	38.022	- 57.734	- 60.536	4.134
3300	14.540	77.229	65.267	39.475	- 57.944	- 60.618	4.015
3400	14.561	77.664	65.626	40.930	- 58.156	- 60.697	3.902
3500	14.581	78.086	65.976	42.387	- 58.370	- 60.770	3.795
3600	14.600	78.497	66.318	43.846	- 58.587	- 60.834	3.693
3700	14.619	78.898	66.652	45.307	- 58.806	- 60.893	3.597
3800	14.636	79.288	66.980	46.770	- 59.027	- 60.945	3.505
3900	14.654	79.668	67.330	48.234	- 59.251	- 60.996	3.418
4000	14.671	80.039	67.614	49.701	- 180.655	- 58.892	3.218
4100	14.688	80.402	67.922	51.169	- 180.652	- 55.849	2.977
4200	14.706	80.756	68.223	52.638	- 180.649	- 52.801	2.748
4300	14.724	81.102	68.518	54.110	- 180.649	- 49.758	2.529
4400	14.743	81.441	68.808	55.583	- 180.652	- 46.715	2.320
4500	14.762	81.772	69.093	57.058	- 180.656	- 43.673	2.121
4600	14.783	82.097	69.372	58.536	- 180.661	- 40.626	1.930
4700	14.804	82.415	69.646	60.015	- 180.669	- 37.580	1.747
4800	14.827	82.727	69.915	61.496	- 180.677	- 34.534	1.572
4900	14.851	83.033	70.180	62.980	- 180.667	- 31.495	1.405
5000	14.877	83.333	70.440	64.467	- 180.698	- 28.449	1.244
5100	14.904	83.628	70.696	65.956	- 180.711	- 25.401	1.089
5200	14.934	83.918	70.947	67.448	- 180.723	- 22.359	.940
5300	14.965	84.203	71.195	68.943	- 180.735	- 19.311	.796
5400	14.998	84.483	71.438	70.441	- 180.750	- 16.269	.658
5500	15.034	84.758	71.678	71.942	- 180.762	- 13.217	.525
5600	15.071	85.029	71.914	73.447	- 180.777	- 10.178	.397
5700	15.111	85.297	72.146	74.957	- 180.790	- 7.129	.273
5800	15.153	85.560	72.375	76.470	- 180.804	- 4.082	.154
5900	15.197	85.819	72.601	77.987	- 180.816	- 1.034	.038
6000	15.244	86.075	72.823	79.509	- 180.827	2.014	.073

Dec. 31, 1960; Dec. 31, 1964; Dec. 31, 1975

BORON HYDRIDE OXIDE (HBO) (IDEAL GAS) GFW = 27.8174 BHO

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = [48.4 ± 0.5] gibbs/mol

Ground State Configuration [$^1\Sigma^+$]

ΔHf°_0 = −47.2 ± 3.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −47.4 ± 3.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[1]	[35000]	[6]
[30000]	[3]	[40000]	[3]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[2802](1)
757 (2)
1822 (1)

Bond Distances: H-B = [1.17] Å
H-O = [1.19] Å

Bond Angle: H-B-O = [180°] σ = 1

Rotational Constant: B_0 = [1.34111]cm^{-1}

Heat of Formation

We calculate ΔHf° from a selected value (−47.9$_5$ kcal/mol) for the heat of formation of DBO(g) by combining this value *with zero-point energies and relative enthalpies ($H^\circ_{298}-E^\circ_0$) for HBO, D_2, DBO and H_2. All ancillary data are from JANAF* (1) unless otherwise indicated. The zero-point energies are estimated as one-half the sum of the vibrational frequencies. The vibrational frequencies for DBO are taken from the matrix-isolation results of Lory and Porter (2). We assume that DBO and HBO have similar structures, and we calculate the relative enthalpy for DBO as ($H^\circ_{298}-E^\circ_0$) = −2.27 kcal/mol. Data for D_2 are taken from a NBS compilation (3).

The selected value of ΔHf° for DBO is obtained from the results of a mass-spectrometric study (4, 5) of the reaction of $D_2(g)$ with $B_2O_3(\ell)$. The thermal results which were initially reported (4) for a study of the reactions (A) $D_2(g) + B_2O_3(\ell)$ = DBO(g) + DOBO(g) and (B) $D_2O(g) + B_2O_3(\ell)$ = 2DOBO(g) are unreliable due to erroneous equilibrium constants. Second-law heats for these two reactions have been reported in revised form in a later publication (5). Apparently, no attempt was made in this study to perform calibration experiments which would have allowed the ion intensity data to be converted to absolute partial pressures; thus, precluding a third law analysis. We combine their second-law values (5) for ΔHr at 1296 K for reactions (A) and (B) to give ΔHr_{1296} = 135±4 kcal/mol for the process $2D_2(g) + B_2O_3(\ell) = 2DBO(g) + D_2O(g)$. Corrected to 298.15 K this value is 144.1 kcal/mol which leads to ΔHf°_{298}(DBO,g) = −47.95±2.3 kcal/mol with $\Delta Hf^\circ_{298}(D_2O,g)$ = −59.561±0.02 kcal/mol (3) and $\Delta Hf^\circ_{298}(B_2O_3,\ell)$ = −299.56± 0.6 kcal/mol (1).

Comparison of values for the stretching force constants in HBO, BH_3(6), BO, and B_2O_2 (1) suggests a similarity in the bonds of these molecules. Using D°_{298}(H-B) = $\bar{D}^\circ_{298}(BH_3)$ = 87.9 kcal/mol and D°_{298}(B=O) = (D°_{298}(BO) + $\bar{D}^\circ_{298}(B_2O_2)$)/2=202 kcal/mol (1), we calculate a heat of atomization for HBO of 289.9 kcal/mol. This corresponds to ΔHf°_{298}(HBO,g) = −45.4 kcal/mol which lends support to the experimental measurements of Farber et al. (4, 5). Previous JANAF estimates (7) of ΔHf° via bond energy calculations led to results which were too positive due to the use of an inaccurate value (168 kcal/mol) for D° of B=O. A recent ab-initio LCAO-MO-SCF investigation (8) of HBO yields ΔHa = 232.2 kcal/mol; however, this value does not include a contribution from correlation effects (9, 16) and therefore is too low.

Heat Capacity and Entropy

The B=O stretching (ν_3) and bending (ν_2) frequencies for the isotopes $H^{11}BO$ and $H^{10}BO$ have been measured in a low-temperature argon matrix (2). These values are corrected for the natural isotopic abundances of boron. The H-B stretching frequency (ν_1) is calculated from an estimated force constant by the valence force method (10). The stretching force constant K_1 is estimated from the ratio $K_1/K_D/\ell_1\ell_2$ = 17.47 which is the value we calculate for DBO from the measured frequencies of Lory and Porter (2). These workers (2) used a slightly different value for K_1 and obtained a value for ν_1 which is roughly 50 cm^{-1} higher than our result. We believe our estimate is probably more nearly correct, since it agrees much better with the H-B stretching frequency (2808 cm^{-1}) observed for BH_3 (6). MO calculations show that the pattern of valence orbitals for HBO is similar to that in HCN (8) and HCP (11, 16). The ordering is substantiated by the photoelectron spectra (12) which have been observed for HCN and HCP. This suggests that the ground and excited electronic states for these isoelectronic molecules are quite similar. We assume that the ground state configuration is $^1\Sigma^+$ by analogy with those for HCN and HCP (1). We also include three triplet levels which are estimated from those observed for HCP (1) and predicted for HCN (13).

There have been no measurements reported for HBO which provide direct experimental information on its structure. However, the millimeter-wave spectra of the related species HBS (14) have been observed. These results show that this molecule is linear and has a B=S bond length which is 0.01 Å less than that for BS (1). We assume a similar decrease in r_e(B=O) for the HBO-BO pair, and we obtain r_e(HB=O) = 1.19 Å with r_e(B=O) = 1.20 Å (1). The H-B bond length is assumed the same as that for HBS (14). Ab-initio calculations (8) of bond lengths for HBO by an optimization procedure predict values only slightly lower (∼0.01 Å) than our estimates. We note that bond lengths computed by this procedure are normally slightly lower (∼0.005 Å) than the true values as indicated by the results for HCP (16) and HBS (17). By analogy with HBS (14), we assume HBO to be linear. This assumption is in agreement with predictions from the Walsh diagram (15) for HAB molecules with ten valence electrons. Indirect evidence available from product rule calculations (2) also tend to support a linear configuration. The moment of inertia is 2.0871 x 10^{-39} g cm^2.

References

1. JANAF Thermochemical Tables: $H_2(g)$, 3-31-61; $B_2O_3(\ell)$, 6-30-71; BO(g), 6-30-68; $B_2O_2(g)$ and $BH_3(g)$, 12-31-64; HCP(g) and HCN(g), 12-31-69; BS(g), 6-30-72.
2. E. R. Lory and R. F. Porter, J. Amer. Chem. Soc. 93, 6301 (1971).
3. U. S. Natl. Bur. Std. Report No. 10904, July, 1972.
4. M. Farber, M. A. Greenbaum, and M. A. Frisch, Rocket Power, Inc., Report No. AFRPL-TR-66-220, Contract AF 04-(611)-10929, September, 1966.
5. M. Farber and M. A. Frisch, Proc. First Intern. Conf. Calorimetry and Thermodynamics, Warsaw, August-September, 1969.
6. A. Kaldor and R. F. Porter, J. Amer. Chem. Soc. 93, 2140 (1971).
7. JANAF Thermochemical Tables, 2nd Edition, NSRDS-NBS-37, June, 1971.
8. C. Thomson and B. J. Wishart, Theoret. Chim. Acta, 35, 267 (1974).
9. C. Thomson, J. Chem. Phys. 58, 216 (1973).
10. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, Inc., New York, 1945.
11. J. Robert, H. Marsmann, I. Absar, and J. R. VanWazer, J. Amer. Chem. Soc. 93, 3320 (1971).
12. D. C. Frost, S. T. Lee, and C. A. McDowell, Chem. Phys. Letters, 23, 472 (1973).
13. G. M. Schwenzer, S. V. O'Neil, H. F. Schaefer, C. P. Baskin, and C. F. Bender, J. Chem. Phys. 60, 2787 (1974).
14. E. F. Pearson and R. V. McCormick, J. Chem. Phys. 58, 1619 (1973).
15. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
16. C. Thomson, Theoret. Chim. Acta, 35, 237 (1974).
17. C. Thomson, Chem. Phys. Letters, 25, 59 (1974).

Boron Hydride Oxide Unipos. Ion (HBO^+) BHO^+
(Ideal Gas) GFW=27.8169

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.304	51.255	51.255	.000	283.830	279.437	-204.833
300	8.322	51.307	51.256	.015	283.836	279.409	-203.549
400	9.250	53.831	51.593	.895	284.189	277.880	-151.826
500	10.041	55.982	52.261	1.861	284.523	276.264	-120.755
600	10.711	57.874	53.042	2.899	284.856	274.561	-100.016
700	11.282	59.569	53.855	4.000	285.197	272.842	-85.185
800	11.767	61.108	54.667	5.153	285.550	271.052	-74.048
900	12.181	62.519	55.462	6.351	285.916	269.218	-65.375
1000	12.534	63.821	56.234	7.587	286.291	267.344	-58.428
1100	12.837	65.030	56.979	8.856	286.671	265.430	-52.736
1200	13.099	66.159	57.698	10.153	287.054	263.483	-47.987
1300	13.328	67.216	58.390	11.474	287.438	261.502	-43.962
1400	13.529	68.211	59.056	12.818	287.822	259.494	-40.509
1500	13.707	69.151	59.698	14.179	288.201	257.456	-37.511
1600	13.865	70.041	60.317	15.558	288.576	255.394	-34.885
1700	14.007	70.886	60.914	16.952	288.947	253.309	-32.565
1800	14.134	71.690	61.490	18.359	289.313	251.202	-30.500
1900	14.249	72.457	62.048	19.778	289.676	249.075	-28.650
2000	14.352	73.191	62.587	21.208	290.036	246.929	-26.983
2100	14.446	73.893	63.108	22.648	290.393	244.765	-25.473
2200	14.530	74.567	63.614	24.097	290.747	242.583	-24.098
2300	14.606	75.215	64.104	25.554	291.098	240.386	-22.842
2400	14.675	75.838	64.580	27.018	291.445	238.176	-21.689
2500	14.737	76.438	65.043	28.489	286.400	236.056	-20.636
2600	14.793	77.017	65.492	29.965	286.746	234.035	-19.672
2700	14.843	77.577	65.930	31.447	287.093	232.003	-18.779
2800	14.888	78.117	66.355	32.934	287.438	229.955	-17.949
2900	14.929	78.641	66.770	34.425	287.783	227.900	-17.175
3000	14.965	79.147	67.174	35.919	288.126	225.827	-16.451
3100	14.997	79.638	67.568	37.417	288.468	223.742	-15.774
3200	15.026	80.115	67.953	38.919	288.808	221.650	-15.138
3300	15.052	80.578	68.329	40.423	289.147	219.547	-14.540
3400	15.075	81.028	68.695	41.929	289.483	217.433	-13.976
3500	15.095	81.465	69.054	43.437	289.817	215.307	-13.444
3600	15.113	81.890	69.405	44.948	290.148	213.175	-12.941
3700	15.129	82.305	69.748	46.460	290.476	211.032	-12.465
3800	15.142	82.708	70.084	47.974	290.804	208.883	-12.014
3900	15.154	83.102	70.412	49.488	291.127	206.720	-11.584
4000	15.165	83.486	70.734	51.004	170.268	206.696	-11.293
4100	15.174	83.860	71.050	52.521	170.818	207.600	-11.066
4200	15.181	84.226	71.359	54.039	171.366	208.495	-10.849
4300	15.188	84.583	71.663	55.558	171.910	209.371	-10.641
4400	15.193	84.932	71.960	57.077	172.450	210.235	-10.442
4500	15.198	85.274	72.252	58.596	172.986	211.085	-10.252
4600	15.201	85.608	72.539	60.116	173.521	211.929	-10.069
4700	15.204	85.935	72.821	61.636	174.051	212.760	-9.893
4800	15.206	86.255	73.097	63.157	174.578	213.579	-9.725
4900	15.208	86.569	73.369	64.678	175.102	214.382	-9.562
5000	15.209	86.876	73.636	66.198	175.622	215.177	-9.405
5100	15.209	87.177	73.899	67.719	176.138	215.966	-9.255
5200	15.210	87.472	74.157	69.240	176.652	216.740	-9.109
5300	15.209	87.762	74.411	70.761	177.162	217.508	-8.969
5400	15.209	88.046	74.661	72.282	177.668	218.260	-8.833
5500	15.208	88.325	74.907	73.803	178.170	219.014	-8.703
5600	15.207	88.599	75.149	75.324	178.669	219.745	-8.576
5700	15.206	88.869	75.387	76.844	179.163	220.476	-8.454
5800	15.204	89.133	75.622	78.365	179.654	221.197	-8.335
5900	15.203	89.393	75.853	79.885	180.142	221.910	-8.220
6000	15.201	89.648	76.081	81.405	180.625	222.614	-8.109

June 30, 1968; Dec. 31, 1975

BORON HYDRIDE OXIDE UNIPOSITIVE ION (HBO^+) (IDEAL GAS) GFW = 27.8169

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [51.26 ± 1.5] gibbs/mol

ΔHf°_0 = [282.6 ± 12.0] kcal/mol BHO^+

$\Delta Hf^\circ_{298.15}$ = [283.8 ± 12.0] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Pi$	0	[4]
$A^2\Sigma^+$	[6000]	[2]
$B^2\Sigma^+$	[40000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[2559](1)
[801](2)
[1617](1)

Bond Distances: H-B = [1.19] Å B-O = [1.25] Å

Bond Angle: H-B-O = [180]° σ = 1

Rotational Constant: B_o = [1.22858] cm^{-1}

Heat of Formation

The HBO^+ ion has been detected mass spectrometrically by Sholette and Porter (1) and Farber and Frisch (2). However, no appearance potential data have been reported for the ion. Kroto et al. (3) recently attempted to measure the photoelectron spectrum of HBO by passing water vapor over heated boron. The spectrum showed no bands which could be definitely assigned to HBO monomer. Unfortunately, the region of their spectrum (∿14-15 eV) where the first photoelectron band of HBO would be expected to lie shows a broad band which also appeared in the spectrum of HBS above 1150°C. Kroto et al. (4) have assigned this band to diborane. We believe the HBO band may well be hidden under this broad band.

We employ Koopmans' theorem (4) to obtain the ionization potential (IP) of HBO as 14.3 eV from the one electron orbital energies reported by Thomson and Wishart (5). A comparison of Koopmans' theorem IP's for the related species HBS (6), HCN (5), and HCP (7) with experimental values (8, 9) shows that the theoretical calculations correctly predict these ionization potentials to within about ±0.4 eV. We adopt $\Delta Hr^\circ = 329.7_6 \pm 9$ kcal/mol for the ionization process $HBO(g) + e^- = HBO^+(g) + 2e^-$ at 0 K, and we obtain $\Delta Hf^\circ_0(HBO^+,g) = 282.5 \pm 12.0$ kcal/mol when the former value is combined with $\Delta Hf^\circ_0(HBO,g) = -47.2 \pm 3.0$ kcal/mol (8). ΔHf° at 298.15 K is 283.8±12.0 kcal/mol.

Heat Capacity and Entropy

Extensive ab initio MO calculations (5) reported for HBO show that the highest occupied orbital is of Π-symmetry and is localized mainly on the oxygen atom. The Walsh diagram (10) for HAB molecules predicts that this orbital is bonding. We would expect therefore that the ion is less strongly bound than the parent molecule. For HCN which has the same orbital ordering as HBO (5), ionization (11) occurs with a 2.2% increase in the H-C bond length and a 4.7% increase in the C≡N bond length. We assume a similar increase in the bond lengths of HBO (8) upon loss of the bonding electron. A linear configuration is assumed by analogy with that for HBS^+ (8). This assumption is supported by predictions from the Walsh diagram (10). The moment of inertia is 2.2783×10^{-39} g cm^2. The enthalpy between 0 K and 298.15 K is -2.172 kcal/mol.

All vibrational frequencies are calculated from estimated force constants by a valence force method (12). The force constants are estimated from those for HBO (8) by comparison with the changes in the force constants for HCN (8) produced on ionization (9). The electronic states and levels are estimated from those observed for isoelectronic ions HBS^+ (8), HCN^+, and HCP^+ (9). We estimate the uncertainties in our calculated frequencies as ±50 cm^{-1} which introduces an error of only about ±0.1 gibbs/mol in the value of S°_{298}. The uncertainty in the electronic levels contribute the majority of the error in the entropy. We predict that the energy separation of the $^2\Pi$-$^2\Sigma$ states is small. Thus, it is possible that the ground state is $^2\Sigma$ as is the case for the isoelectronic ions CO^+ and N_2^+ (13). If the ground state is $^2\Sigma$, then our entropies should be decreased by roughly 1.5 gibbs/mol at all temperatures above 298.15 K. The enthalpy is much more certain than the entropy. Below 2000 K the uncertainty in our relative enthalpies probably does not exceed a few calories. The uncertainty increases at higher temperatures and is about 1.0 kcal/mol at 4000 K. All excited states are expected to be linear as observed for HBS^+ (3).

References

1. W. P. Sholette and R. F. Porter, J. Phys. Chem. 67, 177 (1963).
2. M. Farber and M. A. Frisch, Proc. 1st Intern. Conf. Calorimetry and Thermodynamics, Warsaw, August-September, 1969.
3. H. W. Kroto, R. J. Suffolk, and N. P. C. Westwood, Chem. Phys. Letters, 22, 495 (1973).
4. T. Koopmans, Physica, 1, 104 (1934).
5. C. Thomson and B. J. Wishart, Theoret. Chim. Acta, 35, 267 (1974).
6. C. Thomson, Chem. Phys. Letters, 25, 59 (1974).
7. C. Thomson, Theoret. Chim. Acta, 35, 237 (1974).
8. JANAF Thermochemical Tables: HBS(g), HBO(g), and HBS^+(g), 12-31-75; HCN(g), 12-31-69.
9. D. C. Frost, S. T. Lee, and C. A. McDowell, Chem. Phys. Letters, 23, 472 (1973).
10. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
11. S. P. So and W. G. Richards, J. Chem. Soc. Faraday Trans. II 71, 62 (1975).
12. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, Inc., New York, 1962.
13. B. Rosen, ed., "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, New York, 1970.

BORON HYDRIDE OXIDE UNINEG. ION (HBO^-) BHO^-
(IDEAL GAS) GFW=27.8179

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	8.413	54.241	54.241	.000	-58.430	-60.739	44.523
300	8.423	54.293	54.241	.016	-58.441	-60.753	44.259
400	9.036	56.797	54.579	.887	-59.091	-61.427	33.562
500	9.706	58.885	55.236	1.825	-59.779	-61.933	27.071
600	10.334	60.712	56.000	2.827	-60.476	-62.298	22.692
700	10.882	62.347	56.792	3.889	-61.166	-62.546	19.526
800	11.342	63.831	57.580	5.001	-61.848	-62.697	17.128
900	11.721	65.190	58.351	6.154	-62.521	-62.763	15.241
1000	12.033	66.441	59.099	7.343	-63.187	-62.753	13.715
1100	12.289	67.600	59.819	8.559	-63.854	-62.679	12.453
1200	12.501	68.679	60.513	9.799	-64.520	-62.541	11.390
1300	12.678	69.687	61.181	11.058	-65.193	-62.350	10.482
1400	12.827	70.632	61.822	12.333	-65.870	-62.105	9.695
1500	12.955	71.521	62.440	13.623	-66.557	-61.813	9.006
1600	13.067	72.361	63.034	14.924	-67.253	-61.473	8.397
1700	13.165	73.156	63.606	16.236	-67.957	-61.090	7.854
1800	13.254	73.911	64.158	17.557	-68.671	-60.667	7.366
1900	13.336	74.630	64.690	18.886	-69.392	-60.203	6.925
2000	13.412	75.316	65.204	20.224	-70.118	-59.700	6.524
2100	13.483	75.972	65.702	21.568	-70.849	-59.160	6.157
2200	13.551	76.601	66.183	22.920	-71.586	-58.586	5.820
2300	13.616	77.205	66.649	24.278	-72.328	-57.980	5.509
2400	13.678	77.786	67.101	25.643	-73.074	-57.338	5.221
2500	13.739	78.345	67.540	27.014	-79.213	-56.561	4.945
2600	13.797	78.685	67.966	28.391	-79.958	-55.638	4.677
2700	13.854	79.407	68.380	29.773	-80.705	-54.688	4.427
2800	13.910	79.912	68.783	31.162	-81.452	-53.713	4.192
2900	13.963	80.401	69.175	32.555	-82.198	-52.705	3.972
3000	14.015	80.875	69.557	33.954	-82.945	-51.678	3.765
3100	14.065	81.336	69.930	35.358	-83.689	-50.624	3.569
3200	14.113	81.783	70.293	36.767	-84.435	-49.545	3.384
3300	14.159	82.218	70.648	38.181	-85.181	-48.442	3.208
3400	14.203	82.641	70.994	39.599	-85.927	-47.318	3.042
3500	14.245	83.054	71.333	41.021	-86.673	-46.174	2.883
3600	14.285	83.455	71.664	42.448	-87.418	-45.004	2.732
3700	14.323	83.847	71.988	43.878	-88.165	-43.815	2.588
3800	14.359	84.230	72.305	45.313	-88.911	-42.605	2.450
3900	14.393	84.603	72.616	46.750	-89.659	-41.360	2.319
4000	14.425	84.968	72.920	48.191	-211.585	-37.987	2.075
4100	14.455	85.325	73.218	49.635	-212.102	-33.641	1.793
4200	14.483	85.673	73.511	51.082	-212.619	-29.278	1.524
4300	14.509	86.014	73.798	52.532	-213.138	-24.908	1.266
4400	14.533	86.348	74.079	53.984	-213.659	-20.527	1.020
4500	14.556	86.675	74.355	55.438	-214.180	-16.132	.783
4600	14.576	86.995	74.627	56.895	-214.703	-11.722	.557
4700	14.595	87.309	74.893	58.354	-215.228	-7.303	.340
4800	14.612	87.616	75.155	59.814	-215.755	-2.873	.131
4900	14.628	87.918	75.413	61.276	-216.284	1.562	-.070
5000	14.642	88.214	75.666	62.739	-216.813	6.015	-.263
5100	14.655	88.504	75.915	64.204	-217.347	10.460	-.449
5200	14.666	88.788	76.159	65.670	-217.882	14.949	-.628
5300	14.676	89.068	76.400	67.137	-218.420	19.433	-.801
5400	14.684	89.342	76.637	68.605	-218.961	23.922	-.968
5500	14.692	89.612	76.871	70.074	-219.502	28.432	-1.130
5600	14.699	89.876	77.101	71.544	-220.049	32.937	-1.285
5700	14.704	90.137	77.327	73.014	-220.599	37.463	-1.436
5800	14.708	90.392	77.550	74.485	-221.152	41.995	-1.582
5900	14.712	90.644	77.770	75.956	-221.707	46.536	-1.724
6000	14.715	90.891	77.987	77.427	-222.266	51.090	-1.861

Dec. 31, 1975

BORON HYDRIDE OXIDE UNINEGATIVE ION (HBO^-) (IDEAL GAS) GFW = 27.8179

Point Group C_s
$S°_{298.15}$ = [54.2 ± 2.0] gibbs/mol
Ground State Quantum Weight = [2]

$\Delta Hf°_0$ = [-57 ± 24] kcal/mol BHO^-
$\Delta Hf°_{298.15}$ = [-58.4 ± 24] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[10000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[2000] (1)
[1000] (1)
[1500] (1)

Bond Distances: H-B = [1.25] Å B-O = [1.37] Å
Bond Angle: H-B-O = 123° σ = 1
Product of Moments of Inertia: $I_AI_BI_C$ = [9.0890×10^{-118}] g^3 cm^6

Heat of Formation

The identification of the HBO^- radical has been made from observations of its electron spin resonance (esr) spectra which was measured (1, 2) in γ-irradiated polycrystalline potassium borohydride. This assignment is confirmed by the fact that hyperfine coupling constants calculated by INDO (3) and UHF (4, 5) methods are in reasonable agreement with the spectral data (2). *No experimental measurement of the electron affinity (EA) has been reported; however, recent MO calculations (6) predict* that the value is small. We note that these calculations predict incorrectly the relative stabilities of HBO and HBO^- and therefore are of no use in the establishment of the absolute value of EA. This inversion in the predicted stabilities of the radical and parent molecule most likely arises from the neglect of correlation effects.

We estimate ΔHf° from a consideration of bond-energy schemes. For the dissociative process $HBO^-(g) = H(g) + B(g) + O^-(g)$, we assume $\Delta Ha°_0 = \Delta Ha°_0$ (HBO) = 289.4 kcal/mol (7). This atomization energy gives $\Delta Hf°_0(HBO^-, g)$ = -81.0 kcal/mol which we believe is an upper limit since the unpaired electron in HBO^- is antibonding (8) and consequently, one would expect $\Delta Ha°(HBO^-) < \Delta Ha°(HBO)$. A lower limit of ΔHf° can be obtained from a consideration of the H-B bond dissociation energy. It is very unlikely that $D°_0(H\text{-}BO^-) < D°_0(H\text{-}CO)$ which is equal to 14.1 kcal/mol. Using this value for $D°_0(H\text{-}BO^-)$, we obtain $\Delta Hf°_0(HBO^-,g)$ = -33 kcal/mol with $\Delta Hf°_0(H,g)$ = 52.103 kcal/mol (7) and $\Delta Hf°_0(BO^-, g)$ = -71.0 kcal/mol (9). We adopt an average (-57±24 kcal/mol) of the upper and lower limit values. Our adopted ΔHf° value corresponds to an $EA(HBO^-)$ of 0.42±1.0 eV.

Heat Capacity and Entropy

The bond lengths are those reported by Thomson (3) who performed an INDO calculation in which the bond lengths were *determined by minimization of the total energy. The esr spectrum (1, 2) of HBO^- is consistent with a bent structure. Catton* et al. (2) obtained bond angles of 121° and 125° from the p:s ratios deduced from estimated and observed anisotropic components of the hyperfine tensors. A similar calculation (2) for HCO and HCN^- led to bond angles which agreed with independent values to within ±5°. We adopt a bond angle of 123±5°. MO calculations (3) give an angle of 129°. However, the energy minimization procedure with the INDO method generally over-estimates the angle as evidenced by the results for HCO (10) and HCN (2, 3). The individual moments of inertia are: $I_A = 2.5500 \times 10^{-39}$, $I_B = 2.4015 \times 10^{-39}$, and $I_C = 0.1484 \times 10^{-39}$ g cm^2. The enthalpy between 0 K and 298.15 K is -2.397 kcal/mol.

The electronic levels and quantum weights are taken from those for HCO (7), which is isoelectronic with HBO^-. The vibrational frequencies are estimated by comparison with the corresponding values for HBO, HBO^+, HCO and HCO^+ (7).

References

1. M. C. R. Symons and H. W. Wardale, Chem. Commun. 1968, 1483 (1968).
2. R. C. Catton, M. C. R. Symons, and H. W. Wardale, J. Chem. Soc. (A), 1969, 2622 (1966).
3. C. Thomson, Theoret. Chim. Acta, 17, 320 (1970).
4. T. A. Claxton and N. A. Smith, Trans. Faraday Soc. 67, 1859 (1971).
5. T. A. Claxton, Trans. Faraday Soc. 67, 897 (1971).
6. C. Thomson and B. J. Wishart, Theoret. Chim. Acta, 35, 267 (1974).
7. JANAF Thermochemical Tables: HBO(g) and HBO^+(g), 12-31-75; H(g), 6-30-74; B(g), 12-31-64; O^-(g), 6-30-65; HCO(g) and HCO^+(g), 12-31-70.
8. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
9. R. D. Srivastava, O. M. Uy, and M. Farber, Trans. Faraday Soc. 67, 2941 (1971).
10. M. S. Gordon and J. A. Pople, J. Chem. Phys. 49, 4643 (1968).

BHO^-

BORON HYDRIDE SULFIDE (HBS) BHS

(IDEAL GAS) GFW=43.8780

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.220	12.137	12.137	INFINITE
100	6.969	43.127	58.373	- 1.525	12.283	9.494	- 20.749
200	7.610	48.095	52.116	- .804	12.229	6.704	- 7.325
298	8.793	51.351	51.351	.000	12.000	4.036	- 2.958
300	8.815	51.405	51.351	.016	11.995	3.986	- 2.904
400	9.874	54.093	51.710	.953	11.163	1.381	- .755
500	10.677	56.386	52.422	1.982	10.492	- .987	.431
600	11.290	58.390	53.253	3.082	9.910	- 3.226	1.175
700	11.779	60.168	54.116	4.236	9.397	- 5.350	1.670
800	12.181	61.768	54.974	5.435	- 4.127	- 8.693	2.375
900	12.519	63.223	55.811	6.670	- 4.252	- 9.256	2.248
1000	12.805	64.557	56.620	7.937	- 4.370	- 9.805	2.143
1100	13.049	65.789	57.398	9.230	- 4.487	- 10.345	2.055
1200	13.258	66.934	58.146	10.546	- 4.601	- 10.870	1.980
1300	13.436	68.002	58.863	11.881	- 4.717	- 11.388	1.914
1400	13.590	69.004	59.552	13.232	- 4.837	- 11.896	1.857
1500	13.723	69.946	60.214	14.598	- 4.963	- 12.398	1.806
1600	13.838	70.835	60.850	15.976	- 5.095	- 12.888	1.760
1700	13.939	71.677	61.463	17.365	- 5.233	- 13.371	1.719
1800	14.026	72.477	62.052	18.763	- 5.379	- 13.847	1.681
1900	14.103	73.237	62.621	20.170	- 5.528	- 14.312	1.646
2000	14.171	73.962	63.170	21.584	- 5.682	- 14.770	1.614
2100	14.230	74.655	63.701	23.004	- 5.841	- 15.221	1.584
2200	14.284	75.318	64.214	24.430	- 6.003	- 15.663	1.556
2300	14.331	75.954	64.711	25.860	- 6.170	- 16.099	1.530
2400	14.373	76.565	65.192	27.296	- 6.341	- 16.526	1.505
2500	14.412	77.153	65.659	28.735	- 11.903	- 16.839	1.472
2600	14.446	77.719	66.112	30.178	- 12.074	- 17.033	1.432
2700	14.478	78.264	66.552	31.624	- 12.245	- 17.220	1.394
2800	14.507	78.791	66.980	33.073	- 12.418	- 17.404	1.358
2900	14.534	79.301	67.396	34.525	- 12.590	- 17.575	1.324
3000	14.559	79.794	67.801	35.980	- 12.763	- 17.745	1.293
3100	14.583	80.272	68.195	37.437	- 12.935	- 17.910	1.263
3200	14.606	80.735	68.580	38.897	- 13.109	- 18.067	1.234
3300	14.629	81.185	68.955	40.358	- 13.283	- 18.219	1.207
3400	14.651	81.622	69.321	41.822	- 13.458	- 18.364	1.180
3500	14.674	82.047	69.679	43.288	- 13.634	- 18.510	1.156
3600	14.697	82.461	70.028	44.757	- 13.809	- 18.645	1.132
3700	14.721	82.864	70.370	46.228	- 13.987	- 18.776	1.109
3800	14.747	83.257	70.704	47.701	- 14.162	- 18.902	1.087
3900	14.774	83.640	71.031	49.177	- 14.339	- 19.028	1.066
4000	14.803	84.015	71.351	50.656	- 135.694	- 16.997	.929
4100	14.834	84.380	71.664	52.138	- 135.639	- 14.032	.748
4200	14.867	84.738	71.971	53.623	- 135.582	- 11.062	.576
4300	14.904	85.089	72.272	55.111	- 135.525	- 8.101	.412
4400	14.943	85.432	72.567	56.604	- 135.468	- 5.139	.255
4500	14.986	85.768	72.857	58.100	- 135.410	- 2.178	.106
4600	15.032	86.098	73.141	59.601	- 135.348	.783	- .037
4700	15.082	86.422	73.420	61.107	- 135.286	3.742	- .174
4800	15.136	86.740	73.694	62.618	- 135.221	6.699	- .305
4900	15.194	87.052	73.964	64.134	- 135.154	9.656	- .431
5000	15.256	87.360	74.229	65.657	- 135.084	12.608	- .551
5100	15.323	87.663	74.489	67.186	- 135.012	15.564	- .667
5200	15.393	87.961	74.745	68.721	- 134.934	18.515	- .778
5300	15.468	88.255	74.997	70.265	- 134.852	21.464	- .885
5400	15.548	88.545	75.246	71.815	- 134.767	24.413	- .988
5500	15.632	88.831	75.490	73.374	- 134.676	27.363	- 1.087
5600	15.720	89.113	75.731	74.942	- 134.581	30.304	- 1.183
5700	15.813	89.392	75.968	76.518	- 134.480	33.249	- 1.275
5800	15.910	89.668	76.202	78.105	- 134.373	36.190	- 1.364
5900	16.011	89.941	76.432	79.701	- 134.258	39.128	- 1.449
6000	16.115	90.211	76.660	81.307	- 134.138	42.070	- 1.532

Dec. 31, 1975

BORON HYDRIDE SULFIDE (HBS) (IDEAL GAS) GFW = 43.8780

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = [51.35 ± 0.1] gibbs/mol

Ground State Configuration $[^1\Sigma^+]$

ΔHf°_0 = [12.1 ± 10.0] kcal/mol BHS

$\Delta Hf^\circ_{298.15}$ = [12.0 ± 10.0] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[1]	[35000]	[1]
[25000]	[3]	[37000]	[2]
[30000]	[6]	[40000]	[6]
[31000]	[3]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
2742(1)
[715](2)
[1156](1)

Bond Distances: H-B = 1.1692 Å

B-S = 1.5994 Å

Bond Angle = 180° σ = 1

Rotational Constant: B_0 = 0.64359 cm^{-1}

Heat of Formation

The transient thioborine molecule, HBS, has been identified by Kirk and Timms (1) in the mass spectra of the products formed by the high temperature (1150-1300°C) reaction of hydrogen sulfide on crystalline boron. The best yields of HBS were found at low pressures (<1 torr) but even under these conditions the half-life is relatively short (<3 min) (1, 2). No experimental measurement of its heat of formation has been reported.

We estimate ΔHf° from a consideration of bond-energy schemes. A comparison of the values for the H-B stretching force constants in HBS (K = 4.021 x 10^5 dynes/cm) and HBO (K = 4.080 x 10^5 dynes/cm, 3) suggests that the H-B bonds in these two molecules are quite similar. Assuming D°_{298} (H-BS) = D°_{298}(H-BO) = 99.5 kcal/mol (3), we calculate ΔHf°_{298}(HBS,g) = 10.7 kcal/mol with ΔHf°_{298}(H,g) = 52.103 kcal/mol and ΔHf°_{298}(BS,g) = 58.1±4.0 kcal/mol (3).

A comparison of force constants also suggests that the H-B bonds in BH_3 (4) and the B=S bond in BS (3) are similar to those in HBS. Using D°_{298}(H-B) = $\bar{D}^\circ_{298}(BH_3)$ = 87.9 kcal/mol and D°_{298}(B=S) = D°_{298}(BS) = 141.0 kcal/mol, we calculate ΔHa°_{298} = 228.9 kcal/mol which leads to ΔHf°_{298}(HBS,g) = 22.3 kcal/mol. All bond dissociation energies are derived from JANAF data (3).

A value for ΔHa°_{298} can also be obtained from the results of MO calculations on HBS. Thomson (5) has shown that dissociation energies obtained from MO calculations when combined with estimates of the molecular extra correlation energy (MECE) give reliable atomization energies. The change in the relativistic energy between the isolated atoms and molecule is assumed small. It is reasonable to assume that the contribution to the atomization energy from correlation effects would be similar for the isoelectronic molecules HBS and HBO. We estimate the MECE for HBO as 56.5 kcal/mol from the difference in the experimental ΔHa° (3) and the reported Hartree-Fock dissociation energy (6). This value of MECE when added to the computed dissociation energy of 191.7 kcal/mol (7) for HBS gives ΔHa°_{298} = 248.2 kcal/mol which corresponds to ΔHf°_{298}(HBS,g) = 3.0 kcal/mol.

We believe these three estimates of ΔHf°(10.7, 22.3, 3.0 kcal/mol) to be equally probable; therefore, we adopt the mean value of 12.0 kcal/mol. An uncertainty of ±10.0 kcal/mol is assigned which covers the range of possible values.

Heat Capacity and Entropy

The microwave measurements on HBS by Pearson and McCormick (8) have shown that the molecule is linear in its ground state. They observed the millimeter-wave spectra for eight isotopic species and evaluated structural parameters by the substitution method. We adopt their mean values for the H-B and B=S bond lengths. The moment of inertia is 4.3491 x 10^{-39} g cm^2.

Sams and Maki (2) have observed the ν_1 *vibrational fundamental (2742* cm^{-1}*) in the high-resolution infrared spectra of* gaseous HBS. Frequencies (ν_1) were recorded for four isotopic species. The value of ν_1 (2742 cm^{-1}) is corrected for the natural isotopic abundances of boron; the correction for the sulfur isotopes is negligible. Values of ν_2 and ν_3 are calculated from force constants by a valence force method (9). The B=S stretching force constant (K = 6.9 x 10^5 dynes/cm) is estimated from the value for BS (K = 6.7 x 10^5 dynes/cm)by comparison with the B=O stretching force constants for BO and HBO (3). The bending force constant (K_D = 3.2 x 10^{-12} dynes/cm) is taken equal to the value for HBO (3). Sams and Maki (2) also performed a detailed force field calculation on HBS which gave ν_2 = 635 cm^{-1} and ν_3 = 1194 cm^{-1} for $H^{11}B^{32}S$. Results of a similar calculation on HCN led these workers to conclude that their ν_2 values were probably much lower (~50 cm^{-1}) than the true values. They suggested a better estimate of ν_2 for HBS as 690±30 cm^{-1}. Pearson and McCormick (8) estimated ν_2 = 680 cm^{-1} from the ℓ-doubling constant determined from their microwave measurements. These latter two values support our selection of ν_2 = 715 cm^{-1}. Photoelectron spectrometric results (10, 11) have led to predictions of ν_3 = 1100 cm^{-1} from the changes observed in vibrational frequencies produced upon ionization. We believe our calculated frequencies are uncertain to no more than ±50 cm^{-1} which amounts to an error in the value of S°_{298} of ±0.1 gibbs/mol.

Evidence is available which suggests that the ground state configuration and excited states of HBS are similar to those for the isoelectronic molecule HCP. Theoretical calculations (7, 12) predict the same ordering of valence orbitals for these two molecules. This orbital order is corroborated by the results (10, 11, and 13) of photoelectron spectroscopy where the similarity (11) in their PE spectra has been noted. In addition, we note that the Zeeman parameters recently reported for HBS and HCP by Pearson et al. (14) are nearly identical. We assume the same ground state configuration $(^1\Sigma^+)$ for HBS as that for HCP (3), and we estimate the electronic levels by analogy with those observed for HCP.

References

1. R. W. Kirk and P. L. Timms, Chem. Commun. 3, 18 (1967).
2. R. L. Sams and A. G. Maki, J. Mol. Struct. 26, 107 (1975).
3. JANAF Thermochemical Tables: BH_3(g), 12-31-64; BS(g), 6-30-72; HBO(g), 12-31-75; HCP(g), 12-31-69; H(g), 6-30-74; BO(g), 6-30-68.
4. A. Kaldor and R. F. Porter, J. Amer. Chem. Soc. 93, 2140 (1971).
5. C. Thomson, J. Chem. Phys. 58, 216 (1973).
6. C. Thomson and B. J. Wishart, Theoret. Chim. Acta, 35, 267 (1974).
7. C. Thomson, Chem. Phys. Letters, 25, 59 (1974).
8. E. F. Pearson and R. V. McCormick, J. Chem. Phys. 58, 1619 (1973).
9. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, Inc., New York, 1962.
10. T. P. Fehler and D. W. Turner, J. Amer. Chem. Soc. 95, 7175 (1973).
11. H. W. Kroto, R. J. Suffolk, and N. P. C. Westwood, Chem. Phys. Letters, 22, 495 (1973).
12. C. Thomson, Theoret. Chim. Acta, 35, 237 (1974).
13. D. C. Frost, S. T. Lee, and C. A. McDonell, Chem. Phys. Letters, 23, 472 (1973).
14. E. F. Pearson, C. L. Norris, and W. H. Flygare, J. Chem. Phys. 60, 1761 (1974).

BHS

BORON HYDRIDE SULFIDE UNIPOS. ION (HBS$^+$) BHS$^+$

(IDEAL GAS) GFW=43.8775

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	9.430	53.833	53.833	.000	269.950	259.758	-190.406
300	9.449	53.891	53.833	.017	269.955	259.695	-189.187
400	10.387	56.744	54.216	1.011	269.678	256.255	-140.011
500	11.105	59.142	54.967	2.087	269.550	252.915	-110.549
600	11.660	61.218	55.840	3.227	269.505	249.594	-90.914
700	12.107	63.050	56.742	4.416	269.523	246.298	-76.898
800	12.478	64.692	57.635	5.646	256.527	241.708	-66.032
900	12.789	66.180	58.503	6.909	256.927	239.832	-58.239
1000	13.051	67.541	59.339	8.202	257.332	237.912	-51.996
1100	13.274	68.796	60.143	9.518	257.735	235.949	-46.879
1200	13.463	69.959	60.913	10.855	258.138	233.951	-42.608
1300	13.624	71.043	61.651	12.210	258.539	231.920	-38.989
1400	13.762	72.058	62.358	13.579	258.934	229.858	-35.882
1500	13.880	73.012	63.037	14.962	259.322	227.765	-33.185
1600	13.982	73.911	63.689	16.355	259.761	225.650	-30.822
1700	14.071	74.761	64.315	17.758	260.073	223.511	-28.734
1800	14.148	75.568	64.918	19.169	260.438	221.348	-26.875
1900	14.215	76.334	65.499	20.587	260.797	219.169	-25.210
2000	14.274	77.065	66.059	22.011	261.151	216.969	-23.709
2100	14.327	77.763	66.600	23.442	261.498	214.750	-22.349
2200	14.373	78.430	67.123	24.877	261.842	212.517	-21.112
2300	14.414	79.070	67.628	26.316	262.181	210.266	-19.980
2400	14.451	79.684	68.118	27.759	262.515	208.004	-18.941
2500	14.484	80.275	68.593	29.206	257.457	205.834	-17.994
2600	14.514	80.844	69.053	30.656	257.769	203.762	-17.128
2700	14.542	81.392	69.500	32.109	258.121	201.678	-16.325
2800	14.567	81.921	69.934	33.564	258.452	199.578	-15.578
2900	14.590	82.433	70.356	35.022	258.783	197.474	-14.882
3000	14.612	82.928	70.767	36.482	259.112	195.354	-14.232
3100	14.632	83.407	71.167	37.944	259.441	193.220	-13.622
3200	14.651	83.872	71.557	39.409	259.769	191.080	-13.050
3300	14.668	84.323	71.937	40.874	260.096	188.929	-12.512
3400	14.685	84.761	72.308	42.342	260.422	186.769	-12.005
3500	14.702	85.187	72.670	43.812	260.746	184.595	-11.527
3600	14.717	85.602	73.023	45.282	261.069	182.415	-11.074
3700	14.732	86.005	73.369	46.755	261.390	180.227	-10.646
3800	14.747	86.398	73.706	48.229	261.712	178.031	-10.239
3900	14.761	86.782	74.037	49.704	262.032	175.821	-9.853
4000	14.775	87.155	74.360	51.181	141.171	175.755	-9.603
4100	14.789	87.520	74.677	52.659	141.720	176.610	-9.414
4200	14.803	87.877	74.987	54.139	142.268	177.460	-9.234
4300	14.817	88.226	75.291	55.620	142.814	178.288	-9.062
4400	14.830	88.566	75.588	57.102	143.358	179.107	-8.896
4500	14.843	88.900	75.881	58.586	143.900	179.912	-8.738
4600	14.857	89.226	76.167	60.071	144.442	180.707	-8.586
4700	14.870	89.546	76.448	61.557	144.983	181.491	-8.439
4800	14.883	89.859	76.725	63.045	145.521	182.262	-8.299
4900	14.896	90.166	76.996	64.534	146.057	183.022	-8.163
5000	14.909	90.467	77.262	66.024	146.591	183.768	-8.033
5100	14.922	90.762	77.524	67.516	147.123	184.510	-7.907
5200	14.935	91.052	77.781	69.008	147.655	185.237	-7.785
5300	14.948	91.337	78.034	70.503	148.165	185.953	-7.668
5400	14.961	91.616	78.283	71.998	148.711	186.661	-7.555
5500	14.973	91.891	78.528	73.495	149.237	187.362	-7.445
5600	14.986	92.161	78.769	74.993	149.759	188.046	-7.339
5700	14.999	92.426	79.007	76.492	150.279	188.727	-7.236
5800	15.011	92.687	79.240	77.992	150.798	189.396	-7.137
5900	15.024	92.944	79.470	79.494	151.315	190.056	-7.040
6000	15.036	93.197	79.697	80.997	151.828	190.712	-6.947

Dec. 31, 1975

BORON HYDRIDE SULFIDE UNIPOSITIVE ION (HBS$^+$) (IDEAL GAS) GFW = 43.8775

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = [53.83 ± 0.1] gibbs/mol

ΔHf°_0 = [268.4 ± 11.0] kcal/mol BHS$^+$

$\Delta Hf^\circ_{298.15}$ = [270.0 ± 11.0] kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Pi_{1/2}$	0	2
$X^2\Pi_{3/2}$	[300]	2
$A^2\Sigma^+$	19599	2
$B^2\Sigma^+$	38069	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[2550](1)
[764](2)
973 (1)

Bond Distances: H-B = [1.192] Å B-S = [1.680] Å

Bond Angle: H-B-S = 180° σ = 1

Rotational Constant: B_o = [0.58695] cm^{-1}

Heat of Formation

Kroto et al. (1) and Fehler and Turner (2) have independently measured the 584 Å photoelectron spectra of HBS(g). The reported values of 11.11±0.03 eV (1) and 11.12 eV (2) for the first adiabatic ionization potential are in excellent agreement. We adopt an average (11.115±0.03 eV) of these two IP values, and we assume $\Delta Hr^\circ = 256.3_2 \pm 0.7$ kcal/mol refers to the ionization process $HBS(g) + e^- \rightarrow HBS^+(g) + 2e^-$ at 0 K. The latter value yields $\Delta Hf^\circ_0(HBS^+,g)$ = 268.4±11.0 kcal/mol when combined with $\Delta Hf^\circ_0(HBS,g)$ = 12.1±10.0 kcal/mol (3). The adopted ΔHf°_0 value is placed in brackets to emphasize the uncertainty in the estimated ΔHf° value (3) for HBS. ΔHf° at 298.15 K corresponds to 270.0±11.0 kcal/mol.

Heat Capacity and Entropy

Extensive ab initio MO calculations (4) recently reported for HBS show that the highest occupied orbital is of Π-symmetry and is localized mainly on the sulfur atom. The shape of the first photoelectron band in the HBS spectra (1, 2) suggests that this orbital is bonding. The bonding nature of this Π orbital is also predicted from the Walsh diagram (5) for HAB molecules. As a consequence, we would expect the ion to be less strongly bound than the parent molecule. In the related species HCN (6) which has the same orbital ordering as HBS (4), ionization (7) occurs with a 2.2% increase in the H-C bond length and a 4.7% increase in the C≡N bond length. We assume a similar increase in the bond lengths of HBS (3) upon ionization. If the ion was nonlinear, one would expect to find a vibrational spacing in the photoelectron spectra of HBS which could be associated with the bending frequency of the ion. No frequency as low as 764 cm^{-1} has been observed (1, 2); thus, it is likely that HBS$^+$ is linear in its ground state. This prediction is supported by the Walsh diagram (5). We assume that the ion is linear. The moment of inertia is 4.7688×10^{-39} g cm^2. The enthalpy between 0 K and 298.15 K is -2.374 kcal/mol.

The progression in the first photoelectron band of the HBS spectra has been reported as 955±40 cm^{-1} (1) and 990 cm^{-1} (2). *By comparison with changes observed in vibrational frequencies on ionization of HCN and HCP (3, 8), the vibrational mode* excited is most certainly the B=S stretching frequency, ν_3. We adopt the average (973 cm^{-1}) of these two values. The values *of ν_1 and ν_2 are calculated from estimated force constants by a valence force method (9). The two force constants are* estimated from those for HCN$^+$(8), HCN and HBS (3). We estimate the uncertainties in our frequencies are no greater than ±50 *cm^{-1} which corresponds to an error in the value of S°_{298} of only ±0.12 gibbs/mol.*

The electronic states and upper levels are taken from the photoelectron spectrometric study of Kroto et al. (1). Relative term values for the $A^2\Sigma^+$ and $B^2\Sigma^+$ states are calculated as differences in the reported adiabatic ionization potentials (1). Fehler and Turner (2) have estimated the ground state splitting to be ∿300 cm^{-1} from the observed peak widths in the first band of the HBS photoelectron spectra. We adopt this result since it compares favorably with the splitting (∿278 cm^{-1}) observed for the $^2\Pi$ state of the isoelectronic molecule CS$^+$ (10). Relative term values for the two $^2\Sigma$ states calculated from the adiabatic ionization potentials of Fehler and Turner (2) agree within about 160 cm^{-1} with the values adopted here. Fehler and Turner (2) have also reported a photoelectron band at 17.9 eV which was not observed by Kroto et al. (1). This band could not be definitely assigned to HBS$^+$. If this state does exist, it lies above 50000 cm^{-1} and has a negligible effect on the thermodynamic functions of the ion. We prefer not to include it. Kroto et al. (1) have interpreted their photoelectron results in terms of a linear configuration for the three observed states of HBS$^+$. Thus, we feel our functions are not significantly influenced by the use of the ground state vibrational frequencies and rotational constant for the excited states.

References

1. H. W. Kroto, R. J. Suffolk, and N. P. C. Westwood, Chem. Phys. Letters, 22, 495 (1973).
2. T. P. Fehler and D. W. Turner, J. Amer. Chem. Soc. 95, 7175 (1973).
3. JANAF Thermochemical Tables: HBS(g), 12-31-75; HCN(g) and HCP(g), 12-31-69.
4. C. Thomson, Chem. Phys. Letters, 25, 59 (1974).
5. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
6. C. Thomson and B. J. Wishart, Theoret. Chim. Acta, 35, 267 (1974).
7. S. P. So and W. G. Richards, J. Chem. Soc. Faraday Trans. II, 71, 62 (1975).
8. D. C. Frost, S. T. Lee, and C. A. McDowell, Chem. Phys. Letters, 23, 472 (1973).
9. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, Inc., New York, 1962.
10. D. C. Frost, S. T. Lee, and C. A. McDowell, Chem. Phys. Letters, 17, 153 (1972).

Barium Monobromide (BaBr)

(Ideal Gas) GFW = 217.244

T, °K	$C_p°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.438	-24.287	-24.287	INFINITE
100	8.052	55.271	72.324	-1.705	-24.295	-28.364	61.989
200	8.677	61.098	65.404	-.861	-24.644	-32.305	35.302
298	8.842	64.599	64.599	.000	-26.431	-35.815	26.253
300	8.844	64.654	64.599	.016	-26.443	-35.873	26.133
400	8.915	67.209	64.947	.905	-30.397	-38.224	20.884
500	8.955	69.203	65.606	1.798	-30.857	-40.132	17.542
600	8.983	70.838	66.346	2.695	-31.509	-41.924	15.271
700	9.005	72.225	67.089	3.595	-31.968	-43.627	13.621
800	9.024	73.428	67.808	4.496	-32.548	-45.251	12.362
900	9.041	74.492	68.493	5.399	-33.027	-46.810	11.367
1000	9.056	75.445	69.141	6.304	-33.506	-48.315	10.559
1100	9.071	76.309	69.754	7.211	-35.985	-49.577	9.850
1200	9.086	77.099	70.334	8.119	-36.518	-50.789	9.250
1300	9.100	77.827	70.882	9.028	-37.028	-51.957	8.735
1400	9.115	78.502	71.403	9.938	-37.518	-53.088	8.287
1500	9.130	79.131	71.897	10.851	-37.994	-54.183	7.895
1600	9.146	79.721	72.368	11.764	-38.461	-55.248	7.546
1700	9.164	80.276	72.817	12.680	-38.922	-56.282	7.236
1800	9.184	80.800	73.246	13.597	-39.383	-57.290	6.956
1900	9.205	81.298	73.657	14.517	-39.850	-58.272	6.703
2000	9.235	81.771	74.051	15.439	-40.326	-59.230	6.472
2100	9.266	82.222	74.429	16.364	-40.816	-60.163	6.261
2200	9.302	82.654	74.793	17.292	-74.679	-59.847	5.945
2300	9.343	83.068	75.144	18.225	-75.016	-59.164	5.622
2400	9.389	83.467	75.483	19.161	-75.407	-58.467	5.324
2500	9.442	83.851	75.810	20.103	-75.849	-57.752	5.049
2600	9.500	84.222	76.126	21.050	-76.343	-57.018	4.793
2700	9.563	84.582	76.433	22.003	-76.885	-56.265	4.554
2800	9.633	84.931	76.730	22.963	-77.476	-55.491	4.331
2900	9.708	85.270	77.019	23.930	-78.106	-54.694	4.122
3000	9.789	85.601	77.299	24.904	-78.775	-53.876	3.925
3100	9.874	85.923	77.572	25.887	-79.476	-53.034	3.739
3200	9.965	86.238	77.838	26.879	-80.202	-52.170	3.563
3300	10.059	86.546	78.098	27.880	-80.948	-51.283	3.396
3400	10.158	86.848	78.350	28.891	-81.709	-50.373	3.238
3500	10.260	87.144	78.598	29.912	-82.479	-49.440	3.087
3600	10.366	87.434	78.839	30.943	-83.252	-48.485	2.943
3700	10.474	87.720	79.075	31.985	-84.026	-47.509	2.806
3800	10.585	88.001	79.306	33.038	-84.795	-46.511	2.675
3900	10.697	88.277	79.533	34.102	-85.556	-45.493	2.549
4000	10.810	88.549	79.755	35.178	-86.306	-44.458	2.429
4100	10.925	88.818	79.973	36.265	-87.042	-43.403	2.314
4200	11.040	89.082	80.186	37.363	-87.764	-42.329	2.203
4300	11.155	89.343	80.396	38.473	-88.468	-41.238	2.096
4400	11.270	89.601	80.603	39.594	-89.153	-40.131	1.993
4500	11.384	89.856	80.805	40.726	-89.821	-39.010	1.895
4600	11.497	90.107	81.005	41.871	-90.468	-37.873	1.799
4700	11.610	90.356	81.201	43.026	-91.096	-36.722	1.708
4800	11.720	90.601	81.394	44.192	-91.704	-35.560	1.619
4900	11.829	90.844	81.585	45.370	-92.293	-34.384	1.534
5000	11.935	91.084	81.772	46.558	-92.862	-33.197	1.451
5100	12.039	91.321	81.957	47.757	-93.413	-32.000	1.371
5200	12.141	91.556	82.140	48.966	-93.944	-30.789	1.294
5300	12.240	91.788	82.320	50.185	-94.458	-29.569	1.219
5400	12.336	92.018	82.497	51.414	-94.954	-28.341	1.147
5500	12.428	92.245	82.672	52.652	-95.434	-27.101	1.077
5600	12.518	92.470	82.845	53.899	-95.899	-25.856	1.009
5700	12.604	92.692	83.016	55.155	-96.348	-24.601	.943
5800	12.687	92.912	83.185	56.420	-96.782	-23.337	.879
5900	12.767	93.130	83.351	57.693	-97.203	-22.068	.817
6000	12.843	93.345	83.516	58.973	-97.609	-20.793	.757

Dec. 31, 1974

BARIUM MONOBROMIDE (BaBr) (IDEAL GAS) GFW = 217.244

Ground State Configuration $^2\Sigma^+$

$S°_{298.15}$ = 64.6 ± 0.1 gibbs/mol

$\Delta Hf°_0$ = -24.3 ± 10.0 kcal/mol

$\Delta Hf°_{298.15}$ = -26.4 ± 10.0 kcal/mol

BABR

Electronic Levels and Quantum Weights

STATE	ϵ_i, cm^{-1}	g_i	STATE	ϵ_i, cm^{-1}	g_i
X $^2\Sigma^+$	0	2	D$^2\Sigma$	25670.9	2
[A $^2\Pi$]	[13000]	[4]	E$^2\Sigma$	26865.9	2
[B $^2\Sigma$]	[13500]	[2]	[F $^2\Pi$]	[28000]	[4]
C_1 $^2\Pi_{1/2}$	18650.9	2	[G_1 $^2\Delta$]	[29000]	[4]
C_2 $^2\Pi_{3/2}$	19192.5	2	[H $^2\Sigma$]	[30000]	[2]

ω_e = 193.2 cm^{-1} $\omega_e x_e$ = 0.42 cm^{-1} σ = 1

B_e = [0.04052] cm^{-1} α_e = [0.000113] cm^{-1} r_e = [2.87] Å

Heat of Formation

The selected value, $\Delta Hf°_0$ = -24.3 kcal/mol, is obtained from an analysis of spectroscopic data. Herzberg (1) suggested $D°_0$ = 2.8 eV for BaBr(g) which was derived from a linear Birge-Sponer extrapolation of the ground state vibrational levels. Our adopted vibrational constants give $D°_0$ = 2.74 eV by a similar extrapolation. Based on the ionicity correction developed by Hildenbrand (2), this value adjusts to 4.14 eV (95.5 kcal/mol) which is adopted. Gaydon (3) has claimed that the spectroscopic data for BaBr(g) are insufficient to obtain a reliable extrapolation. However, our adopted value for $D°_0$ gives $D°_0(BaBr)/D°_0(BaBr_2)$ = 0.48 which is quite consistent with values of this ratio for other alkaline earth halide systems (4). $\Delta Hf°_{298}$ corresponds to -26.4 kcal/mol.

Ionic model calculations (5, 6) have led to $D°_0$ values of 4.9 eV (5) and 3.76 eV (6). The latter result is believed to represent a minimum value for $D°_0$. Two other experimental values for $D°_0$, which bracket the selected value, have been reported. Flame studies (7) gave $D°_0$ = 3.79 eV, and chemiluminescence (8) from reaction of Ba atoms with Br_2 gave a lower limit to $D°_0$ of 4.54 eV. We assign an uncertainty of ± 10 kcal/mol to $\Delta Hf°_0$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $BaBr_2$ (9) with $r_e(BaBr)/r_e(BaBr_2)$ = 0.96. This value for the ratio is calculated from bond lengths (4) for several other alkaline earth halide systems. Two other estimates (5, 6) of r_e agree with the adopted value to within 0.05 Å. The rotational constant is calculated from the estimated value for r_e. The value of α_e is obtained from a Morse potential function. The moment of inertia is 6.9088 X 10^{-38} g cm^2.

The vibrational constants are taken from the compilation of Rosen (10) and are corrected for the natural isotopic abundances of the elements. The observed electronic levels for BaBr(g) are from Rosen (10). Also included are A, B, F, G, and H states. Their energies are estimated by analogy with those for SrBr(g) (9).

References

1. G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Company, New York, 1950.
2. D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, Ed. by L. Eyring, Academic Press, New York, 1967.
3. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1968.
4. JANAF Thermochemical Tables.
5. J. L. Margrave, J. Phys. Chem. 58, 258 (1954).
6. K. S. Krasnov and N. V. Karaseva, Optics and Spectroscopy 19, 14 (1965).
7. A. N. Khitrov, V. G. Ryabova, and L. V. Gurvich, Teplofiz. Vys. Temp. 11, 1126 (1973).
8. M. Menzinger, Can. J. Chem. 52, 1688 (1974).
9. JANAF Thermochemical Tables: $BaBr_2$(g) and SrBr(g), 12-31-74.
10. B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.

Barium Dibromide ($BaBr_2$)
(Crystal) GFW = 297.148

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	18.407	35.500	35.500	.000	- 181.100	- 176.384	129.293
300	18.416	35.614	35.500	.034	- 181.111	- 176.354	128.474
400	18.933	40.983	36.229	1.902	- 188.205	- 173.301	94.687
500	19.450	45.263	37.622	3.821	- 188.081	- 169.594	74.129
600	19.967	48.855	39.202	5.792	- 188.103	- 165.892	60.426
700	20.483	51.972	40.809	7.814	- 187.886	- 162.210	50.644
800	21.000	54.740	42.380	9.888	- 187.742	- 158.550	43.314
900	21.517	57.244	43.895	12.014	- 187.447	- 154.917	37.619
1000	22.034	59.538	45.346	14.192	- 187.103	- 151.320	33.071
1100	22.551	61.662	46.734	16.421	- 188.710	- 147.565	29.318
1200	23.067	63.646	48.061	18.702	- 188.322	- 143.840	26.197
1300	23.584	65.513	49.333	21.034	- 187.861	- 140.151	23.561
1400	24.101	67.280	50.552	23.419	- 187.330	- 136.501	21.309
1500	24.618	68.960	51.724	25.854	- 186.737	- 132.892	19.362

Dec. 31, 1974

BARIUM DIBROMIDE ($BaBr_2$) (CRYSTAL) GFW = 297.148

$BABR_2$

$S°_{298.15}$ = [35.5 ± 1.0] gibbs/mol
Tm = 1130 ± 2 K

$ΔHf°_0$ = Unknown
$ΔHf°_{298.15}$ = -181.1 ± 0.4 kcal/mol
ΔHm° = 7.64 ± 0.15 kcal/mol
$ΔHs°_{298.15}$ = 79.6 ± 2.0 kcal/mol

Heat of Formation

The selected value is based on results obtained from solution calorimetry performed in aqueous acid media. Ehrlich et al. (1) reported measurements of the heats of solution of Ba(c) and $BaBr_2$(c) in HBr · 555 H_2O. These results lead to $ΔHf°_{298}$ ($BaBr_2$, c) = -181.1 ± 0.4 kcal/mol when combined with the most recent thermal data (2, 3) for aqueous HBr. This value is adopted and is essentially that (-181.0) which has been selected by NBS (4).

Two independent calorimetric values (in kcal/mol) of -180.7 (5) and -181.7 (6) bracket our adopted value. These values are based on results of early heat of solution measurements (5, 6) which are combined with $ΔHf°_{298}$ (Ba^{+2}, aq) = -128.5 kcal/mol (4) and $ΔHf°_{298}$(Br^-, aq) = -29.039 ± 0.035 kcal/mol (2). Use of the newly derived value (See BaO(c) table) for ΔHf° of Ba^{+2} (aq) makes these values less negative by 0.5 kcal/mol.

Heat Capacity and Entropy

Cp° data needed to define $S°_{298}$ are unavailable. The adopted value $S°_{298}$ = 35.5 ± 1.0 gibbs/mol is a compromise between several estimates. JANAF (7) entropies for the other three barium dihalides suggest a value of $S°_{298}$ near 35.3 gibbs/mol for the bromide. Application of the Berthelot principle (8) to the process $SrBr_2$(c) + Ba(c) = $BaBr_2$(c) + Sr(c) gives $S°_{298}$ = 36.7 ± 1.7 gibbs/mol. Literature estimates which were considered are in gibbs/mol 35.0 (4), 35.5 ± 5.0 (9), and 38 (10).

The adopted Cp° data are obtained from JANAF curve fits of the relative enthalpies (825-1130 K) reported by Efremova and Matizen (11). For 27 enthalpy points the average deviation of the fit is ±0.4%; the maximum deviation is -1.0% at 847 K. Two points (1129 and 1130 K) are omitted from the fit, since these points presumably involve pre-melting effects. The derived value of $Cp°_{298}$ = 18.41 gibbs/mol is supported by the value (18.48 gibbs/mol) obtained from the process $BaCl_2$(c) + 2KBr (c) = $BaBr_2$(c) + 2 KCl(c) with ΔCp° = 0. Relative enthalpies (487-1126 K) reported in equation form by Janz et al. (12) suggest a somewhat lower value (17.8 gibbs/mol) for Cp° at 298.15 K. Their smoothed enthalpies show deviations from our adopted ones that are generally less than ±0.3% but show maximum deviations of ∼±1.0% at 500 K and 900 K. The enthalpy measurement of Dworkin and Bredig (13) at the melting point (Tm = 1130 K) is roughly 1% lower than that which is adopted. The values of Cp° above Tm are obtained from the adopted enthalpy equation.

Melting Data

See $BaBr_2$(ℓ) table for details.

Heat of Sublimation

ΔHs° is the difference in the values of ΔHf° for the gas and crystal at 298.15 K.

References

1. P. Ehrlich, K. Peik, and E. Koch, Z. Anorg. Chem. 324, 113 (1963).
2. ICSU - CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
3. U.S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. U.S. Natl. Bur. Std. Tech. Note 270-6, 1971.
5. J. Thomsen, "Thermochemische Untersuchungen," Vol. III, Barth, Leipzig, 1883.
6. R. Varet, Ann. Chim. Phys. 8, 240 (1896).
7. JANAF Thermochemical Tables: BaO(c), 6-30-74; BaF_2(c) and $BaCl_2$(c), 12-31-72; BaI_2(c), 6-30-74.
8. N. N. Drozin, Zhur. Fiz. Khim. 35, 879 (1961).
9. O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," 4th ed., Pergamon Press, New York, 1967.
10. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
11. R. I. Efremova and E. V. Matizen, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk (1), 144 (1970).
12. G. J. Janz, F. J. Kelley, and J. L. Pérano, Trans. Faraday Soc. 59, 2718 (1963).
13. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 67, 697 (1963).

Barium Dibromide ($BaBr_2$)

(Liquid) GFW = 297.148

$BaBr_2$

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	18.407	41.135	41.135	.000	− 174.520	− 171.484	125.701
300	18.416	41.249	41.135	.034	− 174.531	− 171.465	124.912
400	18.933	46.617	41.864	1.902	− 181.625	− 168.975	92.324
500	19.450	50.898	43.256	3.821	− 181.501	− 165.831	72.485
600	19.967	54.490	44.837	5.792	− 181.523	− 162.693	59.261
700	20.483	57.606	46.443	7.814	− 181.306	− 159.574	49.821
800	25.060	60.375	48.015	9.888	− 181.162	− 156.477	42.748
900	25.060	63.327	49.556	12.394	− 180.487	− 153.431	37.258
1000	25.060	65.967	51.067	14.900	− 179.815	− 150.461	32.883
1100	25.060	68.356	52.532	17.406	− 181.145	− 147.363	29.278
1200	25.060	70.536	53.943	19.912	− 180.532	− 144.318	26.284
1300	25.060	72.542	55.297	22.418	− 179.897	− 141.325	23.759
1400	25.060	74.399	56.596	24.924	− 179.245	− 138.383	21.603
1500	25.060	76.128	57.841	27.430	− 178.581	− 135.488	19.741
1600	25.060	77.745	59.035	29.936	− 177.910	− 132.637	18.117
1700	25.060	79.265	60.181	32.442	− 177.236	− 129.827	16.690
1800	25.060	80.697	61.281	34.948	− 176.564	− 127.059	15.427
1900	25.060	82.052	62.339	37.454	− 175.900	− 124.325	14.301
2000	25.060	83.337	63.357	39.960	− 175.250	− 121.630	13.291
2100	25.060	84.560	64.338	42.466	− 174.616	− 118.964	12.381
2200	25.060	85.726	65.284	44.972	− 207.359	− 115.102	11.434
2300	25.060	86.840	66.197	47.478	− 206.581	− 110.925	10.540
2400	25.060	87.906	67.080	49.984	− 205.861	− 106.781	9.724
2500	25.060	88.929	67.933	52.490	− 205.198	− 102.667	8.975
2600	25.060	89.912	68.760	54.996	− 204.593	− 98.578	8.286
2700	25.060	90.858	69.561	57.502	− 204.043	− 94.512	7.650
2800	25.060	91.769	70.338	60.008	− 203.549	− 90.464	7.061
2900	25.060	92.649	71.092	62.514	− 203.102	− 86.433	6.514
3000	25.060	93.498	71.825	65.020	− 202.701	− 82.417	6.004

Dec. 31, 1974

BARIUM DIBROMIDE ($BaBr_2$) (LIQUID) GFW = 297.148

$S^\circ_{298.15}$ = [41.135] gibbs/mol
Tm = 1130 ± 2 K
Tb = 2304 K

$\Delta Hf^\circ_{298.15}$ = −174.520 kcal/mol
ΔHm° = 7.64 ± 0.15 kcal/mol
ΔHv° = 53.3 kcal/mol

B A B R $_2$

Heat of Formation

ΔHf° of the liquid is obtained from that of the crystal by addition of ΔHm° and the difference in the values of (H°_{1130} − H°_{298}) for the crystal and liquid.

Heat Capacity and Entropy

Cp° for the liquid is taken equal to 25.06 gibbs/mol above the assumed glass transition temperature of 800 K. The constant value of Cp° is derived from a curve fit of the relative enthalpies (1134 − 1963 K) reported by Efremova and Matizen (1). For 11 enthalpy points the average deviation of the fit is ±0.3%; the maximum deviation occurs at 1386 K and amounts to −0.7%. Our adopted value for Cp° is supported by the enthalpy measurements of Dworkin and Bredig (2) who found Cp° (ℓ) = 25.6 gibbs/mol. A considerably higher value (31 gibbs/mol) for Cp°(ℓ) is obtained from yet another enthalpy study (3); however, these latter measurements extend over a relatively short temperature interval (∿100°) above Tm and are probably insufficient to accurately establish Cp° of the liquid. Cp° data below the glass transition are those of the crystal.

The value of S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data

Tm is the value determined in two independent drop-calorimetric investigations (1, 2). Nine other reported values for Tm lie within 11° of the adopted value. These other values are 1126 K (3-5), 1119 K (6, 7), 1128 K (8), and 1120 K (9-11).

ΔHm° is calculated as the difference between JANAF values for the enthalpies of the liquid and crystal at Tm. Our value for ΔHm° is in excellent agreement with another drop-calorimetric value (ΔHm° = 7.63 kcal/mol, 2) and is further supported by a value (ΔHm° = 7.7 kcal/mol, 4) obtained by dynamic differential calorimetry. Other published values include in kcal/mol 7.75 ± 0.08 (1), 7.25 ± 0.19 (3), 7.15 ± 0.4 (4), and 7.0 (5).

Vaporization Data

Tb is the temperature at which ΔGr° = 0 for the process $BaBr_2(\ell) = BaBr_2(g)$. ΔHv° is the corresponding difference in the ΔHf° values for the gas and liquid at Tb. Petersen and Hutchison (12) calculated Tb = 2122 K from their measured vapor pressure data which covered the range 1175 − 1321 K. This value is considered somewhat uncertain due to the rather long extrapolation.

References

1. R. I. Efremova and E. V. Matizen, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khin. Nauk (1), 144 (1970).
2. A. S. Dworkin and M. A. Bredig, J. Phys Chem. 67, 697 (1963).
3. G. J. Janz, F. J. Kelley, and J. L. Pérano, Trans. Faraday Soc. 59, 2718 (1963).
4. H. H. Emons and B. Löffelholz, Wiss. Z. Tech. Hochsch. Chem., Leuna − Merseburg 6, 261 (1964).
5. M. Blanc, Compt. rend. 249, 2012 (1959).
6. E. D. Eastman, D. D. Cubicciotti, and C. D. Thurmond in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., National Nuclear Energy Series IV-19B, McGraw − Hill Book Co., New York, 1950.
7. H. H. Emons, Z. Anorg. Chem. 323, 114 (1963).
8. R. Riccardi, C. Sinistri, G. V. Campari, and A. Magistris, Z. Naturforsch. 25a, 781 (1970).
9. G. Kellner, Z. Anorg. Chem 99, 137 (1917).
10. G. Kellner, J. Chem. Soc. 112, 469 (1917).
11. H. Schinke and F. Sauerwald, Z. Anorg. Chem. 304, 25 (1960).
12. D. T. Peterson and J. F. Hutchison, J. Chem. Eng. Data 15, 320 (1970).

Barium Dibromide ($BaBr_2$)

(Ideal Gas) GFW = 297.148

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.646	-97.635	-97.635	INFINITE
100	12.108	67.471	93.591	-2.612	-97.675	-102.320	223.621
200	13.321	76.341	82.968	-1.325	-98.167	-106.787	116.692
298	13.630	81.729	81.729	.000	-101.500	-110.568	81.048
300	13.633	81.813	81.729	.025	-101.520	-110.623	80.589
400	13.751	85.754	82.266	1.395	-109.112	-112.116	61.257
500	13.808	88.829	83.282	2.774	-109.528	-112.824	49.315
600	13.839	91.349	84.423	4.156	-110.139	-113.424	41.315
700	13.857	93.484	85.569	5.541	-110.559	-113.942	35.574
800	13.870	95.335	86.676	6.927	-111.103	-114.386	31.249
900	13.878	96.969	87.731	8.315	-111.546	-114.769	27.870
1000	13.884	98.432	88.729	9.703	-111.992	-115.103	25.156
1100	13.889	99.756	89.672	11.091	-114.440	-115.197	22.888
1200	13.892	100.964	90.564	12.480	-114.944	-115.243	20.989
1300	13.895	102.076	91.407	13.870	-115.425	-115.248	19.375
1400	13.897	103.106	92.206	15.259	-115.890	-115.217	17.986
1500	13.899	104.065	92.965	16.649	-116.342	-115.154	16.778
1600	13.900	104.962	93.687	18.039	-116.787	-115.060	15.717
1700	13.901	105.805	94.376	19.429	-117.229	-114.938	14.776
1800	13.902	106.599	95.033	20.819	-117.673	-114.792	13.938
1900	13.903	107.351	95.662	22.210	-118.124	-114.618	13.184
2000	13.904	108.064	96.264	23.600	-118.590	-114.423	12.504
2100	13.904	108.742	96.842	24.990	-119.072	-114.203	11.885
2200	13.905	109.389	97.398	26.381	-152.930	-112.733	11.199
2300	13.905	110.007	97.933	27.771	-153.268	-110.897	10.538
2400	13.906	110.599	98.448	29.162	-153.663	-109.046	9.930
2500	13.906	111.167	98.946	30.552	-154.116	-107.178	9.370
2600	13.906	111.712	99.426	31.943	-154.626	-105.291	8.850
2700	13.907	112.237	99.891	33.334	-155.191	-103.384	8.368
2800	13.907	112.743	100.341	34.724	-155.813	-101.453	7.919
2900	13.907	113.231	100.777	36.115	-156.481	-99.499	7.498
3000	13.907	113.702	101.200	37.506	-157.195	-97.523	7.105
3100	13.907	114.158	101.611	38.896	-157.952	-95.521	6.734
3200	13.908	114.600	102.010	40.287	-158.742	-93.495	6.385
3300	13.908	115.028	102.398	41.678	-159.562	-91.444	6.056
3400	13.908	115.443	102.776	43.069	-160.407	-89.369	5.745
3500	13.908	115.846	103.143	44.460	-161.272	-87.265	5.449
3600	13.908	116.238	103.502	45.850	-162.152	-85.138	5.169
3700	13.908	116.619	103.851	47.241	-163.042	-82.988	4.902
3800	13.908	116.990	104.192	48.632	-163.940	-80.812	4.648
3900	13.908	117.351	104.525	50.023	-164.841	-78.611	4.405
4000	13.909	117.703	104.850	51.414	-165.743	-76.391	4.174
4100	13.909	118.047	105.168	52.805	-166.643	-74.147	3.952
4200	13.909	118.382	105.478	54.195	-167.541	-71.879	3.740
4300	13.909	118.709	105.782	55.586	-168.433	-69.590	3.537
4400	13.909	119.029	106.080	56.977	-169.318	-67.279	3.342
4500	13.909	119.342	106.371	58.368	-170.197	-64.952	3.154
4600	13.909	119.647	106.656	59.759	-171.068	-62.602	2.974
4700	13.909	119.946	106.936	61.150	-171.931	-60.233	2.801
4800	13.909	120.239	107.210	62.541	-172.787	-57.851	2.634
4900	13.909	120.526	107.479	63.932	-173.634	-55.446	2.473
5000	13.909	120.807	107.743	65.323	-174.473	-53.026	2.318
5100	13.909	121.082	108.001	66.713	-175.306	-50.591	2.168
5200	13.909	121.353	108.256	68.104	-176.129	-48.137	2.023
5300	13.909	121.618	108.505	69.495	-176.945	-45.666	1.883
5400	13.909	121.878	108.750	70.886	-177.754	-43.183	1.748
5500	13.909	122.133	108.991	72.277	-178.556	-40.680	1.616
5600	13.909	122.383	109.228	73.668	-179.353	-38.170	1.490
5700	13.909	122.630	109.461	75.059	-180.144	-35.640	1.367
5800	13.909	122.871	109.690	76.450	-180.928	-33.096	1.247
5900	13.909	123.109	109.916	77.841	-181.708	-30.542	1.131
6000	13.909	123.343	110.138	79.232	-182.482	-27.977	1.019

Dec. 31, 1974

BARIUM DIBROMIDE ($BaBr_2$) *(IDEAL GAS)* *GFW = 297.148*

$BaBr_2$

Point Group = C_{2v}

$S°_{298.15}$ = [81.7 ± 2.0] gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -97.6 ± 3.0 kcal/mol

$\Delta Hf°_{298.15}$ = -101.5 ± 3.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[160] (1)
[28] (1)
[223] (1)

Bond Distance: Ba-Br = 2.99 ± 0.03 Å

Bond Angle: Br-Ba-Br = [150±30]°

σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = [3.71757 x 10^{-112}] g^3cm^6

Heat of Formation

The heat of formation is calculated from the selected value for the heat of vaporization ($\Delta Hv°_{298}$ = 73.04 ± 0.24 kcal/mol) and the adopted value for ΔHf°(ℓ). The selected value of ΔHv° is obtained from a third law analysis of the vapor pressures for the liquid (1175-1321 K) reported by Peterson and Hutchison (1, 2). These measurements were made by the Knudsen effusion method on a sample of anhydrous $BaBr_2$ which had been prepared by direct union of high purity elements. The second law ΔHv° = 73.7 kcal/mol is in agreement with the third law value; thus, the entropy deviation is small ($\Delta Sv°_r$ (2nd law) - $\Delta Sv°_r$ (3rd law) = 0.5 ± 0.8 gibbs/mol). The dominant vapor species is assumed to be the dihalide monomer. This assumption is supported by the fact that negligible concentrations of polymeric species have been observed for some of the other alkaline-earth dihalides by use of mass spectrometry (see $CaBr_2(g)$ table (9)).

A third law analysis of a single sublimation pressure reported by Stock and Heynemann (3) leads to ΔHf°(g) = -104.3 kcal/mol. This result suggests a possible uncertainty in the adopted value for ΔHf° of as much as ± 3 kcal/mol. This also brings our value in agreement with the selection (-105 kcal/mol) of NBS (4).

Heat Capacity and Entropy

Experimental evidence which has been presented in favor of a linear or nonlinear structure for $BaBr_2$ is conflicting. Electron diffraction analysis by Akishin and Spiridonov (5) showed $BaBr_2$ to be linear (180 ± 30°). Later studies by Klemperer et al. (6, 7), *using electric quadrupole deflection of molecular beams, have shown that this molecule possesses a permanent* dipole moment and therefore must be bent. A simple explanation of the observed trends in the geometries of the alkaline-earth dihalides as established by the electric deflection experiments (6, 7) has been presented by Hayes (8), and it appears quite likely that $BaBr_2$ is probably bent. The bond angle is arbitrarily taken to be greater than that for $BaCl_2$ (100°, 9) but less than that for BaI_2 (170°, 9). The bond distance is that measured in the gas phase by an electron diffraction study of Akishin and Spiridonov (5). The individual moments of inertia are: I_A = 2.2868 x 10^{-37}, I_B = 2.21335 x 10^{-37}, and I_C = 7.3448 x 10^{-39} g cm^2.

The vibrational frequencies are calculated from estimated force constants by the valence force method (10). The stretching force constant (K = 1.117 x 10^5 dynes/cm) is taken equal to that for BaBr (9). The ratio of the stretching to bending force constants is estimated as 125. This value for the ratio is to be compared with that for BaF_2 (93, 9) and $BaCl_2$ (119, 9). The uncertainty in the adopted value for ν_2 is believed to be no greater than ± 20 cm^{-1} which corresponds to roughly 1 gibbs/mol in the value of $S°_{298}$. Other sets (11-13) of estimated vibrational frequencies compare favorably with ours; the maximum deviation is 35 cm^{-1} in ν_3 (13). The ground state quantum weight of one is assigned by analogy with that for $BaCl_2$(9). Our free energy functions differ by roughly 2 gibbs/mol in the range 298-2000 K from those given by Brewer et al. (11). However, their values are based on a linear structure for the bromide which now appears to be incorrect.

References

1. D. T. Peterson and J. F. Hutchison, J. Chem. Eng. Data 15, 320 (1970).
2. J. F. Hutchison, Ames Laboratory, Iowa State University, AEC Contract No. W-7405-eng-82, Report No. IS-T-50, November, 1965.
3. A. Stock and H. Heynemann, Chem. Ber. 42, 4088 (1909).
4. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.
5. P. A. Akishin and V. P. Spiridonov, Kristallografiya 2, 475 (1957).
6. L. Wharton, R. A. Berg, and W. Klemperer, J. Chem. Phys. 39, 2023 (1963).
7. A. Büchler, J. L. Stauffer, and W. Klemperer, J. Amer. Chem. Soc. 86, 4544 (1964).
8. E. F. Hayes, J. Phys. Chem. 70, 3740 (1966).
9. *JANAF Thermochemical Tables:* $BaCl_2(g)$ *and* $BaF_2(g)$, 12-31-72; $BaI_2(g)$, 6-30-74; *BaBr(g)*, 12-31-74; $CaBr_2(g)$, 6-30-74.
10. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1962.
11. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
12. K. S. Krasnov and V. I. Svettsov, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 6, 167 (1963).
13. V. I. Baikov, Opt. Spektrosk. 27, 502 (1969).

$BaBr_2$

BARIUM MONOHYDROXIDE (BAOH) BAHO
(IDEAL GAS) GFW=154.3474

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.561	-53.000	-53.000	INFINITE
100	7.373	50.443	69.235	-1.879	-53.431	-54.371	118.828
200	9.672	56.259	61.391	-1.026	-53.835	-55.145	60.259
298	11.079	60.416	60.416	.000	-54.120	-55.724	40.847
300	11.097	60.485	60.416	.021	-54.125	-55.734	40.602
400	11.797	63.784	60.861	1.169	-54.401	-56.231	30.723
500	12.174	66.461	61.722	2.369	-54.828	-56.643	24.759
600	12.408	68.703	62.704	3.599	-55.430	-56.948	20.743
700	12.581	70.629	63.702	4.849	-55.832	-57.171	17.850
800	12.731	72.319	64.675	6.115	-56.353	-57.326	15.661
900	12.871	73.827	65.610	7.395	-56.769	-57.422	13.444
1000	13.008	75.190	66.501	8.689	-57.181	-57.473	12.561
1100	13.141	76.436	67.348	9.996	-59.590	-57.286	11.382
1200	13.269	77.585	68.154	11.317	-60.050	-57.056	10.391
1300	13.391	78.652	68.921	12.650	-60.484	-56.789	9.547
1400	13.507	79.648	69.652	13.995	-60.896	-56.489	8.816
1500	13.615	80.584	70.350	15.351	-61.292	-56.160	8.182
1600	13.718	81.466	71.017	16.718	-61.679	-55.806	7.623
1700	13.816	82.301	71.657	18.095	-62.059	-55.427	7.126
1800	13.910	83.093	72.270	19.481	-62.439	-55.026	6.681
1900	14.000	83.848	72.860	20.876	-62.824	-54.603	6.281
2000	14.089	84.568	73.427	22.281	-63.219	-54.161	5.918
2100	14.178	85.258	73.974	23.694	-63.628	-53.698	5.588
2200	14.266	85.919	74.502	25.117	-97.410	-51.969	5.165
2300	14.355	86.555	75.013	26.548	-97.668	-49.918	4.743
2400	14.446	87.168	75.507	27.988	-97.980	-47.835	4.356
2500	14.538	87.760	75.985	29.437	-98.347	-45.740	3.999
2600	14.633	88.332	76.449	30.895	-98.765	-43.627	3.667
2700	14.729	88.886	76.899	32.363	-99.235	-41.497	3.359
2800	14.828	89.423	77.337	33.841	-99.754	-39.350	3.071
2900	14.928	89.945	77.763	35.329	-100.315	-37.181	2.802
3000	15.030	90.453	78.177	36.827	-100.917	-34.995	2.549
3100	15.134	90.948	78.581	38.335	-101.552	-32.787	2.311
3200	15.239	91.430	78.975	39.854	-102.216	-30.559	2.087
3300	15.344	91.900	79.360	41.383	-102.903	-28.308	1.875
3400	15.450	92.360	79.736	42.922	-103.608	-26.039	1.674
3500	15.555	92.809	80.103	44.473	-104.325	-23.747	1.483
3600	15.660	93.249	80.462	46.033	-105.049	-21.433	1.301
3700	15.764	93.679	80.813	47.605	-105.778	-19.100	1.128
3800	15.866	94.101	81.157	49.186	-106.506	-16.748	.963
3900	15.967	94.515	81.495	50.778	-107.231	-14.377	.806
4000	16.066	94.920	81.825	52.380	-107.949	-11.967	.655
4100	16.162	95.318	82.149	53.991	-108.658	-9.579	.511
4200	16.255	95.709	82.468	55.612	-109.357	-7.154	.372
4300	16.346	96.092	82.780	57.242	-110.045	-4.712	.239
4400	16.433	96.469	83.087	58.881	-110.719	-2.255	.112
4500	16.516	96.839	83.388	60.528	-111.381	.216	-.011
4600	16.596	97.203	83.685	62.184	-112.028	2.707	-.129
4700	16.672	97.561	83.976	63.847	-112.663	5.207	-.242
4800	16.744	97.913	84.263	65.518	-113.283	7.722	-.352
4900	16.812	98.258	84.545	67.196	-113.890	10.247	-.457
5000	16.876	98.599	84.823	68.880	-114.485	12.785	-.559
5100	16.936	98.934	85.096	70.571	-115.067	15.339	-.657
5200	16.991	99.263	85.365	72.267	-115.637	17.899	-.752
5300	17.043	99.587	85.631	73.969	-116.195	20.476	-.844
5400	17.091	99.906	85.892	75.676	-116.743	23.057	-.933
5500	17.134	100.220	86.150	77.387	-117.281	25.653	-1.019
5600	17.174	100.529	86.404	79.103	-117.811	28.254	-1.103
5700	17.210	100.834	86.654	80.822	-118.332	30.867	-1.183
5800	17.242	101.133	86.901	82.545	-118.844	33.490	-1.262
5900	17.271	101.428	87.145	84.270	-119.350	36.120	-1.338
6000	17.296	101.719	87.385	85.999	-119.848	38.760	-1.412

June 30, 1975; Dec. 31, 1975

BARIUM MONOHYDROXIDE (BaOH) (IDEAL GAS) GFW = 154.3474

Point Group $[C_{\infty v}]$

$S^\circ_{298.15}$ = [60.4 ± 2] gibbs/mol

ΔHf°_0 = -53.0 ± 7.0 BAHO

$\Delta Hf^\circ_{298.15}$ = -54.12 ± 7.0

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	[19500]	[2]
[11800]	[4]	[20500]	[2]
[13500]	[2]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[469](1)
[431](2)
[3650](1)

Bond Distance: Ba-O=[2.17] Å
O-H = [0.96] Å

Bond Angle: Ba-O-H = [180°]

Rotational Constant: B_0=[0.22204]cm^{-1}
σ = 1

Heat of Formation

The adopted $\Delta Hf^\circ_0(BaOH,g)$ = -53.0±7.0 kcal/mol is based on an assessment of dissociation energies derived from Knudsen-cell mass-spectrometric measurements of Stafford and Berkowitz (1) and of Newbury (2) and from flame spectral work (3-6).

The results from a third law analysis of the available experimental data are tabulated below.

Investigator	Rxn. No.	No. of Points	Temp. Range, K	ΔHr°_{298}, kcal/mol 3rd Law	Drift gibbs/mol	ΔHf°_{298} [a] kcal/mol	D°_0 [b] kcal/mol
Stafford and	1	2	1755-1785	115.23±3.55	-83.6	-51.58±6	102.8
Berkowitz (1)	2	1	1785	62.11	--	-55.82	108.1
Newbury (2)	3	1	1851	77.33	--	-53.67	104.8
Cotton and Jenkins(5)	4	2	1570-1800	2.40±2.39	7.3	-64.70	115.9

Rxn. No. 1: $BaO(c) + BaO(g) + H_2O(g) = 2BaOH(g) + 0.5\ O_2(g)$
Rxn. No. 2: $2BaO(g) + H_2O(g) = 2BaOH(g) + O(g)$
Rxn. No. 3: $BaO(c) + 0.5\ H_2(g) = BaOH(g)$
Rxn. No. 4: $Ba(g) + H_2O(g) = BaOH(g) + H(g)$

[a] Auxiliary data from the JANAF Thermochemical Tables (7). [b] D°_0 is calculated for the reaction BaOH(g) = Ba(g) + OH(g).

Ryabova and Gurvich (3) considered the reaction $Ba(g) + H_2O(g) = BaOH(g) + H(g)$ to be dominant and derived D°_0 (as defined in the table above) = 111±8 kcal/mol. Sugden and Schofield (4) considered the reaction $Ba(g) + 2H_2O(g) = Ba(OH)_2(g) + 2H(g)$ *to be dominant. Cotton and Jenkins (5) found both the mono- and dihydroxide to be present in significant amounts in fuel-*rich hydrogen-oxygen-nitrogen flames and derived D°_0 = 114±5 kcal/mol. Cotton and Jenkins (5) recalculated the work of Ryabova and Gurvich (3) and of Sugden and Schofield (4) considering both BaOH and $Ba(OH)_2$ to be present and obtained recalculated values of D°_0 = 110 and 114 kcal/mol, respectively. Ryabova et al. (6) made further measurements, considered BaOH as dominant, and reported D°_0 = 109±3 kcal/mol. The D°_0 calculation from the third law analysis of Cotton and Jenkins (5) data above, using auxiliary data (7) is about 2 kcal/mol higher than theirs. Applying this correction to the values from Ryabova and Gurvich (3) and Sugden and Schofield (4) as recalculated by Cotton and Jenkins (5), gives D°_0 = 112 and 116 kcal/mol, respectively. The value of D°_0 = 109±3 kcal/mol given by Ryabova et al. (6) is an average of four calculations with two sets of molecular constants assumed for BaOH. The value has not been recalculated with the present auxiliary data but probably it would be higher.

The dissociation energies derived from flame spectra are higher, as a group, than those derived from the Knudsen cell mass spectrometric measurements. The ratio of D°_0 (monohydroxide)/D°_0(dihydroxide), where D°_0 of the dihydroxide is defined by the reaction $Ba(OH)_2(g) = Ba(g) + 2\ OH(g)$ and is 209.6 kcal/mol (7), is approximately 0.53-0.55 for the flame spectral measurements and 0.50 for the average D°_0 = 105.3 kcal/mol for the Knudsen-cell mass spectrometric measurements. The ratio for the barium mono- and difluoride (7) is 0.51, and the ratio for the other alkaline earth halides fall in the 0.40 to 0.51 range (7) with an average close to 0.46 (8). The similarity of the halides and hydroxides, particularly the fluorides, has been established (1, 9-11). D°_0 = 105.3 kcal/mol is adopted from which is calculated ΔHf°_0 = -53.0±7.0 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh (12) and the evidence that gaseous alkali metal hydroxides are linear (13-15). The ground state is assumed to be $^2\Sigma^+$ by analogy with BaF and BaCl (7). The electronic levels are estimated from the observed band spectra (16-20) and the comparison with BaF and BaCl (7).

The Ba-O bond distance is estimated to be slightly larger, 0.02 Å, than the Ba-F distance (7) after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is that in water (7). The moment of inertia is $12.6063\times10^{-39}g\ cm^2$. The Ba-O stretching frequency, 469 cm^{-1}, is estimated to be the same as in BaF (7, 11). The O-H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 431 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant *is 0.022, which is the* average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz (11, 15).

The entropy in the present table is lower by 1.25 gibbs/mol at 298 K and 1.77 gibbs/mol at 1000 K than that proposed by Jackson (11); the vibrational frequencies and electronic levels adopted here differ from those of Jackson (11). The moment of inertia in Jackson (11) appears to be in error.

References

1. *F. E. Stafford and J. Berkowitz, J. Chem. Phys.* 40, 2963 (1964).
2. R. S. Newbury, U. S. At. Energy Comm. UCRL-12225-T, 1965.
3. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 3, 318 (1965).
4. T. M. Sugden and K. Schofield, Trans. Faraday Soc. 62, 566 (1966).
5. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 64, 2988 (1968).
6. V. G. Ryabova, A. N. Khitrov, and L. V. Gurvich, Teplofiz. Vys. Temp. 10, 744 (1972).
7. JANAF Thermochemical Tables: BaO(c), BaO(ℓ), H(g), O(g), 6-30-74; $H_2(g)$, $H_2O(g)$, 3-31-61; $O_2(g)$, 9-30-65; Ba(g), 12-30-70; BaCl(g), BaF(g), $BaF_2(g)$ 12-31-72.
8. G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, Nature 199, 804 (1963).
9. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
10. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
11. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Dec. 8, 1971.
12. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
13. N. Acquista, S. Abramowitz, and R. Lide, J. Chem. Phys. 49, 780 (1968).
14. R. L. Kuczkowski and R. Lide, J. Chem. Phys. 44, 3131 (1966).
15. N. Acquista and S. Abramowitz, U. S. Natl. Bur. Std. Report 9905, July, 1968.
16. C. G. James and T. M. Sugden, Nature 175, 333 (1955).
17. E. M. Bulewicz, Nature 177, 670 (1956).
18. M. Charton and A. G. Gaydon, Proc. Phys. Soc. (London) 69A, 520 (1956).
19. V. F. Zhitkevich, A. I. Lyutyi, N. A. Nesterko, V. S. Rossikhin, and I. L. Tsikora, Optika i Spektroskopiya 14, 35 (1963).
20. J. Van der Hurk, Tj. Hollander, and C. Th. J. Alkemade, J. Quant. Spectrosc. Radiat. Transfer. 13, 273 (1973).

BAHO

BARIUM MONOHYDROXIDE UNIPOS. ION ($BaOH^+$) BAHO$^+$
(IDEAL GAS) GFW=154.3469

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.587	64.380		
100							
200							
298	11.104	59.071	59.071	0.000	64.746	62.056	-45.489
300	11.121	59.140	59.071	0.021	64.751	62.040	-45.196
400	11.814	62.445	59.517	1.171	64.974	61.100	-33.383
500	12.186	65.125	60.379	2.373	65.046	60.119	-26.276
600	12.417	67.369	61.362	3.604	64.941	59.146	-21.544
700	12.588	69.296	62.361	4.854	65.035	58.170	-18.161
800	12.736	70.987	63.336	6.121	65.013	57.191	-15.624
900	12.875	72.495	64.271	7.401	65.094	56.210	-13.650
1000	13.011	73.858	65.163	8.696	65.179	55.218	-12.066
1100	13.144	75.105	66.011	10.003	63.268	54.414	-10.811
1200	13.271	76.254	66.817	11.324	63.303	53.608	-9.763
1300	13.392	77.321	67.585	12.657	63.367	52.797	-8.876
1400	13.505	78.318	68.316	14.002	63.452	51.981	-8.115
1500	13.610	79.253	69.014	15.358	63.552	51.159	-7.454
1600	13.707	80.134	69.682	16.724	63.661	50.327	-6.874
1700	13.796	80.968	70.322	18.099	63.776	49.492	-6.363
1800	13.877	81.759	70.935	19.483	63.891	48.648	-5.907
1900	13.952	82.511	71.525	20.874	63.999	47.799	-5.498
2000	14.020	83.229	72.092	22.273	64.095	46.942	-5.130
2100	14.081	83.914	72.639	23.678	64.174	46.083	-4.796
2200	14.137	84.571	73.167	25.089	30.677	46.446	-4.614
2300	14.189	85.200	73.676	26.505	31.102	47.149	-4.480
2400	14.235	85.805	74.169	27.927	31.267	47.844	-4.357
2500	14.278	86.387	74.646	29.352	31.375	46.531	-4.243
2600	14.317	86.948	75.109	30.782	31.423	49.216	-4.137
2700	14.353	87.489	75.557	32.216	31.416	49.901	-4.039
2800	14.386	88.011	75.993	33.653	31.353	50.586	-3.946
2900	14.416	88.517	76.416	35.093	31.241	51.277	-3.864
3000	14.443	89.006	76.827	36.536	31.082	51.970	-3.786
3100	14.469	89.480	77.228	37.981	30.880	52.666	-3.713
3200	14.493	89.940	77.618	39.429	30.642	53.374	-3.645
3300	14.514	90.386	77.998	40.880	30.374	54.090	-3.582
3400	14.534	90.820	78.369	42.332	30.078	54.811	-3.523
3500	14.553	91.241	78.731	43.787	29.762	55.544	-3.466
3600	14.571	91.651	79.084	45.243	29.430	56.286	-3.417
3700	14.587	92.051	79.429	46.701	29.084	57.036	-3.369
3300	14.602	92.440	79.766	48.160	28.731	57.797	-3.324
3900	14.616	92.820	80.096	49.621	28.373	58.566	-3.282
4000	14.629	93.190	80.419	51.083	28.011	59.344	-3.242
4100	14.641	93.551	80.735	52.547	27.651	60.132	-3.205
4200	14.653	93.904	81.044	54.011	27.293	60.929	-3.170
4300	14.663	94.249	81.347	55.477	26.938	61.735	-3.138
4400	14.673	94.586	81.644	56.944	26.589	62.548	-3.107
4500	14.683	94.916	81.936	58.412	26.244	63.367	-3.078
4600	14.692	95.239	82.221	59.881	25.906	64.199	-3.050
4700	14.700	95.555	82.502	61.350	25.575	65.035	-3.024
4800	14.708	95.865	82.777	62.821	25.251	65.878	-3.000
4900	14.716	96.168	83.047	64.292	24.935	66.726	-2.976
5000	14.723	96.465	83.313	65.764	24.623	67.580	-2.954
5100	14.729	96.757	83.573	67.236	24.320	68.444	-2.933
5200	14.736	97.043	83.830	68.710	24.024	69.310	-2.913
5300	14.742	97.324	84.082	70.183	23.735	70.188	-2.894
5400	14.747	97.599	84.329	71.658	23.452	71.064	-2.876
5500	14.753	97.870	84.573	73.133	23.174	71.950	-2.859
5600	14.758	98.136	84.813	74.609	22.901	72.837	-2.843
5700	14.763	98.397	85.049	76.085	22.634	73.731	-2.827
5800	14.767	98.654	85.281	77.561	22.372	74.632	-2.812
5900	14.772	98.906	85.510	79.038	22.114	75.534	-2.798
6000	14.776	99.155	85.735	80.515	21.861	76.442	-2.784

Dec. 31, 1975; June 30, 1976

BARIUM MONOHYDROXIDE UNIPOSITIVE ION ($BaOH^+$) (IDEAL GAS) GFW = 154.3469

Point Group [$C_{\infty v}$]

ΔHf°_0 = 64.38 ± 15.0 kcal/mol BAHO$^+$

$S^\circ_{298.15}$ = [59.07 ± 2.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 64.75 ± 15.0 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[460](1)
[430](2)
[3650](1)

Bond Distances: Ba-O = [2.17] Å O-H = [0.96] Å
Bond Angle: Ba-O-H = [180°] σ = 1
Rotational Constant: B_0 = [0.2220] cm^{-1}

Heat of Formation

The ionization potential of BaOH(g) was deduced by Kelly and Padley (1) to be 5.25±0.1 ev. These authors quantitatively examined the total positive ion concentrations produced from Ba aqueous salt additives in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data (2), we recalculate the ionization potential to be 5.36 ev.

Jensen (3) determined the heat of reaction ΔHr°_0 = 6±10 kcal/mol for Ba(g) + OH(g) = $BaOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for $BaOH^+$; The value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data (2), we derive an ionization potential of 4.83 ev, which is not in good agreement with the value derived from the data of Kelly and Padley (1).

We adopt an ionization potential of 5.09 ev (117.38 kcal/mol) which is an average of the above two studies (1,3). This leads to ΔHf°_0 = 64.38 kcal/mol and ΔHf°_{298} = 64.75 kcal/mol for $BaOH^+(g)$. We assign an uncertainty of ±15 kcal/mol.

For comparison, the ionization potential of BaF(g) is 4.83 ev (2) while that of Ba(g) is 5.21 ev (4). The average of these two values is very close to the ionization potential adopted for $BaOH^+$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear (2,5,6,7). In addition, Walsh (8) had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons ($BaOH^+$ has eight valence electrons) will be linear in their ground state. The molecule $BaOH^+$ is isoelectronic with CsOH.

The bond dissociation energy for $BaOH^+$ (D°_0 = 108.2 kcal/mol, 4, 2) for the process $BaOH^+(g) = Ba^+(g) + OH(g)$ is nearly the same as that for BaOH (D°_0 = 105.3 kcal/mol, 2). This suggests that the bonding in these two molecules is quite similar. Thus, the bond distances are assumed to be the same as those adopted for BaOH(g,2). The moment of inertia is 12.6062×10^{-39} g cm^2. The vibrational frequencies are assumed to be similar to those adopted for BaOH(g,2). The ground state quantum weight is assumed to be the same as that of CsOH(g,2). The enthalpy change between 0 and 298.15 K is -2.587 kcal/mol.

References

1. R. Kelly and P. J. Padley, Trans. Faraday Soc. 67, 1384 (1971).
2. JANAF Thermochemical Tables: e^-, 3-31-65; $H_2(g)$ and $H_2O(g)$, 3-31-61; OH(g) and Ba(g), 12-31-70; H(g), 6-30-74; BaOH(g) and $Ba(OH)_2(g)$, 12-31-75; BaF(g), 12-31-72; CsOH(g), 6-30-71.
3. D. E. Jensen, Combustion and Flame 12, 261 (1968).
4. C. E. Moore, Natl. Bur. Stds., Circ. 467, Vol. III (1958).
5. N. Acquista, S. Abramowitz, and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
6. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. 44, 3131 (1966).
7. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9905, July, 1968.
8. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

BARIUM DIHYDROXIDE, ALPHA (α-Ba(OH)$_2$) (CRYSTAL) GFW=171.3548

BAH_2O_2

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	24.290	25.600	25.600	.000	− 226.170	− 205.435	150.588
300	24.330	25.750	25.600	.045	− 226.163	− 205.307	149.566
400	26.920	33.145	26.591	2.622	− 225.713	− 198.420	108.412
500	28.360	39.321	28.537	5.392	− 225.285	− 191.649	83.770
600	29.330	44.577	30.783	8.276	− 224.961	− 184.949	67.366
700	30.300	49.171	33.089	11.258	− 224.371	− 178.328	55.677
800	31.270	53.280	35.360	14.336	− 223.831	− 171.786	46.930
900	32.240	57.019	37.562	17.512	− 223.114	− 165.322	40.146
1000	33.210	60.466	39.682	20.784	− 222.321	− 158.942	34.737

Dec. 31, 1975

BARIUM DIHYDROXIDE, ALPHA (α-Ba(OH)$_2$) (CRYSTAL) GFW = 171.3548

BAH_2O_2

$S°_{298.15}$ = [25.6 ± 2]gibbs/mol

ΔHf$°_0$ = unknown

ΔHf$°_{298.15}$ = −226.17 ± 1.5 kcal/mol

Tm = 681.15 ± 1 K

ΔHm°=4.00 ± 0.30 kcal/mol

Tt = 521 ± 2 K (β−α)

ΔHt° = Unknown

Heat of Formation

The adopted ΔHf$°_{298}$=−226.17±1.5 kcal/mol is obtained from the heat of formation of the liquid (1) minus the heat of *melting and the enthalpy difference of the* liquid and the crystal between the melting point and 298.15 K. Using auxiliary data (1), our second and third law analysis of the dissociation pressure equation of Kondakov et al. (2) for the reaction Ba(OH)$_2$(c)=BaO(c)+H$_2$O(g) is given below.

Temp. Range, K	ΔHr$_{298}$, kcal/mol 2nd Law	ΔHr$_{298}$, kcal/mol 3rd Law	Drift gibbs/mol	ΔHf$°_{298}$(Ba(OH)$_2$, c)* kcal/mol
559-682	46.4	38.04±1.63	−13.5±0.2	−226.84±2

*ΔHf$°_{298}$ is calculated from the third law value for ΔHr$°_{298}$.

While this is in good agreement with the adopted value, there is an inconsistency in the measurements of Kondakov et al. (2) for the crystal and the liquid and the adopted heat of melting. The liquid state dissociation pressures are in good agreement with other measurements (see the Ba(OH)$_2$(ℓ) table (1)) and are judged more reliable than the solid state measurements. The adopted value for the alpha crystal is also in good agreement with −225.8 kcal from another recent evaluation (4).

Heat Capacity and Entropy

The heat capacities at 298.15 K and above are derived from the drop-ice-calorimeter enthalpy measurements of Powers and Blalock (3, 425-681 K) combined with a graphical comparison of the heat capacities of Mg(OH)$_2$(c) and Ca(OH)$_2$(c)(1). From the information referenced in the Transition Data Section below, it is concluded that the α-form is maintained on cooling to 273.15 K. This JANAF Table is a single-phase alpha-crystal table.

The adopted entropy, $S°_{298}$ = *[25.6±2] gibbs/mol,* is calculated from Kelley's additive entropy constants for cations and anions (5).

Melting Data

Seward (6) determined a melting point of 408±1 °C and a cryoscopic heat of fusion of 3400±100 cal/mol. Powers and Blalock (3) chose a melting point of 395°C where they found ΔHm = 24 cal/g (4113 cal/mol) by drop calorimetry. However, their enthalpy measurements show a possible melting range of 395 to 421°C. (At the adopted temperature of melting, 408°C, our smoothing of Powers and Blalock's experimental enthalpies (3) leads to ΔHm = 4051 cal/mol). Kondakov et al. observed barium dihydroxide to melt at 682 K (ca. 409°C) while investigating the dissociation pressures of the crystal and liquid states. Michaud (7,8) determined a melting point of 408±1°C and a cryoscopic heat of fusion of 3720±200 cal/mol (8). From a consideration of all of these data a melting point of 681.15±1 K (408±1°C) and a heat of fusion of 4000±300 cal/mol are adopted.

Transition Data

Michaud has observed a β to α crystal transition, on heating anhydrous barium dihydroxide, at 250°C (7) and at 246°C (8) by both thermal and dilatometric techniques. In the absence of water vapor, the high temperature α-form is maintained on cooling to room temperature (7). This "metastable" state has been confirmed by others (9, 10), and x-ray diffraction and infrared absorption studies further establish the existence of two crystalline forms (9, 10). This present JANAF Table considers only the α-form. A transition temperature of 521±2 K (248±2°C) is adopted.

References

1. JANAF Thermochemical Tables: Ba(OH)$_2$(ℓ), 12-31-75; BaO(c), 6-30-74; H$_2$O(g), 3-31-61; Mg(OH)$_2$(c), 12-31-75; Ca(OH)$_2$(c), 12-31-75.
2. B. V. Kondakov, P. V. Kovtunenko, and A. A. Bundel, Zh. Fiz. Khim. 38, 190 (1964).
3. W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm., ORNL-1653(1954).
4. U.S. Natl. Bur. Std. Tech. Note 270-6, 1971.
5. K. K. Kelley in Chap. 13, D. R. Stull and H. Prophet, "The Characterization of High Temperature Vapors," J. L. Margrave, Ed., John Wiley and Sons, New York, 1967.
6. R. P. Seward, J. Am. Chem. Soc. 67, 1189 (1945).
7. M. Michaud, Compt. Rend. Ser. C 262, 1143 (1966).
8. M. Michaud, Rev. Chim. Miner. 5, 89 (1968).
9. P. Buck and H. Baernighausen, Acta Crystallogr., Sect. B 24, 1705 (1968).
10. H. D. Lutz, R. Heider, and R. A. Becker, Z. Naturforsch. B 24, 1657 (1969).

BARIUM DIHYDROXIDE (Ba(OH)$_2$) (LIQUID) GFW=171.3548

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							
296	24.290	29.483	29.483	.000	− 223.260	− 203.683	149.304
300	24.330	29.634	29.484	.045	− 223.253	− 203.562	148.294
400	26.920	37.028	30.474	2.622	− 222.803	− 197.064	107.670
500	33.700	43.799	32.451	5.674	− 222.093	− 190.696	83.353
600	33.700	49.944	34.870	9.044	− 221.283	− 184.491	67.201
700	33.700	55.138	37.404	12.414	− 220.305	− 178.439	55.711
800	33.700	59.638	39.908	15.784	− 219.473	− 172.515	47.129
900	33.700	63.608	42.325	19.154	− 218.562	− 166.699	40.480
1000	33.700	67.158	44.634	22.524	− 217.671	− 160.984	35.183
1100	33.700	70.370	46.830	25.894	− 218.800	− 155.162	30.826
1200	33.700	73.303	48.916	29.264	− 218.002	− 149.411	27.212
1300	33.700	76.000	50.897	32.634	− 217.199	− 143.728	24.163
1400	33.700	78.498	52.780	36.004	− 216.395	− 138.107	21.560
1500	33.700	80.823	54.573	39.374	− 215.596	− 132.542	19.311
1600	33.700	82.998	56.282	42.744	− 214.807	− 127.033	17.352
1700	33.700	85.041	57.915	46.114	− 214.028	− 121.569	15.629
1800	33.700	86.967	59.476	49.484	− 213.267	− 116.153	14.103
1900	33.700	88.789	60.971	52.854	− 212.528	− 110.778	12.742
2000	33.700	90.517	62.405	56.224	− 211.815	− 105.443	11.522

Dec. 31, 1975

BARIUM DIHYDROXIDE (Ba(OH)$_2$) (LIQUID) GFW = 171.3548

$S^\circ_{298.15}$ = [29.483] gibbs/mol
Tm = 681.15 ± 1 K
Td = 1325 K

$\Delta Hf^\circ_{298.15}$ = −223.26 ± 1.0 kcal/mol
ΔHm° = 4.00 ± 0.30 kcal/mol

Heat of Formation

The adopted ΔHf°_{298} = −223.26±1.0 kcal/mol is the average of values derived from the third law analysis of dissociation pressure measurements of Tamaru and Shiomi (1) and of Kondakov et al. (2). Auxiliary data used in the analysis are from the JANAF Thermochemical Tables (3). Johnston (4) has also determined pressures for the dissociation reaction $Ba(OH)_2(\ell) = BaO(c) + H_2O(g)$.

Investigator	No. of Points	Temperature Range, K	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	Drift gibbs/mol	$\Delta Hf^\circ_{298}(\ell)$* kcal/mol
Tamaru and Shiomi (1)	7	788-1018	32.1	34.56±0.48	2.8±0.5	−223.35±1
Kondakov et al. (2)	Equation	682-993	34.0	34.37±0.21	0.4	−223.17±0.7
Johnston (4)	11	918-1263	34.4	33.86±0.38	−0.5±0.5	−222.66±0.9

*ΔHf°_{298} is calculated from the third law value for ΔHr°_{298}.

The heat of formation derived from Johnston's measurements is in good agreement with the adopted value but is not averaged in because, as indicated by Kondakov et al. (2), the measurements are believed less accurate.

Heat Capacity and Entropy

Cp° is based on the enthalpy measurements of Powers and Blalock (5) and is assumed constant at 33.7 gibbs/mol over the range of 450 to 1600 K. A glass transition is assumed at 450 K below which Cp° is that of the alpha crystal. The entropy at 298.15 K is derived from the value adopted for the alpha crystal.

Decomposition Data

Td = 1325 K is calculated as the temperature at which ΔGr° = 0 for the reaction $Ba(OH)_2(\ell) = BaO(c) + H_2O(g)$. Auxiliary data used in the calculations are from the JANAF Thermochemical Tables (3).

References

1. S. Tamaru and K. Shiomi, Z. physik. Chem. A171, 221 (1935).
2. B. V. Kondakov, P. V. Kovtunenko, and A. A. Bundel, Zh. Fiz. Khim. 38, 190 (1964).
3. JANAF Thermochemical Tables: BaO(c), 6-30-74; $H_2O(g)$, 3-31-61.
4. J. Johnston, Z. physik. Chem. 62, 330 (1908).
5. W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm., ORNL-1653 (1954).

BARIUM DIHYDROXIDE ($Ba(OH)_2$) BaH_2O_2

(IDEAL GAS) GFW=171.3548

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.966	-147.967	-147.967	INFINITE
100	10.839	59.333	89.662	-3.033	-148.893	-147.433	322.215
200	15.744	68.402	76.879	-1.695	-149.462	-145.727	159.243
298	18.464	75.263	75.263	.000	-149.752	-143.825	105.426
300	18.498	75.378	75.264	.034	-149.756	-143.768	104.749
400	19.809	80.901	76.008	1.957	-149.960	-141.769	77.459
500	20.506	85.403	77.451	3.976	-150.283	-139.667	61.057
600	20.938	89.182	79.099	6.050	-150.769	-137.521	50.092
700	21.261	92.435	80.778	8.160	-151.051	-135.292	42.240
800	21.544	95.293	82.417	10.301	-151.448	-133.014	36.338
900	21.814	97.846	83.992	12.469	-151.739	-130.691	31.736
1000	22.079	100.158	85.495	14.663	-152.024	-128.336	28.048
1100	22.338	102.275	86.925	16.884	-154.302	-125.759	24.986
1200	22.589	104.229	88.287	19.131	-154.627	-123.149	22.426
1300	22.827	106.047	89.584	21.402	-154.923	-120.513	20.260
1400	23.051	107.747	90.821	23.696	-155.195	-117.857	18.396
1500	23.259	109.344	92.003	26.011	-155.451	-115.180	16.782
1600	23.452	110.852	93.135	28.347	-155.696	-112.489	15.365
1700	23.629	112.279	94.219	30.701	-155.933	-109.779	14.113
1800	23.790	113.634	95.260	33.072	-156.171	-107.058	12.999
1900	23.938	114.924	96.262	35.459	-156.415	-104.322	12.000
2000	24.073	116.156	97.226	37.859	-156.672	-101.576	11.100
2100	24.195	117.333	98.155	40.273	-156.945	-98.613	10.284
2200	24.307	118.461	99.053	42.698	-190.597	-94.812	9.419
2300	24.409	119.544	99.921	45.134	-190.727	-90.455	8.595
2400	24.502	120.585	100.760	47.580	-190.918	-86.090	7.840
2500	24.587	121.587	101.573	50.034	-191.171	-81.721	7.144
2600	24.664	122.553	102.362	52.497	-191.481	-77.334	6.501
2700	24.736	123.485	103.127	54.967	-191.851	-72.937	5.904
2800	24.801	124.386	103.870	57.444	-192.279	-68.527	5.349
2900	24.861	125.257	104.593	59.927	-192.758	-64.095	4.830
3000	24.916	126.101	105.295	62.416	-193.287	-59.651	4.346
3100	24.967	126.919	105.980	64.910	-193.859	-55.188	3.891
3200	25.014	127.712	106.647	67.409	-194.471	-50.706	3.463
3300	25.057	128.482	107.297	69.912	-195.116	-46.203	3.060
3400	25.097	129.231	107.931	72.420	-195.790	-41.682	2.679
3500	25.135	129.959	108.550	74.932	-196.487	-37.139	2.319
3600	25.169	130.668	109.155	77.447	-197.202	-32.574	1.978
3700	25.201	131.358	109.745	79.966	-197.934	-27.991	1.653
3800	25.231	132.030	110.323	82.487	-198.676	-23.387	1.345
3900	25.259	132.686	110.888	85.012	-199.425	-18.767	1.052
4000	25.285	133.326	111.441	87.539	-200.180	-14.125	.772
4100	25.310	133.950	111.982	90.069	-200.936	-9.464	.504
4200	25.333	134.561	112.513	92.601	-201.693	-4.784	.249
4300	25.354	135.157	113.032	95.135	-202.449	-.086	.004
4400	25.374	135.740	113.542	97.672	-203.201	4.626	-.230
4500	25.393	136.311	114.042	100.210	-203.952	9.357	-.454
4600	25.411	136.869	114.532	102.750	-204.697	14.112	-.670
4700	25.428	137.415	115.013	105.292	-205.439	18.876	-.878
4800	25.443	137.951	115.485	107.836	-206.174	23.656	-1.077
4900	25.458	138.476	115.949	110.381	-206.905	28.448	-1.269
5000	25.472	138.990	116.405	112.927	-207.632	33.255	-1.454
5100	25.486	139.495	116.853	115.475	-208.354	38.086	-1.632
5200	25.498	139.990	117.293	118.025	-209.069	42.920	-1.804
5300	25.510	140.476	117.726	120.575	-209.781	47.781	-1.970
5400	25.522	140.953	118.151	123.127	-210.488	52.639	-2.130
5500	25.532	141.421	118.570	125.679	-211.191	57.523	-2.286
5600	25.543	141.881	118.982	128.233	-211.892	62.410	-2.436
5700	25.552	142.333	119.388	130.788	-212.588	67.315	-2.581
5800	25.562	142.778	119.787	133.343	-213.282	72.235	-2.722
5900	25.570	143.215	120.181	135.900	-213.972	77.162	-2.856
6000	25.579	143.645	120.568	138.458	-214.658	82.103	-2.991

Dec. 31, 1975

BARIUM DIHYDROXIDE ($Ba(OH)_2$) (IDEAL GAS) GFW = 171.3548

Point Group [C_{2v}]
$S°_{298.15}$ = [75.3 ± 3.0] gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -147.97 ± 9.0 kcal/mol BAH_2O_2
$\Delta Hf°_{298.15}$ = -149.75 ± 9.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[413](1)	[3650](2)
[64](1)	[431](4)
[390](1)	

Bond Distances: Ba-O = [2.34] Å O-H = [0.96] Å
Bond Angles: O-Ba-O = [95°] Ba-O-H = [180°] σ = 2
Product of the Moments of Inertia: $I_AI_BI_C$ = [6363.1658] x $10^{-117} g^3 cm^6$

Heat of Formation

The adopted $\Delta Hf°_{298}(Ba(OH)_2,g)$ = -149.75±9.0 kcal/mol is derived from the Knudsen-cell mass-spectrometric equilibrium study of Newbury (1). Tabulated below are the results of a second and third law analysis of this study (1), the Knudsen-cell mass-spectrometric work of Stafford and Berkowitz (2), and the flame-spectral work of Cotton and Jenkins (3)

Investigator	Rxn No.	No. of Points	Temp. Range, K	$\Delta Hr°_{298}$, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	$\Delta Hf°_{298}(g)^b$ kcal/mol	$D°_0{}^c$ kcal/mol
Stafford and Berkowitz(2)	1	24^a	1485-1727	56.4	45.37±1.82	-6.7±1.7	-143.42±2.5	203.3
Newbury (1)	1	44^a	1428-1899	39.0	39.05±0.17	0.0±0.1	-149.75±0.7	209.6
Cotton and Jenkins (3)	2	2	1570-1800	8.1	23.04±2.98	8.8±0.0	-153.96±4.0	213.8

Reaction 1. $BaO(c) + H_2O(g) = Ba(OH)_2(g)$ Reaction 2. $Ba(g) + 2H_2O(g) = Ba(OH)_2(g) + 2H(g)$

a. Two points rejected by a statistical test.

b. $\Delta Hf°_{298}(g)$ is calculated from the third law $\Delta Hr°_{298}$ using auxiliary data (4).

c. $D°_0$ is the dissociation energy for the reaction $Ba(OH)_2(g) = Ba(g) + 2OH(g)$

In addition to the three investigations above, dissociation energies ($D°_0$ as defined in the table above) have been derived from flame spectra by Ryabova and Gurvich (5) and by Sugden and Schofield (6). Ryabova and Gurvich (5) believed the dominant reaction to be $Ba(g) + H_2O(g) = BaOH(g) + H(g)$, but they also considered the possibility that the reaction $Ba(g) + 2H_2O(g) = Ba(OH)_2 + 2H(g)$ was dominant and derived $D°_0$ = 205±20 kcal/mol. Sugden and Schofield (6) considered the dihydroxide to be the dominant product and derived $D°_0$ = 229±12 kcal/mol. Cotton and Jenkins (3) found both BaOH and $Ba(OH)_2$ to be present in significant amounts in fuel-rich hydrogen-oxygen-nitrogen flames and derived $D°_0$ = 213±5 kcal/mol. Cotton and Jenkins (3) recalculated the work of Ryabova and Gurvich (5) and of Sugden and Schofield (6) *considering both BaOH and* $Ba(OH)_2$ to be present and obtained recalculated $D°_0$ values of 208 and 212 kcal/mol, respectively.

The third law analysis of the data of Cotton and Jenkins (3) above combined with current JANAF Thermochemical Table data (4) leads to $D°_0$ = 213.8 kcal/mol which is 0.8 kcal/mol higher than the 213 kcal/mol derived by Cotton and Jenkins (3). Applying this difference to the values of Ryabova and Gurvich (5) and of Sugden and Schofield (6) as recalculated by Cotton and Jenkins (3) gives $D°_0$ = 208.8 and 212.8 kcal/mol, respectively.

The average of the dissociation energies from the flame-spectral measurements (208.8, 212.8, and 213.8) and the dissociation energy from the Knudsen-cell mass-spectrometric work of Stafford and Berkowitz (203.3) is 209.7 kcal/mol which happens to be in agreement with the 209.6 kcal/mol calculated from Newbury's data.

$\Delta Hf°_{298}(Ba(OH)_2,g)$ = -149.75±9.0 kcal/mol is adopted because of the excellent agreement in the second and third law heats of reaction from Newbury's data (1) and because of the larger uncertainty associated with dissociation energies derived from flame spectra.

The heat of dissociation listed by Jackson (9) leads to $\Delta Hf°_{298}(Ba(OH)_2,g)$ = -151.22 kcal/mol. Another recent compilation (10) lists $\Delta Hf°_{298}$ = -140 kcal/mol.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized (2, 7-9). The O-Ba-O bond angle is assumed to be the same as the F-Ba-F bond angle (4); the Ba-O-H bond angle is considered to be linear as in BaOH(4). The Ba-O bond distance is estimated to be slightly larger, 0.02 Å, than the Ba-F distance in BaF_2 (4) after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is taken to be the same as in water (4).

The vibrational frequencies are assumed to be the same as in BaF_2 (4) (O-Ba-O symmetrical and asymmetrical stretch, and bend) and as in BaOH (4) (O-H stretch and Ba-O-H bend). The three principal moments of inertia are $I_A = 29.7952 \times 10^{-39}$, $I_B = 17.7916 \times 10^{-39}$, and $I_C = 12.0036 \times 10^{-39} g\ cm^2$.

Jackson (9) has used a different molecular configuration and different vibrational frequencies to estimate $S°_{298.15}$ = 78.045 gibbs/mol. We assign an uncertainty of ±3 gibbs/mol to the adopted entropy.

References

1. R. S. Newbury, U. S. At. Energy Comm. UCRL-12225-T (1965).
2. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
3. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 64, 2988 (1968).
4. JANAF Thermochemical Tables: BaO(c), H(g), 6-30-74; $H_2O(g)$, 3-31-61; BaOH(g), 12-31-75; Ba(g), HO(g), 12-31-70; $BaF_2(g)$, 12-31-72.
5. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSR 3, 318 (1965).
6. T. M. Sugden and K. Schofield, Trans. Faraday Soc. 62, 566 (1966).
7. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
8. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
9. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Contract No. W-7405-Eng.-48, Dec. 8, 1971.
10. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.

BAH_2O_2

BERYLLIUM MONOBROMIDE (BEBR)

(IDEAL GAS) GFW=88.91618

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.144	29.960	29.960	INFINITE
100	6.966	46.690	61.180	-1.449	30.312	26.299	-57.476
200	7.286	51.589	55.291	-.740	30.297	22.271	-24.336
298	7.791	54.594	54.594	.000	28.707	18.534	-13.585
300	7.799	54.642	54.594	.014	28.698	18.471	-13.456
400	8.178	56.942	54.905	.815	24.939	15.827	-8.648
500	8.424	58.795	55.504	1.646	24.825	13.562	-5.928
600	8.585	60.346	56.185	2.497	24.690	11.322	-4.124
700	8.696	61.678	56.877	3.361	24.536	9.106	-2.843
800	8.776	62.845	57.551	4.235	24.366	6.912	-1.888
900	8.837	63.882	58.198	5.116	24.181	4.742	-1.152
1000	8.884	64.816	58.814	6.002	23.977	2.593	-.567
1100	8.922	65.664	59.399	6.892	23.753	.466	-.093
1200	8.954	66.442	59.954	7.786	23.506	-1.641	.299
1300	8.982	67.160	60.481	8.683	23.238	-3.725	.626
1400	9.006	67.827	60.982	9.582	22.949	-5.789	.904
1500	9.027	68.449	61.459	10.484	22.636	-7.832	1.141
1600	9.047	69.032	61.915	11.388	19.547	-9.773	1.335
1700	9.065	69.581	62.350	12.293	19.304	-11.598	1.491
1800	9.083	70.100	62.766	13.201	19.058	-13.409	1.628
1900	9.099	70.591	63.165	14.110	18.808	-15.206	1.749
2000	9.114	71.058	63.548	15.020	18.554	-16.990	1.857
2100	9.129	71.503	63.916	15.933	18.296	-18.761	1.952
2200	9.143	71.928	64.271	16.846	18.034	-20.520	2.038
2300	9.157	72.335	64.613	17.761	17.767	-22.264	2.116
2400	9.170	72.725	64.943	18.677	17.496	-23.998	2.185
2500	9.183	73.100	65.261	19.595	17.221	-25.723	2.249
2600	9.196	73.460	65.570	20.514	16.942	-27.434	2.306
2700	9.209	73.807	65.869	21.434	16.659	-29.136	2.358
2800	9.222	74.142	66.158	22.356	-54.657	-29.719	2.320
2900	9.235	74.466	66.439	23.279	-54.696	-28.826	2.172
3000	9.248	74.780	66.712	24.203	-54.736	-27.934	2.035
3100	9.261	75.083	66.977	25.128	-54.777	-27.042	1.906
3200	9.275	75.377	67.235	26.055	-54.817	-26.144	1.786
3300	9.288	75.663	67.486	26.983	-54.860	-25.248	1.672
3400	9.302	75.940	67.731	27.913	-54.904	-24.351	1.565
3500	9.317	76.210	67.969	28.844	-54.950	-23.453	1.464
3600	9.332	76.473	68.202	29.776	-54.999	-22.550	1.369
3700	9.348	76.729	68.429	30.710	-55.051	-21.650	1.279
3800	9.364	76.978	68.650	31.646	-55.107	-20.746	1.193
3900	9.381	77.222	68.867	32.583	-55.165	-19.838	1.112
4000	9.400	77.460	69.079	33.522	-55.229	-18.935	1.035
4100	9.419	77.692	69.286	34.463	-55.297	-18.029	.961
4200	9.439	77.919	69.489	35.406	-55.370	-17.118	.891
4300	9.460	78.141	69.688	36.351	-55.448	-16.203	.824
4400	9.482	78.359	69.882	37.298	-55.532	-15.290	.759
4500	9.506	78.573	70.073	38.247	-55.623	-14.375	.698
4600	9.530	78.782	70.260	39.199	-55.720	-13.459	.639
4700	9.556	78.987	70.444	40.153	-55.824	-12.539	.583
4800	9.584	79.188	70.624	41.110	-55.936	-11.617	.529
4900	9.612	79.386	70.801	42.070	-56.054	-10.691	.477
5000	9.642	79.581	70.974	43.033	-56.180	-9.761	.427
5100	9.673	79.772	71.145	43.999	-56.315	-8.834	.379
5200	9.706	79.960	71.313	44.968	-56.456	-7.905	.332
5300	9.740	80.145	71.477	45.940	-56.607	-6.967	.287
5400	9.775	80.328	71.640	46.916	-56.765	-6.031	.244
5500	9.811	80.507	71.799	47.895	-56.932	-5.089	.202
5600	9.849	80.685	71.956	48.878	-57.107	-4.145	.162
5700	9.888	80.859	72.111	49.865	-57.290	-3.195	.123
5800	9.928	81.032	72.263	50.855	-57.481	-2.241	.084
5900	9.970	81.202	72.413	51.850	-57.680	-1.291	.048
6000	10.012	81.370	72.561	52.849	-57.887	-.338	.012

Dec. 31, 1961; Sept. 30, 1964; June 30, 1975

BERYLLIUM MONOBROMIDE (BeBr) (IDEAL GAS) GFW = 88.91618

Ground State Configuration $^2\Sigma^+$

$S°_{298.15}$ = 54.6 ± 0.1 gibbs/mol

$\Delta Hf°_0$ = 30.0 ± 10.0 kcal/mol

$\Delta Hf°_{298.15}$ = 28.7 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A_1\,^2\Pi_{1/2}$	26353.2	2
$A_2\,^2\Pi_{3/2}$	26550.2	2
$B[^2\Sigma]$	[27000]	[2]
$C[^2\Pi]$	[40000]	[4]

ω_e = 715.06 cm^{-1} $\omega_e x_e$ = 4.30 cm^{-1} σ = 1

B_e = [0.62155] cm^{-1} α_e = [0.005285] cm^{-1} r_e = [1.83] Å

Heat of Formation

No thermochemical measurement of the heat of formation has been made. The selected value, $\Delta Hf°_0(BeBr,g)$ = 30.0 ± 10.0 kcal/mol, is obtained from an analysis of spectroscopic data. The adopted values for the ground state vibrational constants give $D°_0 = 3.64_1$ eV by a linear Birge-Sponer extrapolation (1). Based on the ionicity correction developed by Hildenbrand (2), this value adjusts to $D°_0 = 3.27_2$ eV (75.46 kcal/mol) which is adopted. $\Delta Hf°_{298}$ corresponds to 28.7 kcal/mol.

Ionic model calculations (4, 6) and bond energy correlations (5) have led to $D°_0$ values of (in eV) 1.7 (4), 4.1 (5), and 2.1 (6). The latter value which is based on a Rittner potential (7) is believed to represent a minimum value for $D°_0$. Additional support for the adopted value of ΔHf° is provided by a comparison of values for the ratio $D°_{298}(MX)/\Delta Ha°_{298}(MX_2)$ for the alkaline-earth halides (3). We find $D°_{298}(BeBr)/\Delta Ha°_{298}(BeBr_2)$ = 0.41 which is quite consistent with values of this ratio for other alkaline-earth halides.

Heat Capacity and Entropy

We estimate r_e to be 0.08 Å less than that for $BeBr_2$ (3). This estimation is made based on the observation that the ratio $r_e(MX)/r_e(MX_2)$ is near 0.96 for several alkaline-earth halides (3). The value of Be is calculated from r_e. The value of α_e is obtained from the other constants by assuming a Morse potential function. The moment of inertia is 4.5034×10^{-39} g cm^2.

The ground state vibrational constants are taken from the results of a recent vibrational analysis of the $A^2\Pi$-$X^2\Sigma$ system by Reddy et al. (8). Other values (9) for these constants are slightly different than ours, but we consider them to be less accurate. It should also be noted that the values for $\omega_e x_e$ tabulated by Rosen (9) for the ground and first excited states have been inadvertently reversed. The electronic level for the $A_1\,^2\Pi_{1/2}$ state is also taken from Reddy et al. (8). The doublet splitting of this state is assumed to be 197 cm^{-1} as was observed in the emission spectrum of BeBr by Reddy and Rao (10, 11). We also include a $B^2\Sigma$ level at 27000 cm^{-1} and a $C^2\Pi$ level at 40000 cm^{-1}. These levels are estimated by analogy with those for CaBr, SrBr, and BaBr (3).

References

1. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1968.
2. D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, Ed. by L. Eyring, Academic Press, New York, 1967.
3. JANAF Thermochemical Tables: $BeBr_2(g)$, 6-30-75; CaBr(g), SrBr(g), and BaBr(g), 12-31-74.
4. J. L. Margrave, J. Phys. Chem. 58, 258 (1954).
5. S. P. Tandon and K. Tandon, Indian J. Phys. 38, 460 (1964).
6. K. S. Krasnov and N. V. Karaseva, Optics and Spectroscopy 19, 14 (1965).
7. E. S. Rittner, J. Chem. Phys. 19, 1030 (1951).
8. B. R. Reddy, Y. P. Reddy, and P. T. Rao, J. Phys. B, 3, L1 (1970).
9. B. Rosen, Ed.,"Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.
10. Y. P. Reddy and P. T. Rao, Proc. Phys. Soc., London, At. Mol. Phys. 1, 482 (1968).
11. Y. P. Reddy and P. T. Rao, Curr. Sci. 36, 399 (1967).

BERYLLIUM DIBROMIDE ($BeBr_2$)

(CRYSTAL) GFW=168.82018

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	15.780	24.000	24.000	.000	-85.000	-80.628	59.102
300	15.810	24.098	24.000	.029	-85.011	-80.600	58.717
400	16.880	28.794	24.633	1.664	-92.055	-77.667	42.435
500	17.880	32.674	25.864	3.405	-91.701	-74.110	32.394
600	18.550	35.996	27.283	5.228	-91.308	-70.628	25.726
700	19.050	38.895	28.739	7.109	-90.892	-67.215	20.985
800	19.440	41.465	30.172	9.034	-90.458	-63.862	17.446
900	19.750	43.773	31.557	10.994	-90.013	-60.564	14.707
1000	20.020	45.868	32.885	12.982	-89.565	-57.315	12.526
1100	20.270	47.787	34.154	14.997	-89.116	-54.112	10.751
1200	20.520	49.562	35.365	17.036	-88.669	-50.950	9.279
1300	20.770	51.214	36.521	19.101	-88.221	-47.824	8.040
1400	21.000	52.762	37.626	21.189	-87.775	-44.734	6.983
1500	21.250	54.219	38.685	23.302	-87.330	-41.676	6.072

Dec. 31, 1961; June 30, 1965; June 30, 1975

BERYLLIUM DIBROMIDE ($BeBr_2$) (CRYSTAL)

$S^\circ_{298.15}$ = [24.0±1.0] gibbs/mol
Tm = 781±15 K
Ts = 752 K (to monomer)

GFW = 168.82018
Hf°_0 = Unknown
$\Delta Hf^\circ_{298.15}$ = [-85.0±3.0] kcal/mol
ΔHm° = [2.35±2.0] kcal/mol
$\Delta Hs^\circ_{298.15}$ = 30.2 ± 1.0 kcal/mol

Heat of Formation

A direct measurement of the heat of formation has not been made. *An estimate of ΔHf° is obtained by a method suggested* by Vivian Parker (1). Biltz and Messerknecht (2) have measured the heats of solution of $BeCl_2$(c) and $BeBr_2$(c) in aqueous HCl (18.69%). Samples (3) of the dihalides were prepared from reactions of BeO-C mixtures with the halogens at elevated temperatures. *We assume that the two dihalides had similar structures, i.e. α form. ΔHf°_{298}($BeBr_2$, in 18.7% HCl) is estimated* as -140.1 kcal/mol by combining ΔH_{soln} of $BeCl_2$(c) with ΔHf°_{298}(α-$BeCl_2$,c) = -117.3±0.8 kcal/mol (4) and twice the difference in ΔHf°_{298}($HCl \cdot 8.8H_2O$) and ΔHf°_{298} ($HBr \cdot 8.8H_2O$) which is -21.2 kcal/mol (5). The heat associated with the interchange of the *aqueous anions is assumed to be negligible. Combination of the estimated value for ΔHf°_{298}($BeBr_2$, in 18.7% HCl) with ΔH_{soln}* = -55.7 kcal/mol (2) gives ΔHf°_{298}($BeBr_2$,c) = -84.4 kcal/mol which is essentially the value adopted by NBS (6). Subsequent measurements by Biltz et al. (7) in less concentrated HCl(1.48%) solutions lead to ΔHf°_{298} equal to -85.6 kcal/mol by a similar route. We adopt an average value of -85.0 kcal/mol but emphasize that the uncertainty in ΔHf° is much greater than that indicated (∿1.0 kcal/mol) by the agreement of these two results. A combined total uncertainty of ±3.0 kcal/mol is believed to be more realistic.

Heat Capacity and Entropy

No low-temperature heat capacity or high-temperature enthalpy measurements have been reported. We estimate Cp°_{298} = 15.78 gibbs/mol from the reaction $BeF_2(c) + 2LiBr(c) = BeBr_2(c) + 2LiF(c)$ by assuming ΔCp° = 0. Comparison of this value with Cp° data for α,β-$BeCl_2$ (4) suggests that our estimate is reasonable. Cp° data above 298K are estimated graphically by comparison with those for α,β-$BeCl_2$ and $MgCl_2$ (4).

Several methods of estimation predict that the value of S°_{298} should lie near 24.0 gibbs/mol. Application of the Berthelot principle (8) to the process $SrBr_2(c) + Be(c) = Sr(c) + BeBr_2(c)$ and additive entropy constants (9) give values of 24.1 and 24.0 gibbs/mol, respectively. A graphical comparison of the standard entropies for other alkaline-earth dihalides (4) suggests values for S°_{298} in the range 23.5-24.5 gibbs/mol. Literature estimates have included (in gibbs/mol) 29 (10) and 22 (11). We adopt S°_{298} = 24.0±1.0 gibbs/mol.

Melting Data

The reported melting points for $BeBr_2$ show an unusual amount of scatter. Values of Tm include 761 K (12), 763 K (13), and 779-781 K (14). Semenenko and Naumova (14) reported encountering difficulties in handling $BeBr_2$ due to its hygroscopic nature and susceptibility to oxidation by traces of oxygen. These factors could account for the discrepancies in the Tm values. We tentatively adopt the highest value of 781 K (14) but believe that Tm is more uncertain (∿15°) than the accuracy (±5°) claimed in their temperature measurements.

A thermal analysis (14) of $BeBr_2$ up to temperatures near the melting point showed no polymorphic modifications. Also, the interpretation of electron-diffraction patterns for freshly sublimed $BeBr_2$ indicated that it is isostructural with the α form of $BeCl_2$. Thus, we estimate ΔHm° = 2.35±2.0 kcal/mol from ΔSm° = 3.0 gibbs/mol which is calculated for α-$BeCl_2$ (4).

Sublimation Data

ΔHs°_{298} is obtained from an analysis of the sublimation pressures reported by Rahlfs and Fischer (12). Further details of the analysis are given on the gas-phase table. The value of Ts is the temperature at which ΔG approaches zero for the process *$BeBr_2(c) = BeBr_2(g)$. Ts has been measured as 746 K (12). The good agreement between the calculated and observed* values of Ts is believed to indicate the presence of only small amounts of dimer in the saturated vapor of $BeBr_2$ near the melting point. However, this conflicts with other evidence which is discussed on the gas-phase table. Our results show *that Ts< Tm which implies that the liquid phase is thermodynamically unstable under ordinary conditions.*

References

1. V. B. Parker, private communication, Natl. Bur. Std., March, 1975.
2. W. Biltz and C. Messerknecht, Z. Anorg. Chem. 148, 157 (1925).
3. C. Messerknecht and W. Biltz, Z. Anorg. Chem. 148, 152 (1925).
4. JANAF Thermochemical Tables: α,β-$BeCl_2$(c), 6-30-65; $MgCl_2$(c), 12-31-65.
5. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
6. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.
7. W. Biltz, K. A. Klatte, and E. Rahlfs, Z. Anorg. Chem. 166, 339 (1927).
8. N. N. Drozin, Zhur. Fiz. Khim. 35, 879 (1961).
9. D. R. Stull and H. Prophet in "The Characterization of High Temperature Vapors," J. L. Margrave, Ed., John Wiley and Sons, Inc., New York, 1966.
10. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., National Nuclear Energy Series IV-19B, McGraw-Hill Book Co., New York, 1950.
11. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
12. O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 349 (1933).
13. P. Lebeau, Ann. Chim. Phys. 16, 472 (1899).
14. K. N. Semenenko and T. N. Naumova, Russ. J. Structural Chem. 4, 59 (1963).

BERYLLIUM DIBROMIDE (BeBr$_2$)

(IDEAL GAS) GFW=168.82018

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 3.087	- 51.560	- 51.560	INFINITE
100	9.661	52.991	76.095	- 2.310	- 51.461	- 55.461	121.209
200	11.866	63.522	66.579	- 1.211	- 51.671	- 59.394	64.903
298	12.742	65.439	65.439	.000	- 54.800	- 62.783	46.021
300	12.755	65.518	65.439	.024	- 54.816	- 62.832	45.773
400	13.340	69.272	65.947	1.330	- 62.189	- 63.992	34.964
500	13.744	72.295	66.924	2.686	- 62.220	- 64.440	28.167
600	14.023	74.827	68.036	4.075	- 62.261	- 64.880	23.633
700	14.218	77.005	69.165	5.487	- 62.314	- 65.313	20.392
800	14.358	78.913	70.267	6.917	- 62.375	- 65.738	17.959
900	14.461	80.610	71.324	8.358	- 62.449	- 66.154	16.064
1000	14.537	82.138	72.330	9.808	- 62.539	- 66.560	14.547
1100	14.596	83.526	73.286	11.265	- 62.648	- 66.957	13.303
1200	14.643	84.798	74.193	12.727	- 62.778	- 67.343	12.265
1300	14.679	85.972	75.054	14.193	- 62.929	- 67.717	11.384
1400	14.709	87.061	75.873	15.662	- 63.102	- 68.080	10.628
1500	14.733	88.077	76.653	17.135	- 63.297	- 68.430	9.970
1600	14.753	89.028	77.397	18.609	- 66.271	- 68.686	9.382
1700	14.769	89.923	78.108	20.085	- 66.398	- 68.832	8.849
1800	14.784	90.768	78.788	21.563	- 66.529	- 68.973	8.374
1900	14.796	91.567	79.440	23.042	- 66.665	- 69.103	7.949
2000	14.806	92.326	80.065	24.522	- 66.807	- 69.230	7.565
2100	14.815	93.049	80.667	26.003	- 66.953	- 69.347	7.217
2200	14.823	93.738	81.245	27.485	- 67.105	- 69.458	6.900
2300	14.829	94.397	81.803	28.967	- 67.263	- 69.559	6.610
2400	14.835	95.029	82.341	30.450	- 67.426	- 69.654	6.343
2500	14.841	95.634	82.861	31.934	- 67.595	- 69.745	6.097
2600	14.845	96.216	83.363	33.419	- 67.768	- 69.826	5.869
2700	14.849	96.777	83.850	34.903	- 67.947	- 69.904	5.658
2800	14.853	97.317	84.321	36.388	- 139.162	- 68.864	5.375
2900	14.857	97.838	84.778	37.874	- 139.099	- 66.353	5.000
3000	14.860	98.342	85.222	39.360	- 139.039	- 63.847	4.651
3100	14.862	98.829	85.653	40.846	- 138.982	- 61.343	4.325
3200	14.865	99.301	86.072	42.332	- 138.926	- 58.836	4.018
3300	14.867	99.759	86.480	43.819	- 138.874	- 56.336	3.731
3400	14.869	100.202	86.877	45.306	- 138.825	- 53.837	3.461
3500	14.871	100.633	87.264	46.793	- 138.780	- 51.338	3.206
3600	14.873	101.052	87.641	48.280	- 138.740	- 48.839	2.965
3700	14.875	101.460	88.009	49.767	- 138.704	- 46.344	2.737
3800	14.876	101.857	88.369	51.255	- 138.674	- 43.848	2.522
3900	14.878	102.243	88.719	52.743	- 138.649	- 41.349	2.317
4000	14.879	102.620	89.062	54.230	- 138.632	- 38.859	2.123
4100	14.880	102.987	89.397	55.718	- 138.621	- 36.367	1.939
4200	14.881	103.346	89.725	57.206	- 138.617	- 33.872	1.763
4300	14.882	103.696	90.046	58.695	- 138.620	- 31.374	1.595
4400	14.883	104.038	90.360	60.183	- 138.633	- 28.880	1.434
4500	14.884	104.373	90.668	61.671	- 138.655	- 26.387	1.282
4600	14.885	104.700	90.969	63.160	- 138.686	- 23.892	1.135
4700	14.886	105.020	91.265	64.648	- 138.727	- 21.395	.995
4800	14.886	105.333	91.555	66.137	- 138.779	- 18.900	.861
4900	14.887	105.640	91.839	67.625	- 138.841	- 16.400	.731
5000	14.888	105.941	92.118	69.114	- 138.913	- 13.898	.607
5100	14.888	106.236	92.392	70.603	- 138.998	- 11.400	.489
5200	14.889	106.525	92.661	72.092	- 139.093	- 8.900	.374
5300	14.890	106.809	92.925	73.581	- 139.201	- 6.391	.264
5400	14.890	107.087	93.185	75.070	- 139.321	- 3.888	.157
5500	14.891	107.360	93.440	76.559	- 139.453	- 1.376	.055
5600	14.891	107.628	93.691	78.048	- 139.598	1.134	- .044
5700	14.891	107.892	93.938	79.537	- 139.755	3.652	- .140
5800	14.892	108.151	94.181	81.026	- 139.924	6.173	- .233
5900	14.892	108.406	94.420	82.515	- 140.107	8.689	- .322
6000	14.893	108.656	94.655	84.005	- 140.301	11.206	- .408

Dec. 31, 1961; June 30, 1965; June 30, 1975

BERYLLIUM DIBROMIDE (BeBr$_2$) (IDEAL GAS) GFW = 168.82018

Point Group $D_{\infty h}$
$S^\circ_{298.15}$ = 65.4 ± 0.5 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = [-51.6±4.0] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [-54.8±4.0] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
[227]	(1)
220	(2)
1010	(1)

Bond Distance: Be-Br = 1.91 ± 0.02 Å   Bond Angle: Br-Be-Br = 180°   σ = 2
Rotational Constant: B_0 = 0.02892 cm^{-1}

Heat of Formation

Rahlfs and Fischer (1) have reported measurements of the sublimation pressures (624-695 K) and vapor densities (736-799 K) for BeBr$_2$. Both measurements were complicated by significant reaction of the dibromide with the quartz apparatus. Assuming the reaction to be $2BeBr_2(c) + SiO_2(c) = SiBr_4(g) + 2BeO(c)$, Rahlfs and Fischer (1) corrected their measured total pressure for the partial pressure of the tetrabromide. Results of a second and third law analyses of their data are tabulated below.

MEASUREMENT	No. Of Points	Temp. Range K	ΔHs°_{298}, Kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(BeBr$_2$, g)[d] Kcal/mol
Sublimation Pressures[a]	8[b]	624-695	31.0	30.2±0.1	-1.0±0.8	-54.8
Vapor Densities-Total Pressures[c]	4	736-799	23.9	33.4±1.0	12.4±9.0	-51.6

[a] Pressures assigned to monomer.
[b] One point rejected due to failure of a statistical test.
[c] Pressures corrected for dimer.
[d] Third Law Values based on ΔHf°_{298} (BeBr$_2$, c) = -85.0 ± 3.0 kcal/mol.

The vapor density measurements (1) predict about 50% dimerization at temperatures near the melting point (Tm = 781 K). This value appears to be unusually high when compared with dimerization data which are available for BeCl$_2$, MgBr$_2$, MgCl$_2$, and MgF$_2$ (2). Mass spectral studies of these alkaline-earth dihalides show the presence of only small amounts (1-5%) of dimer in the saturated vapors up to temperatures near their melting points. Electron-diffraction experiments on BeBr$_2$ vapor are also inconsistent with high concentrations of dimer. It is quite likely that the monomer and dimer pressures reported by Rahlfs and Fischer (1) from their vapor density measurements are unreliable. Thus, we choose to adopt ΔHf°_{298} = -54.8 kcal/mol rather than the average value (-53.2 kcal/mol) of these two results. The sublimation pressures (1) are assigned solely to the monomer pending resolution of the dimerization problem. Also, ΔHf°(g) is placed in brackets to emphasize the uncertainties in ΔHf°(c).

Heat Capacity and Entropy

Information available on the structure of BeBr$_2$ tend to indicate that the molecule is linear. Electron-diffraction patterns (3, 4) for BeBr$_2$ vapor have been successfully interpreted in terms of a linear configuration. Büchler et al. (5), using electric quadruple deflection of molecular beams to detect permanent dipole moments in molecules, have shown that for the gaseous alkaline-earth dihalides the linear form is favored by a light metal-heavy halogen combination. The matrix-isolation spectrum (6) of BeBr$_2$ shows the two infrared-active vibrations which would be expected for a linear molecule. We adopt the linear configuration. The bond length is taken from the electron-diffraction studies of Akishin (3, 4). The moment of inertia is 9.6803X10^{-38} g cm^2.

The asymmetric stretching (ν_3) and bending (ν_2) frequencies have been observed in the matrix-isolation spectrum of BeBr$_2$ by Snelson (6). The adopted frequencies are gas-phase values which were estimated by Snelson (6) from the matrix data. The infrared-inactive symmetrical stretching frequency (ν_1) is calculated from an estimated force constant by a simple valence force field approximation (7). The stretching force constant (K=2.430X10^5 dynes/cm) is assumed equal to that for BeBr (2). *Literature estimates of* ν_1 *include (in cm^{-1}) 230* (6, 8) *and 209* (9). *The ground state quantum weight of one* is assigned by analogy with BaCl$_2$ (2).

Brewer et al. (8) have tabulated free energy functions for BeBr$_2$ up to 1500 K. Their values are consistently lower *than ours by about 2.5 gibbs/mol. These differences are due entirely to the higher bending frequency* (ν_2 = 446 cm^{-1}) *which* was used by Brewer et al. (8). This estimated value is now known to be incorrect.

References

1. O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 349 (1933).
2. JANAF Thermochemical Tables: Be$_2$Cl$_4$(g), 6-30-65; Mg$_2$Br$_4$(g), 6-30-74; Mg$_2$Cl$_4$(g), 12-31-69; Mg$_2$F$_4$(g), 3-31-66; BeBr(g), 6-30-75; BaCl$_2$(g), 12-31-72.
3. P. A. Akishin and V. P. Spiridonov, Kristallografiya 2, 472 (1957).
4. P. A. Akishin, V. P. Spiridonov, and G. A. Sobalev, Dokl. Akad. Nauk SSSR 118, 1134 (1958).
5. A. Büchler, J. L. Stauffer, and W. Klemperer, J. Amer. Chem. Soc. 86, 4544 (1964).
6. A. Snelson, J. Phys. Chem. 72 250 (1968).
7. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1962.
8. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
9. K. S. Krasnov and V. I. Svettsov, Izv. Vysshikh Uchekn. Zavedenii, Khim. i Khim. Tekhnol. 6, 167 (1963).

BERYLLIUM MONOHYDROXIDE (BEOH) BEHO
(IDEAL GAS) GFW=26.01958

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.277	-27.160	-27.160	INFINITE
100	7.004	41.565	57.388	-1.582	-27.201	-28.056	61.316
200	7.964	46.658	50.868	-.842	-27.249	-28.904	31.585
298	9.159	50.067	50.067	.000	-27.400	-29.690	21.763
300	9.179	50.124	50.067	.017	-27.403	-29.704	21.640
400	10.113	52.899	50.439	.984	-27.578	-30.445	16.635
500	10.793	55.233	51.171	2.031	-27.749	-31.142	13.612
600	11.293	57.247	52.020	3.137	-27.913	-31.805	11.585
700	11.678	59.018	52.896	4.286	-28.076	-32.441	10.128
800	11.992	60.599	53.761	5.470	-28.239	-33.054	9.030
900	12.260	62.027	54.602	6.683	-28.406	-33.645	8.170
1000	12.495	63.331	55.410	7.921	-28.581	-34.218	7.478
1100	12.706	64.532	56.186	9.181	-28.767	-34.773	6.909
1200	12.896	65.646	56.928	10.461	-28.967	-35.310	6.431
1300	13.067	66.685	57.639	11.759	-29.181	-35.830	6.024
1400	13.221	67.659	58.320	13.074	-29.412	-36.333	5.672
1500	13.361	68.576	58.974	14.403	-29.661	-36.819	5.365
1600	13.486	69.442	59.601	15.746	-32.685	-37.209	5.083
1700	13.599	70.263	60.205	17.100	-32.858	-37.486	4.819
1800	13.701	71.044	60.785	18.465	-33.034	-37.754	4.584
1900	13.792	71.787	61.345	19.840	-33.213	-38.011	4.372
2000	13.875	72.496	61.885	21.223	-33.395	-38.260	4.181
2100	13.950	73.175	62.406	22.614	-33.581	-38.498	4.007
2200	14.017	73.826	62.911	24.013	-33.773	-38.728	3.847
2300	14.078	74.450	63.399	25.418	-33.968	-38.947	3.701
2400	14.134	75.051	63.872	26.828	-34.170	-39.158	3.566
2500	14.184	75.629	64.331	28.244	-34.380	-39.365	3.441
2600	14.230	76.186	64.776	29.665	-34.593	-39.557	3.325
2700	14.272	76.724	65.209	31.090	-34.812	-39.744	3.217
2800	14.311	77.243	65.629	32.519	-106.068	-38.816	3.030
2900	14.346	77.746	66.039	33.952	-106.048	-36.411	2.744
3000	14.378	78.233	66.437	35.388	-106.033	-34.012	2.478
3100	14.408	78.705	66.825	36.828	-106.019	-31.614	2.229
3200	14.436	79.163	67.204	38.270	-106.009	-29.212	1.995
3300	14.461	79.608	67.573	39.715	-106.003	-26.812	1.776
3400	14.485	80.040	67.933	41.162	-106.003	-24.413	1.569
3500	14.507	80.460	68.285	42.612	-106.007	-22.015	1.375
3600	14.528	80.869	68.629	44.063	-106.017	-19.612	1.191
3700	14.548	81.267	68.965	45.517	-106.033	-17.213	1.017
3800	14.566	81.655	69.294	46.973	-106.056	-14.812	.852
3900	14.584	82.034	69.616	48.431	-106.085	-12.409	.695
4000	14.601	82.403	69.931	49.890	-106.123	-10.009	.547
4100	14.617	82.764	70.240	51.351	-106.169	-7.607	.406
4200	14.633	83.117	70.542	52.813	-106.222	-5.202	.271
4300	14.649	83.461	70.838	54.277	-106.285	-2.793	.142
4400	14.664	83.798	71.129	55.743	-106.357	-.387	.019
4500	14.678	84.128	71.414	57.210	-106.439	2.021	-.098
4600	14.693	84.451	71.694	58.679	-106.532	4.434	-.211
4700	14.708	84.767	71.969	60.149	-106.635	6.846	-.318
4800	14.722	85.076	72.239	61.620	-106.748	9.263	-.422
4900	14.737	85.380	72.504	63.093	-106.872	11.680	-.521
5000	14.752	85.678	72.765	64.568	-107.008	14.102	-.616
5100	14.766	85.970	73.021	66.043	-107.156	16.528	-.708
5200	14.782	86.257	73.272	67.521	-107.315	18.948	-.796
5300	14.797	86.539	73.520	69.000	-107.486	21.384	-.882
5400	14.813	86.816	73.764	70.480	-107.669	23.812	-.964
5500	14.828	87.088	74.003	71.962	-107.864	26.250	-1.043
5600	14.845	87.355	74.240	73.446	-108.072	28.689	-1.120
5700	14.861	87.618	74.472	74.931	-108.291	31.135	-1.194
5800	14.878	87.876	74.701	76.418	-108.522	33.587	-1.266
5900	14.896	88.131	74.926	77.907	-108.766	36.035	-1.335
6000	14.913	88.381	75.148	79.397	-109.021	38.490	-1.402

Dec. 31, 1960; Sept. 30, 1963; June 30, 1975; Dec. 31, 1975

BERYLLIUM MONOHYDROXIDE (BeOH) (IDEAL GAS) GFW = 26.01958 BEHO

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [50.07±2] gibbs/mol

ΔHf°_0 = -27.2 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -27.4 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[30000]	[4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1266] (1)
[606] (2)
[3650] (1)

Bond Distance: Be-O = [1.38] Å O-H = [0.96] Å σ=1

Bond Angle: Be-O-H = [180]° Rotational Constant: B_0 = [1.29312]cm^{-1}

Heat of Formation

The adopted ΔHf°_{298} = -27.4±10 kcal/mol, which corresponds to D°_0(Be-OH) = 113.9±10 kcal/mol, is derived from third law analysis of Knudsen-cell mass-spectrometric studies and Knudsen-cell weight-loss studies of several BeOH(g) producing reactions (1-3). The results are tabulated below. The earlier Knudsen-cell mass-spectrometric measurement by Hildenbrand et al. (4) had indicated a minimum absolute value for ΔHf°_{298}(BeOH,g) of -25±10 kcal/mol.

Investigator	Reaction	No. of Points	Temp. Range K	$-\Delta Hr_{298}$, 3rd Law kcal/mol	Drift gibbs/mol	$-\Delta Hf^\circ_{298}$ kcal/mol
Inami and Ju (1)	A	3	2422-2485	9.73±0.93	-13.0±2.0	27.2
	B	3	2422-2485	0.82±0.59	6.2±5.5	37.3
	C	3	2422-2485	75.56±1.3	-5.3±17	16.1
	D	3	2422-2485	12.09±1.8	3.6±25	29.0
Inami and Ju (2)	E	3	2425-2518	22.11±2.1	-21.3±8.6	27.1
Ko, Greenbaum, and Farber (3)	F	3	2107-2368	106.01±1.40	5.1±1.7	39.4

(A) $BeO(g)+OH(g)=BeOH(g)+O(g)$

(B) $Be_2O(g)+OH(g)=BeOH(g)+BeO(g)$

(C) $\beta\text{-}BeO(c)+H(g)=BeOH(g)$

(D) $Be_2O(g)+H(g)=BeOH(g)+Be(g)$

(E) $BeCl(g)+OH(g)=BeOH(g)+Cl(g)$

(F) $\alpha\text{-}BeO(c)+0.5H_2(g)=BeOH(g)$

Auxiliary heats of formation used in the analysis are from current JANAF Tables (5).

The average ΔHf°_{298}(BeOH,g) from the measurements of Inami and Ju (1, 2) is -27.4 kcal/mol. The D°_{298}(Be-OH) of 115 kcal/mol from ΔHf°_{298} of -27.4 kcal/mol appears more reasonable than a D°_{298}(Be-OH) of 127 kcal/mol from the ΔHf°_{298} of -39.4 kcal/mol, derived from Ko, Greenbaum, and Farber (3) above. This is based on a comparison of the trends in D°_0 values of the alkaline earth monofluorides and monochlorides and in the adopted D°_0 values for the other alkaline earth monohydroxides (5). The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has already been recognized (6-9). Accordingly, ΔHf°_{298}(BeOH,g)=-27.4±10 kcal/mol is adopted.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh (10) and the evidence that the gaseous alkali metal monohydroxides are linear (11-13). By analogy with BeF and BeCl (5) the ground state is assumed to be $^2\Sigma^+$ and the first excited state is estimated at 30000 cm^{-1}.

The Be-O bond distance is estimated to be slightly larger, 0.02 Å, than the Be-F bond distance (5) after noting the close similiarity in bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is that in water (5). The moment of inertia is 2.1646×10^{-39} g cm^2.

The Be-O stretching frequency, 1266 cm^{-1}, is estimated to be the same as the Be-F stretching frequency (5, 9). The O-H stretching frequency, 3650 cm^{-1}, is estimated from the alkali metal hydroxides series. The bending frequency, 606 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz (9, 13).

The entropy in the present table is higher by 1.83 gibbs/mol at 298K and 1.76 gibbs/mol at 1000 K than that proposed by Jackson (9); the moment of inertia as calculated by Jackson (9) appears to be in error.

References

1. Y. H. Inami and F. Ju, Philco-Ford Corp., Aeronutronic Div., Report U-4307, Contract F 04611-68-C-0012, Feb. 1, 1968.
2. Y. H. Inami and F. Ju, Philco-Ford Corp., Aeronutronic Div., Report U-4352, Contract F 06411-68-C-0012, May 1, 1968.
3. H. C. Ko, M.A. Greenbaum, and M. Farber, J. Phys. Chem. 71, 1815 (1967).
4. D. L. Hildenbrand, L. P. Theard, E. Murad, and F. Ju, Philco Corp., Aeronutronic Div., Report U-3068, Contract AF 04(611)-8523, April 1, 1965.
5. JANAF Thermochemical Tables: Be(g), 9-30-61; BeCl(g), 9-30-66; BeO (c,α), BeO(c,β), BeO(g), 12-31-74; Be_2O(g), 9-30-63; Cl(g), 6-30-72; H(g), O(g), 6-30-74; OH(g) 12-31-70; BaOH(g), CaOH(g), MgOH(g), SrOH(g), 12-31-75; BeF(g), 12-31-71; BeCl(g), 9-30-66; H_2O(g) 3-31-61.
6. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
7. J. Berkowitz, D. J. Meschi, and N. A. Chupka, J. Chem. Phys. 33, 533 (1960).
8. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
9. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Contract No. W-7405-Eng.-48, Dec. 8, 1971
10. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
11. N. Acquista, S. Abramowitz, and R. Lide, J. Chem. Phys. 49, 780 (1968).
12. R. L. Kuczkowski and R. Lide, J. Chem. Phys. 44, 3131 (1966).
13. N. Acquista and S. Abramowitz, U. S. Natl. Bur. Std. Report 9905, July, 1968.

BERYLLIUM MONOHYDROXIDE UNIPOSITIVE ION (BEOH^{+})BEHO^{+}

(IDEAL GAS) GFW=26.01903

T, °K	Cp°	S°	-(G°-H°$_{298}$)/T	H°-H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	9.187	48.711	48.711	.000	181.635	178.262	-130.669
300	9.207	48.768	48.711	.017	181.641	178.241	-129.848
400	10.138	51.551	49.084	.987	181.966	177.058	-96.740
500	10.814	53.890	49.818	2.036	182.294	175.794	-76.839
600	11.310	55.908	50.668	3.144	182.628	174.463	-63.548
700	11.692	57.681	51.546	4.294	182.963	173.075	-54.036
800	12.004	59.263	52.414	5.480	183.299	171.638	-46.889
900	12.270	60.693	53.255	6.694	183.630	170.162	-41.321
1000	12.504	61.998	54.065	7.933	183.953	168.649	-36.858
1100	12.713	63.200	54.842	9.194	184.264	167.103	-33.200
1200	12.902	64.314	55.585	10.474	184.561	165.529	-30.147
1300	13.072	65.354	56.297	11.773	184.845	163.932	-27.559
1400	13.226	66.328	56.979	13.088	185.112	162.313	-25.338
1500	13.365	67.245	57.633	14.418	185.360	160.676	-23.410
1600	13.490	68.112	58.261	15.761	182.832	159.100	-21.732
1700	13.602	68.933	58.865	17.116	183.156	157.607	-20.262
1800	13.704	69.714	59.446	18.481	183.478	156.095	-18.953
1900	13.795	70.457	60.006	19.856	183.796	154.565	-17.779
2000	13.877	71.167	60.547	21.240	184.111	153.018	-16.721
2100	13.952	71.846	61.069	22.631	184.422	151.456	-15.762
2200	14.019	72.496	61.574	24.030	184.727	149.878	-14.889
2300	14.080	73.121	62.062	25.435	185.029	148.289	-14.091
2400	14.135	73.721	62.536	26.846	185.324	146.688	-13.358
2500	14.186	74.299	62.995	28.262	185.612	145.068	-12.682
2600	14.232	74.857	63.440	29.683	185.894	143.443	-12.057
2700	14.273	75.394	63.873	31.108	186.172	141.805	-11.478
2800	14.312	75.914	64.294	32.537	115.413	141.264	-11.026
2900	14.347	76.417	64.703	33.970	115.930	142.181	-10.715
3000	14.379	76.904	65.102	35.406	116.443	143.076	-10.423
3100	14.408	77.376	65.490	36.846	116.953	143.952	-10.149
3200	14.436	77.834	65.869	38.288	117.460	144.818	-9.891
3300	14.461	78.278	66.238	39.733	117.963	145.665	-9.647
3400	14.484	78.710	66.599	41.180	118.460	146.496	-9.417
3500	14.505	79.131	66.951	42.629	118.953	147.312	-9.199
3600	14.525	79.540	67.295	44.081	119.439	148.118	-8.992
3700	14.544	79.938	67.631	45.535	119.919	148.906	-8.796
3800	14.561	80.326	67.960	46.990	120.393	149.685	-6.609
3900	14.577	80.704	68.282	48.447	120.860	150.450	-8.431
4000	14.592	81.074	68.597	49.905	121.317	151.200	-8.261
4100	14.606	81.434	68.906	51.365	121.768	151.940	-8.099
4200	14.619	81.786	69.208	52.826	122.210	152.672	-7.944
4300	14.632	82.130	69.505	54.289	122.643	153.396	-7.796
4400	14.643	82.467	69.796	55.753	123.066	154.104	-7.654
4500	14.654	82.796	70.081	57.218	123.477	154.803	-7.518
4600	14.664	83.118	70.361	58.684	123.879	155.496	-7.388
4700	14.674	83.434	70.636	60.150	124.270	156.179	-7.262
4800	14.683	83.743	70.906	61.618	124.650	156.855	-7.142
4900	14.691	84.046	71.171	63.087	125.018	157.521	-7.026
5000	14.699	84.342	71.431	64.556	125.374	158.181	-6.914
5100	14.707	84.634	71.687	66.027	125.717	158.836	-6.807
5200	14.714	84.919	71.939	67.498	126.049	159.476	-6.703
5300	14.721	85.200	72.186	68.970	126.367	160.122	-6.603
5400	14.727	85.475	72.430	70.442	126.673	160.751	-6.506
5500	14.733	85.745	72.670	71.915	126.965	161.380	-6.413
5600	14.739	86.011	72.906	73.389	127.245	162.002	-6.322
5700	14.745	86.272	73.138	74.863	127.512	162.623	-6.235
5800	14.750	86.528	73.366	76.338	127.765	163.240	-6.151
5900	14.755	86.780	73.592	77.813	128.005	163.846	-6.069
6000	14.760	87.028	73.814	79.289	128.231	164.449	-5.990

June 30, 1968; Dec. 31, 1975

BERYLLIUM MONOHYDROXIDE UNIPOSITIVE ION (BeOH^{+}) (IDEAL GAS) GFW = 26.01903

Point Group [$C_{\infty v}$]

$S^{\circ}_{298.15}$ = [48.7 ± 1.5] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_{0} = 180.39 ± 12.0 kcal/mol BEHO^{+}

$\Delta Hf^{\circ}_{298.15}$ = 181.63 ± 12.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[1260](1)
[600](2)
[3650](1)

Bond Distance: Be-O = [1.38] Å O-H = [0.96] Å
Bond Angle: Be-O-H = [180°] σ = 1
Rotational Constant: B_0 = [1.2932] cm^{-1}

Heat of Formation

Using mass spectrometric techniques, Inami and Ju (1) determined the appearance potential of BeOH(g) to be 9.0±0.5 ev (207.55±11.53 kcal/mol). In the same study, Porter (2) was reported to have said that the appearance potential of a metal hydroxide is expected to be about the same as the corresponding fluoride. In this case, the appearance potential of BeF(g) is 9.1 ev (1), which is within 0.1 ev of the value for BeOH(g). It is also interesting to note that the ionization potential of Be(g) is 9.32 ev (3). We adopt the experimentally determined appearance potential of 9.0±0.5 ev which refers to the process BeOH(g) + e^- = BeOH^{+}(g) + 2e^-. Using auxiliary data (3), we calculate ΔHf°_{0} = 180.39±12.0 kcal/mol for BeOH^{+}(g). *This leads to* ΔHf°_{298} = *181.63±12.0 kcal/mol.*

Heat Capacity and Entropy

The molecular configuration is assumed to be linear since experimental evidence indicates that the gaseous alkali metal hydroxides are linear (3,4,5,6). In addition, Walsh (7) had predicted that BAH molecules (H=hydrogen atom) with ten or less valence electrons (BeOH^{+} has 8 valence electrons) will be linear in their ground state. The molecule BeOH^{+} is isoelectronic with LiOH.

The bond dissociation energy for BeOH^{+}(D°_{0} = 121.2 kcal/mol, 3) for the process BeOH^{+}(g) = Be^{+}(g) + OH(g) is fairly close to that for *BeOH*(D°_{0} = *113.9 kcal/mol, 3). This suggests a similar bonding in these two molecules.* Thus, bond distances are assumed to be the same as those adopted for BeOH(g,3). The moment of inertia is 2.1645 x 10^{-39} g cm^{2}. The vibrational frequencies are assumed to be similar to those adopted for BeOH(g,3). The ground state quantum weight is assumed to be the same as that of LiOH(g,3). The enthalpy change between 0 and 298.15K is -2.281 kcal/mol.

References

1. Y. H. Inami and F. Ju, Philco-Ford Corp., Aeronutronic Dev., Report U-4307, Contract F 04611-68-C-0012, Feb. 1, 1968.
2. R. F. Porter, private communication, as referenced in (1).
3. JANAF Thermochemical Tables : e^-, 3-31-65; Be^{+}(g), *6-30-65; LiOH(g), 6-30-71; BeOH(g), 12-31-75.*
4. N. Acquista, S. Abramowitz, and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
5. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. 44, 3131 (1966).
6. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9905, July, 1968.
7. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

BERYLLIUM DIHYDROXIDE, ALPHA (α-Be$(OH)_2$) BeH$_2$O$_2$

(CRYSTAL) GFW=43.02698

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	15.703	12.800	12.800	.000	− 215.800	− 195.021	142.954
300	15.737	12.897	12.800	.029	− 215.804	− 194.892	141.979
400	19.814	18.029	13.473	1.823	− 215.854	− 187.906	102.667
500	22.226	22.726	14.862	3.932	− 215.679	− 180.936	79.087
600	23.754	26.920	16.529	6.235	− 215.373	− 174.015	63.385
700	24.846	30.667	18.286	8.667	− 214.993	− 167.150	52.187
800	25.692	34.042	20.048	11.195	− 214.564	− 160.346	43.805
900	26.386	37.109	21.776	13.800	− 214.102	− 153.595	37.298
1000	26.985	39.921	23.452	16.469	− 213.618	− 146.898	32.104

Dec. 31, 1966; Dec. 31, 1975

BERYLLIUM DIHYDROXIDE, ALPHA (α-Be$(OH)_2$) CRYSTAL GFW = 43.02698

ΔHf°_0 = unknown BeH$_2$O$_2$

$S^\circ_{298.15}$ = [12.8 ± 2.0] gibbs/mol $\Delta Hf^\circ_{298.15}$ = −215.8 ± 0.5 kcal/mol

Td = [354] K

Heat of Formation

Bear and Turnbull (1) measured the heat of solution of α-Be$(OH)_2$ and Be in 22.6% HF(aq) at 21°C. Combining these results, adjusting to 25°C, and correcting for the small HF concentration differences in the two systems, we calculate ΔHr°_{298} = −79.16 kcal/mol for the reaction Be(c) + $2H_2O(\ell)$ = Be$(OH)_2$(α,c) + H_2(g). Using auxiliary data (2, 3), we derive ΔHf°_{298} = −215.8 kcal/ mol for α-Be$(OH)_2$. Since this adopted value is calorimetrically determined and based on well characterized samples, we assign an uncertainty of ±0.5 kcal/mol.

Parker (4) recently reviewed data pertaining to the heat of formation of the beryllium hydroxides. Her analyses were intended to give additional support to the thermochemical values chosen for BeO(c). Our interpretation would differ slightly due to the fact that our ΔHf° value for BeO(c) is different (by 0.3 kcal/mol at 298.15 K) from that adopted by Parker (4). Discussed in her review were the heat of solution studies by Fricke and Wullhorst (5) [involving BeO and α-Be$(OH)_2$ in 11.59% HF] and Matignon and Marchal (6, 7) [amorphous Be$(OH)_2$ in 30% HF]. In addition there is also an earlier study by Mulert (8) involving amorphous Be$(OH)_2$ in 20% HF. All these studies are in fair agreement with our adopted value for ΔHf°_{298}. These latter studies are thought to be less reliable, however, due to incomplete characterization of the beryllium compounds.

Heat Capacity and Entropy

The heat capacity is assumed to be identical to that of the β-phase. The entropy difference between the α and β phases may be obtained from the solubility data of Fricke and Humme (9). Both crystalline forms of Be$(OH)_2$ were dissolved in varying concentrations of aqueous NaOH. By relating the quantities dissolved, we calculate ΔG°_{303} = −0.5 (±0.2) kcal/mol for the process α-Be$(OH)_2$ = β-Be$(OH)_2$. Using auxiliary data (2), we find ΔS°_{303} = −0.8 gibbs/mol, from which we calculate and adopt S°_{298} = 12.8 gibbs/mol for α-Be$(OH)_2$. We assign an uncertainty of ±2 gibbs/mol to reflect the possible error in this calculation of ΔS°_{303}.

Phase Data

The structural information for α-Be$(OH)_2$ via x-ray techniques is not complete (1, 9, 10, 11). A tetragonal unit cell has been suggested by Guillemat and Lecocq (11) without supporting data. Bear and Turnbull (1), following this suggestion and using their x-ray data, calculated a crystal density which was consistent with the two experimentally determined values of Fricke and Severin (12, helium densitometry and a pycnometric method). This lends support to the premise that α-Be$(OH)_2$ has a tetragonal unit cell. The alpha phase is metastable.

Decomposition Data

Td is calculated as the temperature at which ΔGr° is zero for the reaction Be$(OH)_2$(α,c) = BeO(α,c) + H_2O(g).

References

1. I. J. Bear and A. G. Turnbull, J. Phys. Chem. 69, 2828 (1965).
2. JANAF Thermochemical Tables: Be(c), 9-30-61; H_2(g) and H_2O(g), 3-31-61; BeO(α,c), 6-30-75; Be$(OH)_2$(β,c), 12-31-75.
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. V. B. Parker, J. Res. Natl. Bur. Std. 77A, 227 (1973); U. S. Natl. Bur. Std. Rept. 10004, pp. 58-81, Jan., 1969.
5. R. Fricke and B. Wullhorst, Z. anorg. allgem. Chem 205, 127 (1932).
6. C. Matignon and G. Marchal, Bull. soc. chim. France 39, 167 (1926).
7. C. Matignon and G. Marchal, Compt. rend. 181, 859 (1925).
8. O. Mulert, Z. anorg. allgem. Chem. 75, 198 (1912).
9. R. Fricke and H. Humme, Z. anorg. allgem. Chem. 178, 400 (1929).
10. M. Bernier, Commission Energie Atomique (France) Rapport CEA2326 (1963).
11. A. Guillemat and A. Lecocq, Compt. rend. 257, 1260 (1963).
12. R. Fricke and H. Severin, Z. anorg. allgem. Chem. 205, 287 (1932).

BERYLLIUM DIHYDROXIDE, BETA (β-BE(OH)$_2$) BEH$_2$O$_2$

(CRYSTAL) GFW=43.02698

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							
100							
200							
298	15.703	12.000	12.000	.000	- 216.500	- 195.483	143.293
300	15.787	12.097	12.000	.029	- 216.504	- 195.352	142.314
400	19.814	17.229	12.673	1.823	- 216.554	- 188.286	102.875
500	22.226	21.926	14.062	3.932	- 216.379	- 181.236	79.218
600	23.754	26.120	15.729	6.235	- 216.073	- 174.235	63.465
700	24.846	29.867	17.486	8.667	- 215.693	- 167.290	52.230
800	25.692	33.242	19.248	11.195	- 215.264	- 160.406	43.821
900	26.386	36.309	20.976	13.800	- 214.802	- 153.575	37.293
1000	26.985	39.121	22.652	16.469	- 214.318	- 146.798	32.083

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1966;
Dec. 31, 1975

BERYLLIUM DIHYDROXIDE, BETA (β-Be(OH)$_2$) (CRYSTAL) GFW = 43.02698

ΔHf°_0 = unknown BEH$_2$O$_2$

$S^\circ_{298.15}$ = [12.0 ± 1.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -216.5 ± 0.5 kcal/mol

Td = [366] K

Heat of Formation

Bear and Turnbull (1) measured the heat of solution of β-Be(OH)$_2$ and Be in 22.6% HF(aq) at 21°C. Combining these results, adjusting to 25°C, and correcting for the small HF concentration differences in the two systems, we calculate ΔHr°_{298} = -79.89 kcal/mol for the reaction $Be(c) + 2H_2O(\ell) = Be(OH)_2(\beta,c) + H_2(g)$. Using auxiliary data (2, 3), we derive ΔHf°_{298} = -216.5 kcal/mol for β-Be(OH)$_2$. Since this adopted value is calorimetrically determined and based on well characterized samples, we assign an uncertainty of ±0.5 kcal/mol.

Parker (4) recently reviewed data pertaining to the heat of formation of the beryllium hydroxides. Her analyses were intended to give additional support to the thermochemical values chosen for BeO(c). Our interpretation would differ slightly due to the fact that our ΔHf° value for BeO(c) is different (by 0.3 kcal/mol at 298.15 K) from that adopted by Parker (4). Discussed in her review were the heat of solution studies by Fricke and Wullhorst (5) [involving BeO and β-Be(OH)$_2$ in 11.59% HF] and Matignon and Marchal (6, 7) [amorphous Be(OH)$_2$ in 30% HF]. In addition there is also an earlier study by Mulert (8) involving amorphous Be(OH)$_2$ in 20% HF. These latter three studies are in fair agreement with our adopted value for ΔHf°_{298} but are thought to be less reliable, however, due to incomplete characterization of the beryllium compounds.

Fricke and Severin (9) and Baur and Lecocq (10) measured the decomposition pressure of water vapor over β-Be(OH)$_2$. Fricke and Severin (9) observed a decomposition temperature of 105°C at a pressure of 100 mm Hg while Baur and Lecocq (10) observed 223°C for the equilibrium with saturated water vapor at 24.2 atm. We reduce the latter data to a standard state value ΔG°_{496} = -3028 cal/mol for the decomposition reaction $Be(OH)_2(\beta,c) = BeO(\alpha,c) + H_2O(g)$. The third law analyses for these two decomposition studies are given below where ΔHf°_{298} refers to the heat of formation of β-Be(OH)$_2$.

Source	temp, K	method	ΔHr°_{298} (kcal/mol)	ΔHf°_{298} (kcal/mol)
Fricke and Severin (9)	378	Kp	15.27	≥-218.5
Baur and Lecocq (10)	496	Kp	14.88	≥-218.1

These values are within 2 kcal/mol of our adopted ΔHf°_{298} value. The difference may be due to the formation of metastable BeO. Fricke and Severin (9) reported that BeO had a distorted lattice which would suggest a ΔHf° value more positive than -145.4 kcal/mol. Thus, we conclude that these two studies (9, 10) are consistent with our adopted value but are not sufficiently definitive for further consideration.

Heat Capacity and Entropy

The heat capacity is estimated from that for Mg(OH)$_2$ by subtracting the values for MgO(c) and adding those for BeO(α,c)(2). The entropy is estimated to be S°_{298} = 12.0 gibbs/mol. This value is a compromise of values suggested by two different paths. Additive entropy constants of Kelley (11) yield S°_{298} = 13.20 gibbs/mol whereas a comparison of entropy differences for the alkali metal and alkaline earth chlorides and hydroxides suggest values in the range 10.2 to 12.4 gibbs/mol. Our adopted value is the same as that selected by NBS (12).

Phase Data

Bear and Turnbull (1) and Seitz et al. (13), using x-ray powder techniques, determined that β-Be(OH)$_2$ has an orthohombic structure, the ε-Zn(OH)$_2$ structure. The β-structure is the stable crystalline form for Be(OH)$_2$ whereas the α-structure is metastable.

Decomposition Data

Td is calculated as the temperature at which ΔGr° is zero for the reaction $Be(OH)_2(\beta,c) = BeO(\alpha,c) + H_2O(g)$.

References

1. I. J. Bear and A. G. Turnbull, J. Phys. Chem. 69, 2828 (1965).
2. JANAF Thermochemical Tables: Be(c), 9-30-61; H_2(g) and H_2O(g), 3-31-61; BeO(α,c), 6-30-75; BeO(β,c) and MgO(c), 12-31-74; Mg(OH)$_2$(c), 12-31-75.
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. V. B. Parker, J. Res. Natl. Bur. Std. 77A, 227 (1973); U. S. Natl. Bur. Std. Rept 10004, pp 58-81, Jan., 1969.
5. R. Fricke and B. Wullhorst, Z. anorg. allgem. Chem. 205, 127 (1932).
6. C. Matignon and G. Marchal, Bull. soc. chim. France 39, 167 (1926).
7. C. Matignon and G. Marchal, Compt. rend. 181, 859 (1925).
8. O. Mulert, Z. anorg. allgem. Chem. 178, 198 (1912).
9. R. Fricke and H. Severin, Z. anorg. allgem. 205, 287 (1932).
10. A. Baur and A. Lecocq, Comm. Energie At. (France), Rappt. CEA-R2611, 17 pp (1964).
11. D. R. Stull and H. Prophet in "The Characterization of High Temperature Vapors", J. L. Margrave, ed., John Wiley and Sons, Inc., New York 1966.
12. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.
13. A. Seitz, U. Rosler, and K. Schubert, Z. anorg. allgem. Chem. 261, 94 (1960).

BEH$_2$O$_2$

BERYLLIUM DIHYDROXIDE ($Be(OH)_2$) BEH_2O_2

(IDEAL GAS) GFW=43.02698

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.008	-160.141	-160.141	INFINITE
100	7.760	43.986	66.966	-2.298	-160.894	-158.701	346.842
200	11.756	50.518	57.180	-1.332	-161.365	-156.319	170.818
298	15.157	55.893	55.893	.000	-161.700	-153.769	112.716
300	15.208	55.987	55.893	.028	-161.705	-153.720	111.985
400	17.385	60.684	56.519	1.666	-161.911	-151.025	82.516
500	18.792	64.725	57.766	3.480	-162.031	-148.288	64.817
600	19.773	68.243	59.225	5.411	-162.097	-145.532	53.010
700	20.512	71.348	60.740	7.426	-162.134	-142.768	44.574
800	21.112	74.128	62.242	9.508	-162.151	-140.002	38.247
900	21.626	76.645	63.705	11.646	-162.156	-137.231	33.324
1000	22.080	78.947	65.116	13.831	-162.156	-134.462	29.387
1100	22.489	81.071	66.471	16.060	-162.156	-131.692	26.165
1200	22.859	83.044	67.771	18.328	-162.159	-128.923	23.480
1300	23.194	84.887	69.017	20.631	-162.169	-126.153	21.208
1400	23.497	86.617	70.213	22.966	-162.188	-123.382	19.261
1500	23.770	88.248	71.362	25.329	-162.222	-120.609	17.573
1600	24.017	89.790	72.466	27.719	-165.026	-117.756	16.085
1700	24.240	91.253	73.528	30.132	-164.975	-114.801	14.759
1800	24.441	92.644	74.552	32.566	-164.925	-111.852	13.581
1900	24.622	93.971	75.539	35.019	-164.876	-108.904	12.527
2000	24.785	95.238	76.493	37.490	-164.828	-105.961	11.579
2100	24.933	96.451	77.414	39.976	-164.784	-103.018	10.721
2200	25.067	97.614	78.306	42.476	-164.746	-100.078	9.942
2300	25.188	98.731	79.170	44.989	-164.711	-97.139	9.230
2400	25.298	99.805	80.008	47.513	-164.684	-94.198	8.578
2500	25.398	100.840	80.820	50.048	-164.666	-91.268	7.979
2600	25.489	101.838	81.610	52.592	-164.652	-88.328	7.425
2700	25.572	102.801	82.377	55.146	-164.645	-85.393	6.912
2800	25.648	103.733	83.123	57.707	-235.677	-81.351	6.350
2900	25.718	104.634	83.849	60.275	-235.435	-75.839	5.715
3000	25.782	105.507	84.557	62.850	-235.199	-70.342	5.124
3100	25.840	106.353	85.246	65.431	-234.966	-64.854	4.572
3200	25.895	107.174	85.919	68.018	-234.739	-59.367	4.055
3300	25.945	107.972	86.575	70.610	-234.519	-53.890	3.569
3400	25.991	108.747	87.216	73.207	-234.306	-48.422	3.113
3500	26.034	109.501	87.842	75.808	-234.100	-42.959	2.682
3600	26.073	110.235	88.454	78.413	-233.902	-37.497	2.276
3700	26.110	110.950	89.052	81.023	-233.713	-32.045	1.893
3800	26.145	111.647	89.638	83.635	-233.533	-26.596	1.530
3900	26.177	112.326	90.211	86.251	-233.362	-21.152	1.185
4000	26.206	112.990	90.772	88.871	-233.201	-15.715	.859
4100	26.234	113.637	91.322	91.493	-233.051	-10.282	.548
4200	26.260	114.270	91.861	94.117	-232.912	-4.849	.252
4300	26.285	114.888	92.389	96.745	-232.783	.583	-.030
4400	26.308	115.492	92.907	99.374	-232.668	6.005	-.298
4500	26.329	116.084	93.416	102.006	-232.565	11.427	-.555
4600	26.349	116.663	93.915	104.640	-232.474	16.853	-.801
4700	26.368	117.229	94.405	107.276	-232.397	22.270	-1.036
4800	26.386	117.785	94.886	109.914	-232.332	27.690	-1.261
4900	26.403	118.329	95.359	112.553	-232.281	33.103	-1.476
5000	26.419	118.863	95.824	115.194	-232.244	38.518	-1.684
5100	26.434	119.386	96.281	117.837	-232.222	43.938	-1.883
5200	26.449	119.899	96.730	120.481	-232.213	49.344	-2.074
5300	26.462	120.403	97.172	123.127	-232.219	54.769	-2.258
5400	26.475	120.898	97.607	125.774	-232.240	60.175	-2.435
5500	26.487	121.384	98.035	128.422	-232.275	65.594	-2.606
5600	26.499	121.861	98.456	131.071	-232.327	71.006	-2.771
5700	26.510	122.331	98.871	133.722	-232.391	76.426	-2.930
5800	26.520	122.792	99.279	136.373	-232.472	81.850	-3.084
5900	26.530	123.245	99.681	139.026	-232.567	87.265	-3.233
6000	26.540	123.691	100.078	141.679	-232.677	92.685	-3.376

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1966;
March 31, 1967; Dec. 31, 1975

BERYLLIUM DIHYDROXIDE ($Be(OH)_2$) (IDEAL GAS) GFW = 43.02698

Point Group = [$C_{\infty h}$]
$S°_{298.15}$ = [55.89 ± 3.0] gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -160.1 ± 9.0 kcal/mol BEH_2O_2
$\Delta Hf°_{298.15}$ = -161.7 ± 9.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[670](1)	[3650](2)
[345](2)	[606](4)
[1530](1)	

Bond Distances: Be-O = [1.42] Å O-H = [0.96]Å σ = 2
Bond Angles: Be-O-H = [180°] O-Be-O = [180°]
Rotational Constant: B_o = [0.22198] cm^{-1}

Heat of Formation

The equilibrium reaction $BeO(\alpha,c) + H_2O(g) = Be(OH)_2(g)$ has been studied by several investigators (1-6); all inferred that $Be(OH)_2$ was the major product, but there was no direct proof of this. A second and third law analysis is given below.

			$\Delta Hr°_{298}$, kcal/mol*		drift	$\Delta Hf°_{298}$*
	No. of Pts.	Range, K	2nd Law	3rd Law	gibbs/mol	kcal/mol
Stuart and Price (1)	15**	1338-1653	40.66±0.70	41.76±0.26	0.7±0.4	-161.74
Young (2)	7	1576-1839	42.25±1.46	41.58±0.43	-0.4±0.9	-161.92
Grossweiner and Seifert (3)	24**	1472-1873	42.23±0.17	42.27±0.69	0.0±0.7	-161.23
	11	1673		41.09±1.47		-161.81
Blauer et al. (4)	4	1567-1808	38.2±4.3	35.26±0.82	-1.8±2.5	-168.24
Brewer and Elliott (5)	6	1527-1583	74.8±68.8	44.12±4.4	-20±44	-159.38
Morize et al. (6)	eqn		49.1	37.7	-6.9	-165.80

*$\Delta Hf°_{298}$ is the heat of formation for $Be(OH)_2(g)$ as derived from the third law $\Delta Hr°_{298}$.
$\Delta Hr°_{298}$ refers to the reaction $BeO(\alpha,c) + H_2O(g) = Be(OH)_2(g)$
**One (or two) point(s) rejected due to a statistical test.

Three of these studies (1-3) were conducted under similar conditions. Each of these investigations (1-3) varied the $H_2O(g)$ flow rate without a detectable change in Kp values. However, one study (3) used a considerably larger flow rate than the others (1, 2). The residence times in all cases were quite comparable. Blauer et al. (4) studied the same system using molecular flow effusion techniques. They reported a larger variation of Kp with surface area, operated at pressures near the upper limits of the molecular flow regime, and encountered unexpected variations of the blank experiments with sample size. Brewer and Elliott (5) also studied the same system but details of the sample are not available and the results show considerable drift. Baur and Lecocq (7) cited a study by Morize et al. (6). No details are given and the results are presented in equation form. It is presumed that the results were obtained in the vicinity of 1673 K.

We adopt $\Delta Hf°_{298}$ = -161.7 kcal/mol for $Be(OH)_2(g)$ which is an average value of three studies (1-3). We assign an uncertainty of ±9.0 kcal/mol. The remaining studies are in reasonable agreement with our adopted value (and its uncertainty). As is suggested by Blauer et al. (4), the results of the transpiration studies are greatly affected by surface effects. The larger ΔHf value derived from Blauer et al. (4) is due to a consideration of sample size and surface effects. Thus, it is possible that the earlier studies (1, 2, 3) had not achieved equilibrium.

Hildenbrand et al. (8) *examined the* $BeO-H_2O$ system at 2300 °C mass-spectrometrically and detected BeOH and $Be(OH)_2$. They reported a maximum value for the equilibrium constant for the reaction $BeO(g) + H_2O(g) = Be(OH)_2(g)$. From this maximum value, we calculate $\Delta Hf°_{298} \geq -161.3$ kcal/mol for $Be(OH)_2(g)$. This gives additional support for our adopted value. Qualitative support is found by comparing the dissociation energies of BeOH(g) and $Be(OH)_2(g)$ into Be(g) and OH(g); the ratio for the mono- to dihydroxide dissociation is (113.9/256.1) = 0.445; a value which is consistent with similar ratios for the other alkaline earth hydroxides and halides.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and di-*fluorides, has been recognized* (9-11). *The* O-Be-O angle is assumed to be the same as the F-Be-F angle, (12), i.e. 180°; the Be-O-H angle is assumed to be linear as in MgOH(g) (12). The Be-O bond distance is estimated to be slightly larger, 0.02 Å, than the Be-F distance in BeF_2(12) after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is taken to be the same as in water (12). The moment of inertia is 1.26096×10^{-39} g cm^2.

The vibrational frequencies are estimated to be the same as in BeF_2 (12) (O-Be-O symmetrical and antisymmetrical stretch and bend) and as in BeOH (12) (O-H stretch and Be-O-H bend).

Jackson (13) has used a different molecular configuration and different vibrational frequencies to estimate $S°_{298}$ = 59.076 gibbs/mol. We assign an uncertainty of ±3 gibbs/mol to the adopted entropy.

One vibrational frequency, 649 cm^{-1}, *was reported by Farber* et al. (14) based on infrared spectral data. We do not adopt this value for the following reasons. It is within 21 cm^{-1} of an adopted value and will not drastically change the entropy. For consistency we estimate all the vibrational frequencies for the alkaline earth dihydroxides in the same manner since the result of Farber et al. (14) is the only reported value.

References

1. W. I. Stuart and G. H. Price, J. Nucl. Mater. 14, 417 (1964).
2. W. A. Young, J. Phys. Chem. 64, 1003 (1960).
3. L. I. Grossweiner and R. L. Seifert, J. Amer. Chem. Soc. 74, 2701 (1952).
4. J. Blauer, M. A. Greenbaum, and M. Farber, J. Phys. Chem. 70, 973 (1966).
5. L. Brewer and G. R. B. Elliott, UCRL 1831 (1952).
6. Morize, Roudier, and Besson, DM/948.
7. A. Baur and A. Lecocq, Comm. Energie At. (France), Rappt. CEA-R2611 (1964).
8. D. F. Hildenbrand, L. P. Theard, and F. Ju., Aeronautronic, 3rd Quarterly Technical Report No. U-2231, Contract AF 03(611)-8523, 31 July 1963.
9. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
10. J. Berkowitz, D. J. Mescki, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
11. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
12. JANAF Thermochemical Tables: $BeF_2(g)$, 12-31-71; Mg(OH)(g) and Be(OH)(g), 12-31-75; $H_2O(g)$, 3-31-61.
13. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., UCRL-51137, Contract No. W-7405-Eng.-48, Dec. 8, 1971.
14. M. Farber, et al., Rocket Power, Inc., AFRPL-TR-66-220, September, 1966.

BEH_2O_2

BERYLLIUM MONOIODIDE (BeI) BeI

(IDEAL GAS) GFW=135.91668

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.174	40.500	40.500	INFINITE
100	6.983	48.642	63.430	-1.479	40.821	36.699	-80.205
200	7.464	53.602	57.404	-.760	40.812	32.564	-35.584
298	8.001	56.688	56.688	.000	40.629	28.546	-20.924
300	8.009	56.738	56.689	.015	40.625	28.471	-20.741
400	8.353	59.093	57.007	.834	38.420	24.527	-13.401
500	8.561	60.981	57.620	1.681	33.001	21.571	-9.429
600	8.694	62.555	58.315	2.544	32.874	19.297	-7.029
700	8.785	63.902	59.019	3.418	32.726	17.045	-5.322
800	8.850	65.080	59.704	4.300	32.563	14.816	-4.048
900	8.900	66.125	60.361	5.188	32.381	12.609	-3.062
1000	8.939	67.065	60.985	6.080	32.181	10.422	-2.278
1100	8.972	67.918	61.577	6.975	31.959	8.257	-1.641
1200	9.000	68.700	62.139	7.874	31.714	6.113	-1.113
1300	9.024	69.422	62.671	8.775	31.449	3.990	-.671
1400	9.046	70.091	63.178	9.679	31.160	1.889	-.295
1500	9.066	70.716	63.660	10.584	30.849	-.193	.028
1600	9.085	71.302	64.119	11.492	27.761	-2.172	.297
1700	9.103	71.853	64.558	12.401	27.519	-4.035	.519
1800	9.119	72.374	64.978	13.312	27.274	-5.885	.714
1900	9.135	72.867	65.380	14.225	27.024	-7.720	.888
2000	9.151	73.336	65.767	15.139	26.770	-9.543	1.043
2100	9.166	73.783	66.138	16.055	26.513	-11.352	1.181
2200	9.180	74.210	66.495	16.973	26.250	-13.149	1.306
2300	9.195	74.618	66.839	17.891	25.984	-14.932	1.419
2400	9.209	75.010	67.172	18.811	25.714	-16.705	1.521
2500	9.223	75.386	67.493	19.733	25.438	-18.468	1.615
2600	9.237	75.748	67.803	20.656	25.159	-20.218	1.699
2700	9.251	76.097	68.104	21.580	24.876	-21.958	1.777
2800	9.265	76.434	68.396	22.506	-46.440	-22.579	1.762
2900	9.279	76.759	68.678	23.433	-46.479	-21.725	1.637
3000	9.294	77.074	68.953	24.362	-46.520	-20.872	1.521
3100	9.309	77.379	69.220	25.292	-46.560	-20.018	1.411
3200	9.324	77.675	69.480	26.224	-46.600	-19.159	1.308
3300	9.340	77.962	69.732	27.157	-46.643	-18.300	1.212
3400	9.357	78.241	69.978	28.092	-46.688	-17.442	1.121
3500	9.374	78.512	70.218	29.028	-46.733	-16.582	1.035
3600	9.392	78.777	70.452	29.967	-46.782	-15.718	.954
3700	9.410	79.034	70.681	30.907	-46.833	-14.857	.878
3800	9.430	79.285	70.904	31.849	-46.888	-13.991	.805
3900	9.450	79.531	71.122	32.793	-46.946	-13.122	.735
4000	9.471	79.770	71.335	33.739	-47.009	-12.257	.670
4100	9.493	80.004	71.544	34.687	-47.076	-11.388	.607
4200	9.517	80.233	71.748	35.637	-47.147	-10.516	.547
4300	9.541	80.458	71.948	36.590	-47.224	-9.642	.490
4400	9.566	80.677	72.144	37.546	-47.307	-8.768	.435
4500	9.592	80.892	72.336	38.504	-47.396	-7.890	.383
4600	9.619	81.104	72.524	39.464	-47.492	-7.012	.333
4700	9.647	81.311	72.709	40.427	-47.594	-6.133	.285
4800	9.676	81.514	72.890	41.394	-47.704	-5.248	.239
4900	9.706	81.714	73.068	42.363	-47.820	-4.361	.195
5000	9.737	81.910	73.243	43.335	-47.944	-3.471	.152
5100	9.769	82.103	73.415	44.310	-48.076	-2.581	.111
5200	9.802	82.293	73.584	45.289	-48.217	-1.692	.071
5300	9.835	82.481	73.750	46.271	-48.366	-.793	.033
5400	9.870	82.665	73.914	47.256	-48.523	.106	-.004
5500	9.905	82.646	74.074	48.245	-48.689	1.007	-.040
5600	9.940	83.025	74.233	49.237	-48.863	1.911	-.075
5700	9.977	83.201	74.388	50.233	-49.045	2.822	-.108
5800	10.013	83.375	74.542	51.232	-49.236	3.736	-.141
5900	10.051	83.546	74.693	52.235	-49.436	4.647	-.172
6000	10.088	83.716	74.842	53.242	-49.644	5.564	-.203

Dec. 31, 1961; Sept 30, 1964; Dec. 31, 1975

BERYLLIUM MONOIODIDE (BeI) (IDEAL GAS) GFW = 135.91668

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 56.69 ± 0.05 gibbs/mol

ΔHf° = 40.5 ± 10.0 kcal/mol BeI

$\Delta Hf^\circ_{298.15}$ = 40.6 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A_1\,^2\Pi_{1/2}$	23541	2
$A_2\,^2\Pi_{3/2}$	23898	2

ω_e = 611.7 cm^{-1}

B_e = 0.4406 cm^{-1}

$\omega_e x_e$ = [3.36] cm^{-1}

α_e = [0.0042] cm^{-1}

σ = 1

r_e = 2.132 Å

Heat of Formation

No thermochemical measurement of the heat of formation has been made. The selected value, ΔHf°_0(BeI,g) = 40.5 kcal/mol, is obtained from an analysis of spectroscopic data. The adopted values for the ground state vibrational constants give $D^\circ_0 = 3.41_4$ eV (78.73 kcal/mol) via a linear Berge-Sponer extrapolation (1). Based on the ionicity correction developed by Hildenbrand (2), this value adjusts to $D^\circ_0 = 2.70_7$ eV (62.43 kcal/mol). We adopt D°_0 = 62.4±10.0 kcal/mol which corresponds to ΔHf°_0 = 40.5±10.0 kcal/mol.

Support for the adopted D°_0 value is provided by an examination of the trends in the dissociation energies for all alkaline earth monohalides and a comparison of the values for the ratio $D^\circ_{298}(MX)/\Delta Ha^\circ_{298}(MX_2)$ for the alkaline earth halides (3). For the beryllium iodides this ratio is 0.44 which is consistent with the values of this ratio for other alkaline earth halides.

Heat Capacity and Entropy

The ground state vibrational and rotational constants are derived from spectroscopic studies by Murty and Rao (4, 5, 6). The reported value for $\omega_e x_e$ (1.6 cm^{-1}) appears to be inconsistent with the values obtained for other alkaline earth monohalides. By a comparison of $(\omega_e/\omega_e x_e)$ and $x_e\mu^{1/2}$ values, we estimate $\omega_e x_e$ = 3.36 cm^{-1} and adopt this value. The reported B_0 value is converted to B_e by using a calculated value for α_e. We calculate α_e from the relation $\alpha_e/B_e = 13.2\,(B_e/\omega_e)$ as suggested by Calder and Ruedenberg (7). Initially we use the B_0 value in this relationship and then iterate to obtain consistent values for B_e and α_e. We calculate r_e = 2.132 Å from B_e. This corresponds well with the 2.12 Å Be-I distance for BeI_2(g) obtained via the electron diffraction study of Akishin et al. (8). The moment of inertia is $63.5^2 \times 10^{-40}$ g cm^2.

The electronic levels are also from the study by Murty and Rao (4, 5, 6). The possibility of additional levels ($^2\Pi$ and $^2\Sigma^+$) near 15000 cm^{-1} is suggested by a comparison with CaI, SrI, and BaI (3). Including these levels does not change the entropy at 298.15 K but does increase the entropy at 6000 K by 0.7 gibbs/mol.

References

1. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1968.
2. D. L. Hildenbrand in "Advances in High Temperature Chemistry", Vol. 1, Ed. by L. Eyring, Academic Press, New York, 1967.
3. *JANAF Thermochemical Tables: BeI_2(g), 12-31-75; BaI(g), SrI(g), and CaI(g), 6-30-74*.
4. P. S. Murty and P. T. Rao, Curr. Sci. 38, 187 (1969).
5. P. S. Murty and P. T. Rao, Curr. Sci. 38, 537 (1969).
6. P. S. Murty and P. T. Rao, *Proc. Roy. Ir. Acad., Sect. A* 72, 71 (1972).
7. G. V. Calder and K. Ruedenberg, J. Chem. Phys. 49, 5399 (1968).
8. P. A. Akishin, V. P. Spiridonov, and G. A. Sobolev, Dokl. Akad. Nauk SSSR, 118, 1134 (1958).

BERYLLIUM DIIODIDE (BeI_2) BeI_2

(CRYSTAL) GFW=262.82118

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	16.482	28.800	28.800	.000	-45.100	-44.731	32.789
300	16.522	28.902	28.800	.031	-45.100	-44.728	32.584
400	18.372	33.926	29.473	1.781	-48.961	-44.466	24.295
500	19.512	38.157	30.798	3.680	-59.089	-42.387	18.528
600	20.122	41.773	32.333	5.664	-58.544	-39.099	14.242
700	20.427	44.899	33.910	7.692	-57.987	-35.902	11.209
800	20.642	47.641	35.459	9.746	-57.429	-32.785	8.956
900	20.825	50.083	36.951	11.819	-56.877	-29.737	7.221
1000	20.982	52.286	38.376	13.910	-56.331	-26.751	5.846
1100	21.113	54.292	39.733	16.015	-55.797	-23.819	4.732
1200	21.219	56.134	41.024	18.132	-55.278	-20.935	3.813
1300	21.299	57.836	42.253	20.258	-54.773	-18.093	3.042
1400	21.353	59.416	43.423	22.391	-54.288	-15.290	2.387
1500	21.382	60.891	44.539	24.528	-53.824	-12.523	1.825

Dec. 31, 1961; June 30, 1965; Dec. 31, 1975

BERYLLIUM DIIODIDE (BeI_2) (CRYSTAL) GFW = 262.82118

BeI_2

$S^\circ_{298.15}$ = [28.8 ± 1.0] gibbs/mol

Tm = 753 ± 15 K

ΔHf°_0 = unknown

$\Delta Hf^\circ_{298.15}$ = [-45.1 ± 5.0] kcal/mol

ΔHm° = [5.0 ± 3.0] kcal/mol

$\Delta Hs^\circ_{298.15}$ = 29.8 ± 2.0 kcal/mol

Heat Of Formation

A direct measurement of the heat of formation has not been made. An estimate of ΔHf° is obtained by a method suggested by Vivian Parker (1) and used in the $BeBr_2$(c) table (2). Biltz and Messerknecht (3) have measured the heats of solution of $BeCl_2$(c) and BeI_2(c) is aqueous HCl(18.69%). Samples (4) of the dihalides were prepared from reactions of BeO-C mixtures with the halogens at elevated temperatures. We assume that the two dihalides had similar structures, i.e. the α-form (orthorhombic). ΔHf°_{298}(BeI_2, in 18.7% HCl) is estimated as -109.1 kcal/mol by combining ΔH_{soln} of $BeCl_2$(c) with ΔHf°_{298}(α-$BeCl_2$(c) = -117.3±0.8kcal/mol (2) and twice the difference in $\Delta Hf^\circ_{298}(HCl \cdot 8H_2O)$ and $\Delta Hf^\circ_{298}(HI \cdot 8H_2O)$ which is -52.3 kcal/mol (5). The heat associated with the interchange of the aqueous anions is assumed to be negligible. Combination of the estimated value for ΔHf°_{298}(BeI_2, in 18.8% HCl) with ΔH_{soln} = -62.5 kcal/mol (3) gives ΔHf°_{298} (BeI_2,c) = -46.6 kcal/mol which is within 0.6 kcal/mol of the value suggested by NBS (6). Subsequent measurements by Biltz et al. (7) in less concentrated HCl(1.48%) solution leads to ΔHf°_{298} = -43.6 kcal/mol by a similar route. We adopt an average value of -45.1 kcal/mol but emphasize that the uncertainty in ΔHf° is much greater than indicated (3 kcal/mol) by the closeness of these two values. An uncertainty of ±5.0 kcal/mol is believed to be more realistic.

Heat Capacity and Entropy

No low temperature heat capacity or high-temperature enthalpy measurements have been reported. We estimate Cp°_{298} = 16.482 gibbs/mol from the reaction $BeCl_2(c,\alpha) + 2LiI(c) = BeI_2(c) + 2LiCl(c)$ by assuming ΔCp° = 0. Similar results are obtained using BeF_2(c). Cp° values above 298.15 K are assumed to parallel those for α-$BeCl_2$ (2).

Application of the Berthelot principle (8) to the process $BaI_2(c) + Be(c) \rightarrow Ba(c) + BeI2(c)$ suggests S°_{298} = 26.8 gibbs/mol. A graphical comparison of the standard entropies for other alkaline-earth dihalides (2) indicates that this value is reasonable. Other estimated values are given by additive entropy constants (9, 27.4 gibbs/mol), Brewer (10, 31.0 gibbs/mol), and Brewer et al. (11, 25 gibbs/mol)

For additional information on the heat capacity and entropy, refer to the heat of formation discussion for gaseous BeI_2 (2).

Melting Data

See BeI_2(ℓ) table for details (2).

Phase Data

Semenenko and Naumova (12) studied the BeI_2 crystal modifications by thermal and x-ray techniques. The study was complicated by the extreme hygroscopicity, high vapor pressures near the melting point, and susceptibility to oxidation on heating by traces of oxygen. As stated by Semenenko and Naumova (12), the sequence of polymorphic conversions and the character of the resulting modifications of BeI_2, which are largely dependent on the heating and cooling conditions, parallel those of $BeCl_2$ (13). They detected thermally transitions at 290°C, 370°C, 470°C, and a melting at 490°C. However, this data does not appear to be fully consistent in terms of crystallographic structures with that proposed by Johnson, Staritzky, and Douglas (14) and Messerknecht and Biltz (15). These latter works suggested two structures with a transition at 350°C.

We assume the similarity with $BeCl_2$ with a transition in the vicinity of 350 - 370°C. Further study is necessary to resolve all possible phases and their structures.

Sublimation Data

See BeI_2(g) table for details (2).

Reference

1. V. B. Parker, private communication, Natl. Bur. Std., March, 1975.
2. JANAF Thermochemical Tables: $BeBr_2$(c), 6-30-75; BeI_2(ℓ) and BeI_2(g), 12-31-75; $BeCl_2$(c,α), 6-30-75.
3. W. Biltz and C. Messerknecht, Z. Anorg. Chem. 148, 157 (1925).
4. C. Messerknecht and W. Biltz, Z. Anorg. Chem. 148. 152 (1925).
5. U.S. Natl. Bur. Std. Tech. Note 270-3, 1968.
6. U.S. Natl. Bur. Std. Tech. Note 270-6, 1971.
7. W. Biltz, K.A. Klatte, and E. Rahlfs, Z. Anorg. Chem. 166, 339 (1927).
8. N. N. Drozin, Zhur. Fiz. Khim. 35, 879 (1961).
9. D. R. Stull and H. Prophet in "The Characterization of High Temperature Vapors," J. L. Margrave, Ed., John Wiley and Sons, Inc., New York, 1966.
10. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quil , Ed., National Nuclear Engery Series IV-19B, McGraw-Hill Book Co., New York, 1950.
11. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
12. K. N. Semenenko and T. N. Naumova, Russ J. Structural Chem. 4, 59 (1963)
13. O. N. Kuvyrkin, O. N. Breusov, A. V. Novoselova, and K. N. Semenenko, Zhur. Fiz. Khim. 34, 343 (1960).
14. R. E. Johnson, E. Staritzky, and R. M. Douglas, J. Amer. Chem. Soc. 79, 2037 (1957).
15. C. Messerknecht and W. Biltz, Z. anorg. allgem. Chem. 48, 152 (1925).

BERYLLIUM DIIODIDE (BeI_2)
(LIQUID) GFW=262.82118

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	16.482	30.832	30.831	.000	-42.633	-42.870	31.424
300	16.522	30.934	30.832	.031	-42.634	-42.871	31.231
400	27.000	35.955	31.504	1.780	-46.495	-42.811	23.391
500	27.000	41.980	33.019	4.480	-55.822	-41.031	17.935
600	27.000	46.902	34.935	7.180	-54.561	-38.193	13.912
700	27.000	51.064	36.950	9.880	-53.332	-35.562	11.103
800	27.000	54.670	38.944	12.580	-52.128	-33.106	9.044
900	27.000	57.850	40.872	15.280	-50.949	-30.799	7.479
1000	27.000	60.695	42.714	17.980	-49.794	-28.622	6.255
1100	27.000	63.268	44.468	20.680	-48.665	-26.560	5.277
1200	27.000	65.617	46.134	23.380	-47.563	-24.600	4.480
1300	27.000	67.778	47.717	26.080	-46.484	-22.729	3.821
1400	27.000	69.779	49.222	28.780	-45.432	-20.942	3.269
1500	27.000	71.642	50.655	31.480	-44.405	-19.230	2.802

Dec. 31, 1961; June 30, 1965; Dec. 31, 1975

BERYLLIUM DIIODIDE(BeI_2) (LIQUID) GFW = 262.82118

$S^\circ_{298.15}$ = [30.832] gibbs/mol
Tm = 753 ± 15 K
Tb = 759.4 K (to monomer)

$\Delta Hf^\circ_{298.15}$ = [-42.633] kcal/mol
ΔHm° = [5.0 ± 3.0] kcal/mol
ΔHv° = 22.300 kcal/mol

Heat of Formation

The heat of formation is obtained from that of the crystal by adding ΔHm° and the difference between $H^\circ_{753} - H^\circ_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with the measured value for $BeCl_2$ (1). A glass transition is assumed at 400 K below which the heat capacity is that of the crystal. The entropy is obtained in a manner analogous to that used for the heat of formation.

Melting Data

Rahlfs and Fischer (2) reported a melting point of 753 K. Semenenko and Naumova (3), using thermal analysis techniques, implied a melting point of 763 K. Since this latter value was derived from a thermogram, it is probable that this value represents a maximum, with the true melting point somewhat lower. We adopt Tm = 753±15 K.

We estimate the heat of melting, ΔHm° = 5.0±3.0 kcal/mol. This estimate includes a contribution for melting (based on the entropy of melting for other alkaline earth dihalides) and a contribution for a phase transition. There is no experimental data available pertaining to the heat of melting.

Vaporization Data

Tb is the temperature at which ΔGr° = 0 for the process $BeI_2(\ell) = BeI_2(g)$. ΔHv° is the cooresponding difference in the ΔHf° values for the liquid and gas at Tb.

Reference

1. JANAF Thermochemical Tables: $BeCl_2(\ell)$, 6-30-65.
2. O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 349 (1933).
3. K.N. Semenenko and J.N. Naumova, Russ. J. Structural Chem. 4, 59 (1963).

BERYLLIUM DIIODIDE (BeI_2) BeI_2
(IDEAL GAS) GFW=262.82118

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.258	- 14.936	- 14.936	INFINITE
100	10.661	56.513	80.755	- 2.424	- 14.841	- 19.021	41.571
200	12.373	64.557	70.827	- 1.254	- 14.987	- 23.157	25.305
298	13.131	69.649	69.649	.000	- 15.300	- 27.110	19.872
300	13.142	69.730	69.649	.024	- 15.307	- 27.183	19.803
400	13.660	73.587	70.171	1.366	- 19.576	- 30.945	16.908
500	14.003	76.674	71.173	2.751	- 30.218	- 32.775	14.326
600	14.231	79.249	72.311	4.163	- 30.245	- 33.285	12.124
700	14.386	81.455	73.463	5.594	- 30.285	- 33.789	10.549
800	14.495	83.384	74.585	7.039	- 30.336	- 34.286	9.366
900	14.574	85.096	75.660	8.492	- 30.404	- 34.776	8.445
1000	14.632	86.634	76.682	9.953	- 30.488	- 35.257	7.705
1100	14.677	88.031	77.651	11.418	- 30.594	- 35.729	7.099
1200	14.711	89.310	78.570	12.888	- 30.722	- 36.190	6.591
1300	14.739	90.488	79.442	14.360	- 30.871	- 36.639	6.160
1400	14.760	91.581	80.270	15.835	- 31.044	- 37.077	5.788
1500	14.778	92.600	81.059	17.312	- 31.240	- 37.503	5.464
1600	14.793	93.555	81.810	18.791	- 34.214	- 37.833	5.168
1700	14.805	94.452	82.528	20.271	- 34.343	- 38.056	4.892
1800	14.816	95.298	83.214	21.752	- 34.477	- 38.270	4.647
1900	14.825	96.100	83.871	23.234	- 34.617	- 38.477	4.426
2000	14.832	96.860	84.502	24.717	- 34.762	- 38.679	4.227
2100	14.839	97.584	85.108	26.200	- 34.913	- 38.869	4.045
2200	14.844	98.275	85.691	27.685	- 35.069	- 39.055	3.880
2300	14.849	98.935	86.252	29.169	- 35.232	- 39.230	3.728
2400	14.854	99.567	86.794	30.654	- 35.400	- 39.399	3.588
2500	14.858	100.173	87.317	32.140	- 35.575	- 39.565	3.459
2600	14.861	100.756	87.823	33.626	- 35.755	- 39.720	3.339
2700	14.864	101.317	88.312	35.112	- 35.941	- 39.869	3.227
2800	14.867	101.857	88.786	36.599	- 107.162	- 38.902	3.036
2900	14.869	102.379	89.246	38.086	- 107.107	- 36.464	2.748
3000	14.872	102.883	89.692	39.573	- 107.056	- 34.031	2.479
3100	14.874	103.371	90.126	41.060	- 107.007	- 31.599	2.228
3200	14.876	103.843	90.547	42.547	- 106.960	- 29.165	1.992
3300	14.877	104.301	90.957	44.035	- 106.917	- 26.734	1.770
3400	14.879	104.745	91.356	45.523	- 106.878	- 24.306	1.562
3500	14.880	105.177	91.745	47.011	- 106.842	- 21.878	1.366
3600	14.881	105.596	92.124	48.499	- 106.812	- 19.450	1.181
3700	14.883	106.003	92.493	49.987	- 106.787	- 17.026	1.006
3800	14.884	106.400	92.854	51.475	- 106.768	- 14.600	.840
3900	14.885	106.787	93.206	52.964	- 106.754	- 12.171	.682
4000	14.886	107.164	93.551	54.452	- 106.748	- 9.751	.533
4100	14.887	107.531	93.887	55.941	- 106.748	- 7.325	.390
4200	14.887	107.890	94.216	57.430	- 106.756	- 4.898	.255
4300	14.888	108.240	94.538	58.918	- 106.773	- 2.474	.126
4400	14.889	108.583	94.854	60.407	- 106.799	- .049	.002
4500	14.889	108.917	95.163	61.896	- 106.834	2.380	- .116
4600	14.890	109.245	95.465	63.385	- 106.879	4.806	- .228
4700	14.891	109.565	95.762	64.874	- 106.933	7.231	- .336
4800	14.891	109.878	96.053	66.363	- 106.999	9.664	- .440
4900	14.892	110.185	96.338	67.852	- 107.075	12.097	- .540
5000	14.892	110.486	96.618	69.342	- 107.162	14.531	- .635
5100	14.893	110.781	96.893	70.831	- 107.261	16.964	- .727
5200	14.893	111.070	97.163	72.320	- 107.373	19.396	- .815
5300	14.893	111.354	97.428	73.809	- 107.497	21.839	- .901
5400	14.894	111.632	97.688	75.299	- 107.632	24.282	- .983
5500	14.894	111.906	97.944	76.788	- 107.781	26.723	- 1.062
5600	14.894	112.174	98.196	78.278	- 107.942	29.168	- 1.138
5700	14.895	112.438	98.443	79.767	- 108.116	31.621	- 1.212
5800	14.895	112.697	98.687	81.257	- 108.302	34.077	- 1.284
5900	14.895	112.951	98.927	82.746	- 108.502	36.530	- 1.353
6000	14.896	113.202	99.162	84.236	- 108.714	38.989	- 1.420

Dec. 31, 1961; June 30, 1965; Dec. 31, 1975

BERYLLIUM DIIODIDE (BeI_2) (IDEAL GAS) GFW = 262.82118

Point Group $D_{\infty h}$
$S^\circ_{298.15}$ = [69.65 ± 0.05] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -14.9 ± 8.0 kcal/mol BeI_2
$\Delta Hf^\circ_{298.15}$ = -15.3 ± 8.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[160] (1)
[175] (2)
873 (1)

Bond Distance: Be-I = 2.12 ± 0.05 Å σ = 2
Bond Angle: I-Be-I = 180° ± 10°
Rotational Constant: B_o = 0.01478 cm^{-1}

Heat of Formation

Rahlfs and Fischer (1) have reported measurements of the sublimation pressures (578-703 K, 9 pts) for BeI_2. The measurements were complicated by reaction of the diiodide with the quartz apparatus. Assuming the reaction to be $BeI_2(c) + SiO_2(c) = SiI_4(g) + 2BeO(c)$, Rahlfs and Fischer (1) corrected their measured total pressure for the partial pressure of the tetraiodide. A second and third law analysis of their corrected data yields ΔHs°_{298} = 29.81±0.29 kcal/mol (3rd law) and 28.34±0.74 kcal/mol (2nd law) with a drift of 2.2±1.1 gibbs/mol. We adopt ΔHs°_{298} = 29.8±2.0 kcal/mol. We have assumed negligible dimer formation. ΔHf°_{298} = -15.3 kcal/mol for $BeI_2(g)$ when the adopted ΔHs°_{298} value is added to the ΔHf°_{298} value for $BeI_2(c)$.

The drift could be reduced by further adjusting the free energy functions for the crystal. These functions may be changed by altering the Cp° values and/or the S°_{298} value. Such changes would yield values which are unreasonable when compared to other alkaline earth dihalides. *Note also that a similar sublimation study for* $BeCl_2$ *(2) gives a drift of -1.3±2.6* gibbs/mol. We tentatively assume the drift is due to the data rather than our choice of functions.

Heat Capacity and Entropy

Electron diffraction patterns for BeI_2 vapor (3, 4) have been interpreted in terms of a linear configuration, with the latter study reporting the Be-I bond distance as 2.12 Å. Other studies also suggest a linear molecule. For example, the electric deflection of mass spectrometrically detected molecular beams (5) showed that all the beryllium dihalides are linear.

Snelson (6) observed the infrared spectra of BeI_2 in the spectral range 4000-200 cm^{-1} using a matrix isolation technique. Assuming a linear geometry, ν_3 was assigned as 873 cm^{-1}. Snelson (6) estimated a value for ν_2 based on force constant values for the other three beryllium dihalides. The values of ν_1 were calculated using a simple valence force field approximation. We adopt the two estimated and one measured vibrational frequency as reported by Snelson (6). The ground state quantum weight of one is assigned by analogy with $BaCl_2$ (2).

Brewer et al. (7) have tabulated free energy functions for BeI_2 up to 2000 K. Their values are consistently lower than ours due primarily to their use of a higher bending frequency (ν_2 = 395 cm^{-1}).

References

1. O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 349 (1933).
2. JANAF Thermochemical Tables: $BeCl_2(\ell)$, 6-30-65.
3. P. S. Ahishin and V. P. Spiridonov, Kristallografiya 2, 472 (1957).
4. P. A. Ahishin, V. P. Spiridonov, and G. A. Sobalev, Dokl. Akad. Nauk SSSR 118, 1134 (1958).
5. A. Buchler, J. L. Stauffer, and W. Klemperer, J. Amer. Chem. Soc. 86, 4544 (1964).
6. A. Snelson, J. Phys. Chem. 72, 250 (1968).
7. L. Brewer, G. R. Somoyajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).

BERYLLIUM OXIDE, ALPHA (α-BeO) BeO

(CRYSTAL) GFW=25.0116

T, °K	gibbs/mol C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	kcal/mol $H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-.677	-144.572	-144.572	INFINITE
100	.630	.197	6.821	-.662	-144.914	-142.851	312.200
200	3.384	1.407	3.766	-.472	-145.209	-140.667	153.714
298	6.109	3.291	3.291	.000	-145.400	-138.396	101.447
300	6.153	3.329	3.291	.011	-145.402	-138.353	100.790
400	8.068	5.381	3.558	.729	-145.479	-135.989	74.301
500	9.302	7.323	4.119	1.602	-145.476	-133.615	58.403
600	10.128	9.097	4.804	2.576	-145.421	-131.247	47.807
700	10.713	10.704	5.534	3.619	-145.339	-128.891	40.242
800	11.151	12.165	6.273	4.714	-145.238	-126.549	34.572
900	11.494	13.499	7.002	5.846	-145.130	-124.218	30.164
1000	11.774	14.724	7.714	7.010	-145.019	-121.901	26.641
1100	12.011	15.858	8.404	8.200	-144.913	-119.594	23.761
1200	12.217	16.912	9.069	9.411	-144.815	-117.297	21.363
1300	12.400	17.897	9.711	10.642	-144.724	-115.007	19.334
1400	12.567	18.822	10.329	11.891	-144.644	-112.725	17.597
1500	12.721	19.695	10.925	13.155	-144.575	-110.448	16.092
1600	12.865	20.520	11.499	14.435	-147.273	-108.096	14.765
1700	13.001	21.304	12.053	15.728	-147.114	-105.652	13.582
1800	13.132	22.051	12.588	17.035	-146.949	-103.218	12.532
1900	13.257	22.765	13.105	18.354	-146.780	-100.793	11.594
2000	13.378	23.448	13.605	19.686	-146.607	-98.378	10.750
2100	13.496	24.103	14.089	21.030	-146.428	-95.970	9.988
2200	13.611	24.734	14.559	22.385	-146.247	-93.572	9.296
2300	13.724	25.341	15.014	23.752	-146.061	-91.180	8.664
2400	13.834	25.928	15.457	25.130	-145.872	-88.797	8.086
2500	13.943	26.495	15.887	26.519	-145.681	-86.426	7.555
2600	14.051	27.044	16.306	27.918	-145.486	-84.057	7.066
2700	14.157	27.576	16.713	29.329	-145.286	-81.698	6.613
2800	14.263	28.093	17.111	30.750	-216.114	-78.240	6.107
2900	14.367	28.595	17.498	32.181	-215.656	-73.321	5.526
3000	14.471	29.084	17.876	33.623	-215.193	-68.422	4.985
3100	14.574	29.560	18.245	35.075	-214.722	-63.540	4.480
3200	14.676	30.024	18.606	36.538	-214.245	-58.668	4.007
3300	14.778	30.478	18.959	38.011	-213.762	-53.814	3.564
3400	14.879	30.920	19.304	39.493	-213.275	-48.975	3.148
3500	14.980	31.353	19.643	40.986	-212.781	-44.152	2.757

Dec. 31, 1960; Sept. 30, 1963; June 30, 1971;
Dec., 31, 1974; June 30, 1975

BERYLLIUM OXIDE, ALPHA (α-BeO) (CRYSTAL) GFW = 25.0116 BeO

$S^\circ_{298.15}$ = 3.291 ± 0.05 gibbs/mol
Tt = 2373 ± 15 K (α→β)
Tm = [2821.2 ± 100]K (β→ℓ)
Tm = 2780 ± 100 K (α→ℓ)

ΔHf°_0 = -144.6 ± 0.8 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -145.4 ± 0.8 kcal/mol
ΔHt° = 1.60 ± 0.4 kcal/mol
ΔHm° = [18.895 ± 1.5] kcal/mol
ΔHm° = 20.3 ± 1.5 kcal/mol

Heat of Formation

Parker (1) thoroughly reviewed the data as of 1969 and selected -145.4 ± 0.8 kcal/mol. She later revised (1) this value to -145.7 ± 0.6 kcal/mol due to new HF-solution calorimetry on BeF_2(amorphous) performed by Kilday et al. (2). Values of ΔHf° from Parker's revised analysis (1) are summarized below. We adopt -145.4 ± 0.8, rather than the revised selection, as a compromise between the indirect results based on Be(c) and those based on BeF_2(am). The latter depend on ΔHf° for HF(n H_2O). Use of the JANAF ΔHf° (4) in place of the NBS value (3) causes a change of +0.9 kcal/mol in the results based on BeF_2(am). Recent data for HF suggest that the change could be even larger.

Direct Determinations of ΔHf°

kcal/mol	Source
-136.2	Mielenz & von Wartenberg (1921)
-134.4	Moose & Parr (1924)
-145.3	Neumann et al. (1934)
-147.3	Roth et al. (1938)
-143.1	Cosgrove & Snyder (1953)

Indirect Determinations of ΔHf°

kcal/mol	Source
-144.9	Neumann et al. (1934, 1932), ΔHc & ΔHf of Be_3N_2
-141.1	Smirnov & Chukreev (1958), Emf data
-145.7±1.5	Kilday et al. (1969), Thomson et al. (1962)[a]
-143.9±1.5	Kilday et al. (1969), Armstrong & Coyle (1965)[b]
-145.7±0.6	Kolesov et al. (1959), Bear & Turnbull (1965)[b]
-146.2, -145.65, -145.65, -145.3±0.6	Kilday et al. (1969), Bear & Turnbull (1965)[b]
-144.7(-145.6)[d], -144.5(-145.4)[d]±1.2	Kilday et al. (1971), Churney & Armstrong (1969)[c]

[a] HCl-solution calorimetry of BeO(c) and Be(c). [b] HF-solution calorimetry of BeO(c) and Be(c). [c] HF-solution calorimetry of BeO(c) and BeF_2(am) and ΔHf° of the latter. [d] Values in parentheses based on ΔHf° of HF(n H_2O) from NBS (3) instead of JANAF (4).

Heat Capacity and Entropy

The adopted Cp° and S° below 298 K are taken from Furukawa and Reilly (5) who measured Cp° from 15 to 370 K. The authors give a detailed comparison with the earlier data of Gmelin (6, 5 to 75 K) and Kelley (7, 56 to 292 K). Gmelin's results *deviate by roughly +20% from 15 to 75 K and Kelley's results deviate by about +50% at 56 K, +8% at 100 K and +1% at 200 K.* The deviations of Kelley are probably due to the sensitivity limit of his calorimeter and to non-standard-state effects of finely powdered BeO.

The adopted Cp° above 298 K is from a constrained fit of the Cp° data (5) and enthalpy data of Victor and Douglas (8, 323 to 1173 K), Conway and Hein (9, 2161 to 2365 K) and Shpil'rain et al. (10, 2023 to 2708 K). The latter data show no evidence of transition even though they extend more than 300° above Tt = 2373 K. Deviations of the data (8) from the adopted enthalpies are <±0.15% above 373 K and -0.4% at 323 K. Deviations above 2000 K are -0.3 to +0.8% (9) and -1.8 to +0.4% (10) excluding the point at 2266 K (10). Enthalpy measurements not used in the fit deviate by -2.1 to +2.9% (11, 1142 to 2697 K), -17±8% (12, 2273 to 2523 K), -2.1±0.8% (13, 400 to 1100 K) and +0.4 to -0.7% (14, 363 to 1128 K). Cp° data from the cooling-rate method (15) deviate by <2% (1300 to 1700 K) but by -5% at 2000 K.

Transition Data See BeO(β, c).

Melting Data See BeO(ℓ).

References

1. V. B. Parker, J. Res. Natl. Bur. Std. 77A, 227 (1973); U. S. Natl. Bur. Std. Rept. 10004, pp. 58-81, Jan., 1969.
2. M. V. Kilday, E. J. Prosen and D. D. Wagman, J. Res. Natl. Bur. Std. 77A, 217 (1973).
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. JANAF THERMOCHEMICAL TABLES: HF(g), 12-31-68; BeF_2(c, ℓ) 6-30-70.
5. G. T. Furukawa and M. L. Reilly, U. S. Natl. Bur. Std. Rept. 9905, pp. 28-47, July, 1968.
6. E. Gmelin, Compt. Rend. 262, 1452 (1966).
7. K. K. Kelley, J. Amer. Chem. Soc. 61, 1217 (1939).
8. A. C. Victor and T. B. Douglas, J. Res. Natl. Bur. Std. 67A, 325 (1963).
9. J. B. Conway and R. A. Hein, Nucleonics 22 (6), 71 (1964).
10. E. E. Shpil'rain, D. N. Kagan and L. S. Barkhatov, High Temperature (USSR) 9, 842 (1971).
11. V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, Dokl. Akad. Nauk SSSR 131, 566 (1960).
12. M. A. Greenbaum, J. Weiher and M. Farber, J. Phys. Chem. 69, 4035 (1965).
13. B. E. Walker, C. T. Ewing and R. R. Miller, J. Chem. Eng. Data 7, 595 (1962); B. E. Walker, personal communication, U. S. Naval Res. Lab., Washington, April 18, 1963.
14. E. N. Rodigina and K. Z. Gomel'skii, Russ. J. Phys. Chem. 35, 898 (1961).
15. R. A. McDonald, F. L. Oetting and H. Prophet, CPIA Working Group on Thermochemistry, Proc. 1st Meeting, Nov., 1963, CPIA Publ. No. 44(U), pp. 213-245, Feb., 1964.

Beryllium Oxide, Beta (β-BeO) BeO

(Crystal) GFW = 25.0116

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.109	3.965	3.965	.000	− 143.800	− 136.997	100.422
300	6.153	4.003	3.965	.011	− 143.802	− 136.955	99.772
400	8.068	6.055	4.232	.729	− 143.879	− 134.658	73.574
500	9.302	7.998	4.794	1.602	− 143.876	− 132.352	57.851
600	10.128	9.771	5.478	2.576	− 143.821	− 130.052	47.371
700	10.713	11.379	6.208	3.619	− 143.739	− 127.763	39.889
800	11.151	12.839	6.947	4.714	− 143.638	− 125.488	34.282
900	11.494	14.173	7.677	5.846	− 143.530	− 123.225	29.923
1000	11.774	15.399	8.388	7.010	− 143.419	− 120.975	26.439
1100	12.011	16.532	9.078	8.200	− 143.313	− 118.736	23.591
1200	12.217	17.586	9.744	9.411	− 143.215	− 116.506	21.219
1300	12.400	18.572	10.385	10.642	− 143.124	− 114.284	19.213
1400	12.567	19.497	11.003	11.891	− 143.044	− 112.069	17.495
1500	12.721	20.369	11.599	13.155	− 142.975	− 109.859	16.006
1600	12.865	21.195	12.173	14.435	− 145.673	− 107.575	14.694
1700	13.001	21.979	12.727	15.728	− 145.514	− 105.198	13.524
1800	13.132	22.726	13.262	17.035	− 145.349	− 102.832	12.485
1900	13.257	23.439	13.779	18.354	− 145.180	− 100.474	11.557
2000	13.378	24.122	14.279	19.686	− 145.007	− 98.127	10.723
2100	13.496	24.778	14.763	21.030	− 144.828	− 95.786	9.969
2200	13.611	25.408	15.233	22.385	− 144.647	− 93.455	9.284
2300	13.724	26.016	15.689	23.752	− 144.461	− 91.131	8.659
2400	13.834	26.602	16.131	25.130	− 144.272	− 88.816	8.088
2500	13.943	27.169	16.562	26.519	− 144.081	− 86.511	7.563
2600	14.051	27.718	16.980	27.918	− 143.886	− 84.210	7.079
2700	14.157	28.250	17.388	29.329	− 143.686	− 81.919	6.631
2800	14.263	28.767	17.785	30.750	− 214.514	− 78.528	6.129
2900	14.367	29.269	18.172	32.181	− 214.056	− 73.677	5.552
3000	14.471	29.758	18.550	33.623	− 213.593	− 68.845	5.015
3100	14.574	30.234	18.920	35.075	− 213.122	− 64.030	4.514
3200	14.676	30.699	19.281	36.538	− 212.645	− 59.226	4.045
3300	14.778	31.152	19.633	38.011	− 212.162	− 54.439	3.605
3400	14.879	31.595	19.979	39.493	− 211.675	− 49.668	3.193
3500	14.980	32.027	20.317	40.986	− 211.181	− 44.912	2.804

June 30, 1971; Dec. 31, 1974

BERYLLIUM OXIDE, BETA (β-BeO) (CRYSTAL) GFW = 25.0116 BEO

$S^\circ_{298.15}$ = [3.965] gibbs/mol
Tt = 2373 ± 15 K (α→β)
Tm = [2821.2±100] K (β→ℓ)
$\Delta Hf^\circ_{298.15}$ = [−143.8] kcal/mol
ΔHt° = 1.60 ± 0.4 kcal/mol
ΔHm° = [18.895±1.5] kcal/mol

Heat of Formation

ΔHf° is obtained from that of BeO(α, c) by addition of ΔHt°, since the difference of $(H^\circ_{2373}-H^\circ_{298})$ for α- and β-phases is zero according to the adopted functions.

Heat Capacity and Entropy

Cp° is taken to be the same as that of BeO(α, c). Enthalpy data for β-BeO (1) extend from 2377 to 2501 K, a range too short for obtaining an accurate Cp° curve. The enthalpy data deviate from the adopted functions by −0.2 to +1.4%. Other enthalpy data (2-4) show no obvious transition to β-BeO; this suggests that experimental uncertainties masked the transition or that these samples failed to transform. S° is obtained in a manner analogous to that of ΔHf°.

Transition Data

Studies of X-ray diffraction (5-7), optical properties (6, 8), thermal expansion (1, 9), thermal analysis (10-14), enthalpy (1), and decrepitation of single crystals (6, 9, 15) indicate the existence of a reversible transition near 2100°C. β-BeO is tetragonal with a structure related to rutile (5), while α-BeO is hexagonal close-packed with a wurtzite-type structure (16, 17).

Tt is lower on cooling than on heating. Earlier studies gave temperature differences of about 40° (11, 12), 50° (7) and 80° (14), but a recent DTA study (10) gave Tt values on cooling which were only ∿15° below those on heating. Tt = 2107 ± 7°C (IPTS-68) was proposed as a DTA standard temperature because it is reproducible and relatively unchanged by oxide impurities (10). Reported values of Tt on heating include 2100±10°C (1), 2107±7°C (10), 2095°C (11), 2075±15°C (12), 2050-2100°C (7), 2100-2250°C (7), 2144±40°C (14) and 2050±25°C (6). We adopt 2100±15°C.

Reported values of ΔHt° include 1.35±0.1 (1), 1.40±0.25 (10), 1.25 ± 0.25 (14) and 0.95±0.3 kcal/mol (13). The first value is from enthalpy data and the others are from thermal analysis. It is not clear why the transition fails to appear in two other enthalpy studies (2, 3). We adopt ΔHt° = 1.6±0.4 kcal/mol derived from the difference between the enthalpy data for β-BeO (1) and the JANAF enthalpy for α-BeO.

Melting Data

See BeO(ℓ).

References

1. J. B. Conway and R. A. Hein, Nucleonics 22 (6), 71 (1964).
2. E. E. Shpil'rain, D. N. Kagan and L. S. Barkhatov, High Temperature (USSR) 9, 842 (1971).
3. V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, Dokl. Akad. Nauk SSSR 131, 566 (1960).
4. M. A. Greenbaum, J. Weiher and M. Farber, J. Phys. Chem. 69, 4035 (1965).
5. D. K. Smith, C. F. Cline and S. B. Austerman, Acta Crystallogr. 18, 393 (1965).
6. D. K. Smith, C. F. Cline and V. D. Frechette, J. Nucl. Mater. 6, 265 (1962).
7. T. W. Baker and P. J. Baldock, J. Nucl. Mater. 19, 210 (1966); Nature 193, 1172 (1962).
8. S. B. Austerman, J. Nucl. Mater. 6, 332 (1962).
9. C. J. Engberg and E. H. Zehms, J. Amer. Ceram. Soc. 42, 300 (1959).
10. T. Sata and T. Takahashi, Colloq. Int. Cent. Nat. Rech. Sci., No. 205, 331 (1972); Yogyo Kyokai Shi 80, 142 (1972).
11. R. E. Latta, E. C. Duderstadt and R. E. Fryxell, J. Nucl. Mater. 35, 350 (1970).
12. Yu. A. Kocherzhinskii, E. A. Shishkin and L. M. Yupko, Refractories (USSR) 1969, 314; Ogneupory 34 (5), 50 (1969).
13. A. I. Kaznoff and L. N. Grossman, in "Thermodynamics of Nuclear Materials 1967," pp. 25-39, Intl. At. Energy Agency, Vienna, 1968.
14. S. B. Austerman, U. S. At. Energy Comm. NAA-SR-7654, 14 pp. (1963); Bull. Amer. Phys. Soc. II 7, 28 (1962).
15. S. B. Austerman, U. S. At. Energy Comm. NAA-SR-6428 (1961).
16. D. K. Smith, H. W. Newkirk and J. S. Kahn, J. Electrochem. Soc. 111, 78 (1964).
17. P. J. Baldock, W. E. Spindler and T. W. Baker, J. Nucl. Mater. 19, 169 (1966).

Beryllium Oxide (BeO) BeO

(Liquid) GFW = 25.0116

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.109	8.588	8.588	.000	- 129.710	- 124.285	91.103
300	6.153	8.626	8.588	.011	- 129.712	- 124.251	90.517
400	8.068	10.678	8.855	.729	- 129.788	- 122.417	66.885
500	9.302	12.620	9.416	1.602	- 129.785	- 120.573	52.702
600	10.128	14.393	10.100	2.576	- 129.731	- 118.735	43.249
700	10.713	16.001	10.830	3.619	- 129.648	- 116.908	36.500
800	11.151	17.461	11.569	4.714	- 129.548	- 115.096	31.443
900	11.494	18.795	12.299	5.846	- 129.439	- 113.295	27.512
1000	11.774	20.021	13.011	7.010	- 129.329	- 111.507	24.370
1100	12.011	21.155	13.700	8.200	- 129.223	- 109.730	21.801
1200	12.217	22.209	14.366	9.411	- 129.124	- 107.962	19.663
1300	12.400	23.194	15.007	10.642	- 129.034	- 106.202	17.854
1400	12.567	24.119	15.626	11.891	- 128.953	- 104.450	16.305
1500	12.721	24.991	16.221	13.155	- 128.884	- 102.702	14.964
1600	12.865	25.817	16.795	14.435	- 131.582	- 100.880	13.780
1700	13.001	26.601	17.349	15.728	- 131.423	- 98.966	12.723
1800	13.132	27.348	17.884	17.035	- 131.259	- 97.061	11.785
1900	13.257	28.061	18.401	18.354	- 131.090	- 95.166	10.947
2000	19.000	29.036	18.909	20.254	- 130.348	- 93.296	10.195
2100	19.000	29.963	19.413	22.154	- 129.613	- 91.460	9.518
2200	19.000	30.847	19.913	24.054	- 128.887	- 89.661	8.907
2300	19.000	31.691	20.407	25.954	- 128.168	- 87.893	8.352
2400	19.000	32.500	20.894	27.854	- 127.457	- 86.156	7.846
2500	19.000	33.276	21.374	29.754	- 126.755	- 84.452	7.383
2600	19.000	34.021	21.846	31.654	- 126.059	- 82.771	6.958
2700	19.000	34.738	22.310	33.554	- 125.370	- 81.120	6.566
2800	19.000	35.429	22.767	35.454	- 195.719	- 78.386	6.118
2900	19.000	36.096	23.215	37.354	- 194.793	- 74.210	5.593
3000	19.000	36.740	23.655	39.254	- 193.871	- 70.068	5.104
3100	19.000	37.363	24.087	41.154	- 192.953	- 65.959	4.650
3200	19.000	37.966	24.511	43.054	- 192.038	- 61.874	4.226
3300	19.000	38.551	24.928	44.954	- 191.128	- 57.821	3.829
3400	19.000	39.118	25.337	46.854	- 190.223	- 53.796	3.458
3500	19.000	39.669	25.739	48.754	- 189.322	- 49.799	3.110
3600	19.000	40.204	26.133	50.654	- 188.427	- 45.822	2.782
3700	19.000	40.724	26.521	52.554	- 187.538	- 41.874	2.473
3800	19.000	41.231	26.901	54.454	- 186.656	- 37.949	2.183
3900	19.000	41.725	27.275	56.354	- 185.779	- 34.046	1.908
4000	19.000	42.206	27.642	58.254	- 184.910	- 30.168	1.648
4100	19.000	42.675	28.003	60.154	- 184.048	- 26.312	1.403
4200	19.000	43.133	28.358	62.054	- 183.194	- 22.475	1.170
4300	19.000	43.580	28.707	63.954	- 182.348	- 18.654	.948
4400	19.000	44.017	29.050	65.854	- 181.511	- 14.859	.738
4500	19.000	44.444	29.387	67.754	- 180.684	- 11.081	.538
4600	19.000	44.861	29.719	69.654	- 179.866	- 7.321	.348
4700	19.000	45.270	30.045	71.554	- 179.058	- 3.580	.166
4800	19.000	45.670	30.367	73.454	- 178.261	.147	- .007
4900	19.000	46.062	30.683	75.354	- 177.473	3.854	- .172
5000	19.000	46.445	30.995	77.254	- 176.697	7.549	- .330

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1971; Dec. 31, 1974

BERYLLIUM OXIDE (BeO) (LIQUID) GFW = 25.0116 BEO

$S^\circ_{298.15}$ = [8.588] gibbs/mol
Tm = [2821.2±100] K ($\beta \to \ell$)
Tm = 2780±100 K ($\alpha \to \ell$)

$\Delta Hf^\circ_{298.15}$ = [-129.710] kcal/mol
ΔHm° = [18.895±1.5] kcal/mol
ΔHm° = 20.3±1.5 kcal/mol

Heat of Formation

ΔHf° is obtained from that of α-BeO by adding ΔHm° and the difference of ($H^\circ_{2780}-H^\circ_{298}$) for α and liquid phases.

Heat Capacity and Entropy

Cp° is taken to be 19 gibbs/mol based on the lower two of three enthalpy points (2867-3159 K) measured by Shpil'rain et al. (1). The upper two points yield 24.9 gibbs/mol, which is too large in our opinion. Earlier enthalpy data (2, 3) are inadequate for deriving Cp°. Below the assumed glass transition at 1900 K, Cp° is taken to be the same as that of the crystal. S° is calculated in a manner analogous to that of ΔHf°.

Melting Data

Conflicting evidence suggests that the melting points of α- and β-BeO are quite uncertain. Schneider's review (4) listed six values (Tm/°C, IPTS-48, with dates in parentheses): 2410(1916), 2452(1956), 2508(1937), 2557(1930), 2570(1948) and 2573°C (1913). Subsequent Tm values include 2430±10 (5), 2560±10 (6), 2444±30 (7), 2547±9 (2), 2450±30 and 2470±30°C (8). The reported values fall roughly into two groups near 2450°C and 2560°C. Three enthalpy studies (1-3) avoided the region from 2435°C to 2547°C. Part of the conflict arises because, in most cases, the measurement of Tm of BeO was only an incidental part of the study. Such values are more likely to be in error due to temperature measurement, detection of melting, impurities, volatilization and reaction with the surroundings. The actual discrepancies may be even larger than they appear, since one of the higher Tm values seems to refer to α-BeO which should melt ~40° below β-BeO. Enthalpy data of Kandyba et al. (2) suggest that their sample may have remained as α-BeO, yet they reported Tm = 2547±9°C. In contrast Tm = 2430±10°C was found for β-BeO by Latta et al.(5); their thermal analysis showed both Tt and Tm.

The conflict is epitomized by the two most recent values of Tm, 2430±10°C (5) and 2560±10°C (6). These studies (5, 6) seem to be more satisfactory than their predecessors yet at least one of them has a large bias. They agree (5, 6) on Tm for $A\ell_2O_3$, Mo and Ta but differ in opposite directions for BeO and UO_2. Non-stoichiometry could explain the lower Tm(UO_2) reported by Riley (6), but analogous evidence for BeO is lacking. As a compromise, we adopt Tm(α) = 2507°C = 2780 K and calculate Tm(β) = 2548°C = 2821.2 K from ΔGr° = 0 for BeO(β) → BeO(ℓ).

ΔHm°(α) = 20.3 kcal/mol is calculated by difference from enthalpies (2867-3159 K) of Shpil'rain et al.(1) and the JANAF enthalpy for α-BeO. We assume that BeO(ℓ) reverted to α-BeO and that β-BeO did not form during the drop calorimetry (1). ΔHm°(β) = 18.895 kcal/mol is calculated from BeO(β) → BeO(ℓ) at the corresponding Tm using the adopted tables. Enthalpy data of Greenbaum et al. (3) gave ΔHm = 19.3 kcal/mol (phase uncertain) even though both the crystal and liquid data have large negative bias. Ohta and Sata (9) derived ΔHm = 7.6±2.1 kcal/mol from liquidus data in the binary system BeO-ThO_2. This can be discounted along with other binary data (10, 11) due to the uncertainty in Tm.

Vaporization Data

The vapor over BeO is composed mainly of trimer, tetramer and individual atoms, along with minor amounts of several other molecules.

References

1. E. E. Sphil'rain, D. N. Kagan and L. S. Barkhatov, High Temperature (USSR) 9, 842 (1971).
2. V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, Dokl. Akad. Nauk SSSR 131, 566 (1960).
3. M. A. Greenbaum, J. Weiher and M. Farber, J. Phys. Chem. 69, 4035 (1965).
4. S. J. Schneider, U. S. Natl. Bur. Std. Monograph 68, 1963.
5. R. E. Latta, E. C. Duderstadt and R. E. Fryxell, J. Nucl. Mater. 35, 350 (1970).
6. B. Riley, Rev. Int. Hautes Temp. Refract. 3, 327 (1966).
7. J. Kordis, J. Nucl. Mater. 14, 322 (1964).
8. C. J. Engberg and E. H. Zehms, J. Amer. Ceram. Soc. 42, 300 (1959).
9. T. Ohta and T. Sata, Yogyo Kyokai Shi 82, 397 (1974).
10. E. M. Levin, C. R. Robbins and H. F. McMurdie, "Phase Diagrams for Ceramists," Third Edition and 1969 Supplement, The American Ceramic Soc., Columbus, Ohio, 1964 and 1969.
11. N. A. Toropov, V. P. Barzakovskii, V. V. Lapin and N. N. Kurtseva, "Handbook of Phase Diagrams of Silicate Systems, Vol. I, Binary Systems," Second revised edition (1969), English transl. (avail. NTIS), Israel Program for Scientific Translations, Jerusalem, 1972.

Beryllium Oxide (BeO) BeO

(Ideal Gas) GFW = 25.0116

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.076	32.029	32.029	INFINITE
100	6.957	39.591	53.416	- 1.382	32.366	30.490	- 66.635
200	6.964	44.415	47.847	- .687	32.576	28.517	- 31.162
298	7.046	47.207	47.207	.000	32.600	26.510	- 19.433
300	7.049	47.250	47.207	.013	32.600	26.473	- 19.285
400	7.253	49.304	47.485	.727	32.519	24.440	- 13.354
500	7.510	50.950	48.019	1.465	32.388	22.436	- 9.807
600	7.757	52.341	48.626	2.229	32.232	20.459	- 7.452
700	7.969	53.553	49.245	3.016	32.058	18.511	- 5.779
800	8.146	54.629	49.852	3.822	31.870	16.587	- 4.531
900	8.294	55.598	50.438	4.644	31.668	14.690	- 3.567
1000	8.425	56.478	50.998	5.480	31.450	12.815	- 2.801
1100	8.552	57.287	51.534	6.329	31.216	10.963	- 2.178
1200	8.689	58.037	52.045	7.191	30.965	9.132	- 1.663
1300	8.849	58.739	52.533	8.067	30.701	7.324	- 1.231
1400	9.040	59.401	53.000	8.962	30.427	5.535	- .864
1500	9.270	60.033	53.448	9.877	30.147	3.767	- .549
1600	9.543	60.639	53.879	10.817	27.110	2.096	- .286
1700	9.855	61.227	54.294	11.787	26.945	.538	- .069
1800	10.205	61.800	54.695	12.789	26.805	- 1.011	.123
1900	10.584	62.362	55.084	13.829	26.694	- 2.553	.294
2000	10.984	62.915	55.462	14.907	26.614	- 4.092	.447
2100	11.393	63.461	55.829	16.026	26.568	- 5.625	.585
2200	11.802	64.000	56.189	17.185	26.553	- 7.158	.711
2300	12.199	64.534	56.540	18.386	26.573	- 8.689	.826
2400	12.575	65.061	56.884	19.625	26.623	- 10.222	.931
2500	12.923	65.581	57.221	20.900	26.700	- 11.761	1.028
2600	13.235	66.094	57.553	22.208	26.804	- 13.299	1.118
2700	13.507	66.599	57.879	23.545	26.930	- 14.844	1.202
2800	13.737	67.095	58.199	24.908	- 43.956	- 15.287	1.193
2900	13.923	67.580	58.514	26.291	- 43.546	- 14.268	1.075
3000	14.067	68.055	58.824	27.691	- 43.125	- 13.266	.966
3100	14.169	68.518	59.129	29.103	- 42.694	- 12.281	.866
3200	14.234	68.969	59.430	30.524	- 42.259	- 11.304	.772
3300	14.264	69.407	59.726	31.949	- 41.824	- 10.344	.685
3400	14.263	69.833	60.017	33.376	- 41.392	- 9.397	.604
3500	14.235	70.246	60.303	34.801	- 40.966	- 8.464	.529
3600	14.184	70.647	60.585	36.222	- 40.550	- 7.538	.458
3700	14.113	71.034	60.862	37.637	- 40.146	- 6.629	.392
3800	14.027	71.409	61.135	39.044	- 39.757	- 5.727	.329
3900	13.929	71.773	61.403	40.442	- 39.382	- 4.836	.271
4000	13.821	72.124	61.667	41.829	- 39.025	- 3.957	.216
4100	13.706	72.464	61.926	43.206	- 38.687	- 3.086	.164
4200	13.587	72.793	62.181	44.570	- 38.368	- 2.221	.116
4300	13.465	73.111	62.431	45.923	- 38.070	- 1.360	.069
4400	13.342	73.419	62.677	47.263	- 37.793	- .512	.025
4500	13.219	73.717	62.919	48.591	- 37.537	.333	- .016
4600	13.098	74.007	63.157	49.907	- 37.304	1.172	- .056
4700	12.979	74.287	63.391	51.211	- 37.092	2.005	- .093
4800	12.863	74.559	63.621	52.503	- 36.903	2.836	- .129
4900	12.750	74.823	63.847	53.783	- 36.735	3.660	- .163
5000	12.642	75.080	64.069	55.053	- 36.588	4.486	- .196
5100	12.538	75.329	64.287	56.312	- 36.465	5.307	- .227
5200	12.439	75.571	64.502	57.561	- 36.362	6.120	- .257
5300	12.344	75.807	64.713	58.800	- 36.282	6.940	- .286
5400	12.254	76.037	64.921	60.030	- 36.221	7.752	- .314
5500	12.169	76.261	65.125	61.251	- 36.182	8.567	- .340
5600	12.088	76.480	65.326	62.464	- 36.163	9.380	- .366
5700	12.012	76.693	65.523	63.669	- 36.163	10.194	- .391
5800	11.941	76.902	65.718	64.866	- 36.183	11.012	- .415
5900	11.874	77.105	65.909	66.057	- 36.222	11.821	- .438
6000	11.811	77.304	66.097	67.241	- 36.279	12.635	- .460

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1974

BERYLLIUM OXIDE (BeO) (IDEAL GAS) GFW = 25.0116

Symmetry Number = 1

$S^\circ_{298.15}$ = 47.207 ± 0.1 gibbs/mol

ΔHf°_0 = 32.03 ± 3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 32.6 ± 3 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	1.3310	1.6510	0.0190	1487.3	11.83
(1-7)	$^3\Pi$	[8000]	6	[1.463]	[1.366]	[0.0163]	1130.8	8.2
(1)	A $^1\Pi$	9234.8	2	1.4632	1.3661	0.0163	1144.2	8.42
(4-7)	$^3\Sigma^+$	[16000]	3	[1.362]	[1.576]	[0.015]	[1370]	[7.8]
(1)	B $^1\Sigma^+$	21197.	1	1.3623	1.5758	0.0154	1370.8	7.75
(4)	$^3\Sigma^+$	[37000]	3	[1.49]	[1.31]	[0.01]	[1082]	[9.]
(4)	$^3\Delta$	[38000]	6	[1.49]	[1.31]	[0.01]	[1082]	[9.]
(1)	D $^1\Delta$	38918.	2	1.49	1.31	0.01	1081.5	9.1
(1, 4)	$^3\Sigma^-$	[40000]	3	[1.49]	[1.31]	[0.01]	1012.2	8.4
(1, 4)	$^1\Sigma^-$	38956.	1	[1.49]	[1.31]	[0.01]	[1082]	[9.]
(4)	$^1\Sigma^+$	[47000]	1	[1.49]	[1.31]	[0.01]	[1082]	[9.]

Heat of Formation

We adopt D°_0 = 104.2 ± 3 and ΔHf°_{298} = 32.6 ± 3 kcal/mol based on two mass-spectrometric studies (8, 9) analyzed below. The adopted values correspond to the average of the two results for reaction A and also to the average for reaction B. Improved agreement between reactions A and B is due to recalculation of Kp of reaction B using the current table (4) for BeO(α). Our analysis should be compared to the analysis of Brewer and Rosenblatt (10), using "functions based upon calculated levels."

The controversy over D°_0 of alkaline earth oxides has been reviewed in detail (10-12). Uncertainty in the electronic partition function of BeO due to triplet states now is much reduced (2). Gaydon (12) derived spectroscopic values for D°_0 of 91 and 111 kcal/mol from the X and A states, respectively. D°_0 = 101 kcal/mol was derived (13) by fitting an electronegativity potential function to the X state.

Source	Method	Reaction[a]	Range	No. of	δS[b]	ΔHr°_{298}/(kcal/mol)		ΔHf°_{298}	D°_0
			T/K	Points	gibbs/mol	2nd Law	3rd Law	kcal/mol	
(8)Chupka(1959)	Knudsen mass spec.	A	2100-2474	8	1.6±2.3	-8.4±5	-11.9±3	30.6	106.2
(9)Theard(1964)	Knudsen mass spec.	A	2380	1	-	-	-15.9±3	34.6	102.2
(8)Chupka(1959)	Knudsen mass spec.	B[c]	1914-2304	6	0.7±0.9	107.3±2	105.9±3	31.9	104.9
(9)Theard(1964)	Knudsen mass spec.	B[c]	2380	1	-	-	104.5±3	33.3	103.5

[a] Reactions: A) BeO(g) + O(g) = Be(g) + O_2(g); B) BeO(g) = Be(g) + O(g). [b] δS = ΔS°_r(2nd Law) - ΔS°_r(3rd Law).

[c] Recalculated as in (8) assuming $P_{Be} = P_O$ and JANAF values for BeO(α) = Be(g) + O(g).

Heat Capacity and Entropy

Electronic levels (T_o) and vibrational-rotational constants of the observed states are from Rosen (1). Field (2) concluded that calculations (3, 5-7) of the isoconfigurational $A^1\Pi$ - $^3\Pi$ separation should be adequate for estimating the low-lying $^3\Pi$ state. The adopted separation of 1200 cm^{-1} is consistent with analysis (3) of perturbations. We estimate $^3\Sigma^+$ at 16000 cm^{-1} by assuming that it lies 5200 ± 4000 cm^{-1} (4-7) below the isoconfigurational B state. Other predicted states and their vibrational-rotational constants are estimated in isoconfigurational groups by comparison with MgO, CaO, SrO and BaO(4). Comparisons are facilitated by listing the states in the isoconfigurational order of MgO(4). Our thermodynamic functions correspond to an "effective" ground state with $1<g<2$ instead of $g = 3$ or 6 (10, 11). This comparison is only approximate since our functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\varepsilon_i/T)$.

Sublimation and Vaporization Data

Mass spectra (8, 9) at 1900-2400 K showed the vapor to consist mainly of Be, O, $(BeO)_3$ and $(BeO)_4$ with small amounts of O_2, Be_2O, BeO and other polymers of BeO. Tetramer, trimer and pentamer become dominant at higher temperatures.

References

1. B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970, pp. 65-6.
2. R. W. Field, J. Chem. Phys. 60, 2400(1974).
3. W. M. Huo, K. F. Freed and W. Klemperer, J. Chem. Phys. 46, 3556(1967).
4. JANAF Thermochemical Tables: BeO(α,β,g), MgO(g), CaO(g) 12-31-74; SrO(g), BaO(g) 6-30-74.
5. P. K. Pearson, S. V. O'Neil and H. F. Schaeffer, J. Chem. Phys. 56, 3938(1972); 55, 176(1971); Chem. Phys. Lett. 10, 404(1971).
6. M. L. Sink, Ph.D. Thesis, Case Western Reserve Univ., 1972; Diss. Abstr. B33, 671(1972).
7. G. Verhaegen and W. G. Richards, J. Chem. Phys. 45, 1828(1966).
8. W. A. Chupka, J. Berkowitz and C. F. Giese, J. Chem. Phys. 30, 827(1959).
9. L. P. Theard and D. L. Hildenbrand, J. Chem. Phys. 41, 3416(1964).
10. L. Brewer and G. Rosenblatt, Advan. High Temp. Chem. 2, 1(1969).
11. K. Schofield, Chem. Rev. 67, 707(1967).
12. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall Ltd., London, 1968, pp. 236-244.
13. B. Rai and S. N. Rai, Indian J. Pure Appl. Phys. 10, 401(1972).

Calcium Monobromide (CaBr) BrCa

(Ideal Gas) GFW = 119.984

T, °K	gibbs/mol Cp°	 S°	 -(G°-H°298)/T	kcal/mol H°-H°298	 ΔHf°	 ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.355	-9.861	-9.861	INFINITE
100	7.543	51.457	67.912	-1.645	-9.719	-13.840	30.247
200	8.399	56.998	61.204	-.841	-10.042	-17.848	19.504
298	8.695	60.416	60.416	.000	-11.806	-21.434	15.711
300	8.698	60.470	60.416	.016	-11.818	-21.494	15.658
400	8.828	62.992	60.759	.853	-15.698	-23.934	13.077
500	8.897	64.970	61.411	1.780	-15.899	-25.969	11.351
600	8.947	66.597	62.143	2.672	-16.102	-27.964	10.186
700	8.974	67.978	62.881	3.568	-16.306	-29.925	9.343
800	8.999	69.175	63.594	4.466	-16.648	-31.827	8.695
900	9.021	70.239	64.275	5.367	-17.248	-33.676	8.178
1000	9.040	71.190	64.920	6.270	-17.700	-35.477	7.754
1100	9.057	72.053	65.530	7.175	-18.204	-37.231	7.397
1200	9.073	72.841	66.106	8.082	-20.541	-38.785	7.064
1300	9.088	73.568	66.653	8.990	-20.806	-40.294	6.774
1400	9.103	74.242	67.171	9.899	-21.069	-41.784	6.523
1500	9.118	74.871	67.664	10.811	-21.332	-43.254	6.302
1600	9.132	75.460	68.133	11.723	-21.594	-44.707	6.107
1700	9.146	76.014	68.580	12.637	-21.855	-46.143	5.932
1800	9.161	76.537	69.006	13.552	-59.009	-46.884	5.692
1900	9.176	77.033	69.417	14.469	-59.047	-46.209	5.315
2000	9.193	77.504	69.810	15.388	-59.086	-45.533	4.976
2100	9.210	77.953	70.187	16.308	-59.125	-44.855	4.668
2200	9.229	78.382	70.550	17.230	-59.165	-44.174	4.388
2300	9.250	78.792	70.899	18.154	-59.207	-43.491	4.133
2400	9.273	79.186	71.236	19.080	-59.253	-42.807	3.898
2500	9.299	79.566	71.562	20.008	-59.302	-42.120	3.682
2600	9.328	79.931	71.877	20.940	-59.357	-41.432	3.483
2700	9.360	80.283	72.182	21.874	-59.418	-40.742	3.298
2800	9.395	80.624	72.477	22.812	-59.487	-40.049	3.126
2900	9.433	80.955	72.764	23.753	-59.564	-39.355	2.966
3000	9.475	81.275	73.042	24.698	-59.653	-38.655	2.816
3100	9.521	81.587	73.313	25.648	-59.754	-37.952	2.676
3200	9.570	81.890	73.576	26.603	-59.868	-37.247	2.544
3300	9.623	82.185	73.833	27.562	-60.000	-36.540	2.420
3400	9.679	82.473	74.083	28.527	-60.147	-35.827	2.303
3500	9.739	82.754	74.326	29.498	-60.313	-35.108	2.192
3600	9.802	83.030	74.564	30.475	-60.499	-34.386	2.088
3700	9.869	83.299	74.797	31.459	-60.706	-33.658	1.988
3800	9.938	83.563	75.024	32.449	-60.936	-32.923	1.894
3900	10.011	83.822	75.246	33.446	-61.191	-32.183	1.803
4000	10.086	84.077	75.464	34.451	-61.469	-31.437	1.718
4100	10.163	84.327	75.677	35.464	-61.771	-30.682	1.636
4200	10.243	84.573	75.886	36.484	-62.100	-29.919	1.557
4300	10.325	84.815	76.091	37.512	-62.454	-29.149	1.482
4400	10.409	85.053	76.292	38.549	-62.833	-28.369	1.409
4500	10.495	85.288	76.469	39.594	-63.239	-27.583	1.340
4600	10.582	85.519	76.683	40.648	-63.669	-26.785	1.273
4700	10.670	85.746	76.875	41.711	-64.123	-25.977	1.208
4800	10.759	85.973	77.061	42.782	-64.603	-25.162	1.146
4900	10.849	86.196	77.245	43.862	-65.104	-24.335	1.085
5000	10.940	86.416	77.428	44.952	-65.627	-23.497	1.027
5100	11.031	86.634	77.604	46.050	-66.172	-22.650	.971
5200	11.123	86.849	77.780	47.158	-66.736	-21.791	.916
5300	11.214	87.062	77.953	48.275	-67.318	-20.921	.863
5400	11.306	87.272	78.124	49.401	-67.917	-20.041	.811
5500	11.397	87.480	78.292	50.536	-68.531	-19.148	.761
5600	11.488	87.687	78.458	51.680	-69.159	-18.246	.712
5700	11.578	87.891	78.622	52.834	-69.798	-17.329	.664
5800	11.667	88.093	78.783	53.996	-70.448	-16.402	.618
5900	11.756	88.293	78.943	55.167	-71.108	-15.465	.573
6000	11.844	88.491	79.100	56.347	-71.775	-14.519	.529

Dec. 31, 1974

CALCIUM MONOBROMIDE (CaBr) (IDEAL GAS) GFW = 119.984 BRCA

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 60.42 ± 0.05 gibbs/mol

Hf°_0 = -9.9 ± 10.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -11.8 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

STATE	ϵ_i, cm^{-1}	g_i	STATE	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2	$D\ ^2\Sigma$	30190.6	2
$A_1\ ^2\Pi_{1/2}$	15922.5	2	$E\ ^2\Sigma$	33942.2	2
$A_2\ ^2\Pi_{3/2}$	15985.8	2	$[F\ ^2\Pi]$	[35000]	[4]
$B\ ^2\Sigma$	16380.0	2	$[G\ ^2\Delta]$	[36000]	[4]
$C_1\ ^2\Pi_{1/2}$	25314.0	2	$[H\ ^2\Sigma]$	36798.7	[2]
$C_2\ ^2\Pi_{3/2}$	25537.5	2			

ω_e = 284.56 cm^{-1} $\omega_e x_e$ = 0.86 cm^{-1} σ = 1

B_e = [0.09637] cm^{-1} α_e = [0.000389] cm^{-1} r_e = [2.56] Å

Heat of Formation

The selected value, ΔHf°_0 = -9.9 kcal/mol, is obtained from an analysis of spectroscopic data. The adopted values of the ground state vibrational constants, ω_e and $\omega_e x_e$, give D°_0 = 2.90 eV for CaBr(g) by a linear Birge-Sponer extrapolation. Based on the ionicity correction suggested by Hildenbrand (1), this value adjusts to 3.50 eV (80.78 kcal/mol) which is adopted. The adopted value for D°_0 gives D°_0 (CaBr)/D°_0($CaBr_2$) = 0.43 which is quite consistent with values of this ratio for other alkaline earth halide systems (2). Also, Hildenbrand (3, 4) found that the ionicity parameter brings thermochemical and spectroscopic dissociation energies for CaF(g) and CaCl(g) into reasonable agreement. ΔHf°_{298} corresponds to -11.8 kcal/mol.

Ionic model calculations have led to D°_0 values of 5.29 eV (5) and 3.4 eV (6). The latter result is believed to represent a minimum value for D°_0. Two other experimental values for D°_0, which bracket the selected value, have also been reported. Flame studies (7) gave D°_0 = 3.29 eV and chemiluminescence (8) from reaction of Ca atoms with Br_2 gave a lower limit to D°_0 of 4.22 eV. We assign an uncertainty of ± 10 kcal/mol to ΔHf°_0 to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $CaBr_2$ (9) with r_e(CaBr)/r_e($CaBr_2$) = 0.96. The value of this ratio is calculated from bond lengths (2) for several other alkaline earth halide systems. Our adopted value for r_e is supported by an estimate (r_e = 2.6 Å) of Krasnov and Karaseva (6) while another estimated value (5) is only 0.14 Å larger than ours. The rotational constant is calculated from the estimated value of r_e. The value of α_e is obtained from a Morse potential function. The moment of inertia is 2.9045 X 10^{-38} g cm^2.

The vibrational constants are those recently determined from a complete vibrational analysis of the $D\ ^2\Sigma - X\ ^2\Sigma$ system by Shah (10). These two values are corrected for the natural isotopic abundances of Br. The electronic levels with the exception of those for the D, F, G, and H states are from the compilation of Rosen (11). The D state energy is from Shah (10). The two doublet states (F and G) are estimated by analogy with those for SrBr (9). Recently, Reddy et al. (12) reported observing a new system of bands in the visible emission spectrum of CaBr which was associated with $^2\Sigma - A\ ^2\Pi$ transition. The upper state of this system is assigned the $H\ ^2\Sigma$ state by analogy with SrBr.

References

1. D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, Ed. by L. Eyring, Academic Press, New York, 1967.
2. JANAF Thermochemical Tables.
3. D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).
4. D. L. Hildenbrand, J. Chem. Phys. 52, 5751 (1970).
5. J. L. Margrave, J. Phys. Chem. 58, 258 (1954).
6. K. S. Krasnov and N. V. Karaseva, Optics and Spectroscopy 19, 14 (1965).
7. A. N. Khitrov, V. G. Ryabova, and L. V. Gurvich, Teplofiz. Vys. Temp. 11, 1126 (1973).
8. M. Menzinger, Can. J. Chem. 52, 1688 (1974).
9. JANAF Thermochemical Tables: $CaBr_2$(g), 6-30-74; SrBr(g), 12-31-74.
10. S. G. Shah, Indian J. Pure Appl. Phys. 8, 118 (1970).
11. B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules, "Pergamon Press, New York, 1970.
12. B. R. K. Reddy, Y. P. Reddy, and P. T. Rao, Curr. Sci. 39, 485 (1970).

MAGNESIUM MONOBROMIDE (MGBR) BRMG

(IDEAL GAS) GFW=104.209

T, °K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.290	-6.611	-6.611	INFINITE
100	7.235	49.887	65.777	-1.589	-6.399	-10.516	22.984
200	8.106	55.192	59.285	-.819	-6.776	-14.618	15.973
298	8.518	58.516	58.516	.000	-8.447	-18.140	13.297
300	8.523	58.569	58.517	.016	-8.459	-18.200	13.259
400	8.716	61.051	58.854	.879	-12.330	-20.664	11.290
500	8.820	63.008	59.496	1.756	-12.536	-22.723	9.932
600	8.885	64.622	60.219	2.642	-12.763	-24.741	9.012
700	8.929	65.995	60.949	3.532	-13.012	-26.717	8.341
800	8.962	67.190	61.656	4.427	-13.291	-28.657	7.829
900	8.989	68.247	62.331	5.325	-13.603	-30.559	7.421
1000	9.011	69.195	62.970	6.225	-16.072	-32.243	7.047
1100	9.031	70.055	63.576	7.127	-16.423	-33.845	6.724
1200	9.049	70.841	64.149	8.031	-16.797	-35.413	6.450
1300	9.065	71.566	64.692	8.936	-17.197	-36.947	6.211
1400	9.080	72.239	65.207	9.844	-47.987	-37.971	5.928
1500	9.095	72.866	65.697	10.752	-48.029	-37.255	5.428
1600	9.109	73.453	66.164	11.663	-48.070	-36.536	4.991
1700	9.123	74.006	66.609	12.574	-48.111	-35.812	4.604
1800	9.136	74.527	67.035	13.487	-48.150	-35.089	4.260
1900	9.149	75.022	67.442	14.401	-48.188	-34.361	3.952
2000	9.162	75.491	67.833	15.317	-48.226	-33.633	3.675
2100	9.175	75.939	68.208	16.234	-48.264	-32.904	3.424
2200	9.188	76.366	68.569	17.152	-48.300	-32.170	3.196
2300	9.200	76.775	68.917	18.071	-48.337	-31.435	2.987
2400	9.212	77.166	69.253	18.992	-48.372	-30.700	2.796
2500	9.225	77.543	69.577	19.914	-48.408	-29.964	2.619
2600	9.237	77.905	69.890	20.837	-48.443	-29.224	2.456
2700	9.250	78.254	70.194	21.761	-48.478	-28.486	2.306
2800	9.262	78.590	70.488	22.687	-48.513	-27.745	2.166
2900	9.275	78.915	70.773	23.614	-48.547	-27.001	2.035
3000	9.288	79.230	71.049	24.542	-48.583	-26.259	1.913
3100	9.302	79.535	71.318	25.472	-48.619	-25.513	1.799
3200	9.315	79.830	71.580	26.402	-48.657	-24.768	1.692
3300	9.330	80.117	71.834	27.335	-48.695	-24.022	1.591
3400	9.344	80.396	72.082	28.268	-48.736	-23.271	1.496
3500	9.360	80.667	72.323	29.203	-48.779	-22.524	1.406
3600	9.376	80.931	72.559	30.140	-48.824	-21.772	1.322
3700	9.392	81.188	72.788	31.079	-48.872	-21.019	1.242
3800	9.410	81.439	73.013	32.019	-48.924	-20.265	1.166
3900	9.429	81.684	73.232	32.961	-48.979	-19.512	1.093
4000	9.448	81.922	73.446	33.904	-49.039	-18.756	1.025
4100	9.469	82.156	73.656	34.850	-49.104	-17.999	.959
4200	9.490	82.384	73.861	35.798	-49.173	-17.240	.897
4300	9.513	82.608	74.062	36.748	-49.249	-16.479	.838
4400	9.537	82.827	74.259	37.701	-49.330	-15.714	.781
4500	9.563	83.042	74.451	38.656	-49.418	-14.948	.726
4600	9.589	83.252	74.640	39.614	-49.513	-14.181	.674
4700	9.617	83.459	74.826	40.574	-49.615	-13.411	.624
4800	9.647	83.661	75.008	41.537	-49.725	-12.640	.576
4900	9.677	83.861	75.186	42.503	-49.843	-11.866	.529
5000	9.709	84.056	75.362	43.473	-49.969	-11.089	.485
5100	9.742	84.249	75.534	44.445	-50.105	-1.031	.442
5200	9.777	84.439	75.704	45.421	-50.250	-9.531	.401
5300	9.813	84.625	75.870	46.400	-50.404	-8.743	.361
5400	9.850	84.809	76.034	47.384	-50.567	-7.960	.322
5500	9.888	84.990	76.195	48.370	-50.742	-7.167	.285
5600	9.928	85.168	76.354	49.361	-50.927	-6.376	.249
5700	9.968	85.345	76.510	50.356	-51.123	-5.574	.214
5800	10.010	85.518	76.664	51.355	-51.329	-4.777	.180
5900	10.053	85.690	76.815	52.358	-51.548	-3.969	.147
6000	10.097	85.859	76.965	53.365	-51.779	-3.167	.115

June 30, 1966; June 30, 1975

MAGNESIUM MONOBROMIDE (MgBr) (IDEAL GAS) GFW = 104.209 BRMG

Ground State Configuration $^2\Sigma^+$

$S°_{298.15}$ = 58.52 ± 0.05 gibbs/mol

$\Delta Hf°_0$ = -6.6 ± 10.0 kcal/mol

$\Delta Hf°_{298.15}$ = -8.4 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A_1\,^2\Pi_{1/2}$	25765.2	2
$A_2\,^2\Pi_{3/2}$	25876.3	2
$B[^2\Sigma]$	[26500]	2
$C[^2\Sigma]$	39285.9	2

ω_e = 373.2 cm^{-1} $\omega_e x_e$ = 1.34 cm^{-1} σ = 1

B_e = 0.16241 cm^{-1} α_e = [0.00079] cm^{-1} r_e = 2.36 ± 0.10 Å

Heat of Formation

No thermochemical measurement of the heat of formation has been made. The selected value, $\Delta Hf°_0(MgBr, g)$, = -6.6 ± 10.0 kcal/mol, is based on an analysis of spectroscopic data. Herzberg (1) obtained the value $D°_0 \leq 3.35$ eV from predissociation which sets in above v = 3 of $A^2\Pi$ state. Gaydon (2) recommended $D°_0$ = 3.2 ± 1.0 eV which was obtained from a linear Birge-Sponer extrapolation of the ground state vibrational levels (v, 0-6). Our adopted vibrational constants give this same value by a similar extrapolation. The linear Birge-Sponer $D°_0$ value adjusts to 3.03 eV (69.79 kcal/mol) when corrected for the ionic character of the Mg-Br bond by the method suggested by Hildenbrand (3). This adjusted $D°_0$ value is adopted and corresponds to $\Delta Hf°_{298}$ of -8.4 kcal/mol.

Two lower values of $D°_0$ have been reported from results of ionic model calculations (4, 5). Margrave (4) calculated an ionic binding energy of 135 kcal/mol which gives $D°_0$ (MgBr, g) = 1.75 eV. Krasnov and Karaseva (5), using a Rittner potential function (6), found $D°_0$ = 2.39 eV which probably represents a minimum value for $D°_0$. In addition, we find $D°_{298}$ (MgBr)/$\Delta Ha°_{298}(MgBr_2)$ = 0.44 which is quite consistent with values of this ratio for other alkaline-earth halides (7). This consistency provides further support for our adopted results. An estimated uncertainty of ± 10.0 kcal/mol is believed to be realistic.

Heat Capacity and Entropy

Values for the ground state vibrational constants and bond length are taken from the tabulation of Rosen (8). The adopted value of r_e which was obtained from a rotational analysis of the (0,0) bands of the $A^2\Pi$-$X^2\Sigma$ system by Patel and Patel (9, 10) gives $r_e(MgBr)/r_e(MgBr_2)$ = 1.01. Comparison of values for this ratio for several alkaline-earth halides (7) shows that $r_e(MX)/r_e(MX_2)$ is generally slightly less than one (~0.96). This suggests that the uncertainty in r_e(MgBr) may be as high as 0.1 A, assuming r_e for $MgBr_2$ is correct (7). The value of B_e is calculated from r_e. α_e is obtained from the other constants assuming a Morse potential function. The moment of inertia is 1.7235 x 10^{-38} g cm^2.

The electronic levels except for the two upper most states are from Rosen (8). We estimate a $^2\Sigma$ state to lie at 26500 cm^{-1} by analogy with those observed for CaBr and SrBr (7). The assignment of the level at 39285.9 cm^{-1} is rather uncertain. Rosen (8) has assigned this level as a $C^2\Pi$ state. Very recently, Reddy and Rao (11) observed that the bands were single-headed, and they attributed the system to a $C^2\Sigma$ - $X^2\Sigma$ transition by analogy with that for MgF. Comparison of the observed spectra for MgCl, CaBr, SrBr, and BaBr(7) suggests yet another assignment. It appears likely that the observed level near 40000 cm^{-1} arisen from a $D^2\Sigma$-$X^2\Sigma$ transition, and the $C^2\Pi$ state, estimated to lie near 30000 cm^{-1}, has gone unobserved. We tentatively adopt the assignment of Reddy and Rao (11). However, thermodynamic functions based on the alternate assignments are not significantly different from those adopted below 4500 K.

References

1. G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Company, New York, 1950.
2. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1968.
3. D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, Ed. by L. Eyring, Academic Press, New York, 1967.
4. J. L. Margrave, J. Phys. Chem. 58, 258 (1954).
5. K. S. Krasnov and N. V. Karaseva, Optics and Spectroscopy 19, 14 (1965).
6. E. S. Rittner, J. Chem. Phys. 19, 1030 (1951).
7. JANAF Thermochemical Tables: CaBr(g), SrBr(g), and BaBr(g), 12-31-74; MgCl(g), 3-31-66; $MgBr_2$(g), 6-30-74.
8. B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.
9. M. M. Patel and P. D. Patel, Indian J. Phys. 42, 419 (1968).
10. M. M. Patel and P. D. Patel, J. Phys. B (Atom. Molec. Phys.) 2, 515 (1969).
11. B. R. K. Reddy and P. T. Rao, Curr. Sci. 39, 509 (1970).

Strontium Monobromide (SrBr)

(Ideal Gas) GFW = 167.524

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.415	-19.266	-19.266	INFINITE
100	7.906	53.777	70.681	-1.690	-19.195	-23.329	50.986
200	8.611	59.529	63.812	-.856	-19.536	-27.353	29.889
298	8.809	63.011	63.011	.000	-21.300	-30.936	22.677
300	8.811	63.065	63.011	.016	-21.312	-30.996	22.580
400	8.895	65.613	63.358	.902	-25.205	-33.437	18.269
500	8.942	67.604	64.015	1.794	-25.454	-35.466	15.502
600	8.974	69.237	64.753	2.690	-25.744	-37.443	13.638
700	8.998	70.622	65.495	3.589	-26.083	-39.367	12.291
800	9.018	71.825	66.213	4.490	-26.478	-41.239	11.266
900	9.036	72.888	66.897	5.392	-27.101	-43.041	10.452
1000	9.053	73.841	67.544	6.297	-27.547	-44.788	9.788
1100	9.068	74.705	68.157	7.203	-29.916	-46.381	9.215
1200	9.083	75.494	68.736	8.110	-30.300	-47.860	8.717
1300	9.097	76.222	69.284	9.019	-30.683	-49.308	8.289
1400	9.111	76.897	69.804	9.930	-31.066	-50.726	7.919
1500	9.125	77.526	70.298	10.842	-31.448	-52.118	7.594
1600	9.140	78.115	70.768	11.755	-31.829	-53.483	7.305
1700	9.154	78.670	71.217	12.670	-64.783	-53.919	6.932
1800	9.170	79.193	71.646	13.586	-64.821	-53.279	6.469
1900	9.187	79.690	72.056	14.504	-64.859	-52.636	6.055
2000	9.205	80.161	72.450	15.423	-64.898	-51.993	5.682
2100	9.226	80.611	72.828	16.345	-64.939	-51.347	5.344
2200	9.249	81.041	73.191	17.268	-64.982	-50.699	5.036
2300	9.274	81.452	73.542	18.195	-65.028	-50.048	4.756
2400	9.303	81.848	73.879	19.123	-65.080	-49.396	4.498
2500	9.335	82.228	74.206	20.055	-65.137	-48.741	4.261
2600	9.371	82.595	74.521	20.991	-65.202	-48.083	4.042
2700	9.411	82.949	74.827	21.930	-65.277	-47.425	3.839
2800	9.455	83.292	75.123	22.873	-65.365	-46.761	3.650
2900	9.503	83.625	75.411	23.821	-65.466	-46.095	3.474
3000	9.555	83.948	75.690	24.774	-65.583	-45.426	3.309
3100	9.611	84.262	75.961	25.732	-65.719	-44.751	3.155
3200	9.671	84.568	76.226	26.696	-65.876	-44.072	3.010
3300	9.735	84.867	76.483	27.666	-66.056	-43.389	2.874
3400	9.802	85.158	76.734	28.643	-66.261	-42.699	2.745
3500	9.873	85.443	76.979	29.627	-66.493	-42.002	2.623
3600	9.947	85.723	77.218	30.618	-66.755	-41.299	2.507
3700	10.024	85.996	77.451	31.616	-67.046	-40.588	2.397
3800	10.104	86.265	77.680	32.623	-67.370	-39.868	2.293
3900	10.187	86.528	77.903	33.637	-67.727	-39.139	2.193
4000	10.272	86.787	78.122	34.660	-68.119	-38.403	2.098
4100	10.359	87.042	78.336	35.692	-68.544	-37.655	2.007
4200	10.447	87.292	78.547	36.732	-69.005	-36.896	1.920
4300	10.538	87.539	78.753	37.781	-69.499	-36.125	1.836
4400	10.629	87.783	78.955	38.840	-70.027	-35.342	1.755
4500	10.722	88.023	79.154	39.907	-70.589	-34.548	1.678
4600	10.815	88.259	79.350	40.984	-71.183	-33.741	1.603
4700	10.909	88.493	79.542	42.070	-71.806	-32.919	1.531
4800	11.003	88.724	79.731	43.166	-72.460	-32.086	1.461
4900	11.098	88.951	79.916	44.271	-73.140	-31.238	1.393
5000	11.192	89.177	80.099	45.385	-73.844	-30.375	1.328
5100	11.286	89.399	80.280	46.509	-74.572	-29.500	1.264
5200	11.380	89.619	80.457	47.642	-75.321	-28.608	1.202
5300	11.473	89.837	80.632	48.785	-76.087	-27.701	1.142
5400	11.566	90.052	80.804	49.937	-76.870	-26.783	1.084
5500	11.657	90.265	80.975	51.098	-77.667	-25.846	1.027
5600	11.748	90.476	81.142	52.269	-78.474	-24.898	.972
5700	11.837	90.685	81.308	53.448	-79.292	-23.933	.918
5800	11.925	90.891	81.471	54.636	-80.115	-22.955	.865
5900	12.012	91.096	81.633	55.833	-80.944	-21.962	.814
6000	12.097	91.299	81.792	57.038	-81.775	-20.958	.763

Dec. 31, 1974

STRONTIUM MONOBROMIDE (SrBr) (IDEAL GAS)

Ground State Configuration $^2\Sigma^+$

$S°_{298.15}$ = 63.0 ± 0.1 gibbs/mol

GFW = 167.524

$\Delta Hf°_0$ = -19.3 ± 10.0 kcal/mol

$\Delta Hf°_{298.15}$ = -21.3 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i	State	ε_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2	$E\ ^2\Sigma$	32052.5	2
$A_1\ ^2\Pi_{1/2}$	14699.4	2	$F_1\ ^2\Pi_{1/2}$	33131.7	2
$A_2\ ^2\Pi_{3/2}$	15000.7	2	$F_2\ ^2\Pi_{3/2}$	33215.0	2
$B\ ^2\Sigma$	15352.0	2	$G_1\ ^2\Delta_{3/2}$	34257.0	2
$C_1\ ^2\Pi_{1/2}$	24343.7	2	$G_2\ ^2\Delta_{5/2}$	34282.8	2
$C_2\ ^2\Pi_{3/2}$	24665.8	2	$H^2\Sigma$	34357.7	
$D\ ^2\Sigma$	28958.2	2			

ω_e = 216.5 cm^{-1} $\omega_e x_e$ = 0.51 cm^{-1} σ = 1

B_e = [0.054924] cm^{-1} α_e = [0.000171] cm^{-1} r_e = [2.71] Å

Heat of Formation

The selected value, $\Delta Hf°_0$ = -19.3 kcal/mol, is obtained from an analysis of spectroscopic data. Herzberg (1) suggested $D°_0$ = 2.8 eV for SrBr(g) which was derived from a linear Birge-Sponer extrapolation of the ground state vibrational levels. Later, Gaydon (2) claimed that this value is unreliable and suggested that the true value may be much higher. The adopted ground state vibrational constants give $D°_0$ = 2.84 eV by a similar extrapolation. We note that JANAF analyses (3) of the spectroscopic and thermochemical data for SrF(g) and SrCl(g) show that the ionicity corrections of Hildenbrand (4) bring the Birge-Sponer extrapolations into reasonable agreement with adopted $D°_0$ values. Based on this correction for SrBr(g), we obtain $D°_0$ = 3.76 eV (86.7 kcal/mol) which is adopted. The adopted value of $D°_0$ corresponds to $\Delta Hf°_{298}$ = -21.3 kcal/mol. We also find $D°_0$ (SrBr)/$D°_0$($SrBr_2$) = 0.46 which is quite consistent with values of this ratio for other alkaline earth halide systems (5).

Ionic model calculations (6, 7) have led to $D°_0$ values of 5.07 eV (6) and 3.53 eV (7). The latter result is believed to represent a minimum value for $D°_0$. Two other experimental values for $D°_0$, which bracket the selected value, have been reported. Flame studies (8) gave $D°_0$ = 3.4 eV, and chemiluminescence (9) from reaction of Sr atoms with Br_2 gave a lower limit to $D°_0$ of 4.1 eV. We assign an uncertainty of ± 10 kcal/mol to $\Delta Hf°_0$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $SrBr_2$(3) with r_e(SrBr)/r_e($SrBr_2$) = 0.96. This value for the ratio is *calculated from bond lengths (5) for several other alkaline earth halide systems. Our adopted value for* r_e *agrees with that* (2.74Å) estimated by Krasnov and Karaseva (7), while two other estimated values (6, 10) lie somewhat higher (~0.2 Å). The rotational constant is calculated from the estimated value for r_e. The value of α_e is obtained from a Morse potential function. The moment of inertia is 5.0963×10^{-38} g cm^2.

The vibrational constants and first seven electronic states and levels are taken from the compilation of Rosen (11). The E state energy has been measured by Reddy and Rao (12), while the F, G, and H state energies are due to Reddy et al. (13). The five upper most states were associated with transitions between the excited states of SrBr, and their assignments (13) were made by analogy with the observed spectrum for SrCl(g).

References

1. G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Company, New York, 1950.
2. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1968.
3. JANAF Thermochemical Tables: SrF(g) and SrCl(g), 12-31-72; $SrBr_2$(g), 6-30-74.
4. D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, Ed. by L. Eyring, Academic Press, New York, 1967.
5. JANAF Thermochemical Tables.
6. J. L. Margrave, J. Phys. Chem. 58, 258 (1954).
7. K. S. Krasnov and N. V. Karaseva, Optics and Spectroscopy 19, 14 (1965).
8. A. N. Khitrov, V. G. Ryabova, and L. V. Gurvich, Teplofiz. Vys. Temp. 11, 1126 (1973).
9. M. Menzinger, Can. J. Chem. 52, 1688 (1974).
10. K. M. Guggenheimer, Proc. Phys. Soc. London 58, 456 (1946).
11. B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.
12. Y. P. Reddy and P. T. Rao, Indian J. Pure and App. Phys. 4, 251(1966).
13. B. R. K. Reddy, Y. P. Reddy, and P. T. Rao, Curr. Sci. 40, 317 (1971).

ZIRCONIUM TETRABROMIDE ($ZrBr_4$) Br_4Zr

(CRYSTAL) GFW=410.836

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 6.731	- 175.492	- 175.492	INFINITE
100	22.377	24.695	78.605	- 5.391	- 175.700	- 175.260	383.031
200	27.743	42.188	56.373	- 2.837	- 176.014	- 174.703	190.907
298	29.829	53.702	53.702	.000	- 181.800	- 173.339	127.060
300	29.856	53.887	53.703	.055	- 181.822	- 173.285	126.238
400	30.900	62.630	54.888	3.097	- 195.883	- 167.516	91.526
500	31.460	69.588	57.156	6.216	- 195.181	- 160.506	70.157
600	31.870	75.362	59.722	9.383	- 194.468	- 153.638	55.963
700	32.200	80.300	62.318	12.587	- 193.756	- 146.891	45.861
800	32.480	84.618	64.841	15.821	- 193.047	- 140.244	38.313
900	32.760	88.460	67.256	19.083	- 192.343	- 133.686	32.463
1000	33.040	91.926	69.552	22.373	- 191.642	- 127.205	27.801

March 31, 1962; March 31, 1964; June 30, 1975

ZIRCONIUM TETRABROMIDE ($ZrBr_4$) (CRYSTAL) GFW = 410.836 Br_4Zr

$S^\circ_{298.15}$ = [53.7±1.0] gibbs/mol
Tm = 723±1 K
Ts = 628.5 K

ΔHf°_0 = [-175.5±2.0] kcal/mol
$\Delta Hf^\circ_{298.15}$ = -181.8±1.5 kcal/mol
ΔHm° = unknown
$\Delta Hs^\circ_{298.15}$ = 27.7±0.3 kcal/mol

Heat of Formation

Turnbull (1) measured the heats of reaction for the dissolution of the zirconium tetrahalides in caustic and in water. The reported heats of reaction and the corresponding reactions may be combined to yield the following:

$ZrBr_4(c) + 4NaCl(aq) = ZrCl_4(c) + 4NaBr(aq)$, $\Delta Hr^\circ_{298} = -8.10 \pm 0.9$ kcal/mol
$ZrBr_4(c) + 4\ Cl^-(aq) = ZrCl_4(c) + 4\ Br^-(aq)$, $\Delta Hr^\circ_{298} = -9.83 \pm 0.6$ kcal/mol

Using auxiliary data (2, 4), we calculate ΔHf°_{298} = -182.67 and -181.02 kcal/mol for $ZrBr_4(c)$ from these two reactions. We adopt a mean of these two values, ΔHf°_{298} = -181.8 kcal/mol, and assign an uncertainty of ± 1.5 kcal/mol. This same value was suggested by NBS (3).

Heat Capacity and Entropy

There are no heat capacity and enthalpy data reported in the literature for $ZrBr_4(c)$. The adopted heat capacity values are estimated so as to give reasonable trends in comparison with $ZrCl_4$ and ZrI_4 and to be consistent with the existing sublimation data.

The crystal data compilation of Donnay and Ondik (5) tabulated both $ZrCl_4$ and $ZrBr_4$ as cubic structures. Thus, the adopted heat capacity values are estimated so as to parallel those for $ZrCl_4$. The heat capacity values below 300K are calculated by summing contributions due to hindered translations, librations, and internal vibrations of the crystal. The parameters used in the calculations are determined by a correlation with corresponding parameters for $ZrCl_4$ (6) and a consideration of the sublimation data for $ZrBr_4$ (6). The high temperature heat capacities are obtained graphically.

Melting Data

The melting point was observed by Rahlfs and Fischer (7) to be 723 ± 1 K and by Nisel'son (8) to be 723±0.5 K.

Sublimation Data

The sublimation data is treated in the $ZrBr_4(g)$ table (6). The heat of sublimation is adopted as $\Delta H^\circ_{298.15}$ = 27.7 ± 0.3 kcal/mol. The sublimation temperature, Ts, is calculated as that temperature for which $\Delta Gr^\circ = 0$ for the process $ZrBr_4(c) = ZrBr_4(g)$. Since Ts is less than Tm, the liquid phase is thermodynamically unstable at a pressure of one atmosphere.

References

1. A. G. Turnbull, J. Phys. Chem. 65, 1652 (1961).
2. JANAF Thermochemical Tables: $ZrCl_4(c)$, 6-30-75.
3. U. S. Natl. Bur. Std. Tech Note 270-5, 1971.
4. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
5. J. D. H. Donnay and H. M. Ondik, "Crystal Data, Determinative Tables," 3rd edition, Vol. 2, National Bureau of Standards and Joint Committee on Powder Diffraction Standards, 1973.
6. JANAF Thermochemical Tables: $ZrCl_4(c)$ and $ZrBr_4(g)$, 6-30-75.
7. O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).
8. L. A. Nisel'son, Russ. J. Inorg. Chem. 7, 354 (1962).

ZIRCONIUM TETRABROMIDE ($ZrBr_4$) Br_4Zr

(IDEAL GAS) GFW=410.836

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-5.964	-147.025	-147.025	INFINITE
100	19.385	74.603	119.833	-4.523	-147.132	-151.683	331.503
200	23.255	89.471	101.249	-2.356	-147.833	-155.979	170.445
298	24.538	99.037	99.037	.000	-154.100	-159.155	116.664
300	24.553	99.189	99.038	.045	-154.132	-159.185	115.906
400	25.083	106.335	100.008	2.531	-168.749	-157.864	86.253
500	25.343	111.963	101.856	5.053	-168.644	-155.157	67.819
600	25.489	116.598	103.938	7.596	-168.555	-152.468	55.536
700	25.579	120.534	106.035	10.149	-168.494	-149.793	46.767
800	25.638	123.954	108.066	12.710	-168.458	-147.124	40.192
900	25.678	126.976	110.002	15.276	-168.450	-144.458	35.079
1000	25.707	129.683	111.837	17.846	-168.469	-141.790	30.988
1100	25.729	132.134	113.573	20.417	-168.519	-139.121	27.641
1200	25.746	134.374	115.214	22.991	-169.447	-136.393	24.841
1300	25.758	136.435	116.768	25.566	-169.376	-133.640	22.467
1400	25.769	138.344	118.242	28.143	-169.316	-130.894	20.433
1500	25.777	140.122	119.642	30.720	-169.271	-128.152	18.672
1600	25.784	141.786	120.975	33.298	-169.239	-125.412	17.130
1700	25.789	143.349	122.245	35.877	-169.218	-122.672	15.771
1800	25.794	144.824	123.459	38.456	-169.211	-119.937	14.562
1900	25.798	146.218	124.621	41.036	-169.216	-117.196	13.481
2000	25.801	147.542	125.734	43.616	-169.236	-114.461	12.508
2100	25.804	148.801	126.803	46.196	-169.267	-111.721	11.627
2200	25.807	150.001	127.830	48.776	-174.316	-108.804	10.809
2300	25.809	151.148	128.819	51.357	-174.369	-105.823	10.055
2400	25.811	152.247	129.772	53.938	-174.424	-102.840	9.365
2500	25.813	153.300	130.693	56.519	-174.481	-99.857	8.729
2600	25.814	154.313	131.582	59.101	-174.539	-96.870	8.143
2700	25.816	155.287	132.442	61.682	-174.600	-93.885	7.599
2800	25.817	156.226	133.275	64.264	-174.664	-90.892	7.094
2900	25.818	157.132	134.082	66.846	-174.728	-87.898	6.624
3000	25.819	158.007	134.865	69.428	-174.794	-84.905	6.185
3100	25.820	158.854	135.625	72.010	-174.864	-81.905	5.774
3200	25.821	159.674	136.364	74.592	-174.934	-78.905	5.389
3300	25.822	160.468	137.082	77.174	-175.008	-75.907	5.027
3400	25.822	161.239	137.781	79.756	-175.082	-72.903	4.686
3500	25.823	161.968	138.462	82.338	-175.160	-69.894	4.364
3600	25.823	162.715	139.126	84.920	-175.240	-66.887	4.061
3700	25.824	163.423	139.773	87.503	-175.319	-63.877	3.773
3800	25.824	164.111	140.405	90.085	-175.403	-60.862	3.500
3900	25.825	164.782	141.021	92.668	-175.488	-57.844	3.241
4000	25.825	165.436	141.623	95.250	-175.576	-54.832	2.996
4100	25.826	166.074	142.212	97.833	-175.665	-51.813	2.762
4200	25.826	166.696	142.788	100.415	-175.757	-48.789	2.539
4300	25.826	167.304	143.351	102.998	-175.850	-45.763	2.326
4400	25.827	167.897	143.902	105.581	-175.945	-42.736	2.123
4500	25.827	168.478	144.442	108.163	-176.043	-39.709	1.929
4600	25.827	169.046	144.970	110.746	-176.142	-36.677	1.743
4700	25.827	169.601	145.488	113.329	-176.243	-33.640	1.564
4800	25.828	170.145	145.996	115.911	-317.506	-29.929	1.363
4900	25.828	170.677	146.495	118.494	-317.715	-23.931	1.067
5000	25.828	171.199	146.984	121.077	-317.932	-17.933	.784
5100	25.828	171.711	147.463	123.660	-318.158	-11.937	.512
5200	25.828	172.212	147.935	126.243	-318.388	-5.929	.249
5300	25.829	172.704	148.397	128.826	-318.624	.087	-.004
5400	25.829	173.187	148.852	131.408	-318.869	6.096	-.247
5500	25.829	173.661	149.299	133.991	-319.117	12.123	-.482
5600	25.829	174.126	149.738	136.574	-319.371	18.143	-.708
5700	25.829	174.583	150.170	139.157	-319.631	24.175	-.927
5800	25.829	175.033	150.595	141.740	-319.893	30.213	-1.138
5900	25.830	175.474	151.013	144.323	-320.161	36.249	-1.343
6000	25.830	175.908	151.424	146.906	-320.434	42.283	-1.540

March 31, 1962; March 31, 1964; June 30, 1975

ZIRCONIUM TETRABROMIDE ($ZrBr_4$) (IDEAL GAS) GFW = 410.836

Point Group = T_d

$S^\circ_{298.15}$ = 99.04 ± 0.1 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -147.0 ± 2.0 kcal/mol Br_4Zr

$\Delta Hf^\circ_{298.15}$ = -154.1 ± 2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

223 (1)
60 (2)
315 (3)
72 (3)

Bond Distance: Zr-Br = 2.44 ± 0.02 Å σ = 12
Bond Angle: Br-Zr-Br = 109° 28'
Product of the Moments of Inertia: $I_AI_BI_C = 9.3458X10^{-111}\ g^3cm^6$

Heat of Formation

The heat of formation for $ZrBr_4(g)$ is calculated from the heats of formation and sublimation of $ZrBr_4(c)$ at 298.15 K. The adopted value for the heat of sublimation, ΔHs°_{298} = 27.7 ± 0.3 kcal/mol, is based on the mean of the 3rd law results from the following sublimation data.

In analyzing the vapor pressure data for the four sublimation studies (1, 2, 3, 4), corrections were made for non-ideality by means of the equation $\Delta G^\circ/T = -R\ln p - Bp/T$. The Bertholet equation of state and the critical constants Tc = 805.15 K and pc = 42.9 atm, as reported by Nisel'son and Sokolova (5), are used to calculate B.

Source	Method	No. pts	range, K	ΔHs°_{298}, kcal/mol 2nd law	3rd law	drift gibbs/mol	ΔHf°_{298}(a) kcal/mol
Rahlfs and Fischer (1)	static	15	538-633	27.85±0.24	27.78±0.09	-0.1±0.4	-153.92
Schlafer and Skoludek (2)	static	eqn	494-620	28.59	27.66	-1.7	-154.04
Berdonosova et al. (3)		17	489-606	28.87±0.12	28.03±0.12	-1.5±0.2	-153.67
Normanton and Shelton (4)	effusion	eqn	400-500	26.32	27.30	2.2	-154.40

For the heat of sublimation, we adopt the mean of the third law results and assign an uncertainty of ±0.3 kcal/mol. Combining the adopted ΔHs°_{298} value with the heat of formation of $ZrBr_4(c)$, ΔHf°_{298} = -181.7 ± 1.0 kcal/mol (6), we calculate ΔHf°_{298} = -154.0 kcal/mol for $ZrBr_4(g)$ and assign an uncertainty of ± 1.3 kcal/mol.

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark et al. (7, 8, 9), who recorded the Raman spectra of $ZrBr_4$ in *the vapor phase (380-420°C). These studies by Clark et al. (7, 8, 9) indicated that* $ZrBr_4$ *is a tetrahedral monomer* in the vapor phase. Shimanouchi, in his compilation of molecular vibrational frequencies (10), also adopted the values of Clark et al. (7, 8, 9) for $ZrBr_4(g)$. Rahlfs and Fischer (1), through vapor density measurements, had earlier concluded that $ZrBr_4$ was monomeric in the vapor phase.

Berdonosov et al. (11) referenced an electron diffraction study by Cherkasov (12) which showed that, in the vapor phase, the Zr-Br internuclear distance was 2.44±0.02 Å. We adopt this value. The individual moments of inertia are $I_A=I_B=I_C$ = $2.1064X10^{-37}$ g cm^2.

Much literature has been published on the inter-relationships between force constants and vibrational frequencies. Since the majority of these articles are based on estimated frequencies, they will not be further discussed or referenced. The same situation is true for thermodynamic tabulations of $ZrBr_4(g)$. One exception is that Clark et al. (7) calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is very similar to ours in the range 100-1000 K; the difference in entropy being less than 0.02 gibbs/mol in this range.

References

1. O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).
2. H. L. Schlafer and H. Skoludek, Z. Elektrochem. 66, 367 (1962).
3. S. S. Berdonosova, V. I. Tsirel'nikov, and A. V. Lapitskii, Vestn. Mosk. Univ. Ser. II, Khim. 20, 26 (1965).
4. A. S. Normanton and R. A. J. Shelton, Trans. Faraday Soc. 66, 33 (1970).
5. L. A. Nisel'son and T. D. Sokolova, Russ. J. Inorg. Chem. 7, 1382 (1962).
6. JANAF Thermochemical Tables: $ZrBr_4(c)$, 6-30-75.
7. R. J. H. Clark, B. K. Hunter, and D. M. Rippon, Chem. Ind. (London) 1971, 787 (1971); Inorg. Chem. 11, 56 (1971).
8. R. J. H. Clark and D. M. Rippon, J. Mol. Spectrosc. 44, 479 (1972).
9. R. J. H. Clark and D. M. Rippon, Advan. Raman Spectrosc. 1, 493 (1972).
10. T. Shimanouchi, J. Phys. Chem. Ref. Data 3, 269 (1974).
11. S. S. Berdonosov, D. H. Berdonosova, A. V. Lapitskii, and L. G. Vlasov, Russ. J. Inorg. Chem. 8, 277 (1963).
12. I. A. Cherkasov, Diploma Thesis, Moscow State University, 1961 [as referenced in (11)].

Niobium Pentabromide ($NbBr_5$)
(Crystal) GFW = 492.4264

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	35.350	61.850	61.850	.000	− 132.900	− 121.622	89.152
300	35.350	62.069	61.851	.065	− 132.928	− 121.551	88.550
400	35.350	72.238	63.237	3.600	− 150.592	− 114.095	62.338
500	35.350	80.126	65.856	7.135	− 149.878	− 105.055	45.919
600	35.350	86.571	68.787	10.670	− 149.188	− 96.156	35.025
700	35.350	92.021	71.727	14.205	− 148.520	− 87.371	27.279
800	35.350	96.741	74.565	17.740	− 147.869	− 78.680	21.494

Dec. 31, 1974

NIOBIUM PENTABROMIDE ($NbBr_5$) (CRYSTAL)

$S^\circ_{298.15}$ = [61.85±1.5] gibbs/mol
Tm = 527 ± 3 K

GFW = 492.4264
ΔHf°_0 = unknown
$\Delta Hf^\circ_{298.15}$ = −132.9 ± 3.0 kcal/mol
ΔHm° = 5.74 ± 1.5 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 26.880 kcal/mol

BR_5NB

Heat of Formation

The adopted value for the heat of formation of $NbBr_5$(c), ΔHf°_{298} = −132.9 ± 3.0 kcal/mol is based on the study of the direct bromination of Nb(c) by Gross et al. (1).

Shchukarev et al. (2) studied the hydrolysis of $NbBr_5$(c). Using the experimental results reported by Shchukarev et al. (2) and auxiliary data (4, 5), we calculate, ΔHf°_{298} = −135.5 ± 1.2 kcal/mol. Schäfer and Heine (3) also determined the heat of formation of $NbBr_5$(c) via calorimetric measurements of the heats of solution of Nb(c) and $NbBr_5$(c) in hydrofluoric acid. Using their data and auxiliary results (4, 5), we calculate ΔHf°_{298} = −131.86 ± 1.0 kcal/mol. These two solution results (2, 3) are in reasonable agreement with the adopted value. The direct bromination (1) is thought to be the more reliable.

Heat Capacity and Entropy

The heat capacity and entropy are estimated in comparison with $NbCl_5$(c) (4).

Melting Data

Refer to the $NbBr_5$(ℓ) table for details (4).

Sublimation Data

The heat of sublimation, ΔHs°_{298}, is the difference between the ΔHf°_{298} values for $NbBr_5$(g) and $NbBr_5$(c). Two sublimation studies are summarized in the $NbBr_5$(g) table (4).

As there is no low temperature heat capacity data reported in the literature, the entropy at 298.15 K is calculated from the equation $\Delta Ss^\circ_{298} = S^\circ_{298}(g) - S^\circ_{298}(c)$; $S^\circ_{298}(g)$ = 107.35 gibbs/mol as given in the $NbBr_5$(g) table (4) and ΔSs°_{298} = 45.5 gibbs/mol as suggested by comparison with $NbCl_5$ and $TaCl_5$ (4).

References

1. P. Gross, C. Hayman, D. L. Levi, and G. L. Wilson, Trans. Faraday Soc. 56, 318 (1960).
2. S. A. Shchukarev, E. K. Smirnova, I. V. Vasil'kova, and N. I. Borovkova, Russ. J. Inorg. Chem. 7, 625 (1962).
3. H. Schäfer and H. Heine, Z. Anorg. Allg. Chem. 352, 258 (1967).
4. JANAF Thermochemical Tables: $NbCl_5$(c), $TaCl_5$(c), $NbBr_5$(ℓ), and $NbBr_5$(g), 12-31-74, Nb_2O_5, 12-31-72.
5. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.

Niobium Pentabromide ($NbBr_5$) (Liquid) GFW = 492.4264

Br_5Nb

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	35.350	65.489	65.489	.000	- 130.276	- 120.083	88.023
300	35.350	65.706	65.489	.065	- 130.304	- 120.019	87.434
400	53.740	78.390	67.038	4.541	- 147.027	- 112.991	61.735
500	51.760	90.177	70.538	9.819	- 144.569	- 104.772	45.796
600	49.330	99.405	74.010	14.877	- 142.356	- 97.025	35.341
700	46.470	106.801	78.699	19.671	- 140.430	- 89.627	27.983
800	43.167	112.792	82.599	24.154	- 138.831	- 82.483	22.533
900	39.727	117.679	86.234	28.300	- 137.565	- 75.518	18.338

Dec. 31, 1974

NIOBIUM PENTABROMIDE ($NbBr_5$) (LIQUID)

$S^\circ_{298.15}$ = [65.489] gibbs/mol
Tm = 527±3 K
Tb = 634.6 K

GFW = 492.4264
$\Delta Hf^\circ_{298.15}$ = -130.276 kcal/mol
ΔHm° = 5.74±1.5 kcal/mol
ΔHv° = 18.100 kcal/mol

Br_5Nb

Heat of Formation

The heat of formation of $NbBr_5(\ell)$ is calculated from that of $NbBr_5(c)$ by adding ΔHm°, the heat of melting, and the enthalpy difference ($H^\circ_{527}-H^\circ_{298}$) between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be identical with that of $NbCl_5(\ell)$ (3) including the assumed glass transition at 350 K. The entropy at 298.15 K is calculated in a manner analogous to that used for ΔHf°_{298}.

Melting Data

The adopted melting point, Tm = 527 ± 3 K (254°C), is based on the studies by Nisel'son et al. (1) and Berdonosov et al. (2). The melting point was determined by Nisel'son et al. (1) from cooling curves, Tm = 255°C. Berdonosov et al. (2) determined the melting point by three methods: Tm = 252.0 ± 1.5°C based on an analysis of their vapor pressure data, Tm = 255 ± 2°C based on visual observation, and Tm = 254 ± 1°C based on cooling curves.

The heat of melting is chosen to be ΔHm° = 5.74 ± 1.5 kcal/mol. This value is consistent with the vaporization data and the thermodynamic functions we have adopted. The entropy of melting, ΔSm° = 10.89 gibbs/mol is somewhat lower than anticipated, based on the expected similarity with $NbCl_5$ and $TaCl_5$ as far as condensed phase dimerization is concerned (3).

Vaporization Data

Tb, the normal boiling point, is calculated as that temperature for which the Gibbs free energy approaches zero for the process $NbBr_5(\ell) = NbBr_5(g)$. ΔHv° is calculated as the difference between the ΔHf° values for $NbBr_5(g)$ and $NbBr_5(\ell)$ at Tb. Two vaporization studies are summarized in the $NbBr_5(g)$ table.

References

1. L. A. Nisel'son and J. D. Sokolova, Russ. J. Inorg. Chem. 9, 1117 (1964).
2. S. S. Berdonosov, A. V. Lapitskii, and E. K. Bakov, Russ. J. Inorg. Chem. 10, 173 (1965).
3. JANAF Thermochemical Tables: $NbCl_5$ (ℓ), 12-31-74.

Br_5Nb

Niobium Pentabromide ($NbBr_5$)
(Ideal Gas) GFW = 492.4264

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-7.033	-97.149	-97.149	INFINITE
100	22.936	77.712	132.711	-5.500	-97.476	-101.730	222.331
200	28.355	95.651	110.055	-2.881	-98.287	-105.683	115.485
298	30.068	107.348	107.348	.000	-106.020	-108.308	79.392
300	30.087	107.534	107.348	.056	-106.058	-108.321	78.911
400	30.793	116.299	108.539	3.104	-124.208	-105.335	57.552
500	31.141	123.212	110.806	6.203	-123.930	-100.650	43.994
600	31.335	128.908	113.362	9.327	-123.651	-96.021	34.976
700	31.455	133.748	115.938	12.467	-123.378	-91.439	28.548
800	31.533	137.954	118.433	15.617	-123.112	-86.894	23.738
900	31.588	141.671	120.812	18.773	-122.856	-82.382	20.005
1000	31.627	145.002	123.067	21.934	-122.609	-77.896	17.024
1100	31.656	148.017	125.201	25.098	-122.374	-73.438	14.591
1200	31.678	150.773	127.219	28.265	-122.149	-68.998	12.566
1300	31.695	153.309	129.129	31.434	-121.936	-64.576	10.856
1400	31.709	155.658	130.941	34.604	-121.733	-60.173	9.393
1500	31.720	157.846	132.663	37.775	-121.544	-55.784	8.128
1600	31.729	159.894	134.302	40.948	-121.368	-51.404	7.021
1700	31.736	161.818	135.864	44.121	-121.209	-47.035	6.047
1800	31.742	163.632	137.357	47.295	-121.367	-42.679	5.182
1900	31.748	165.348	138.785	50.469	-120.944	-38.324	4.408
2000	31.752	166.977	140.154	53.644	-120.843	-33.982	3.713
2100	31.756	168.526	141.469	56.820	-120.762	-29.641	3.085
2200	31.760	170.003	142.733	59.996	-120.706	-25.304	2.514
2300	31.763	171.415	143.949	63.172	-120.675	-20.966	1.992
2400	31.765	172.767	145.122	66.348	-120.672	-16.629	1.514
2500	31.768	174.064	146.254	69.525	-120.700	-12.295	1.075
2600	31.770	175.310	147.348	72.702	-120.764	-7.956	.669
2700	31.771	176.509	148.406	75.879	-120.875	-3.619	.293
2800	31.773	177.664	149.430	79.056	-127.348	.844	-.066
2900	31.775	178.779	150.423	82.233	-127.278	5.422	-.409
3000	31.776	179.857	151.386	85.411	-127.210	9.995	-.728
3100	31.777	180.899	152.322	88.588	-127.148	14.571	-1.027
3200	31.778	181.907	153.230	91.766	-127.085	19.141	-1.307
3300	31.779	182.885	154.114	94.944	-127.027	23.705	-1.570
3400	31.780	183.834	154.975	98.122	-126.969	28.272	-1.817
3500	31.781	184.755	155.812	101.300	-126.916	32.840	-2.051
3600	31.782	185.651	156.629	104.478	-126.865	37.402	-2.271
3700	31.782	186.521	157.425	107.656	-126.815	41.963	-2.479
3800	31.783	187.369	158.202	110.835	-126.769	46.526	-2.676
3900	31.784	188.195	158.960	114.013	-126.726	51.090	-2.863
4000	31.784	188.999	159.701	117.191	-126.685	55.641	-3.040
4100	31.785	189.784	160.426	120.370	-126.646	60.198	-3.209
4200	31.785	190.550	161.134	123.548	-126.610	64.756	-3.370
4300	31.785	191.298	161.827	126.727	-126.577	69.315	-3.523
4400	31.786	192.029	162.505	129.905	-126.546	73.872	-3.669
4500	31.786	192.743	163.169	133.084	-126.517	78.424	-3.809
4600	31.787	193.442	163.819	136.263	-126.491	82.980	-3.942
4700	31.787	194.125	164.457	139.441	-126.467	87.538	-4.071
4800	31.787	194.794	165.082	142.620	-126.448	92.082	-4.193
4900	31.788	195.450	165.695	145.799	-126.430	96.639	-4.310
5000	31.788	196.092	166.297	148.978	-126.413	101.193	-4.423
5100	31.788	196.722	166.887	152.156	-126.402	105.738	-4.531
5200	31.788	197.339	167.467	155.335	-291.360	112.344	-4.722
5300	31.789	197.944	168.036	158.514	-291.419	120.114	-4.953
5400	31.789	198.539	168.595	161.693	-291.487	127.872	-5.175
5500	31.789	199.122	169.145	164.872	-291.561	135.647	-5.390
5600	31.789	199.695	169.686	168.051	-291.644	143.408	-5.597
5700	31.789	200.257	170.217	171.230	-291.735	151.182	-5.797
5800	31.790	200.810	170.740	174.409	-291.829	158.957	-5.990
5900	31.790	201.354	171.254	177.588	-291.933	166.727	-6.176
6000	31.790	201.888	171.760	180.767	-292.044	174.491	-6.356

Dec. 31, 1974

NIOBIUM PENTABROMIDE ($NbBr_5$) (IDEAL GAS) GFW = 492.4264

Point Group D_{3h}
$S°_{298.15}$ = 107.35 ± 0.75 gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -97.15 ± 3.0 kcal/mol
$\Delta Hf°_{298.15}$ = -106.02 ± 3.0 kcal/mol

BR5NB

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
234.0 (1)	[357.6] (2)
178.0 (1)	119.0 (2)
[288.9](1)	67.0 (2)
[106.2](1)	101.0 (2)

Bond Distance : Nb-Br = 2.45 ± 0.02 Å σ = 6

Bond Angles: Br* - Nb - Br* = 120° Br* - Nb - Br** = 90° Br** -Nb - Br** = 180°
(* - equatorial ** - axial)

Product of the Moments of Inertia: $I_A I_B I_C = 1.856 \times 10^{-110}\ g^3 cm^6$

Heat of Formation

The vapor pressures over $NbBr_5$(c, ℓ) have been measured by Alexander and Fairbrother (1) and Berdonosov et al. (2). A second and third law analysis of their data is given below. The heat of formation for $NbBr_5$(g) is derived from the sublimation data of Berdonosov et al. (2). Our third law analysis of their data gives $\Delta Hs°_{298}$ = 26.88 kcal/mol which leads to the adopted value, $\Delta Hf°_{298}$ = -106.02 kcal/mol for $NbBr_5$(g). The sublimation data of Alexander and Fairbrother (1) is not acceptable as it leads to a large entropy drift, -45 ± 6 gibbs/mol.

The heat of melting is chosen as 5.74 kcal/mol so as to give reasonable entropy drifts for the vaporization data.

				$\Delta Hr°_{298}$, kcal/mol		drift
$NbBr_5(c) = NbBr_5(g)$	method	no. pts.	range, K	2nd Law	3rd Law	gibbs/mol
Alexander and Fairbrother (1)	static	4	480-517	50.82±2.94	27.77±1.57	-45±6
Berdonosov et al. (2)	static	12*	478-524	27.28±0.16	26.88±0.04	-0.8±0.3
$NbBr_5(\ell) = NbBr_5(g)$						
Alexander and Fairbrother (1)	static	26	528-635	24.07±0.13	24.26±0.06	+0.3±0.2
Berdonosov et al. (2)	static	14	529-606	24.80±0.27	24.23±0.09	-1.0±0.5

* One point rejected due to a statistical test.

Heat Capacity and Entropy

Monomeric $NbBr_5$(g) was shown by Spiridonov and Romanov (4, 5), using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Nb-Br bond lengths being equal within experimental uncertainty, Nb-Br = 2.45±0.02 Å. Skinner and Sutton (3) earlier used electron diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with their experimental results. We adopt the results of Spiridonov and Romanov (4, 5).

A normal coordinate treatment of $NbBr_5$(g) in the Urey-Bradley force fields was performed by So (7) using the reported vibrational frequencies of Beattie and Ozin (6). This work by So (7) was intended to check the correctness of the reported fundamental frequencies and predict those unobserved frequencies (ω_3, ω_4, ω_5). Beattie and Ozin (6) had recorded the gas phase Raman spectra of niobium and tantalum chloride and bromide. We adopt the results of So (7) which support the work of Beattie and Ozin (6).

References

1. K. A. Alexander and F. Fairbrother, J. Chem. Soc. (London) 1949, S223 (1949).
2. S. S. Berdonosov, A. V. Lapitskii, and E. K. Bakov, Russ. J. Inorg. Chem. 10, 173 (1965).
3. H. Skinner and L. Sutton, Trans. Faraday Soc. 36, 668 (1940).
4. V. P. Spiridonov and G. V. Romanov, Vestn. Mosk. Univ., Khim. 21, 109 (1966).
5. V. P. Spiridonov and G. V. Romanov, Vestn. Mosk. Univ., Khim. 24, 65 (1969).
6. I. R. Beattie and G. A. Ozin, J. Chem. Soc. (London) A1969, 1691 (1964).
7. S. P. So, J. Mol. Struct. 16, 311 (1973).

CALCIUM MONOHYDROXIDE (CaOH) CaHO
(IDEAL GAS) GFW=57.0874

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	.000	.000	INFINITE	-2.493	-45.410	-45.410	INFINITE
100	7.205	46.725	64.664	-1.794	-45.672	-46.674	102.006
200	9.169	52.283	57.185	-.980	-46.050	-47.529	51.937
298	10.665	56.252	56.252	.000	-46.338	-48.190	35.325
300	10.686	56.318	56.252	.020	-46.343	-48.202	35.115
400	11.505	59.516	56.682	1.133	-46.569	-48.787	26.656
500	11.965	62.137	57.519	2.309	-46.754	-49.318	21.557
600	12.254	64.346	58.478	3.521	-46.921	-49.815	18.145
700	12.463	66.251	59.455	4.757	-47.078	-50.285	15.700
800	12.638	67.927	60.412	6.012	-47.567	-50.704	13.852
900	12.797	69.425	61.331	7.284	-47.910	-51.076	12.403
1000	12.947	70.781	62.210	8.572	-48.301	-51.407	11.235
1100	13.090	72.022	63.046	9.873	-48.739	-51.697	10.271
1200	13.225	73.167	63.842	11.189	-51.006	-51.793	9.433
1300	13.353	74.231	64.601	12.518	-51.198	-51.851	8.717
1400	13.471	75.225	65.325	13.860	-51.386	-51.894	8.101
1500	13.581	76.158	66.016	15.212	-51.572	-51.923	7.565
1600	13.682	77.037	66.678	16.575	-51.756	-51.941	7.095
1700	13.774	77.870	67.312	17.948	-51.938	-51.946	6.678
1800	13.859	78.659	67.921	19.330	-89.013	-51.261	6.224
1900	13.936	79.411	68.506	20.720	-88.973	-49.165	5.655
2000	14.008	80.128	69.069	22.117	-88.933	-47.072	5.144
2100	14.074	80.813	69.612	23.521	-88.895	-44.979	4.681
2200	14.136	81.469	70.136	24.932	-88.861	-42.889	4.261
2300	14.194	82.098	70.643	26.348	-88.829	-40.800	3.877
2400	14.250	82.704	71.133	27.771	-88.805	-38.711	3.525
2500	14.303	83.287	71.607	29.198	-88.787	-36.626	3.202
2600	14.355	83.849	72.067	30.631	-88.776	-34.539	2.903
2700	14.406	84.391	72.514	32.069	-88.775	-32.453	2.627
2800	14.457	84.916	72.947	33.512	-88.785	-30.367	2.370
2900	14.508	85.424	73.369	34.961	-88.807	-28.278	2.131
3000	14.559	85.917	73.779	36.414	-88.844	-26.192	1.908
3100	14.611	86.395	74.178	37.872	-88.896	-24.102	1.699
3200	14.664	86.860	74.567	39.336	-88.966	-22.012	1.503
3300	14.718	87.312	74.947	40.805	-89.057	-19.918	1.319
3400	14.773	87.752	75.317	42.280	-89.167	-17.822	1.146
3500	14.830	88.181	75.678	43.760	-89.300	-15.721	.982
3600	14.888	88.600	76.031	45.246	-89.458	-13.616	.827
3700	14.947	89.008	76.377	46.737	-89.642	-11.507	.680
3800	15.007	89.408	76.714	48.235	-89.852	-9.391	.540
3900	15.068	89.798	77.045	49.739	-90.091	-7.273	.406
4000	15.131	90.181	77.369	51.249	-90.358	-5.146	.281
4100	15.194	90.555	77.686	52.765	-90.654	-3.012	.161
4200	15.257	90.922	77.996	54.288	-90.981	-.870	.045
4300	15.321	91.282	78.301	55.816	-91.338	1.279	-.065
4400	15.386	91.635	78.600	57.352	-91.725	3.437	-.171
4500	15.450	91.981	78.894	58.894	-92.144	5.603	-.272
4600	15.514	92.322	79.182	60.442	-92.591	7.784	-.370
4700	15.576	92.656	79.465	61.996	-93.068	9.971	-.464
4800	15.642	92.985	79.743	63.557	-93.574	12.168	-.554
4900	15.705	93.308	80.017	65.125	-94.108	14.375	-.641
5000	15.767	93.626	80.286	66.698	-94.668	16.593	-.725
5100	15.828	93.938	80.551	68.278	-95.255	18.827	-.807
5200	15.888	94.246	80.811	69.864	-95.866	21.067	-.885
5300	15.946	94.550	81.067	71.456	-96.501	23.326	-.962
5400	16.004	94.848	81.320	73.053	-97.158	25.589	-1.036
5500	16.059	95.142	81.568	74.656	-97.835	27.870	-1.107
5600	16.113	95.432	81.813	76.265	-98.532	30.159	-1.177
5700	16.166	95.718	82.055	77.879	-99.245	32.465	-1.245
5800	16.216	95.999	82.293	79.498	-99.975	34.783	-1.311
5900	16.265	96.277	82.528	81.122	-100.720	37.112	-1.375
6000	16.312	96.551	82.759	82.751	-101.477	39.455	-1.437

June 30, 1970; June 30, 1975; Dec. 31, 1975

CALCIUM MONOHYDROXIDE (CaOH) (IDEAL GAS) GFW = 57.0874

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [56.25 ± 2] gibbs/mol

ΔHf°_0 = −45.41 ± 5 kcal/mol CaHO

$\Delta Hf^\circ_{298.15}$ = −46.34 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[2]
[16050]	[2]
[16610]	[2]
[18050]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[587] (1)
[466] (2)
[3650] (1)

Bond Distance: Ca-O = [2.03] Å O-H = [0.96] Å

Bond Angle: Ca-O-H = [180]° σ = 1

Rotational Constant: B_0 = [0.31881] cm^{-1}

Heat of Formation

The adopted ΔHf°_0(CaOH,g) = −45.41±5 kcal/mol is based on an assessment of D°_0 values derived from flame spectra of CaOH, SrOH, and BaOH. Cotton and Jenkins (1) found both the monohydroxides and dihydroxides of the alkaline earths to be present in significant amounts in fuel-rich hydrogen-oxygen-nitrogen flames. They determined equilibrium constants for the reactions $M(g) + H_2O(g) = MOH(g) + H(g)$ and $M(g) + 2H_2O(g) = M(OH)_2(g) + 2H(g)$ and derived D°_0 values. In earlier work, Ryabova and Gurvich (2) had considered CaOH to be the dominant compound, and Sugden and Schofield (3) had interpreted $Ca(OH)_2$ as dominant. Cotton and Jenkins (1) have recalculated the work of these last two investigations, considering both CaOH and $Ca(OH)_2$ to be present. Ryabova et al. (4) and Kalff and Alkemade (5) have made additional measurements. The various D°_0 values are summarized below.

	D°_0, kcal/mol $CaOH(g) = Ca(g) + OH(g)$		
Reference	As Published	As Recalculated by Cotton and Jenkins(1)	As Corrected for Current JANAF Auxiliary Data(6)
Ryabova and Gurvich (2)	100±8	99	
Sugden and Schofield (3)		102	
Cotton and Jenkins (1)	104±5		105.5
Ryabova et al. (4)	94±3		97.5[a]
Kalff and Alkemade (5)	102.4		

[a] An approximate correction of +3.5 kcal/mol is made, 2 kcal/mol assumed from the Cotton and Jenkins type calculation for the presence of both CaOH and $Ca(OH)_2$ and 1.5 kcal/mol indicated by the recalculation of Cotton and Jenkins' work (1) using auxiliary data from the current JANAF Tables (6).

The data analyses for BaOH(g) and $Ba(OH)_2(g)$ indicate that flame-spectral data tend to give high dissociation energies. For $Ca(OH)_2(g)$, the lowest value of D°_0 (HO-Ca-OH) was adopted (6). Similarly, D°_0(Ca-OH) = 97.5 kcal/mol is adopted.

The ratio of the dissociation energies of the alkaline earth monohalides to those of the corresponding dihalides range from 0.40 to 0.51 with the ratio for the calcium fluorides being 0.47 (6). The similarity between the halides and hydroxides has been established (7-10). The ratio of the adopted values for the dissociation energies of CaOH(g) and $Ca(OH)_2(g)$ is 0.47 where D°_0 of the dihydroxide is defined by the reaction $Ca(OH)_2 = Ca(g) + 2(OH)(g)$ and is 205.6 kcal/mol.

ΔHf°_0(CaOH,g) = −45.41±5 kcal/mol and is calculated from the adopted dissociation energy.

Heat Capacity and Entropy

The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has been recognized (7-10). The molecular configuration is assumed to be linear in accordance with the prediction of Walsh (11) and the evidence that gaseous alkali metal hydroxides are linear (12-14). The ground state is assumed to be $^2\Sigma^+$ by analogy with CaF and CaCl(6). The electronic levels are estimated from the band spectra observed by James and Sugden (15), Gaydon (16), Zhitkevich et al. (17) and Van der Hurk et al. (18), and the comparison with CaF and CaCl(6).

The Ca-O bond distance is estimated to be slightly larger, 0.02 Å, than the Ca-F distance (6) after noting the close *similarity in bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is that in water (6). The* moment of inertia is 8.7799×10^{-39} g cm^2.

The Ca-O stretching frequency, 587 cm^{-1}, is estimated to be the same as the CaF stretching frequency (6, 10). The O-H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 466 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz (10, 14).

The entropy in the present table is lower by 0.20 gibb/mol at 298K and 0.25 gibb/mol at 1000K than that proposed by Jackson (10); the data relevant to the calculations are nearly the same.

References

1. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 64, 2988 (1968).
2. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 3, 318 (1965).
3. T. M. Sugden and K. Schofield, Trans. Faraday Soc. 62, 566 (1966).
4. V. G. Ryabova, A. N. Khitrov, and L. V. Gurvich, Teplofiz. Vys. Temp. 10, 744 (1972).
5. P. J. Kalff and C. Th. J. Alkemade, J. Chem. Phys. 59, 2572 (1973).
6. JANAF Thermochemical Tables: Ca(g), 12-31-68; $H_2O(g)$, 3-31-61; H(g), 6-30-74; CaCl(g), 6-30-70; CaF(g), 12-31-68; BaOH(g), $Ba(OH)_2(g)$, $Ca(OH)_2(g)$, 12-31-75.
7. R. C. Schoonmaker, and R. F. Porter, J. Chem. Phys. 31, 830(1959).
8. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
9. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
10. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Contract No. W-7405-Eng-48, Dec. 8, 1971.
11. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
12. N. Acquista, S. Abramowitz, and R. Lide, J. Chem. Phys. 49, 780(1968).
13. R. L. Kuczkowski and R. Lide, J. Chem. Phys. 44, 3131 (1966).
14. N. Acquista and S. Abramowitz, U.S. Natl. Bur. Std. Report 9905, July, 1968.
15. C. G. James and T. M. Sugden, Nature 175, 333 (1955).
16. A. G. Gaydon, Proc. Roy. Soc. (London) A231, 437 (1955).
17. V. F. Zhitkevich, A. I. Lyutyi, N. A. Nesterko, V. S. Rossikhin, and I. L. Tsikora, Optika i Spektroskopiya 14, 35 (1963).
18. J. Van der Hurk, Tj. Hollander, and C. Th. J. Alkemade, J. Quant. Spectrosc. Radiat. Transfer 13, 273 (1973).

CaHO

CALCIUM MONOHYDROXIDE UNIPOSITIVE ION (CAOH$^+$) CAHO$^+$

(IDEAL GAS) GFW=57.0869

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	10.707	54.922	54.922	.000	88.213	85.270	-62.504
300	10.727	54.988	54.922	.020	88.217	85.251	-62.105
400	11.535	58.197	55.354	1.137	88.492	84.222	-46.017
500	11.986	60.823	56.193	2.315	88.806	83.120	-36.332
600	12.269	63.035	57.154	3.529	89.138	81.952	-29.851
700	12.476	64.943	58.134	4.767	89.479	80.727	-25.204
800	12.648	66.620	59.092	6.023	89.487	79.483	-21.714
900	12.805	68.119	60.013	7.296	89.642	78.223	-18.995
1000	12.953	69.476	60.892	8.584	89.749	76.948	-16.817
1100	13.095	70.717	61.730	9.886	89.808	75.664	-15.033
1200	13.230	71.863	62.527	11.202	88.038	74.529	-13.574
1300	13.356	72.927	63.287	12.532	88.344	73.391	-12.338
1400	13.474	73.921	64.011	13.873	88.653	72.229	-11.276
1500	13.583	74.854	64.703	15.226	88.965	71.046	-10.351
1600	13.684	75.734	65.365	16.590	89.277	69.840	-9.540
1700	13.775	76.566	66.000	17.963	89.592	68.616	-8.821
1800	13.859	77.356	66.609	19.345	53.014	68.054	-8.263
1900	13.935	78.108	67.195	20.734	53.551	68.875	-7.922
2000	14.004	78.824	67.758	22.131	54.088	69.667	-7.613
2100	14.068	79.509	68.302	23.535	54.621	70.433	-7.330
2200	14.125	80.165	68.826	24.945	55.151	71.174	-7.070
2300	14.177	80.794	69.333	26.360	55.678	71.890	-6.831
2400	14.225	81.398	69.823	27.780	56.198	72.585	-6.610
2500	14.268	81.980	70.298	29.205	56.710	73.256	-6.404
2600	14.308	82.540	70.758	30.633	57.213	73.908	-6.213
2700	14.344	83.081	71.204	32.066	57.705	74.540	-6.034
2800	14.378	83.603	71.638	33.502	58.185	75.155	-5.866
2900	14.408	84.108	72.059	34.942	58.651	75.755	-5.709
3000	14.437	84.597	72.469	36.384	59.100	76.337	-5.561
3100	14.463	85.071	72.868	37.829	59.531	76.903	-5.422
3200	14.487	85.531	73.257	39.276	59.941	77.457	-5.290
3300	14.509	85.977	73.635	40.726	60.328	77.998	-5.166
3400	14.529	86.410	74.005	42.178	60.692	78.528	-5.048
3500	14.548	86.832	74.365	43.632	61.030	79.048	-4.936
3600	14.566	87.242	74.717	45.088	61.338	79.558	-4.830
3700	14.582	87.641	75.061	46.545	61.617	80.061	-4.729
3800	14.598	88.030	75.397	48.004	61.865	80.557	-4.633
3900	14.612	88.409	75.726	49.464	62.080	81.044	-4.542
4000	14.625	88.779	76.048	50.926	62.261	81.527	-4.454
4100	14.638	89.141	76.363	52.389	62.408	82.008	-4.371
4200	14.649	89.494	76.671	53.854	62.521	82.485	-4.292
4300	14.660	89.838	76.973	55.319	62.597	82.960	-4.216
4400	14.670	90.176	77.270	56.786	62.638	83.432	-4.144
4500	14.680	90.505	77.560	58.253	62.641	83.902	-4.075
4600	14.689	90.828	77.845	59.722	62.612	84.379	-4.009
4700	14.698	91.144	78.125	61.191	62.546	84.853	-3.946
4800	14.706	91.454	78.399	62.661	62.446	85.328	-3.885
4900	14.713	91.757	78.669	64.132	62.313	85.805	-3.827
5000	14.720	92.054	78.933	65.604	62.147	86.284	-3.771
5100	14.727	92.346	79.194	67.076	61.949	86.772	-3.718
5200	14.733	92.632	79.449	68.549	61.722	87.258	-3.607
5300	14.740	92.913	79.701	70.023	61.466	87.756	-3.619
5400	14.745	93.188	79.948	71.497	61.183	88.250	-3.572
5500	14.751	93.459	80.191	72.972	60.874	88.755	-3.527
5600	14.756	93.725	80.430	74.447	60.541	89.263	-3.484
5700	14.761	93.986	80.666	75.923	60.186	89.780	-3.442
5800	14.766	94.243	80.898	77.400	59.810	90.304	-3.403
5900	14.770	94.495	81.126	78.876	59.416	90.833	-3.365
6000	14.774	94.743	81.351	80.354	59.002	91.368	-3.328

June 30, 1970; Dec. 31, 1975

CALCIUM MONOHYDROXIDE UNIPOSITIVE ION (CaOH$^+$) (IDEAL GAS) GFW = 57.0869

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [54.92 ± 2.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = 87.65 ± 15 kcal/mol CAHO$^+$

$\Delta Hf^\circ_{298.15}$ = 88.21 ± 15 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[580](1)
[460](2)
[3650](1)

Bond Distances: Ca-O = [2.03] Å O-H = [0.96] Å
Bond Angle: Ca-O-H = [180°] σ = 1
Rotational Constant: B_o = [0.3188] cm^{-1}

Heat of Formation

The ionization potential of CaOH(g) was deduced by Kelly and Padley (1) to be 5.9±0.1 ev. These authors quantitatively examined the total positive ion concentrations produced from Ca aqueous salt additives in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data (2), we recalculate the ionization potential to be 5.79 ev.

Jensen (3) determined the heat of reaction ΔHr°_0 = 35±10 *kcal/mol for* $Ca(g) + OH(g) = CaOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for CaOH$^+$; the value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data (2), we derive an ionization potential of 5.75 ev, which is in good agreement with the value derived from the data of Kelly and Padley (1).

We adopt an ionization potential of 5.77 ev (133.06 kcal/mol) which is average of the above two studies (1,3). This leads to ΔHf°_0 = 87.65 kcal/mol and ΔHf°_{298} = 88.21 kcal/mol for CaOH$^+$(g). We assign an uncertainty of ±15 kcal/mol.

For comparison, the appearance potential of CaF(g) has been reported as 5.8±0.3 ev (4), 5.5±0.3 ev (4) and 6.0±0.5 ev (5). These values are all very similar to the ionization potential adopted here for CaOH(g). In addition, the ionization potential for Ca(g) is 6.11 ev (2).

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear (2,6,7,8). In addition, Walsh (9) had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons (CaOH$^+$ has eight valence electrons) will be linear in their ground state. The molecule CaOH$^+$ is isoelectronic with KOH.

The bond dissociation energy for CaOH$^+$ (D°_0 = 105.4 kcal/mol, 2) for the process $CaOH^+(g) = Ca^+(g) + OH(g)$ is fairly close to that for CaOH (D°_0 = 97.5 kcal/mol, 2). This suggests a similar bonding in these two molecules. Thus, bond distances are assumed to be the same as those adopted for CaOH(g,2). The moment of inertia is 6.779×10^{-39} g cm^2. The vibrational frequencies are assumed to be similar to those adopted for CaOH(g,2). The ground state quantum weight is assumed to be the same as that of KOH(g,2). The enthalpy change between 0 and 298.15 K is -2.501 kcal/mol.

References

1. R. Kelly and P. J. Padley, Trans. Faraday Soc. 67, 1384 (1971).
2. JANAF Thermochemical Tables: e^-, 3-31-65; H_2(g) and H_2O(g), 3-31-61; Ca(g), 12-31-68; OH(g) and Ca^+(g), 12-31-70; H(g), 6-30-74; CaOH(g) and $Ca(OH)_2$(g), 12-31-75.
3. D. E. Jensen, Combustion and Flame 12, 261 (1968).
4. G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, J. Phys. Chem. 67, 877 (1963).
5. D. L. Hildenbrand and E. Murad, J. Chem. Phys. 43, 1400 (1965).
6. N. Acquista, S. Abramowitz, and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
7. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. 44 3131 (1966).
8. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9905, July, 1968.
9. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

CALCIUM DIHYDROXIDE ($Ca(OH)_2$) CaH_2O_2

(CRYSTAL) GFW=74.0948

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 3.384	− 233.594	− 233.594	INFINITE
100	7.777	4.117	35.160	− 3.104	− 235.001	− 228.454	499.285
200	16.390	12.472	21.716	− 1.849	− 235.587	− 221.630	242.180
298	20.910	19.930	19.930	.000	− 235.680	− 214.746	157.413
300	20.980	20.060	19.930	.039	− 235.679	− 214.617	156.348
400	23.520	26.487	20.789	2.279	− 235.481	− 207.620	113.438
500	24.840	31.891	22.484	4.703	− 235.133	− 200.692	87.722
600	25.680	36.495	24.445	7.230	− 234.712	− 193.842	70.607
700	26.460	40.513	26.460	9.837	− 234.238	− 187.067	58.405
800	27.130	44.092	28.444	12.518	− 234.054	− 180.335	49.265
900	27.730	47.323	30.365	15.262	− 233.688	− 173.642	42.166
1000	28.200	50.270	32.210	18.059	− 233.341	− 166.988	36.495

Dec. 31, 1971; Dec. 31, 1975

CALCIUM DIHYDROXIDE ($Ca(OH)_2$) (CRYSTAL) GFW = 74.0948

ΔHf_0° = -233.59 ± 0.3 kcal/mol CaH_2O_2

$S^\circ_{298.15}$ = 19.93 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -235.68 ± 0.3 kcal/mol

Td = 794.8 K

Heat of Formation

Taylor and Wells (1) measured heats of solution of $Ca(OH)_2(c)$ and CaO(c) in dilute HCl and obtained ΔHr°_{298} = -15.58±0.1 kcal/mol for CaO(c) + $H_2O(\ell)$ = $Ca(OH)_2(c)$ which leads to $\Delta Hf^\circ_{298}(Ca(OH)_2, c)$ = -235.68±0.3 kcal/mol using ΔHf°_{298}(CaO, c) = -151.79±0.21 kcal/mol (2) and $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 kcal/mol (3). This value, -235.68±0.3 kcal/mol, is adopted in the tabulation. They also measured directly the heat of hydration of CaO to $Ca(OH)_2$ and found ΔHr°_{298} = -15.43±0.1 kcal/mol which leads to $\Delta Hf^\circ_{298}(Ca(OH)_2, c)$ = -235.53 kcal/mol. Both measurements are in very good agreement. Literature ΔHr° data (4, 5, 6, 7, 8) determined by these two methods were within the limit of -15.4±0.3 kcal/mol which is in good agreement with the value adopted.

JANAF analyses of dissociation pressure data (9, 10, 11) for $Ca(OH)_2(c)$ → CaO(c) + $H_2O(g)$ are listed below. The data of *Halstead and Moore (9) and of Tamaru and Shiomi (10) are in good agreement*, but the pressures reported by Johnston (11) are too low due to failure to reach equilibrium. The heat of formation derived from third law ΔHr of Halstead and Moore (9) or Tamaru and Shiomi (10) is in good agreement with the value adopted. However, the decomposition of $Ca(OH)_2$ may yield non-standard state CaO in the final product which was shown in a similar decomposition of $Mg(OH)_2$. See $Mg(OH)_2$ table (2) for details.

$Ca(OH)_2(c)$ = CaO(c) + $H_2O(g)$

Investigator	Method	Temp (K)	No. of Points	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	$\Delta Hf^\circ_{298}(Ca(OH)_2, c)$* (kcal/mol)
Halstead and Moore (9)	Static	635-776.5	14	25.52	25.75±0.15	0.2±0.4	-235.34
Tamaru and Shiomi (10)	Static	694-776.5	8	26.48	25.90±0.07	-0.8±0.3	-235.49
Johnston (11)	Static	663-804	7	26.92	26.76±0.24	-0.5±1.0	-236.35

*3rd law ΔHr° is used in the calculation.

Heat Capacity and Entropy

The low temperature heat capacities up to 300 K are taken from the adiabatic calorimeter measurements (19-330 K) of Hatton et al. (12). Above 300 K, the heat capacities are based on the heat conduction calorimeter measurements (310-670 K) of Kobayashi (13) joined smoothly at 300°K with the low temperature heat capacities (12) and on a graphical comparison of *the Cp vs. T curve adopted for $Mg(OH)_2(c)$ (2).* The entropy, S°_{298} = 19.93±0.1 gibbs/mol, is derived from the adopted low temperature heat capacities, based on a T^3 extrapolation to obtain S° = 0.070 gibbs/mol at 20 K (12).

Decomposition Data

Td = 794.8 K is calculated as the temperature at which ΔGr° = 0 for the reaction $Ca(OH)_2$ (c) = CaO(c) + $H_2O(g)$. Auxiliary data are from the JANAF Tables (2).

Under a pressure of 1000 bars, Wyllie and Tuttle (14) found that $Ca(OH)_2$ melts congruently at 1108 K.

References

1. K. Taylor and L. S. Wells, J. Res. Natl. Bur. Std. 21, 133 (1938).
2. JANAF Thermochemical Tables: CaO(c), 6-30-73; $Mg(OH)_2(c)$, 12-31-75; $H_2O(g)$, 3-31-61.
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. J. Thomsen, Thermochemische Untersuchungen 3, 247 (1883).
5. M. Bertheolot, Ann. Chim. Phys. 4, 531 (1875).
6. W. A. Roth and P. Chall, Z. Elektrochem. 34, 185 (1928).
7. T. Thorvaldson, W. G. Brown and C. R. Peaker, J. Amer. Chem. Soc. 51, 2687 (1929); 52, 80 (1930); 52, 910 (1930).
8. H. E. Schwietz and E. Hey, Z. Anorg. Chem. 217, 396 (1934).
9. P. E. Halstead and A. E. Moore, J. Chem. Soc., 1957, 3873 (1957).
10. S. Tamuru and K. Shiomi, Z. Phys. Chem. 161, 421 (1932).
11. J. Johnston, Z. physik. Chem. 62, 330 (1908).
12. W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull, J. Amer. Chem. Soc. 81, 5028 (1959).
13. K. Kobayashi, Science Repts. Tohoku Univ., First Ser. 34, 153 (1950); Chem. Abst. 46, 332 (1952).
14. P. J. Wyllie and O. F. Tuttle, J. Petrol. 1, 1(1960).

CaH_2O_2

CALCIUM DIHYDROXIDE ($Ca(OH)_2$) CaH_2O_2

(IDEAL GAS) GFW=74.0948

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.654	-144.160	-144.160	INFINITE
100	9.803	53.596	81.609	-2.801	-144.994	-143.394	313.388
200	14.478	61.815	69.755	-1.588	-145.622	-141.534	154.661
298	17.555	66.234	68.234	.000	-145.976	-139.444	102.215
300	17.595	68.343	68.235	.033	-145.981	-139.404	101.556
400	19.199	73.649	68.947	1.881	-146.175	-137.179	74.951
500	20.079	78.037	70.339	3.849	-146.283	-134.915	58.971
600	20.627	81.749	71.940	5.886	-146.352	-132.635	48.312
700	21.026	84.960	73.575	7.969	-146.402	-130.344	40.695
800	21.360	87.790	75.179	10.089	-146.779	-128.019	34.973
900	21.667	90.324	76.723	12.240	-147.006	-125.660	30.514
1000	21.959	92.622	78.200	14.422	-147.274	-123.274	26.941
1100	22.238	94.728	79.608	16.632	-147.587	-120.860	24.013
1200	22.504	96.674	80.950	18.869	-149.724	-118.262	21.538
1300	22.755	98.485	82.230	21.132	-149.782	-115.638	19.441
1400	22.988	100.180	83.452	23.419	-149.833	-113.010	17.642
1500	23.205	101.774	84.621	25.729	-149.880	-110.377	16.082
1600	23.404	103.278	85.741	28.059	-149.925	-107.744	14.717
1700	23.586	104.702	86.815	30.409	-149.964	-105.104	13.512
1800	23.752	106.055	87.846	32.776	-186.897	-101.784	12.358
1900	23.904	107.344	88.839	35.159	-186.714	-97.060	11.164
2000	24.042	108.573	89.795	37.556	-186.532	-92.348	10.091
2100	24.167	109.749	90.717	39.967	-186.352	-87.642	9.121
2200	24.281	110.876	91.608	42.389	-186.178	-82.946	8.240
2300	24.385	111.958	92.470	44.823	-186.007	-78.258	7.436
2400	24.480	112.998	93.303	47.266	-185.846	-73.574	6.700
2500	24.567	113.999	94.111	49.719	-185.694	-68.903	6.024
2600	24.646	114.964	94.895	52.179	-185.552	-64.232	5.399
2700	24.718	115.895	95.656	54.648	-185.423	-59.569	4.822
2800	24.785	116.796	96.395	57.123	-185.309	-54.911	4.286
2900	24.846	117.666	97.113	59.604	-185.211	-50.251	3.787
3000	24.902	118.510	97.812	62.092	-185.132	-45.601	3.322
3100	24.954	119.327	98.493	64.585	-185.072	-40.951	2.887
3200	25.002	120.120	99.157	67.082	-185.037	-36.303	2.479
3300	25.046	120.890	99.804	69.585	-185.026	-31.656	2.096
3400	25.087	121.638	100.435	72.091	-185.042	-27.010	1.736
3500	25.124	122.366	101.051	74.602	-185.066	-22.360	1.396
3600	25.160	123.075	101.653	77.116	-185.161	-17.709	1.075
3700	25.192	123.764	102.242	79.634	-185.269	-13.055	.771
3800	25.223	124.437	102.817	82.155	-185.409	-8.397	.483
3900	25.251	125.092	103.380	84.678	-185.587	-3.740	.210
4000	25.278	125.732	103.930	87.205	-185.799	.925	-.051
4100	25.302	126.356	104.470	89.734	-186.048	5.597	-.298
4200	25.326	126.966	104.998	92.265	-186.335	10.275	-.535
4300	25.347	127.562	105.516	94.799	-186.660	14.960	-.760
4400	25.368	128.145	106.024	97.335	-187.022	19.651	-.976
4500	25.387	128.716	106.522	99.872	-187.425	24.351	-1.183
4600	25.405	129.274	107.010	102.412	-187.862	29.068	-1.381
4700	25.422	129.820	107.490	104.953	-188.339	33.789	-1.571
4800	25.438	130.356	107.961	107.496	-188.851	38.520	-1.754
4900	25.453	130.880	108.423	110.041	-189.398	43.259	-1.929
5000	25.467	131.395	108.877	112.587	-189.980	48.010	-2.099
5100	25.481	131.899	109.324	115.134	-190.597	52.782	-2.262
5200	25.494	132.394	109.763	117.683	-191.244	57.555	-2.419
5300	25.506	132.880	110.194	120.233	-191.922	62.354	-2.571
5400	25.517	133.357	110.619	122.784	-192.630	67.150	-2.718
5500	25.528	133.825	111.037	125.337	-193.363	71.971	-2.860
5600	25.539	134.285	111.448	127.890	-194.125	76.798	-2.997
5700	25.548	134.737	111.852	130.444	-194.909	81.644	-3.130
5800	25.558	135.182	112.251	133.000	-195.716	86.505	-3.260
5900	25.567	135.619	112.643	135.556	-196.544	91.377	-3.385
6000	25.575	136.048	113.030	138.113	-197.391	96.264	-3.506

Dec. 31, 1975

CALCIUM DIHYDROXIDE ($Ca(OH)_2$) (IDEAL GAS) GFW = 74.0948

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [68.2 ± 2.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -144.16 ± 9.0 kcal/mol CaH_2O_2
$\Delta Hf^\circ_{298.15}$ = -145.98 ± 9.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[484](1)
[163](1)
[554](1)
[3650](2)
[466](4)

Bond Distances: Ca-O = [2.12] Å O-H = [0.96] Å
Bond Angles: O-Ca-O = [135°] Ca-O-H = [180°] σ = 2
Product of the Moments of Inertia: $I_AI_BI_C$ = [1261.5621] x 10^{-117} g^3cm^6

Heat of Formation

Dissociation energies, D°_0, for the reaction $Ca(OH)_2(g) = Ca(g) + 2OH(g)$ have been derived from flame-spectral measurements (1-3). Ryabova and Gurvich (1) believed the dominant reaction to be $Ca(g) + H_2O(g) = CaOH(g) + H(g)$, but they also considered the possibility that $Ca(g) + 2H_2O(g) = Ca(OH)_2(g) + 2H(g)$ was the dominant reaction and derived D°_0 = 200±20 kcal/mol. Sugden and Schofield (2) considered the dihydroxide to be the dominant product and derived D°_0 = 217±12 kcal/mol. Cotton and Jenkins (3) found both CaOH and $Ca(OH)_2$ to be present in significant amounts in fuel-rich hydrogen-oxygen-nitrogen flames and derived D°_0 = 203.8±5 kcal/mol. Cotton and Jenkins (3) recalculated the work of Ryabova and Gurvich (1) and of Sugden and Schofield (2) considering both CaOH and $Ca(OH)_2$ to be present and obtained the recalculated D°_0 values of 199 and 201 kcal/mol, respectively.

A third law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins (3) using current JANAF auxiliary data (4) leads to D°_0 = 210.4 kcal/mol which is 6.6 kcal/mol higher than the 203.8 kcal/mol derived by Cotton and Jenkins (3). Applying this difference to the data of Ryabova and Gurvich (1) and Sugden and Schofield (2) as recalculated by Cotton and Jenkins (3) gives D°_0 = 205.6 and 207.6 kcal/mol, respectively.

For $Ba(OH)_2(g)$ (4), the corrected dissociation energy of Ryabova and Gurvich (4), D°_0 = 208.8 kcal/mol, is in better agreement with the "adopted" value of 209.6 kcal/mol, based on good Knudsen-cell mass-spectrometric measurements, than are the corrected dissociation energies of Sugden and Schofield or Cotton and Jenkins (4). We adopt D°_0 = 205.6 kcal/mol for the dissociation of $Ca(OH)_2$ from which is calculated ΔHf°_0 = -144.16±9.0 kcal/mol.

The heat of dissociation listed by Jackson (8) leads to $\Delta Hf^\circ_{298}(Ca(OH)_2,g)$ = -142.65 kcal/mol. Another recent compilation (9) lists ΔHf°_{298} = -130 kcal/mol.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized (5-8). The O-Ca-O bond angle is assumed to be the same as the F-Ca-F bond angle (4); the Ca-O-H bond angle is considered to be linear as in CaOH (4). The Ca-O bond distance is estimated to be slightly larger, 0.02Å, than the Ca-F bond distance in CaF_2 (4) after noting the close similarity in the bond distance of alkali metal fluorides and hydroxides. The O-H bond distance is taken to be the same as in water (4).

The vibrational frequencies are estimated to be the same as in CaF_2 (4) (O-Ca-O symmetrical and asymmetrical stretch, and bend) and as in CaOH (4) (O-H stretch and Ca-O-H bend). The three principal moments of inertia are I_A=25.2623 x 10^{-39}, I_B=23.1017 x 10^{-39}, and I_C=2.1616 x 10^{-39} g cm^2.

Jackson (8) has used a different molecular configuration and different vibrational frequencies to estimate S°_{298} = 68.530 gibbs/mol. We assign an uncertainty of ±2.0 to the adopted entropy.

References

1. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 3, 318 (1965).
2. T. M. Sugden and K. Schofield, Trans. Faraday Soc. 62, 566 (1966),
3. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 64, 2988 (1968).
4. JANAF Thermochemical Tables: Ca(g), CaF_2(g), 12-31-68; HO(g), 12-31-70; H_2O(g), 3-31-61; H(g), 6-30-74; CaOH(g), $Ca(OH)_2$(g), $Ba(OH)_2$(g), 12-31-75.
5. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
6. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
7. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
8. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Contract No. W-7405-Eng-48, Dec. 8, 1971.
9. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.

Calcium Oxide (CaO) CaO

(Ideal Gas) GFW = 56.0794

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 2.140	10.769	10.769	INFINITE
100	6.964	44.603	59.049	− 1.445	10.883	8.874	− 19.393
200	7.261	49.494	53.180	− .737	10.700	6.927	− 7.569
298	7.757	52.487	52.487	.000	10.500	5.118	− 3.751
300	7.765	52.535	52.487	.014	10.496	5.084	− 3.703
400	8.147	54.824	52.796	.811	10.300	3.310	− 1.808
500	8.398	56.671	53.393	1.639	10.117	1.584	− .692
600	8.564	58.219	54.071	2.488	9.937	− .105	.038
700	8.679	59.548	54.761	3.351	9.758	− 1.765	.551
800	8.763	60.712	55.434	4.223	9.236	− 3.370	.921
900	8.830	61.748	56.079	5.103	8.859	− 4.923	1.196
1000	8.895	62.682	56.693	5.989	8.426	− 6.432	1.406
1100	8.970	63.533	57.277	6.882	7.942	− 7.895	1.569
1200	9.069	64.318	57.831	7.784	5.628	− 9.159	1.668
1300	9.206	65.049	58.359	8.697	5.393	− 10.382	1.745
1400	9.391	65.737	58.861	9.626	5.170	− 11.587	1.809
1500	9.631	66.393	59.342	10.577	4.965	− 12.777	1.862
1600	9.951	67.024	59.802	11.555	4.784	− 13.953	1.906
1700	10.258	67.637	60.245	12.565	4.634	− 15.119	1.944
1800	10.697	68.236	60.673	13.614	− 32.376	− 15.597	1.894
1900	11.147	68.826	61.086	14.706	− 32.231	− 14.669	1.687
2000	11.626	69.410	61.488	15.844	− 32.042	− 13.750	1.503
2100	12.118	69.989	61.879	17.031	− 31.810	− 12.840	1.336
2200	12.589	70.564	62.261	18.266	− 31.533	− 11.943	1.186
2300	13.094	71.135	62.634	19.553	− 31.214	− 11.060	1.051
2400	13.528	71.702	63.000	20.884	− 30.857	− 10.191	.928
2500	13.932	72.262	63.359	22.257	− 30.466	− 9.338	.816
2600	14.287	72.816	63.712	23.668	− 30.047	− 8.501	.715
2700	14.538	73.361	64.060	25.113	− 29.606	− 7.681	.622
2800	14.832	73.896	64.401	26.584	− 29.151	− 6.877	.537
2900	15.020	74.420	64.738	28.077	− 28.689	− 6.088	.459
3000	15.154	74.931	65.069	29.586	− 28.229	− 5.317	.387
3100	15.238	75.430	65.395	31.106	− 27.775	− 4.561	.322
3200	15.277	75.914	65.717	32.632	− 27.336	− 3.819	.261
3300	15.276	76.384	66.033	34.160	− 26.918	− 3.092	.205
3400	15.243	76.840	66.344	35.686	− 26.526	− 2.376	.153
3500	15.181	77.281	66.650	37.208	− 26.163	− 1.671	.104
3600	15.098	77.708	66.951	38.722	− 25.836	− .975	.059
3700	14.998	78.120	67.248	40.227	− 25.547	− .288	.017
3800	14.886	78.518	67.539	41.721	− 25.299	.391	− .023
3900	14.765	78.904	67.826	43.204	− 25.096	1.063	− .060
4000	14.639	79.275	68.107	44.674	− 24.937	1.731	− .095
4100	14.511	79.636	68.384	46.131	− 24.824	2.397	− .128
4200	14.382	79.984	68.656	47.576	− 24.757	3.060	− .159
4300	14.255	80.321	68.923	49.008	− 24.740	3.723	− .189
4400	14.131	80.647	69.186	50.427	− 24.768	4.385	− .218
4500	14.011	80.963	69.444	51.834	− 24.844	5.048	− .245
4600	13.896	81.270	69.698	53.230	− 24.965	5.715	− .272
4700	13.786	81.568	69.948	54.614	− 25.132	6.383	− .297
4800	13.682	81.857	70.193	55.987	− 25.343	7.056	− .321
4900	13.584	82.138	70.434	57.350	− 25.597	7.731	− .345
5000	13.491	82.411	70.670	58.704	− 25.891	8.415	− .368
5100	13.403	82.678	70.903	60.049	− 26.224	9.106	− .390
5200	13.322	82.937	71.132	61.385	− 26.595	9.800	− .412
5300	13.245	83.190	71.357	62.713	− 27.001	10.506	− .433
5400	13.174	83.437	71.579	64.034	− 27.441	11.215	− .454
5500	13.107	83.676	71.797	65.348	− 27.912	11.937	− .474
5600	13.045	83.914	72.011	66.656	− 28.412	12.664	− .494
5700	12.987	84.144	72.222	67.957	− 28.938	13.403	− .514
5800	12.933	84.369	72.429	69.253	− 29.491	14.152	− .533
5900	12.882	84.590	72.633	70.544	− 30.066	14.909	− .552
6000	12.835	84.806	72.835	71.830	− 30.663	15.677	− .571

Dec. 31, 1974

CALCIUM OXIDE (CaO) (IDEAL GAS) GFW = 56.0794

Symmetry Number = 1

$S^\circ_{298.15}$ = 52.486 ± 0.1 gibbs/mol

ΔHf°_0 = 10.77 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 10.5 ± 5 kcal/mol

CaO

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}
(1-3)	X $^1\Sigma^+$	0.0	1	1.822	0.44452	0.00338	733.4	5.28
(1)	a $^3\Pi$	8225.	6	2.097	0.3353	0.0015	556.2	3.30
(1)	A' $^1\Pi$	8612.	2	2.092	0.3372	0.0021	545.7	2.54
(1, 4, 5)	$^3\Sigma^+$	[10000]	3	[1.906]	[0.4059]	[0.0014]	[719]	[2.1]
(1-3)	A $^1\Sigma^+$	11549.	1	1.906	0.40592	0.00137	718.9	2.11
(5)	$^3\Sigma^+$	[21000]	3	[2.00]	[0.369]	[0.003]	[560]	[4.]
(5)	$^3\Delta$	[21000]	6	[2.00]	[0.369]	[0.003]	[560]	[4.]
(5)	$^1\Delta$	[23000]	2	[2.00]	[0.369]	[0.003]	[560]	[4.]
(5)	$^3\Sigma^-$	[23000]	3	[2.00]	[0.369]	[0.003]	[560]	[4.]
(5)	$^1\Sigma^-$	[23000]	1	[2.00]	[0.369]	[0.003]	[560]	[4.]
(6)	C $^1\Sigma^+$	28772.	1	1.989	0.3731	0.0032	560.9	4.0
(5)	$^3\Pi$	[24000]	6	[1.95]	[0.3882]	[0.0055]	[581]	[3.3]
(7)	B $^1\Pi$	25913.	2	1.950	0.3882	0.0055	581.0	[3.3]

Heat of Formation

We adopt D°_0 = 91 ± 5 and ΔHf°_{298} = 10.5 ± 5 kcal/mol based on mass-spectrometric data (8, 9) for four reactions analyzed below. We give "<" or ">" for ΔH° and D°_0 values which may be biased due to our auxiliary data. JANAF differences in ΔHf°_{298} for WO_3-WO_2 and MoO_3-MoO_2 (5) may be biased by up to -3.5 and +4.1 kcal/mol, respectively, leading to bias of the opposite sign in D°_0 values derived from reactions B and C. Adjustments for this possible bias would improve the agreement in D°_0 but leave the mean value almost unchanged. Kalff (10) used spectrometry of CO-N_2O flames to derive D°_0 = 86.5 ± 4.6 kcal/mol. This value becomes ∿89.5 kcal/mol when adjusted to be consistent with JANAF free energy functions. Our adopted D°_0 = 91 ± 5 is similar to that of Rosen (6) and is comparable with other selected values (8, 11), considering the difference in functions for CaO.

The controversy over D°_0 of alkaline earth oxides has been reviewed in detail (8, 11-13). Uncertainty in the electronic partition function of CaO due to triplet states now is much reduced (1). Schofield's criticism (12) of flame studies is supported by new evidence for importance of hydroxides (10, 14, 15); thus, we dismiss higher flame values for D°_0 (12). Valid criticism (8) also causes us to dismiss higher D°_0 values derived from vaporization data. A linear Birge-Sponer extrapolation yields a very low estimate for D°_0, just as it does for the alkali halides (13), unless $X^1\Sigma$ fails to dissociate to an excited state atom as predicted (17, 1).

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	3rd Law	ΔHf°_{298} kcal/mol	D°_0 kcal/mol
(8)Drowart(1964)	Knudsen mass spec.	A	2168-2410	4	-2.3±9.7	24±22	29.4±3	12.7	88.8
	Knudsen mass spec.	B	2328-2334	2	67	209	51.9±3	>6.5	<95.0
	Knudsen mass spec.	C	2393-2410	3	12±83	85±100	55.8±3	<15.5	>85.9
(9)Colin(1964)[c]	Knudsen mass spec.	D	2180-2386	3	1±31	31±72	27.9±6	5.6	95.8[c]

[a] Reactions: A) Ca(g) + O_2(g) = CaO(g) + O(g); B) Ca(g) + WO_3(g) = CaO(g) + WO_2(g); C) Ca(g) + MoO_3(g) = CaO(g) + MoO_2(g); D) Ca(g) + SO(g) = CaO(g) + S(g).

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

[c] Ion intensities and D°_0 reported (9) at 2180 K are discrepant by ∿8 kcal/mol; we use ion intensities.

Heat Capacity and Entropy

Electronic levels (T_o) and vibrational-rotational constants of the observed states are from (1, 2, 3, 6, 7). The long-sought $a^3\Pi$ and $A'^1\Pi$ states of CaO, SrO and BaO were characterized by Field (1) using a new method for assignment of perturbations. This study resolved the long-standing controversy over low-lying electronic levels and confirmed that $X^1\Sigma^+$ is the ground state. We estimate the other potentially low-lying state ($^3\Sigma^+$) at 10000 cm^{-1} by assuming that it lies 1500 ± 1200 cm^{-1}(1, 4) below the isoconfigurational A state. Other predicted states and their vibrational-rotational constants are estimated in isoconfigurational groups by comparison with BeO, MgO, SrO and BaO(5). Comparisons are facilitated by listing the states in the isoconfigurational order of MgO(5). Rotational analysis of a band near 5470 Å was attributed (16) to CaO, but we question this assignment. Our thermodynamic functions are calculated using first-order anharmonic corrections to Q^i_r and Q^i_v in the partition function $Q = Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2\varepsilon_i/T)$.

References

1. R. W. Field, J. Chem. Phys. 60, 2400(1974); R. W. Field, G. A. Capelle & C. R. Jones, J. Mol. Spectrosc. 54, 156 (1975).
2. L. Brewer and R. Hauge, J. Mol. Spectrosc. 25, 330 (1968).
3. H. Johansen, Ph.D. Thesis, Univ. California, Berkeley, UCRL-19649, 1970.
4. K. D. Carlson, K. Kaiser, C. Moser and A. C. Wahl, J. Chem. Phys. 52, 4678 (1970).
5. JANAF Thermochemical Tables: CaO(g), MgO(g), BeO(g) 12-31-74; SrO(g), BaO(g) 6-30-74; WO_2(g), WO_3(g) 9-30-66; MoO_2(g), MoO_3(g) 6-30-68.
6. B. Rosen, "Spectroscopic Data Relative to Diatomics," Pergamon Press, New York, 1970, pp. 112-3.
7. A. Lagerqvist, Arkiv. Fysik 8, 83 (1954).
8. J. Drowart, G. Exsteen and G. Verhaegen, Trans. Faraday Soc. 60, 1290 (1964).
9. R. Colin, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. 60, 306 (1964).
10. P. J. Kalff and C. Th. J. Alkemade, J. Chem. Phys. 59, 2572 (1973); 60, 1698 (1974).
11. L. Brewer and G. Rosenblatt, Advan. High Temp. Chem. 2, 1 (1969).
12. K. Schofield, Chem. Rev. 67, 707 (1967).
13. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall Ltd., London, 1968, pp. 236-244, 109.
14. J. van der Hurk, Tj. Hollander and C. Th. J. Alkemade, J. Quant. Spectrosc. Radiat. Transfer 13, 273 (1973).
15. V. G. Ryabova, Teplofiz. Vys. Temp. 10, 744 (1972); 9, 290, 755 (1971).
16. G. A. Volynets, G. V. Kovalenok and V. A. Sokolov, Opt. Spektrosk. 36, 1034 (1974).
17. N. J. Stag and W. G. Richards, Mol. Phys. 27, 787 (1974).

CaO

Dicalcium (Ca_2)

Ca_2

(Ideal Gas) GFW = 80.16

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.615	82.787	82.787	INFINITE
100	8.641	51.403	69.446	-1.804	83.130	78.752	-172.112
200	9.226	57.598	62.133	-.907	82.943	74.431	-81.334
298	9.152	61.289	61.289	.000	82.660	70.309	-51.538
300	9.145	61.345	61.289	.017	82.653	70.232	-51.164
400	8.699	63.918	61.643	.910	82.272	66.147	-36.141
500	8.270	65.811	62.296	1.758	81.828	62.167	-27.173
600	7.947	67.289	63.009	2.568	81.336	58.281	-21.229
700	7.716	68.495	63.709	3.350	80.812	54.479	-17.009
800	7.552	69.514	64.373	4.113	79.589	50.813	-13.882
900	7.433	70.397	64.994	4.862	78.634	47.272	-11.479
1000	7.344	71.175	65.574	5.601	77.563	43.844	-9.582
1100	7.278	71.872	66.116	6.332	76.378	40.528	-8.052
1200	7.226	72.503	66.622	7.057	71.519	37.629	-6.853
1300	7.186	73.079	67.097	7.777	70.799	34.834	-5.856
1400	7.154	73.611	67.543	8.494	70.076	32.095	-5.010
1500	7.128	74.103	67.964	9.208	69.350	29.407	-4.285
1600	7.107	74.563	68.363	9.920	68.622	26.768	-3.656
1700	7.089	74.993	68.740	10.630	67.892	24.175	-3.108
1800	7.075	75.398	69.099	11.338	-6.628	22.986	-2.791
1900	7.062	75.780	69.441	12.045	-6.919	24.639	-2.834
2000	7.052	76.142	69.767	12.750	-7.214	26.307	-2.875
2100	7.043	76.486	70.078	13.455	-7.513	27.990	-2.913
2200	7.035	76.813	70.377	14.159	-7.817	29.689	-2.949
2300	7.029	77.126	70.664	14.862	-8.130	31.401	-2.984
2400	7.024	77.425	70.939	15.565	-8.453	33.126	-3.016
2500	7.020	77.711	71.205	16.267	-8.787	34.866	-3.048
2600	7.016	77.987	71.460	16.969	-9.137	36.618	-3.078
2700	7.014	78.251	71.707	17.670	-9.506	38.384	-3.107
2800	7.013	78.506	71.945	18.372	-9.894	40.166	-3.135
2900	7.012	78.753	72.176	19.073	-10.307	41.962	-3.162
3000	7.013	78.990	72.399	19.774	-10.750	43.771	-3.189
3100	7.014	79.220	72.615	20.475	-11.225	45.597	-3.215
3200	7.017	79.443	72.825	21.177	-11.735	47.438	-3.240
3300	7.020	79.659	73.029	21.879	-12.287	49.294	-3.265
3400	7.024	79.869	73.227	22.581	-12.881	51.169	-3.289
3500	7.029	80.072	73.420	23.284	-13.522	53.063	-3.313
3600	7.035	80.270	73.607	23.987	-14.215	54.975	-3.337
3700	7.042	80.463	73.790	24.691	-14.961	56.908	-3.361
3800	7.050	80.651	73.968	25.395	-15.765	58.860	-3.385
3900	7.059	80.834	74.142	26.101	-16.629	60.834	-3.409
4000	7.068	81.013	74.311	26.807	-17.553	62.832	-3.433
4100	7.079	81.188	74.477	27.514	-18.540	64.854	-3.457
4200	7.090	81.359	74.639	28.223	-19.591	66.902	-3.481
4300	7.102	81.526	74.797	28.932	-20.710	68.972	-3.506
4400	7.114	81.689	74.952	29.643	-21.891	71.073	-3.530
4500	7.128	81.849	75.103	30.355	-23.141	73.198	-3.555
4600	7.141	82.006	75.252	31.069	-24.453	75.354	-3.580
4700	7.156	82.160	75.397	31.784	-25.830	77.539	-3.606
4800	7.170	82.310	75.539	32.500	-27.272	79.753	-3.631
4900	7.186	82.458	75.679	33.218	-28.774	81.998	-3.657
5000	7.201	82.604	75.816	33.937	-30.335	84.275	-3.684
5100	7.217	82.746	75.951	34.658	-31.954	86.584	-3.710
5200	7.233	82.887	76.083	35.380	-33.628	88.924	-3.737
5300	7.250	83.025	76.212	36.105	-35.353	91.297	-3.765
5400	7.266	83.160	76.340	36.830	-37.128	93.702	-3.792
5500	7.283	83.294	76.465	37.558	-38.948	96.141	-3.820
5600	7.300	83.425	76.588	38.287	-40.811	98.614	-3.849
5700	7.317	83.555	76.709	39.018	-42.712	101.122	-3.877
5800	7.334	83.682	76.828	39.751	-44.651	103.662	-3.906
5900	7.351	83.807	76.946	40.485	-46.623	106.236	-3.935
6000	7.368	83.931	77.061	41.221	-48.625	108.844	-3.965

Dec. 31, 1974

DICALCIUM (Ca_2) (IDEAL GAS) GFW = 80.16

Ground State Configuration $^1\Sigma_g^+$

$S^\circ_{298.15}$ = 61.29 ± 0.2 gibbs/mol

ΔHf°_0 = 82.79 ± 0.7 kcal/mol

$\Delta H^\circ_{298.15}$ = 82.66 ± 0.7 kcal/mol

CA 2

Electronic Levels and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma_g^+$	0	1
$A^1\Sigma_\mu^+$	19401	1

The contribution of the ground state vibrational levels is approximated by direct summation of the following levels (in cm^{-1}) : 32.27, 95.14, 155.79, 214.22, 270.43, 324.42, 376.19, 425.74, 473.07, 518.18, 561.07, 601.74, 640.19, 676.42, 710.43, 742.22, 771.79, 799.14, 824.27, 847.18, 867.87, 886.34, 902.59, 916.62, 928.43, 938.02.

$\omega_e = 65.09 cm^{-1}$ $\omega_e x_e = 1.11\ cm^{-1}$ $\sigma = 2$

$B_e = 0.0460 cm^{-1}$ $\alpha_e = [0.00076] cm^{-1}$ $r_e = 4.28 Å$

Heat of Formation

Hamada (1, 2) investigated the emission spectra of Ca and concluded that the spectra suggested the presence of $Ca_2(g)$. A *dissociation limit was reported, $D_0^\circ \geq 4.15$ kcal/mol. This interpretation was later supported in studies by Espenhain* et al. (7) and Weniger (8). Balfour and Whitlock (15) examined at high resolution the absorption spectrum from calcium vapor in a King furnace at 2300 K. They observed 249 levels involving five vibrational states and estimated, by extrapolation, a dissociation energy, $D_0^\circ = 2.69 \pm 0.11$ kcal/mol. [A linear Birge-Sponer extrapolation using the values of ω_e and $\omega_e x_e$ tabulated above yields 2.63 kcal/mol for D_0°.] We adopt $\Delta Hf^\circ_{298} = 82.73 \pm 0.7$ kcal/mol for Ca_2 which is calculated from the D_0° value suggested by Balfour and Whitlock (15).

Brewer (5) tabulated a value of $\Delta Hs^\circ_{298} = 79 \pm 1$ kcal/mol for the process $2Ca(c) = Ca_2(g)$. This value was quoted later by Verhaegen et al. (6). Mellor (12) calculated a value of 66.0 ± 5.2 kcal/mol for the same process. This latter calculation was based on Lennard-Jones potential parameters which were estimated via approximate relations based on pVT data for gases. These ΔHs°_{298} values are actually ΔHf°_{298} values for $Ca_2(g)$. Brewer's value (5) is in good agreement with our adopted value (within 4 kcal/mol) whereas Mellor's value (12) is roughly 16 kcal/mol less positive.

Heat Capacity and Entropy

The molecular data are from the spectroscopic study of Balfour and Whitlock (15). The value of α_e is calculated from the reported values of B_e, ω_e, and $\omega_e x_e$, assuming a Morse potential. The absolute vibrational numbering in the $A^1\Sigma_\mu^+$ state is not known (15) so the $A^1\Sigma_\mu^+ \rightarrow X^1\Sigma_g^+$ separation is not known exactly. We adopt the value $19401.0 cm^{-1}$ which is actually the v'- 0 transition value. Treatment of $Ca_2(g)$ as an harmonic oscillator or an anharmonic oscillator gives heat capacity values which appear unreasonably large (∿24 gibbs/mol at 6000 K). Thus the heat capacity values are generated using a summation over 26 vibrational levels of the ground state.

There are four studies reported in the literature which incorrectly assign bands to gaseous Ca_2 (3, 4, 9, 10). The more recent work by Kovalenok (13) also refers to the observation of Ca_2 bands. However, this article could not be obtained for review. The matrix isolation studies of Williams (16) and Francis and Webber (17) also suggested the presence of Ca_2. Other comments on Ca_2 are given in Liberale and Weniger (11) and Baetzold (14).

References

1. H. Hamada, Phil. Mag. 12, 50 (1931).
2. H. Hamada, Nature 127, 555 (1931).
3. R. F. Sanford, Publ. astron. Soc. Pacific 52, 325 (1940).
4. A. S. King, Publ. astron. Soc. Pacific 54, 6 (1942).
5. L. Brewer, UCRL-2854, February, 1955.
6. G. Verhaegen, F. E. Stafford, P. Goldfinger, and M. Ackerman, Trans. Faraday Soc. 58, 1926 (1962).
7. M. *Espenhain, H. J. Kusch, and W. Lochte - Holtgreven, Z. Astrophys.* 61, *77 (1965); Chem. Abstr.* 63, *10870e (1965).*
8. S. Weniger, Proceedings of I.A.U. Colloquium on Late-type Stars, ed. M. Hack, Trieste, 1966, p. 25; as reference by Balfour and Whitlock (15).
9. G. V. Kovalenok and V. A. Sokolov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 4, 118 (1967).
10. G. V. Kovalenok and V. A. Sokolov, Izv. Vyssh. Ucheb. Zaved., Fiz. 11, 27 (1968).
11. G. Liberale and S. Weniger, Physica 41, 47 (1969).
12. A. M. Mellor, J. Chem. Phys. 51, 1678 (1969).
13. G. V. Kovalenok, Izv. Tomsk. Politekh. Inst., No. 184, 40(1970); Chem. Abstr. 76, 52159x(1972).
14. R. C. Baetzold, J. Chem. Phys. 55, 4355 (1971).
15. W. J. Balfour and R. F. Whitlock, Chem. Comm. 1971, 1231 (1971).
16. D. A. Williams, Observatory 92(900), 174 (1972); Chem. Abstr. 79, 98801r (1973).
17. J. E. Francis, Jr. and S. E. Webber, J. Chem. Phys. 56, 5879 (1972).

Cobalt Dichloride ($CoCl_2$) Cl_2Co

(Ideal Gas) GFW = 129.8392

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	.000	.000	INFINITE	-3.650	-22.717	-22.717	INFINITE
100	12.333	56.580	83.625	-2.705	-22.592	-23.551	51.470
200	13.792	65.713	72.607	-1.379	-22.449	-24.576	26.856
298	14.250	71.316	71.316	.000	-22.400	-25.634	18.790
300	14.256	71.404	71.316	.026	-22.400	-25.654	18.689
400	14.497	75.542	71.879	1.465	-22.405	-26.740	14.610
500	14.655	78.794	72.948	2.923	-22.454	-27.818	12.159
600	14.787	81.478	74.153	4.395	-22.543	-28.883	10.521
700	14.913	83.767	75.367	5.880	-22.662	-29.931	9.345
800	15.031	85.766	76.544	7.378	-22.910	-30.946	8.454
900	15.139	87.543	77.669	8.886	-23.091	-31.939	7.756
1000	15.233	89.143	78.738	10.405	-23.320	-32.911	7.193
1100	15.311	90.599	79.751	11.932	-23.607	-33.857	6.727
1200	15.374	91.934	80.712	13.467	-23.960	-34.773	6.333
1300	15.421	93.166	81.623	15.007	-24.418	-35.658	5.995
1400	15.455	94.311	82.489	16.551	-25.010	-36.500	5.698
1500	15.479	95.378	83.313	18.097	-25.362	-37.308	5.436
1600	15.494	96.377	84.098	19.646	-25.651	-38.095	5.203
1700	15.502	97.317	84.849	21.196	-25.917	-38.863	4.996
1800	15.505	98.203	85.566	22.746	-30.073	-39.548	4.802
1900	15.505	99.041	86.253	24.297	-30.402	-40.063	4.608
2000	15.502	99.837	86.913	25.847	-30.735	-40.564	4.433
2100	15.497	100.593	87.546	27.397	-31.068	-41.048	4.272
2200	15.492	101.314	88.156	28.947	-31.404	-41.516	4.124
2300	15.487	102.002	88.743	30.496	-31.742	-41.966	3.988
2400	15.482	102.661	89.309	32.044	-32.083	-42.404	3.861
2500	15.478	103.293	89.856	33.592	-32.427	-42.827	3.744
2600	15.475	103.900	90.385	35.140	-32.772	-43.236	3.634
2700	15.473	104.484	90.896	36.687	-33.121	-43.632	3.532
2800	15.471	105.047	91.392	38.234	-33.473	-44.014	3.435
2900	15.471	105.590	91.872	39.781	-33.827	-44.385	3.345
3000	15.473	106.114	92.338	41.329	-34.183	-44.744	3.260
3100	15.475	106.622	92.791	42.876	-34.543	-45.090	3.179
3200	15.478	107.113	93.231	44.424	-124.023	-44.589	3.045
3300	15.482	107.589	93.658	45.972	-124.051	-42.106	2.789
3400	15.487	108.052	94.075	47.520	-124.081	-39.621	2.547
3500	15.493	108.501	94.481	49.069	-124.116	-37.139	2.319
3600	15.500	108.937	94.876	50.619	-124.153	-34.652	2.104
3700	15.507	109.362	95.262	52.169	-124.195	-32.165	1.900
3800	15.515	109.776	95.639	53.720	-124.240	-29.678	1.707
3900	15.524	110.179	96.006	55.272	-124.290	-27.188	1.524
4000	15.533	110.572	96.366	56.825	-124.345	-24.698	1.349
4100	15.542	110.956	96.717	58.379	-124.403	-22.207	1.184
4200	15.551	111.330	97.060	59.933	-124.467	-19.714	1.026
4300	15.561	111.696	97.396	61.489	-124.535	-17.220	.875
4400	15.571	112.054	97.725	63.046	-124.607	-14.720	.731
4500	15.581	112.404	98.048	64.603	-124.686	-12.225	.594
4600	15.591	112.747	98.364	66.162	-124.767	-9.724	.462
4700	15.601	113.082	98.673	67.721	-124.855	-7.221	.336
4800	15.610	113.411	98.977	69.282	-124.947	-4.719	.215
4900	15.620	113.733	99.275	70.843	-125.046	-2.211	.099
5000	15.630	114.048	99.567	72.406	-125.148	.295	-.013
5100	15.639	114.358	99.854	73.969	-125.255	2.809	-.120
5200	15.648	114.662	100.136	75.534	-125.368	5.321	-.224
5300	15.657	114.960	100.413	77.099	-125.487	7.833	-.323
5400	15.666	115.253	100.685	78.665	-125.612	10.349	-.419
5500	15.674	115.540	100.952	80.232	-125.742	12.870	-.511
5600	15.683	115.823	101.215	81.800	-125.877	15.389	-.601
5700	15.690	116.100	101.474	83.369	-126.019	17.910	-.687
5800	15.698	116.373	101.729	84.938	-126.166	20.441	-.770
5900	15.705	116.642	101.979	86.508	-126.320	22.967	-.851
6000	15.712	116.906	102.226	88.079	-126.480	25.500	-.929

Dec. 31, 1973; Dec. 31, 1974

COBALT DICHLORIDE ($CoCl_2$) (IDEAL GAS) GFW = 129.8392

Cl_2Co

Point Group $D_{\infty h}$
$S^\circ_{298.15}$ = [71.3 ± 2.0] gibbs/mol
T_b(to monomer) = 1360 K

ΔHf°_0 = -22.7 ± 2.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -22.4 ± 2.0 kcal/mol
ΔHv° = [34.8] kcal/mol
ΔHs° = 52.3 ± 1.7 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i	State	ε_i, cm^{-1}	g_i
$^4\Sigma_g^-$	0	[4]	$^4\Sigma_g^-$	[10425]	[4]
$^4\Phi_g$	[210]	[8]	$^4\Delta_g$	[14197]	[8]
$^4\Pi_g$	[2408]	[8]	$^4\Pi_g$	[21270]	[8]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[325] (1)
94.5 (2)
493 (1)

Bond Distance: Co-Cl = 2.117 Å Bond Angle: Cl-Co-Cl = 180° Rotational Constant: B_0 = 0.05305 cm^{-1} σ = 2

Heat of Formation

ΔHf° is calculated from ΔHs° = 52.3 ± 1.7 kcal/mol by addition of $\Delta Hf^\circ_{298}(CoCl_2, c)$ = -74.7 ± 0.3 kcal/mol (1). The adopted value for ΔHs° is based on results of a second and third law analysis of extensive sublimation data reported by Hill et al. (2). These studies included both Knudsen-effusion and torsion-effusion measurements which were performed in platinum-10% rhodium effusion cells. Orifice diameters of the cells varied from 0.0518 cm to 0.1645 cm. The extent of dimerization (~1-2%) was also determined from mass spectrometric measurements, and the measured vapor pressures were corrected to represent equilibrium pressures of the monomer. Results of our analysis of sixty-four vapor pressure points measured in five different cells are given below. Derived ΔHf values show no significant trends with orifice size; thus, a mean value of the five results is adopted. Also included in this table is a value for ΔHf which was obtained from an analysis of equilibrium data (3) for $CoO(c) + Cl_2(g) = CoCl_2(g) + \frac{1}{2} O_2(g)$. Orlov (3) has not reported sufficient information to allow a small correction to be made for dimerization; even so, his results still give a value for ΔHf (-22.1 kcal/mol) which agrees fairly well with that adopted.

References	Method	Temp. Range K	No. of Points	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	$-\Delta Hf^\circ_{298}$ kcal/mol
(2)	Knudsen-Cell A	680-800	13		52.35±0.13	0.4±0.5	22.4±0.4
(2)	Knudsen-Cell B	697-814	14(a)	51.9	52.29±0.10	0.5±0.4	22.4±0.4
(2)	Knudsen-Cell C	715-810	10	52.9	52.14±0.16	-0.9±0.9	22.6±0.5
(2)	Torsion-Cell A	759-834	10	56.7	52.38±0.52	-5.4±3.2	22.3±0.8
(2)	Torsion-Cell B	745-824	15	55.0	52.30±0.17	-3.4±0.4	22.4±0.5
(3)	Transpiration	1323-1523	Equation	16.6	34.77±2.1	12.7	22.1±2.2(b)

(a)Two points rejected due to failure of a statistical test. (b)$\Delta Hf^\circ_{298}(CoO, c)$ = -56.82 ± 0.10 kcal/mol (1).

Other vapor pressures for $CoCl_2(c, \ell)$ have been measured by static (4) and transpiration (5, 6) methods. In all three studies the presence of a small amount of dimer in the saturated vapor was not considered. JANAF pressures based on (a) selected values of the heats of sublimation and vaporization for the monomer and dimer, (b) the mass spectrometric value of 2ΔHs(monomer)- ΔHs(dimer) = -38.99 kcal/mol (see $Co_2Cl_4(g)$ table) at 298 K, and (c) adopted entropies for the condensed and gaseous species are compared with the observed total pressures in the table given below.

Investigator	Method	Process	Temp. Range K	Mole Fraction Dimer Calc. Range	P_{calc}/P_{obs} Range
Maier (4)	Static	Sublimation	906-997	0.051-0.086	0.073-0.156
Maier (4)	Static	Vaporization	1022-1256	0.082-0.092	0.198-0.816
Kulkarni and Dadape (5)	Transpiration	Vaporization	1015-1144	0.090-0.092	0.531-0.743
Schäfer and Krehl (6)	Transpiration	Sublimation	925-1010	0.057-0.091	0.875-1.096
Schäfer and Krehl (6)	Transpiration	Vaporization	1019-1073	0.092	0.825-0.883

Our predictions agree reasonably well with the transpiration data of Schäfer and Krehl (6), while the static measurements of Maier (4) show significant deviations from our pressures, particularly at the lower temperatures. We note that JANAF analysis (1) of Maier's vapor pressures for $BaCl_2$, $AlCl_3$, and $FeCl_2$ indicate the existence of temperature dependent errors in his measurements; thus, the results for $CoCl_2$ are probably not reliable. Also, the transpiration data of Kulkarni and Dadape (5) show similar discrepancies.

Heat Capacity and Entropy

Measurements of the infrared (7-9) and electronic (10-12) spectra of both matrix-isolated and gaseous $CoCl_2$ have been interpreted on the basis of a linear structure of $D_{\infty h}$ symmetry. This structure is adopted, and the Co-Cl bond length is taken to be equal to the value determined by Tremmel et al. (13). The antisymmetric stretching frequency (ν_3) is that observed in the infrared absorption spectra of gaseous $CoCl_2$ by Leroi et al. (7). This value has been confirmed from results of two infrared matrix isolation studies (8, 9). The doubly degenerate bending frequency (ν_2) was observed by Thompson and Carlson (8) in the infrared spectra of $CoCl_2$ isolated in an argon matrix. The infrared-inactive symmetric stretching frequency (ν_1) is estimated by comparison with similar data for $FeCl_2$ (1) and $NiCl_2$ (14). Some additional support for this value is provided by calculations of DeKock and Gruen (11). Assuming a linear model, they calculated ν_1 = 332 cm^{-1} from ν_3 = 493 cm^{-1}. Also, Clifton and Gruen (15) observed a vibrational spacing of 332 cm^{-1} in the fluorescence spectrum of argon matrix-isolated $CoCl_2$ which may be ν_1. A similar assignment for $NiCl_2$ was recently proposed by Gruen et al. (14) based on observations of the vibrational spacings in its fluorescence spectrum.

The electronic spectra of $CoCl_2$ have been extensively investigated both in the gas phase (10, 11, and 16) and in various matrices (9, 12, 15, and 17). Unfortunately, most of the results are conflicting and difficult to interpret. It is not certain whether the ground state configuration is $^4\Phi$, or $^4\Sigma$. Theoretical arguments based on a ligand-field model (12, 18) favor the former, but recently Lever and Hollebone (19) interpreted the electronic spectra of $CoCl_2$ in terms of an "orbital angular overlap" model and preferred the latter ground state configuration. Other problems associated with band assignments in the $CoCl_2$ spectra have been dealt with by Smith (18). The adopted states and levels comprise one of two sets of assignments proposed by *Lever and Hollebone* (19). *The alternate functions derived from their second set of assignments* (19) *suggest that the adopted* entropies may be biased by as much as +2 eu at 298 K and +0.2 eu at 4000 K. Functions based on the assignments of Smith (18) agree with those adopted to better than 1 eu at all temperatures.

References: See $Co_2Cl_4(g)$ table.

Cl_2Co

ZIRCONIUM TETRACHLORIDE ($ZrCl_4$) CL_4ZR

(CRYSTAL) GFW=233,032

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 5.957	- 234.598	- 234.598	INFINITE
100	18.640	16.852	66.682	- 4.983	- 235.228	- 227.548	497.305
200	25.880	32.445	45.905	- 2.692	- 234.915	- 219.952	240.353
298	28.630	43.360	43.360	.000	- 234.350	- 212.725	155.931
300	28.660	43.537	43.361	.053	- 234.338	- 212.590	154.872
400	29.970	51.982	44.503	2.991	- 233.683	- 205.439	112.247
500	30.760	58.759	46.699	6.030	- 233.001	- 198.456	86.745
600	31.340	64.420	49.193	9.136	- 232.311	- 191.612	69.794
700	31.820	69.288	51.724	12.294	- 231.615	- 184.884	57.723
800	32.260	73.566	54.192	15.499	- 230.915	- 178.257	48.698
900	32.660	77.389	56.561	18.745	- 230.211	- 171.716	41.698
1000	33.040	80.850	58.820	22.030	- 229.503	- 165.256	36.117

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963;
Dec. 31, 1969; June 30, 1975

ZIRCONIUM TETRACHLORIDE ($ZrCl_4$) (CRYSTAL) CL_4ZR

GFW = 233.032

$S°_{298.15}$ = 43.36±0.7 gibbs/mol

$\Delta Hf°_0$ = -234.43±0.4 kcal/mol

Tm = 710±2 K

$\Delta Hf°_{298.15}$ = -234.18±0.4 kcal/mol

ΔHm° = 12±3 kcal/mol

Ts = 609.05 K

$\Delta Hs°_{298.15}$ = 26.42±0.12 kcal/mol

Heat of Formation

Gal'chenko et al. (1) determined heat of formation of $ZrCl_4$(c) by the direct chlorination of highly pure Zr metal in a bomb calorimeter. Complete chlorination of the metal was accomplished as indicated by the absence of unreacted metal and of lower chlorides. They reported $\Delta Hf°_{298}$ ($ZrCl_4$, c) = -234.17±0.28 kcal/mol.

Gal'chenko et al. (2) had also earlier determined the heat of formation of $ZrCl_4$(c) by a similar technique and reported -234.35 ± 2.1 kcal/mol. Gross et al. (6) measured calorimetrically the chlorination of Zr(c) with liquid chlorine. His results lead to $\Delta Hf°_{298}$ = -234.7 ± 0.4 kcal/mol for $ZrCl_4$(c). We adopt $\Delta Hf°_{298}$ = -234.35 ± 0.4 kcal/mol which is a weighted mean of these three studies. This adopted value is identical to that suggested by NBS (4).

Less reliable studies leading to $\Delta Hf°_{298}$ values have been reported by Siemonsen and Siemonsen (7), and Beck (8). Equilibrium studies by Hildenbrand et al. (3) and Morozov and Korshunov (5) suggest $\Delta Hf°_{298}$ values 1-3 kcal/mol less negative than our adopted value.

Heat Capacity and Entropy

Todd (9) measured the low temperature heat capacities from 52.6 to 296.7 K, and made an extrapolation to 0 K which yielded an entropy of 8.12 gibbs/mol at 51 K. We adopt the measured heat capacities, but make our own extrapolation to 0 K, based on the ratio of the measured heat capacities of ZrF_4(10), TiF_4(11) and $TiCl_4$(12) from 6 to 50 K. This extrapolation gives $S°_{50}$ = 6.758±0.7 gibbs/mol which is adopted. Coughlin and King (13) measured high temperature enthalpy data from 335.9 to 566.8 K by drop calorimetry. Their data are smoothly joined with Todd's low temperature heat capacities.

Melting Data

The melting point, Tm = 710±2 K, has been observed by Rahlfs and Fischer (14), Palko et al. (15), and Denisova et al. (16, 17). Nisel'son (18) observed a melting temperature of 708.7 K. Heat of melting data may be extracted from Palko et al. (15) and Denisova et al. (16, 17). A weighted average ΔHm° = 12±3 kcal/mol is adopted for the heat of melting.

Heat of Sublimation

Several sets of sublimation studies are summarized below, using a second and third analysis.

Source	Method	No. pts	range, K	$\Delta Hs°_{298}$, kcal/mol 2nd law	3rd law	drift gibbs/mol
Rahlfs and Fischer (14)	static	11	535-607	27.36±0.43	26.31±0.13	-1.9±0.8
Palko et al. (15)	static (diaphragm)	50[a]	503-575	25.75±0.20	26.39±0.17	1.1±0.3
	static (cap. bridge)	36[b]	580-689	25.87±0.28	26.40±0.16	0.8±0.4
Funaki and Uchimura (19)	glass Bourdon gage	eqn	503-603	26.19	26.33	0.3
Denesova et al. (16)	static	17[c]	625-709	25.51±0.34	26.42±0.11	1.3±0.5
Khodeev and Tsirel'nikov (20)	mass spec.	eqn	373-448	27.14	26.66	-1.2
Safronov et al. (21)	-	eqn	376-493	26.59	26.44	-0.4

*(a) 3, (b) 2, (c) 1 points rejected due to failure of a statistical test.

A mean of the third law values, $\Delta Hs°_{298}$ = 26.42±0.12 kcal/mol, is adopted. The sublimation temperature, Ts, is obtained from the Gibbs free energy crossover between the crystal and gas. Since Ts is lower than Tm, the liquid phase is thermodynamically unstable at normal conditions.

In analyzing the vapor pressures for the sublimation studies, corrections were made for non-ideality by means of the equation ΔG°/T = -Rln p -Bp/T. The Bertholet equation of state and the critical constants Tc = 776.65 K and pc = 57.4 atm as determined by Nisel'son and Sokolova (22) are used to calculate B.

References

1. G. L. Gal'chenko, D. A. Gedakyan, and B. I. Timofeev, Russ. J. Inorg Chem. 13, 159 (1968).
2. G. L. Gal'chenko, D. A. Gedakyan, B. I. Timofeev, and S. M. Skuratov, Dokl. Akad. Nauk SSSR 161, 1081 (1965).
3. D. L. Hildenbrand, L. P. Theard, W. F. Hall, F. Ju, F. S. La Viola, and N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport, Calif., Pub. No. U-1734, NOw 61-0905-C, June, 1962.
4. U.S. Natl. Bur. Std. Tech Note 270-5, 1971.
5. I. S. Morozov and B. G. Korshunov, Khim. Redkikh Elementov, Akad. Nauk SSSR, Inst. Obshchei i Neorg. Khim., No. 2, 102 (1955); Chem. Abstr. 50 3136c (1956).
6. P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. 53, 1285 (1957).
7. H. Siemonsen and U. Siemonsen, Z. Elektrochem. 56, 643 (1952).
8. G. Beck, Z. anorg. allgem. Chem. 174, 31 (1928).
9. S. S. Todd, J. Amer. Chem. Soc. 72, 2914 (1950).
10. E. F. Westrum, Jr., J. Chem. Eng. Data 10, 140 (1965).
11. R. D. Euler and E. F. Westrum, Jr., J. Phys. Chem. 65, 132 (1961).
12. G. T. Furukawa, private communication, U.S. Natl. Bur. Std., 1964.
13. J. P. Coughlin and E. G. King, J. Amer. Chem Soc. 72, 2262 (1950).
14. O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).
15. A. A. Palko, A. D. Ryon, and D. W. Kuhn, J. Phys. Chem. 62, 319 (1958).
16. N. D. Denisova, E. K. Safronov, and O. N. Bystrova, Russ. J. Inorg. Chem. 11, 1171 (1966).
17. N. D. Denisova, E. K. Safranov, A. I. Pustil'nik, and O. N. Bystrova, Russ. J. Phys. Chem. 41, 30 (1967).
18. L. A. Nisel'son, Russ. J. Inorg. Chem. 7, 354 (1962).
19. K. Funaki and K. Uchimura, Denki Kagaku 33, 167 (1965) [Chem. Abstr. 63, 3688 c (1965)].
20. Yu. S. Khodeev and K. I. Tsirel'nikov, Vestn. Mosk. Univ., Khim 14, 611 (1973).
21. E. K. Safronov, L. N. Shelst, and S. M. Selifonov, Nauck. Tr., Gos. Nauch-Issled. Proekt. Inst. Redkometal. Prom. 20, 127 (1968).
22. L. A. Nisel'son and T. D. Sokolova, Russ. J. Inorg. Chem. 7, 1382 (1962).

ZIRCONIUM TETRACHLORIDE ($ZrCl_4$) CL_4ZR

(IDEAL GAS) GFW=233.032

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-5.392	-207.613	-207.613	INFINITE
100	16.920	65.552	107.204	-4.165	-207.990	-205.180	448.421
200	21.469	78.858	89.954	-2.219	-208.022	-202.342	221.109
298	23.478	87.859	87.859	.000	-207.930	-199.572	146.290
300	23.502	88.004	87.859	.043	-207.928	-199.520	145.350
400	24.426	94.908	88.794	2.445	-207.809	-196.735	107.491
500	24.901	100.414	90.586	4.914	-207.697	-193.980	84.788
600	25.174	104.981	92.616	7.419	-207.608	-191.245	69.661
700	25.343	108.875	94.667	9.945	-207.544	-188.524	58.860
800	25.455	112.267	96.660	12.486	-207.508	-185.811	50.761
900	25.533	115.270	98.564	15.035	-207.501	-183.098	44.462
1000	25.589	117.963	100.371	17.592	-207.521	-180.388	39.424
1100	25.631	120.404	102.083	20.153	-207.571	-177.672	35.300
1200	25.663	122.635	103.704	22.717	-208.503	-174.899	31.853
1300	25.688	124.691	105.241	25.285	-208.433	-172.102	28.933
1400	25.708	126.595	106.699	27.855	-208.376	-169.309	26.430
1500	25.724	128.369	108.085	30.426	-208.333	-166.519	24.262
1600	25.737	130.030	109.405	32.999	-208.304	-163.734	22.365
1700	25.748	131.590	110.665	35.574	-208.285	-160.945	20.691
1800	25.757	133.062	111.869	38.149	-208.282	-158.163	19.204
1900	25.765	134.455	113.021	40.725	-208.291	-155.375	17.872
2000	25.771	135.777	114.126	43.302	-208.316	-152.591	16.674
2100	25.777	137.034	115.187	45.879	-208.352	-149.806	15.591
2200	25.782	138.234	116.208	48.457	-213.407	-146.840	14.587
2300	25.786	139.380	117.190	51.036	-213.466	-143.811	13.665
2400	25.790	140.477	118.138	53.614	-213.530	-140.781	12.820
2500	25.794	141.530	119.053	56.194	-213.598	-137.749	12.042
2600	25.797	142.542	119.937	58.773	-213.669	-134.713	11.324
2700	25.799	143.516	120.792	61.353	-213.745	-131.676	10.658
2800	25.802	144.454	121.621	63.933	-213.827	-128.633	10.040
2900	25.804	145.359	122.424	66.513	-213.913	-125.590	9.465
3000	25.806	146.234	123.203	69.094	-214.004	-122.545	8.927
3100	25.807	147.080	123.960	71.674	-214.102	-119.494	8.424
3200	25.809	147.900	124.695	74.255	-214.205	-116.441	7.953
3300	25.810	148.694	125.410	76.836	-214.314	-113.383	7.509
3400	25.812	149.464	126.106	79.417	-214.427	-110.321	7.091
3500	25.813	150.213	126.785	81.998	-214.548	-107.262	6.698
3600	25.814	150.940	127.445	84.580	-214.672	-104.191	6.325
3700	25.815	151.647	128.090	87.161	-214.803	-101.120	5.973
3800	25.816	152.336	128.719	89.743	-214.937	-98.049	5.639
3900	25.817	153.006	129.333	92.324	-215.078	-94.969	5.322
4000	25.818	153.660	129.933	94.906	-215.224	-91.888	5.021
4100	25.818	154.297	130.520	97.488	-215.372	-88.804	4.734
4200	25.819	154.920	131.093	100.070	-215.526	-85.718	4.460
4300	25.820	155.527	131.655	102.652	-215.682	-82.625	4.199
4400	25.820	156.121	132.204	105.234	-215.842	-79.523	3.950
4500	25.821	156.701	132.742	107.816	-216.006	-76.428	3.712
4600	25.821	157.269	133.269	110.398	-216.170	-73.324	3.484
4700	25.822	157.824	133.785	112.980	-216.338	-70.213	3.265
4800	25.822	158.367	134.292	115.562	-357.665	-66.424	3.024
4900	25.823	158.900	134.789	118.145	-357.940	-60.348	2.692
5000	25.823	159.422	135.276	120.727	-358.222	-54.276	2.372
5100	25.824	159.933	135.755	123.309	-358.509	-48.189	2.065
5200	25.824	160.434	136.224	125.892	-358.801	-42.100	1.769
5300	25.824	160.926	136.686	128.474	-359.100	-36.012	1.485
5400	25.825	161.409	137.139	131.057	-359.402	-29.913	1.211
5500	25.825	161.883	137.585	133.639	-359.709	-23.806	.946
5600	25.825	162.348	138.023	136.221	-360.018	-17.699	.691
5700	25.826	162.805	138.454	138.804	-360.332	-11.589	.444
5800	25.826	163.254	138.877	141.387	-360.646	-5.459	.206
5900	25.826	163.696	139.294	143.969	-360.965	.661	-.024
6000	25.826	164.130	139.705	146.552	-361.286	6.796	-.248

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963;
Dec. 31, 1969; June 30, 1975

ZIRCONIUM TETRACHLORIDE ($ZrCl_4$) (IDEAL GAS) GFW = 233.032

Point Group = T_d

$S^\circ_{298.15}$ = 87.86 ± 0.1 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -207.61 ± 0.5 kcal/mol CL_4ZR

$\Delta Hf^\circ_{298.15}$ = -207.93 ± 0.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
377 (1)	418 (3)
98 (2)	113 (3)

Bond Distance: Zr-Cl = 2.32±0.02 Å

σ = 12

Bond Angle: Cl-Zr-Cl = 109° 28'

Product of the Moments of Inertia: $I_AI_BI_C = 6.03177 \times 10^{-112}\ g^3cm^6$

Heat of Formation

The heat of formation of gaseous $ZrCl_4$, ΔHf°_{298} = -207.76±0.5 kcal/mol is calculated from the heats of formation and sublimation of the crystal (1).

Hildenbrand et al. (14) determined the equilibrium constants by the transpiration method for the reaction:

$$ZrO_2(c) + 4\ HCl(g) = ZrCl_4(g) + 2\ H_2O(g)$$

Second and third law analyses for their data are given below. The heat of formation derived from this study is in fair agreement with the value adopted.

			ΔHr°_{298} kcal/mol		drift	ΔHf°_{298}*
Series	No. pts	range, K	2nd law	3rd law	gibbs/mol	kcal/mol
I	10	1171-1373	28.94±0.44	29.16±0.15	0.17±0.34	-205.80
II	9	1169-1374	31.36±0.60	29.85±0.28	-1.19±0.47	-205.11

* ΔHf°_{298} refers to the heat of formation for $ZrCl_4(g)$ and is calculated from the third law ΔHr°_{298} results, using JANAF auxiliary data (1)

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark et al. (2, 3), who recorded the Raman spectra of $ZrCl_4$ in the vapor phase (380-420°C). These studies by Clark et al. (2, 3) indicated that $ZrCl_4$ is a tetrahedral monomer in the vapor phase. Shimanouchi, in his compilation of molecular vibrational frequencies (4), also adopted the values of Clark et al. (2, 3) for $ZrCl_4(g)$. Pontrelli (5) also observed in the Raman spectra all four fundamental vibrational frequencies (376, 99, 418, and 110 cm^{-1}). These values are in excellent agreement with those of Clark et al. (2, 3).

Other experimental studies involving the vibrational frequencies are as follows. Wilmshurst (6) observed one fundamental *vibrational frequency (421 cm^{-1}) in the infrared spectrum of $ZrCl_4$* vapor, *while* Büchler et al. *(7) found the same fundamental* mode at 423 cm^{-1}. Delwaulle and Francois (8) observed the symmetric stretching vibration (383 cm^{-1}) from the Raman spectra of $ZrCl_4$ in PCl_5 and $POCl_3$. Bobovich (9) reported the symmetric stretching vibration (315 cm^{-1}) from a partially polarized band in his Raman spectrometric studies.

Spiridonov et al. (10) measured the bond distance Zr-Cl=2.32±0.02 Å in the vapor phase by election diffraction. The molecule was also found to be a regular tetrahedron. The same bond distance was also reported by Lister and Sutton (11) and Kimura et al. (12). Rahlfs and Fischer (13), through vapor density measurements, had earlier concluded that $ZrCl_4$ was monomeric in the vapor phase. The individual moments of inertia are $I_A=I_B=I_C=84.4942X10^{-39}$ g cm^2.

Much literature has been published on the inter-relationships between force constants and vibrational frequencies. Since the majority of these articles are based on estimated frequencies, they will not be further discussed or referenced. The same situation is true for thermodynamic tabulations of $ZrCl_4(g)$. One exception is that Clark et al. (2) calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is identical to ours in the range 100-1000 K.

References

1. JANAF Thermochemical Tables: $ZrCl_4(c)$, 6-30-75; $ZrO_2(c)$, 12-31-65; HCl(g), 9-30-64; $H_2O(g)$, 3-31-61.
2. R. J. H. Clark, B. K. Hunter, and D. M. Rippon, Chem. Ind. (London) 1971, 787 (1971); Inorg. Chem. 11, 56 (1971).
3. R. J. H. Clark and D. M. Rippon, J. Mol. Spectrosc. 44, 479 (1972); Advanc. Raman Spectrosc. 1, 493 (1972).
4. T. Shimanouchi, J. Phys. Chem. Ref. Data 3, 269 (1974).
5. G. N. Pontrelli, Diss. Abstr. 23, 4130 (1963).
6. J. K. Wilmshurst, J. Mol. Spectrosc. 5, 343 (1960).
7. A. Büchler, J. B. Berkowitz-Mattuck, and D. H. Dugre, J. Chem. Phys. 34, 2202 (1961).
8. M. L. Dewaulle and F. Francois, Bull. Soc. Chim. 13, 205 (1946); J. Phys. Radium 7, 15 (1946).
9. Ya. S. Bobovich, Optics and Spectrosc. 11, 85 (1961).
10. V. P. Spiridonov, P. A. Akiskin, and V. I. Tsirel'nikov, Zh. Strukt. Khim. 3, 329 (1962).
11. M. W. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941).
12. M. Kimura, R. Kimura, M. Aoki, and S. Shibata, Bull. Chem. Soc. Japan 29, 95 (1956).
13. O. Rahlfs and W. Fischer, Z. anorg allgem. Chem. 211, 349 (1933).
14. D. L. Hildenbrand, L. P. Theard, W. F. Hall, F. Ju, F. S. La Viola, and N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport, Calif., Pub. No. U-1734, NOw 61-0905-C, June, 1962.

CL_4ZR

Niobium Pentachloride ($NbCl_5$) Cl_5Nb
(Crystal) GFW = 270.1714

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	35.350	51.160	51.160	.000	− 190.600	− 163.535	119.874
300	35.350	51.379	51.161	.065	− 190.583	− 163.367	119.013
400	35.350	61.548	52.547	3.600	− 189.722	− 154.428	84.375
500	35.350	69.436	55.166	7.135	− 188.933	− 145.695	63.683
600	35.350	75.881	58.097	10.670	− 188.195	− 137.118	49.945
700	35.350	81.331	61.037	14.205	− 187.490	− 128.662	40.170

Dec. 31, 1974

NIOBIUM PENTACHLORIDE ($NbCl_5$) (CRYSTAL)

$S^\circ_{298.15}$ = [51.16±1.0] gibbs/mol
Tm = 478.9 ± 1.5 K

GFW = 270.1714 CL_5NB
ΔHf°_0 = unknown
$\Delta Hf^\circ_{298.15}$ = -190.6 ± 1.0 kcal/mol
ΔHm° = 8.097 ± 0.23 kcal/mol
ΔHs°_{298} = 22.500 kcal/mol

Heat of Formation

The adopted value for the heat of formation of $NbCl_5(c)$ is ΔHf°_{298} = -190.6 ± 1.0 kcal/mol and is based on the study by Gross et al. (2). This value was determined from measurements of the heat evolved in the reaction $Nb(c) + 5/2Cl_2(\ell) = NbCl_5(c)$. Schäfer and Kahlenberg (1) also determined the heat of formation of $NbCl_5(c)$ via calorimetric measurement of the heats of solution of Nb(c) and $NbCl_5(c)$ in hydrofluoric acid. Their procedure consisted of five steps; four were determined experimentally and one was based on literature data. Using their data and auxiliary results (7), we calculate ΔHf°_{298} = -190.0 ± 1.0 kcal/mol for $NbCl_5(c)$. This value is in good agreement with our adopted value. Shchukarev et al. (3) determined a ΔHf°_{298} value from a heat of hydrolysis for $NbCl_5(c)$. A recalculation of this data, using current auxiliary ΔHf°_{298} data for $Nb_2O_5(c)$ (10), $H_2O(\ell)$ (7), and HCl(g) (10), yields ΔHf°_{298} = -192.8 ± 0.7 kcal/mol.

Three compilations on Nb species suggested a similar or closely related ΔHf°_{298} value for $NbCl_5(c)$ (6, 8, 9); in particular, the NBS Technical Note 270 Series suggested -190.6 kcal/mol (9).

Heat Capacity and Entropy

Keneshea et al. (5) measured the saturation enthalpy increments above 298.15 K for the condensed phases of $NbCl_5$ in a drop calorimeter up to the critical point (804±3K). A figure presented by Keneshea et al. (5) indicated roughly 30 data points, the lowest occurring at approximately 360 K. The differences between the saturation and standard enthalpy increments for the crystal phase are negligible, so that the heat capacity values which we adopt are those which are derived from the reported enthalpy equation, $(H_T-H_{298}) = [-10.53 + 3.535\times10^{-2}T] \pm 0.07$ kcal/mol. This equation is reported to apply to the temperature region 298.15 - 478.9 K.

Schäfer and Kahlenberg (1) estimated the heat capacity of $NbCl_5(c)$ to be given by $Cp^\circ = 38.0 - 3\times10^5T^{-2}$ gibbs/mol. For the crystal range 298.15 - 478.9 K, these estimated Cp° values vary from 34.63 to 36.69 gibbs/mol. These values are in fair agreement with the adopted values and were estimated by comparison with $ZrCl_4(c)$ and $HfCl_4(c)$. Amosov (4) also estimated the heat capacity of $NbCl_5$ based on Neumann and Koppe's rule, $Cp^\circ = 26.71 \pm 35.2\times10^{-3}T$ gibbs/mol. These latter values vary between 37.20 and 43.57 gibbs/mol over the region 298.15 - 478.9 K and differ significantly from those Cp° values derived from the experimental data of Keneshea et al. (5).

As there is no low temperature heat capacity data reported in the literature, the entropy of $NbCl_5(c)$ at 298.15 K is calculated from the equation $\Delta Ss^\circ_{298} = S^\circ_{298}(g) - S^\circ_{298}(c)$; $S^\circ_{298}(g)$ = 96.56 gibbs/mol as given in the $NbCl_5(g)$ table (10) and ΔSs°_{298} = 45.40 gibbs/mol as obtained by Keneshea et al. (5) based on their evaluation of the available vapor pressure data by a modified Σ approach.

Melting Data

Refer to the $NbCl_5(\ell)$ table.

Sublimation Data

The heat of sublimation, ΔHs°_{298}, is the difference between the ΔHf°_{298} values for $NbCl_5(g)$ and $NbCl_5(c)$. Four sublimation studies are summarized in the $NbCl_5(g)$ table.

References

1. H. Schäfer and F. Kahlenberg, Z. anorg. u. allgem. Chem. 305, 291 (1960).
2. P. Gross, C. Hayman, D. L. Levi, and G. L. Wilson, Trans. Faraday Soc. 56, 318 (1960).
3. S. A. Shchukarev, M. A. Oranskaya, and T. S. Shemyakina, Russ. J. Inorg. Chem. 5, 1036 (1960).
4. V. M. Amosov, Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met. 6, 103 (1963).
5. F. J. Keneshea, D. Cubicciotti, G. Withers, and H. Eding, J. Phys. Chem. 72, 1272 (1968).
6. V. I. Lavrentev and Ya. I. Gerassimov, At. Energy Rev. 1968, 7 (1968).
7. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
8. J. O. Hill, I. G. Worsley, and L. G. Hepler, Chem. Rev. 71, 127 (1971).
9. U. S. Natl. Bur. Std. Tech. Note 270-5, 1971.
10. JANAF Thermochemical Tables: $Nb_2O_5(c)$, 12-31-72; HCl(g), 9-30-64; $NbCl_5(g)$, 12-31-74.

Niobium Pentachloride ($NbCl_5$) Cl_5Nb

(Liquid) GFW = 270.1714

	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	35.350	62.373	62.373	.000	- 184.836	- 161.114	118.100
300	35.350	62.592	62.374	.065	- 184.819	- 160.967	117.264
400	53.740	75.275	63.922	4.541	- 183.017	- 153.213	83.712
500	51.760	87.061	67.423	9.819	- 180.485	- 146.059	63.842
600	49.330	96.290	71.494	14.878	- 178.224	- 139.392	50.773
700	46.470	103.685	75.584	19.671	- 176.260	- 133.080	41.549
800	43.167	109.680	79.484	24.157	- 174.634	- 127.028	34.702

Dec. 31, 1974

NIOBIUM PENTACHLORIDE ($NbCl_5$) (LIQUID) GFW = 270.1714 Cl_5Nb

$S^\circ_{298.15}$ = [62.373] gibbs/mol
Tm = 478.9 ± 1.5 K
Tb = 520.9 K

$\Delta Hf^\circ_{298.15}$ = -184.836 kcal/mol
ΔHm° = 8.097 ± 0.23 kcal/mol
ΔHv° = 12.466 kcal/mol

Heat of Formation

The heat of formation of $NbCl_5(\ell)$ is calculated from that of $NbCl_5(c)$ by adding ΔHm°, the heat of melting, and the enthalpy difference ($H_{478.9}-H_{298}$) between the crystal and liquid.

Heat Capacity and Entropy

The liquid phase heat capacity values are derived from the enthalpy equation reported by Keneshea et al. (5). The equation is used for the region 478.9 - 600 K, i.e. that region in which the saturation heat capacity and the heat capacity at constant pressure are essentially the same in value. This equation is used also to extrapolate to 700 K and to an assumed glass transition temperature at Tg = 350 K. Below Tg the heat capacity values are those of the crystal. S°_{298} is obtained in a manner analogous to that used for ΔHf°_{298}.

Melting Data

The adopted value of Tm is that reported by Keneshea et al. (5). This value, 205.7°C or 478.9 K, was obtained by visual observation on four different samples in evacuated capsules. Other values for Tm reported in the literature are: 205.3 ± 1.5°C (6), 204.8°C (4), 206.8 ± 0.3°C (3), 204.5°C(2), and 204.7°C (1). Earlier determinations of the melting point have been summarized by Schäfer and Pietruck (1) and Meyer et al. (3).

The adopted heat of fusion, ΔHm° = 8.097 ± 0.23 kcal/mol, is calculated as the difference at 478.9 K in the enthalpy equations for $NbCl_5(\ell)$ and $NbCl_5(c)$ as reported by Keneshea et al. (5). Meyer et al. (3), from an examination of the $NbCl_5$-$NbOCl_3$ system, reported a value of 8.30 ± 0.4 kcal/mol for ΔHm°. Voitovich et al. (4) studied the $NbCl_5$ - S_2Cl_2 system and calculated ΔHm° = 8.15 kcal/mol. These two latter values are in excellent agreement with our adopted value.

Johnson and Cubicciotti (6), in their study of the orthobaric densities of $NbCl_5$, discussed the possible molecular behavior of $NbCl_5$. The explanation served to explain the large entropy of melting, ΔSm° = 16.91 gibbs/mol. Based on currently available information, they suggested that between the melting point and about 650 K the substance changes from a dimeric solid to a monomeric liquid. This change was suggested to manifest itself in the unusually large volume change (27±2%, 6) and entropy of fusion and in the inverse curvature of the liquid density curve just above the melting point. For additional references, refer to the $NbCl_5(g)$ table.

Vaporization Data

T_b is calculated as that temperature for which ΔG°_r = 0 for the process $NbCl_5(\ell) = NbCl_5(g)$. ΔHv° is calculated as the difference between the ΔHf° values for $NbCl_5(g)$ and $NbCl_5(\ell)$ at Tb. Seven vaporization studies are summarized in the $NbCl_5(g)$ table. Sheka et al. (2) studied the vapor-liquid equilibrium in the $NbCl_5$-$POCl_3$ system and measured a boiling point (at 760 mm) of 521.7 K for pure $NbCl_5$. The vaporization studies discussed in the $NbCl_5(g)$ table which included the boiling point yielded normal boiling points (p = 760 mm) in the range 519.2 - 520.6 K. The normal boiling point should be lower than our calculated Tb which corresponds to f = 760 mm.

References

1. H Schäfer and C. Pietruck, Z. anorg. u. allgem. Chem. 267, 174 (1951).
2. I. A. Sheka, B. A. Voitovich, and L. A. Nisel'son, Russ. J. Inorg. Chem. 4, 813 (1959).
3. G. Meyer, J. F. Oosterom, and W. J. Van Oeversen, Rec. Trav. Chim. 80, 502 (1961).
4. B. A. Voitovich, A. S. Barabanova, and N. Kh. Tumanova, Russ. J. Inorg. Chem. 6, 1286 (1961).
5. F. J. Keneshea, D. Cubicciotti, G. Withers, and H. Eding, J. Phys. Chem. 72, 1272 (1963).
6. J. W. Johnson, and D. Cubicciotti, High Temp. Sci. 2, 9 (1970).

References for $NbCl_5(g)$

1. M. A. Opykhtina and N. A. Fleischer, Zh. Obshch. Khim. 7, 2016 (1937).
2. D. N. Tarasenkov and A. V. Komandin, Zh. Obshch. Khim. 10, 1319 (1940).
3. K. M. Alexander and F. Fairbrother, J. Chem. Soc. (London) 1949, S223 (1949).
4. J. B. Ainscough, R. J. W. Holt, and F. W. Trowse, J. Chem. Soc. (London) 1957, 1034 (1957).
5. W. 't Hart and G. Meyer, Rec. Trav. Chim. 83, 1233 (1964).
6. L. A. Nisel'son, A. I. Pustil'nik, and T. D. Sokolova, Russ. J. Inorg. Chem. 9, 574 (1964).
7. H. Schäfer and W. Pölert, Z. anorg. allg. Chem. 353, 78 (1967).
8. L. A. Reznitskii, Russ. J. Phys. Chem. 41, 737 (1967).
9. J. W. Johnson and D. Cubicciotti, High Temp. Sci. 2, 9 (1970).
10. J. W. Johnson, W. J. Silva, and D. Cubicciotti, High Temp. Sci 2, 20 (1970).
11. JANAF Thermochemical Tables: Nb(c), 12-31-73; $Cl_2(g)$, 9-30-65.
12. H. Skinner and L. Sutton, Trans. Faraday Soc. 36, 668 (1940).
13. A. Zalkin and D. E. Sands, Acta Crystallog. 11, 615 (1958); 12, 723 (1959).
14. J. Gaunt and J. B. Ainscough, Spectrochim. Acta 10, 52 (1957).
15. G. L. Carlson, Spectrochim. Acta 19A, 1291 (1963).
16. D. L. Kepert and R. S. Nyholm, J. Chem. Soc. (London) 1965, 2871 (1965).
17. R. A. Walton and B. J. Brisdon, Spectrochim. Acta 28A, 2489 (1967).
18. R. D. Werder, R. A. Frey, and H. H. Günthard, J. Chem. Phys. 47, 4159 (1967).
19. V. P. Spiridonov and G. V. Romanov, Vestn. Mosk. Univ., Khim. 23, 10 (1968).
20. V. P. Spiridonov and G. V. Romanov, Vestn. Mosk. Univ., Khim. 24, 65 (1969).
21. I. R. Beattie and G. A. Ozin, J. Chem. Soc. (London) A 1969, 1691 (1969).
22. S. P. So, J. Mol. Struct. 16, 311 (1973).

Niobium Pentachloride ($NbCl_5$) Cl_5Nb

(Ideal Gas) GFW = 270.1714

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	.000	.000	INFINITE	-6.296	-167.655	-167.655	INFINITE
100	19.251	70.114	119.736	-4.962	-168.251	-163.675	357.711
200	25.671	85.715	99.086	-2.674	-168.280	-159.060	173.813
298	28.451	96.557	96.557	.000	-168.100	-154.570	113.303
300	28.485	96.733	96.558	.053	-168.096	-154.486	112.543
400	29.782	105.128	97.693	2.974	-167.849	-149.986	81.949
500	30.457	111.853	99.875	5.989	-167.579	-145.550	63.620
600	30.846	117.444	102.351	9.056	-167.310	-141.170	51.421
700	31.088	122.218	104.856	12.153	-167.042	-136.835	42.722
800	31.249	126.381	107.292	15.271	-166.784	-132.539	36.208
900	31.361	130.068	109.622	18.402	-166.533	-128.272	31.149
1000	31.442	133.377	111.835	21.542	-166.292	-124.036	27.108
1100	31.502	136.376	113.932	24.689	-166.061	-119.821	23.806
1200	31.548	139.119	115.918	27.842	-165.842	-115.628	21.059
1300	31.585	141.646	117.801	30.999	-165.633	-111.452	18.737
1400	31.613	143.988	119.589	34.159	-165.435	-107.291	16.749
1500	31.636	146.170	121.289	37.321	-165.251	-103.145	15.028
1600	31.655	148.212	122.909	40.486	-165.080	-99.009	13.524
1700	31.671	150.132	124.454	43.652	-164.925	-94.881	12.198
1800	31.684	151.942	125.931	46.820	-164.789	-90.768	11.021
1900	31.696	153.656	127.346	49.989	-164.672	-86.655	9.968
2000	31.705	155.282	128.702	53.159	-164.579	-82.553	9.021
2100	31.714	156.829	130.005	56.330	-164.504	-78.456	8.165
2200	31.721	158.305	131.258	59.502	-164.457	-74.360	7.387
2300	31.727	159.715	132.465	62.674	-164.435	-70.263	6.676
2400	31.733	161.065	133.629	65.847	-164.443	-66.168	6.025
2500	31.737	162.361	134.752	69.021	-164.486	-62.073	5.426
2600	31.742	163.605	135.838	72.194	-164.566	-57.973	4.873
2700	31.746	164.803	136.889	75.369	-164.698	-53.873	4.361
2800	31.749	165.958	137.907	78.544	-171.192	-49.647	3.875
2900	31.752	167.072	138.893	81.719	-171.150	-45.309	3.415
3000	31.755	168.149	139.851	84.894	-171.115	-40.973	2.985
3100	31.757	169.190	140.780	88.070	-171.086	-36.635	2.583
3200	31.760	170.198	141.684	91.245	-171.066	-32.298	2.206
3300	31.762	171.176	142.563	94.422	-171.052	-27.961	1.852
3400	31.764	172.124	143.419	97.598	-171.043	-23.622	1.518
3500	31.765	173.045	144.252	100.774	-171.044	-19.292	1.205
3600	31.767	173.939	145.064	103.951	-171.050	-14.951	.908
3700	31.768	174.810	145.856	107.128	-171.063	-10.614	.627
3800	31.770	175.657	146.630	110.305	-171.081	-6.282	.361
3900	31.771	176.482	147.384	113.482	-171.107	-1.941	.109
4000	31.772	177.287	148.122	116.659	-171.140	2.396	-.131
4100	31.773	178.071	148.843	119.836	-171.175	6.732	-.359
4200	31.774	178.837	149.548	123.013	-171.218	11.069	-.576
4300	31.775	179.585	150.238	126.191	-171.263	15.409	-.783
4400	31.776	180.315	150.913	129.368	-171.313	19.760	-.981
4500	31.777	181.029	151.575	132.546	-171.367	24.095	-1.170
4600	31.778	181.728	152.222	135.724	-171.422	28.441	-1.351
4700	31.778	182.411	152.858	138.902	-171.482	32.791	-1.525
4800	31.779	183.080	153.480	142.080	-171.544	37.132	-1.691
4900	31.780	183.735	154.091	145.257	-171.609	41.486	-1.850
5000	31.780	184.377	154.690	148.435	-171.673	45.831	-2.003
5100	31.781	185.007	155.279	151.614	-171.737	50.189	-2.151
5200	31.781	185.624	155.856	154.792	-336.773	56.595	-2.379
5300	31.782	186.229	156.424	157.970	-336.911	64.155	-2.645
5400	31.782	186.823	156.981	161.148	-337.052	71.724	-2.903
5500	31.783	187.407	157.529	164.326	-337.199	79.300	-3.151
5600	31.783	187.979	158.068	167.505	-337.350	86.869	-3.390
5700	31.784	188.542	158.597	170.683	-337.509	94.438	-3.621
5800	31.784	189.095	159.118	173.861	-337.669	102.029	-3.845
5900	31.784	189.638	159.631	177.040	-337.836	109.604	-4.060
6000	31.785	190.172	160.136	180.218	-338.007	117.192	-4.209

Dec. 31, 1974

NIOBIUM PENTACHLORIDE ($NbCl_5$) (IDEAL GAS) GFW = 270.1714 CL_5NB

Point Group D_{3h}

$S^\circ_{298.15}$ = 96.56±0.75 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -167.7±2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -168.1±2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
394.0 (1)	[492.4] (2)
317.0 (1)	179.9 (2)
[414.1](1)	54.1 (2)
[143.5](1)	148.0 (2)

Bond Distance: Nb-Cl = 2.28±0.02 Å   σ = 6

Bond Angle: Cl*-Nb-Cl* = 120°   Cl*-Nb-Cl** = 90°   Cl**-Nb-Cl** = 180°

(* = equatorial ** = axial)

Product of the Moments of Inertia = $I_AI_BI_C$ = $1.053\times10^{-111}g^3cm^6$

Heats of Formation

The vapor pressures over $NbCl_5(c)$ and $NbCl_5(\ell)$ have been measured by seven investigators. The reported vapor pressures 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 = 803.5±2K and Pc = 48.2 atm. reported by Johnson et al. (9, 10) are used to calculate B. The corrected vapor pressures are used to calculate ΔHr°_{298} by both second and third law methods. By means of comparison, Nisel'son et al. (6) measured the orthobaric densities of $NbCl_5(\ell)$, as did Johnson et al. (9), and reported Tc = 807 K and Pc = 46 atm.

				ΔHr°_{298}, kcal/mol		drift
$NbCl_5(c) = NbCl_5(g)$	method	range, K	no. pts	2nd law	3rd law	gibbs/mol
Opykhtina and Fleisher (1)	transpiration	373-Tm	Eqn.	20.74	22.28	3.6
Tarasenkov and Komandin (2)	static	446-Tm	Eqn.	19.20	22.41	7.0
Alexander and Fairbrother (3)	static	402-Tm	7*	22.02±0.30	22.69±0.09	1.5±0.7
Schäfer and Pölert (7)	flow	351-384	25	22.71±0.10	22.52±0.03	-0.5±0.3
$NbCl_5(\ell) = NbCl_5(g)$						
Opykhtina and Fleisher (1)	transpiration	Tm-503	Eqn.	16.42	16.55	0.3
Tarasenkov and Komandin (2)	static	Tm-506	Eqn.	18.41	16.73	-3.4
	boiling pt	504-520	Eqn.	15.08	16.70	3.2
Alexander and Fairbrother (3)	static	Tm-528	13	16.98±0.05	16.91±0.01	-0.2±0.1
Ainscough et al. (4)	boiling pt	516-530	Eqn.	16.65	16.76	0.2
Hart and Meyer (5)	static	544-594	32*	16.45±0.08	16.79±0.03	0.6±0.1
Johnson et al. (10)	*boiling pt*	503-594	10	16.42±0.04	16.76±0.04	0.6±0.1

* One point is rejected due to statistical test.

The adopted value for ΔHf°_{298} of $NbCl_5(g)$ is -168.1±2.0 kcal/mol. This value is based on a rounded mean of the third law results for both the sublimation and vaporization studies and the appropriate ΔHf°_{298} value for the crystal or liquid.

Reznitskii (8) measured the heat of chlorination for Nb(c) and reported ΔH°_{680} = -169.1±1.0 kcal/mol for the reaction Nb(c) + 5/2 $Cl_2(g) = NbCl_5(g)$. Using auxiliary data for Nb(c) and $Cl_2(g)$ (11), we calculate ΔHf°_{298} = -170.1±1.0 kcal/mol for $NbCl_5(g)$.

Heat Capacity and Entropy

Monomeric $NbCl_5(g)$ was shown by Spiridonov and Romanov (19, 20), using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Nb-Cl bond lengths being equal within experimental uncertainty, Nb-Cl = 2.28 ± 0.2 Å. Skinner and Sutton (12) earlier used electron diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with the experimental results. We adopt the results of Spiridonov and Romanov (19, 20).

A normal coordinate treatment of $NbCl_5(g)$ in the Urey-Bradley force fields was performed by So (22) using the reported vibrational frequencies of Beattie and Ozin (21). This work by So (22) was intended to check the correctness of the reported *fundamental frequencies and predict those frequencies which had not been observed* (ω_3, ω_4, *and* ω_5). *The calculations of So (22)* suggested that the ω_5 value reported for $NbCl_5(g)$ was incorrect. Beattie and Ozin (21) had recorded the gas phase Raman spectra of $NbCl_5$, $NbBr_5$, $TaCl_5$ and $TaBr_5$ and has assigned ω_5 only in the case of $NbCl_5$. It was noted that this appeared only very weakly in the spectra. We adopt the results of So (22) which support the work of Beattie and Ozin (21) except for the ω_5 assignment.

There are many references in the literature to spectroscopic observations (IR and Raman) of $NbCl_5$ in the solid state, in organic solvents, and in matrices. Many problems arise in any attempt in relating the observed spectra. Niobium pentachloride was shown to be dimeric in the solid phase (13). There are also indications that $NbCl_5$ is dimeric in solution (15, 16, 17).

On the basis of these frequencies and the adopted structure, we calculate $S^\circ_{298.15}$ = 96.56±0.75 gibbs/mol, as was also calculated by So (22). This compares to a value of 90.29 gibbs/mol calculated by Gaunt and Ainscough (14) and 95.52 gibbs/mol by Werder et al. (18).

References

Refer to $NbCl_5(\ell)$ table.

CL_5NB

Tantalum Pentachloride ($TaCl_5$) (Crystal) GFW = 358.212

Cl_5Ta

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	35.350	53.000	53.000	.000	− 205.300	− 178.426	130.790
300	35.350	53.219	53.001	.065	− 205.283	− 178.260	129.862
400	35.350	63.388	54.387	3.600	− 204.435	− 169.383	92.547
500	35.350	71.276	57.006	7.135	− 203.656	− 160.709	70.246
600	35.350	77.721	59.537	10.670	− 202.929	− 152.189	55.435
700	35.350	83.171	62.877	14.205	− 202.235	− 143.788	44.893

Dec. 31, 1974

TANTALUM PENTACHLORIDE ($TaCl_5$) (CRYSTAL)

$S^\circ_{298.15}$ = [53.0±1.5]gibbs/mol
Tm = 489.7 ± 1.5 K

GFW = 358.212
ΔHf°_0 = unknown
$\Delta Hf^\circ_{298.15}$ = −205.3 ± 1.0 kcal/mol
ΔHm° = 8.4 ± 0.5 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 22.5 kcal/mol

Cl_5Ta

Heat of Formation

Gross et al. (3) measured the heat evolved in the reaction Ta(c) + 5/2 Cl_2(ℓ) = $TaCl_5$(c). Using their data for 6 runs we calculate ΔHf°_{298} = −205.6 kcal/mol for $TaCl_5$(c). Gal'chenko et al. (4, 5) also determined the heat of reaction for the direct chlorination of Ta(15 runs involving 2 samples). They reported ΔHf°_{298} = −205.05±0.18 kcal/mol. We adopt an intermediate value, ΔHf°_{298} = −205.3±1.0 kcal/mol, based on these two studies (3, 4, 5).

Schäfer and Kahlenberg (1) determined the heat of formation of $TaCl_5$(c) via calorimetric measurements of the heats of solution of Ta(c) and $TaCl_5$(c) in hydrofluoric acid. Their procedure involved eight steps and resulted in ΔHf°_{298} = −205.0 ± 0.3 kcal/mol. This is in good agreement with our adopted value. In the case of $NbCl_5$(c) [$TaCl_5$(c)] the ΔHf°_{298} value derived from the data of Schäfer and Kahlenberg (1, 2) is 0.6 kcal/mol [0.3 kcal/mol] more positive than that derived from the data of Gross et al. (3).

Heat Capacity and Entropy

The heat capacity for $TaCl_5$(c) is assumed to be the same as that for $NbCl_5$(c) (6). We adopt S°_{298} = 53.0 ± 1.5 gibbs/mol in order to reproduce the sublimation and vaporization data. Schäfer and Kahlenberg (1, 2) assumed a similar relationship based on a comparison with the corresponding values for the halides of Zr, Hf, and U.

Melting Data

Refer to the $TaCl_5$(ℓ) table.

Sublimation Data

The heat of sublimation is discussed in the $TaCl_5$(g) table(6). Seven sublimation studies are analyzed and lead to a third law result of ΔHs°_{298} = 22.5 kcal/mol.

References

1. H. Schäfer and F. Kahlenberg, Z. anorg. u. allgem. Chem. 294, 243 (1958).
2. H. Schäfer and F. Kahlenberg, Z. anorg. u. allgem. Chem. 305, 291 (1960).
3. P. Gross, C. Hayman, D. L. Levi, and G. L. Wilson, Trans. Faraday Soc. 56, 318 (1960).
4. G. L. Gal'chenko, D. A. Gedakyan, B. I. Timofiev, S. M. Skuratov, T. I. Serebryakova, and G. V. Samsonov, Dokl. Akad. Nauk SSSR 170, 132 (1966).
5. G. L. Gal'chenko, D. A. Gedakyan, B. I. Timofiev, Russ. J. Inorg. Chem. 13, 159 (1968).
6. JANAF Thermochemical Tables: $NbCl_5$(c), $TaCl_5$(g), 12-31-74.

Tantalum Pentachloride ($TaCl_5$) Cl_5Ta

(Liquid) GFW = 358.212

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	35.350	64.086	64.086	.000	− 199.414	− 175.845	128.898
300	35.350	64.305	64.086	.065	− 199.397	− 175.699	127.997
400	53.740	76.987	65.635	4.541	− 197.608	− 167.996	91.789
500	51.760	88.774	69.135	9.819	− 195.085	− 160.888	70.324
600	49.330	98.002	73.207	14.877	− 192.836	− 154.264	56.191
700	46.470	105.398	77.296	19.671	− 190.883	− 147.995	46.206
800	43.167	111.392	81.196	24.157	− 189.266	− 141.985	38.788

Dec. 31, 1974

TANTALUM PENTACHLORIDE ($TaCl_5$) (LIQUID) GFW = 358.212 CL5TA

$S^\circ_{298.15}$ = [64.085] gibbs/mol
Tm = 489.7 ± 1.5 K
Tb = 506.9 K
$\Delta Hf^\circ_{298.15}$ = −199.414 kcal/mol
ΔHm° = 8.4 ± 0.5 kcal/mol
ΔHv° = 12.673 kcal/mol

Heat of Formation

The heat of formation of $TaCl_5(\ell)$ is calculated from that of $TaCl_5(c)$ by adding ΔHm°, the heat of melting, and the enthalpy difference, ($H_{489.7}-H_{298}$) between the crystal and liquid.

Heat Capacity and Entropy

The liquid phase heat capacity is assumed to be identical to that for $NbCl_5(\ell)$ (4). As in the case of $NbCl_5(\ell)$, there is a glass transition assumed at 350 K. S°_{298} is obtained in a manner analogous to that used for ΔHf°_{298}.

Melting Data

We adopt Tm = 478.9 ± 1.5 K (216.5°C) based on the work by Schäfer and Pietruck (216.5°C, 1), Sheka et al. (216.5°C, 2), and Voitovich et al. (216.7°C, 3). Earlier reported melting points range between 204°C and 221°C and have been summarized by Schäfer and Pietruck (1).

The adopted heat of fusion, ΔHm° = 8.4 ± 0.5 kcal/mol, is based on the analysis of the S_2Cl_2-$TaCl_5$ system by Voitovich et al. (3). A similar study on the S_2Cl_2-$NbCl_5$ system (3) yielded a heat of melting for $NbCl_5$ which was within 0.063 kcal/mol of the result determined by drop calorimetry (4). The discussion of the molecular behavior of $NbCl_5$ (ℓ) (4) is assumed to also apply to $TaCl_5$: that is, between the melting point and ~650 K, the substance changes from a dimeric solid to a monomeric liquid.

Vaporization Data

Tb is calculated as that temperature for which ΔG°_r = 0 for the process $TaCl_5(\ell)$ = $TaCl_5(g)$. ΔHv° is calculated as the difference between the ΔHf° values for $TaCl_5(g)$ and $TaCl_5(\ell)$ at Tb. Three vaporization studies are summarized in the $TaCl_5(g)$ table (4). Sheka et al. (2) studied the vapor-liquid equilibrium in the $TaCl_5$-$POCl_3$ system and measured a boiling point (at 760 mm) of 507.3 K for pure $TaCl_5$. The vaporization studies discussed in the $TaCl_5(g)$ table which included the boiling point yielded normal boiling points (p = 760 mm) in the range 506.0 - 506.9 K. The normal boiling point should be lower than our calculated Tb which corresponds to f = 760 mm.

References

1. H. Schäfer and C. Pietruck, Z. anorg. u. allgem. Chem. 267, 174 (1951).
2. I. A. Sheka, B. A. Voitovich, and L. A. Nisel'son, Russ. J. Inorg. Chem. 4, 813 (1959).
3. B. A. Voitovich, A. S. Barabanova, and N. Kh. Tumanova, Russ. J. Inorg. Chem. 6, 1286 (1961).
4. JANAF Thermochemical Tables: $NbCl_5(\ell)$, $NbCl_5(g)$, $TaCl_5(g)$, 12-31-74.

Tantalum Pentachloride ($TaCl_5$) (Ideal Gas) GFW = 358.212

Cl_5Ta

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-6.422	-182.379	-182.379	INFINITE
100	19.805	71.767	122.181	-5.041	-182.976	-178.480	390.067
200	26.070	87.700	101.232	-2.706	-182.995	-173.948	190.081
298	28.713	98.675	98.675	.000	-182.800	-169.544	124.279
300	28.745	98.853	98.676	.053	-182.795	-169.462	123.453
400	29.953	107.309	99.820	2.995	-182.540	-165.056	90.183
500	30.575	114.066	102.017	6.025	-182.266	-160.715	70.248
600	30.931	119.675	104.505	9.102	-181.998	-156.430	56.980
700	31.153	124.461	107.023	12.207	-181.734	-152.190	47.516
800	31.300	128.631	109.469	15.330	-181.480	-147.989	40.429
900	31.401	132.324	111.807	18.465	-181.228	-143.817	34.923
1000	31.475	135.636	114.027	21.609	-180.983	-139.675	30.526
1100	31.530	138.639	116.130	24.760	-180.747	-135.556	26.932
1200	31.572	141.384	118.122	27.915	-180.522	-131.457	23.942
1300	31.604	143.913	120.010	31.074	-180.307	-127.377	21.414
1400	31.630	146.256	121.802	34.235	-180.102	-123.313	19.250
1500	31.651	148.439	123.506	37.399	-179.902	-119.264	17.377
1600	31.669	150.482	125.129	40.565	-179.708	-115.227	15.739
1700	31.683	152.402	126.677	43.733	-179.519	-111.200	14.296
1800	31.695	154.214	128.157	46.902	-179.342	-107.189	13.015
1900	31.705	155.928	129.574	50.072	-179.179	-103.181	11.869
2000	31.714	157.554	130.933	53.243	-179.035	-99.187	10.839
2100	31.721	159.102	132.237	56.415	-178.901	-95.199	9.908
2200	31.726	160.577	133.492	59.587	-178.789	-91.217	9.062
2300	31.733	161.988	134.701	62.760	-178.690	-87.236	8.289
2400	31.738	163.339	135.866	65.934	-178.611	-83.261	7.582
2500	31.743	164.634	136.991	69.108	-178.555	-79.290	6.932
2600	31.747	165.879	138.078	72.282	-178.519	-75.319	6.331
2700	31.750	167.078	139.130	75.457	-178.511	-71.352	5.776
2800	31.753	168.232	140.149	78.632	-178.534	-67.380	5.259
2900	31.756	169.347	141.137	81.808	-178.588	-63.412	4.779
3000	31.759	170.423	142.095	84.984	-178.680	-59.441	4.330
3100	31.761	171.465	143.026	88.160	-178.815	-55.464	3.910
3200	31.763	172.473	143.931	91.336	-178.998	-51.482	3.516
3300	31.765	173.450	144.810	94.512	-187.947	-47.380	3.138
3400	31.767	174.399	145.667	97.689	-188.138	-43.115	2.771
3500	31.768	175.320	146.501	100.865	-188.339	-38.852	2.426
3600	31.770	176.215	147.314	104.042	-188.545	-34.574	2.099
3700	31.771	177.085	148.107	107.219	-188.758	-30.293	1.789
3800	31.772	177.932	148.881	110.396	-188.976	-26.012	1.496
3900	31.773	178.758	149.636	113.574	-189.201	-21.717	1.217
4000	31.774	179.562	150.374	116.751	-189.433	-17.420	.952
4100	31.775	180.347	151.096	119.929	-189.668	-13.120	.699
4200	31.776	181.112	151.801	123.106	-189.911	-8.813	.459
4300	31.777	181.860	152.492	126.284	-190.156	-4.499	.229
4400	31.778	182.591	153.168	129.462	-190.405	-.170	.008
4500	31.779	183.305	153.829	132.639	-190.660	4.149	-.202
4600	31.779	184.003	154.478	135.817	-190.915	8.483	-.403
4700	31.780	184.687	155.113	138.995	-191.174	12.824	-.596
4800	31.781	185.356	155.736	142.173	-191.436	17.161	-.781
4900	31.781	186.011	156.348	145.351	-191.701	21.517	-.960
5000	31.782	186.653	156.947	148.530	-191.965	25.866	-1.131
5100	31.782	187.283	157.536	151.708	-192.229	30.232	-1.296
5200	31.783	187.900	158.114	154.886	-192.496	34.598	-1.454
5300	31.783	188.505	158.682	158.064	-192.765	38.961	-1.607
5400	31.784	189.099	159.239	161.243	-193.034	43.336	-1.754
5500	31.784	189.682	159.788	164.421	-193.304	47.720	-1.896
5600	31.784	190.255	160.327	167.599	-193.573	52.100	-2.033
5700	31.785	190.818	160.857	170.778	-193.844	56.483	-2.166
5800	31.785	191.370	161.378	173.956	-370.261	61.311	-2.310
5900	31.785	191.914	161.891	177.135	-370.531	68.746	-2.547
6000	31.786	192.448	162.396	180.313	-370.804	76.198	-2.775

Dec. 31, 1974

TANTALUM PENTACHLORIDE ($TaCl_5$) (IDEAL GAS) GFW = 358.212

CL_5TA

Point Group D_{3h}

$S°_{298.15}$ = 98.68±0.75 gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -182.4 ± 2.0 kcal/mol

$\Delta Hf°_{298.15}$ = -182.8 ± 2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
406.0 (1)	[458.0] (2)
324.0 (1)	180.9 (2)
[377.2](1)	53.9 (2)
[112.1](1)	127.0 (2)

Bond Distances: Ta-Cl = 2.27±0.02 Å   σ = 6

Bond Angle: Cl*-Ta-Cl* = 120°   Cl*-Ta-Cl** = 90°   Cl**-Ta-Cl** = 180°

(* = equatorial   ** = axial)

Product of the Moments of Inertia: $I_AI_BI_C = 1.0257 \times 10^{-111}\ g^3cm^6$

Heat of Formation

The vapor pressures over $TaCl_5$(c) and $TaCl_5$(ℓ) have been measured by eight investigators. The reported vapor pressures are corrected for vapor non-ideality by means of the equation $\Delta G°/T = -R\ln P - BP/T$. The Berthelot equation of state and critical constants Tc = 767 K and Pc = 43 atm reported by Nisel'son et al. (6) are used to calculate B. The corrected vapor pressures are used to calculate $\Delta Hr°_{298}$ by both second and third law methods.

				$\Delta Hr°_{298}$, kcal/mol		drift
$TaCl_5(c) = TaCl_5(g)$	method	range, K	no. pts.	2nd law	3rd law	gibbs/mol
Opykhtina and Fleischer (1)	transpiration	393-Tm	Eqn	23.12	22.46	-1.5
Tarasenkov and Komandin (2)	static	301-475	Eqn	20.63	22.26	4.3
Alexander and Fairbrother (3)	static	412-Tm	10*	22.94±0.09	22.76±0.03	-0.4±0.2
Shchukarev and Kurbanov (5)	membrane	425-Tm	Eqn	23.46	22.67	-1.7
Schäfer and Pölert (7)	flow	350-385	17	22.75±0.06	22.53±0.02	-0.6±0.2
Saeki et al. (8)	static	363-Tm	Eqn.	22.31	22.53	0.6
Brink and Stevenson (9)	transpiration	431-473	28	21.80±0.20	22.59±0.08	1.8±0.4
$TaCl_5(ℓ) = TaCl_5(g)$						
Alexander and Fairbrother (3)	static	Tm-511	6*	17.17±0.13	16.79±0.01	-0.8±0.3
Ainscough et al. (4)	boiling pt.	502-513	Eqn	16.73	16.62	-0.2
Saeki et al. (8)	static	490-505	Eqn	17.17	16.66	-1.0

* One point rejected due to a statistical test.

The adopted value for $\Delta Hf°_{298}$ of $TaCl_5$(g) is -182.8±2.0 kcal/mol. This value is calculated using the rounded mean third law result for the seven sublimation studies, $\Delta Hs°_{298}$ = 22.5 kcal/mol. The rounded mean third law result for the three vaporization studies leads to a $\Delta Hf°_{298}$ value for the gas which is 0.1 kcal/mol more positive.

Heat Capacity and Entropy

Monomeric $TaCl_5$(g) was shown by Spiridonov and Romanov (15, 16), using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Ta-Cl bond lengths being equal within experimental uncertainty, Ta-Cl = 2.27±0.02 Å. Skinner and Sutton (10) earlier used election diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with their experimental results. We adopt the results of Spiridonov and Romanov (15, 16).

A normal coordinate treatment of $TaCl_5$(g) in the Urey-Bradley force fields was performed by So (18) using the reported vibrational frequencies of Beattie and Ozin (17). This work by So (18) was intended to check the correctness of the reported fundamental frequencies and predict those frequencies which had not been observed (ω_3, ω_4, and ω_5). Beattie and Ozin (17) had recorded the gas phase Raman spectra of $NbCl_5$, $NbBr_5$, $TaCl_5$, and $TaBr_5$. We adopt the results of So (18) which support the work of Beattie and Ozin (17).

There are many references in the literature to spectroscopic observations (IR and Raman) of $TaCl_5$ in the solid state and in organic solvents. Many problems arise in any attempt in relating the observed spectra. Tantalum pentachloride was shown to be dimeric in the solid phase (11), while there are indications that it also dimeric in solution (12, 13, 14).

References

1. M. A. Opykhtina and N. A. Fleischer, Zh. Obshch. Khim. 7, 2016 (1937).
2. D. N. Taransenkov and A. V. Komandin, Zh. Obshch. Khim. 10, 1319 (1940).
3. K. M. Alexander and F. Fairbrother, J. Chem. Soc. (London) 1949, S223 (1949).
4. J. B. Ainscough, R. J. W. Holt, and F. W. Trowse, J. Chem. Soc. (London) 1957, 1034 (1957).
5. S. A. Shchukarev and A. R. Kurbanov, Vestn. Leningr. Univ. 17, No. 10, Ser. Fiz. i Khim. No. 2, 144 (1962).
6. L. A. Nisel'son, A. I. Prestil'nik, and T. D. Sokolova, Russ. J. Inorg. Chem. 9, 574 (1964).
7. H. Schäfer and W. Pölert, Z. anorg. u. allgem. Chem. 353, 78 (1967).
8. Y. Saeki, R. Matsuzaki, M. Yanai, and K. Funaki, Kogyo Kagaku Zasshi 71, 350 (1968).
9. J. M. Brink and F. D. Stevenson, J. Chem. Eng. Data 17, 143 (1972).
10. H. Skinner and L. Sutton, Trans. Faraday Soc. 36, 668 (1940).
11. A. Zalkin and D. E. Sands, Acta Crystallog. 11, 615 (1958); 12, 723 (1959).
12. G. L. Carlson, Spectrochim. Acta 19A, 1291 (1963).
13. D. L. Kepert and R. S. Nyholm, J. Chem. Soc. (London) 1965, 2871 (1965).
14. R. A. Walton and B. J. Brisdon, Spectrochim. Acta 28A, 2489 (1967).
15. V. P. Spiridonov and G. V. Romanov, Vestn. Mosk. Univ., Khim. 23, 10 (1968).
16. V. P. Spiridonov and G. V. Romanov. Vestn. Mosk. Univ., Khim. 24, 65 (1969).
17. I. R. Beattie and G. A. Ozin, J. Chem. Soc (London) A 1969, 1691 (1969).
18. S. P. So, J. Mol. Struct. 16, 311 (1973).

CL_5TA

FLUOROSILANE (SiH_3F)
(IDEAL GAS) GFW=50.1084

FH3SI

	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	-2.613	-87.753	-87.753	INFINITE
100	7.963	47.252	65.428	-1.818	-88.508	-87.448	191.118
200	8.948	52.963	57.905	-0.988	-89.214	-86.138	94.128
298	11.280	56.952	56.952	0.000	-90.000	-84.460	61.911
300	11.326	57.022	56.953	0.021	-90.015	-84.426	61.504
400	13.668	60.611	57.426	1.274	-90.695	-82.456	45.052
500	15.590	63.875	58.394	2.740	-91.224	-80.332	35.113
600	17.156	66.860	59.560	4.380	-91.618	-78.116	28.454
700	18.447	69.605	60.802	6.162	-91.900	-75.840	23.678
800	19.516	72.140	62.063	8.062	-92.092	-73.534	20.088
900	20.401	74.492	63.315	10.059	-92.213	-71.204	17.291
1000	21.135	76.680	64.543	12.137	-92.278	-68.867	15.051
1100	21.745	78.724	65.740	14.282	-92.303	-66.524	13.217
1200	22.253	80.639	66.903	16.483	-92.297	-64.180	11.689
1300	22.680	82.437	68.029	18.730	-92.272	-61.839	10.396
1400	23.039	84.132	69.120	21.017	-92.235	-59.498	9.288
1500	23.344	85.732	70.174	23.336	-92.195	-57.159	8.328
1600	23.604	87.247	71.194	25.684	-92.157	-54.828	7.489
1700	23.827	88.685	72.181	28.056	-104.113	-52.388	6.735
1800	24.020	90.052	73.136	30.448	-104.027	-49.349	5.992
1900	24.187	91.355	74.061	32.859	-103.937	-46.314	5.327
2000	24.332	92.600	74.957	35.285	-103.847	-43.282	4.730
2100	24.460	93.790	75.826	37.725	-103.758	-40.257	4.190
2200	24.573	94.931	76.669	40.177	-103.671	-37.236	3.699
2300	24.672	96.025	77.487	42.639	-103.585	-34.217	3.251
2400	24.761	97.077	78.281	45.111	-103.502	-31.200	2.841
2500	24.840	98.090	79.053	47.591	-103.425	-28.194	2.465
2600	24.910	99.065	79.804	50.078	-103.349	-25.183	2.117
2700	24.974	100.007	80.535	52.573	-103.278	-22.180	1.795
2800	25.031	100.916	81.247	55.073	-103.211	-19.178	1.497
2900	25.083	101.795	81.940	57.579	-103.147	-16.173	1.219
3000	25.130	102.646	82.617	60.089	-103.089	-13.181	0.960
3100	25.173	103.471	83.276	62.605	-103.032	-10.186	0.718
3200	25.212	104.271	83.920	65.124	-102.983	-7.189	0.491
3300	25.248	105.047	94.546	67.647	-102.938	-4.194	0.278
3400	25.281	105.802	85.162	70.173	-102.896	-1.206	0.077
3500	25.311	106.535	85.763	72.703	-102.862	1.787	-0.112
3600	25.338	107.248	86.349	75.235	-194.793	7.034	-0.427
3700	25.364	107.943	86.924	77.771	-194.671	12.639	-0.747
3800	25.388	108.620	87.486	80.308	-194.552	18.242	-1.049
3900	25.410	109.279	88.036	82.848	-194.443	23.837	-1.336
4000	25.430	109.923	88.575	85.390	-194.338	29.435	-1.608
4100	25.449	110.551	89.104	87.934	-194.239	35.024	-1.867
4200	25.467	111.165	89.622	90.480	-194.147	40.617	-2.114
4300	25.483	111.764	90.130	93.027	-194.059	46.204	-2.348
4400	25.499	112.350	90.628	95.576	-193.978	51.788	-2.572
4500	25.513	112.923	91.117	98.127	-193.903	57.374	-2.786
4600	25.527	113.484	91.597	100.679	-193.832	62.960	-2.991
4700	25.539	114.033	92.069	103.232	-193.770	68.544	-3.187
4800	25.551	114.571	92.532	105.787	-193.710	74.123	-3.375
4900	25.562	115.098	92.987	108.343	-193.657	79.704	-3.555
5000	25.573	115.615	93.435	110.899	-193.610	85.275	-3.727
5100	25.583	116.121	93.875	113.457	-193.568	90.859	-3.894
5200	25.592	116.618	94.307	116.016	-193.532	96.434	-4.053
5300	25.601	117.105	94.733	118.576	-193.500	102.015	-4.207
5400	25.610	117.584	95.151	121.136	-193.476	107.582	-4.354
5500	25.617	118.054	95.564	123.697	-193.456	113.158	-4.496
5600	25.625	118.516	95.969	126.260	-193.443	118.734	-4.634
5700	25.632	118.969	96.369	128.822	-193.435	124.313	-4.766
5800	25.639	119.415	96.762	131.386	-193.433	129.884	-4.894
5900	25.645	119.854	97.150	133.950	-193.437	135.456	-5.018
6000	25.652	120.285	97.532	136.515	-193.445	141.027	-5.137

Dec. 31, 1960; June 30, 1976

FLUOROSILANE (SiH_3F) (IDEAL GAS) GFW = 50.1084

Point Group C_{3v}
$S^\circ_{298.15}$ = 56.95 ± 0.2 gibbs/mol
Ground State Quantum Weight = [1]

ΔH°_0 = [-88 ± 5] kcal/mol
$\Delta H^\circ_{298.15}$ = -90 ± 5 kcal/mol

FH3SI

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2206(1)	2209(2)
991(1)	961(2)
875(1)	728(2)

Bond Distances: Si-H = 1.486 Å Si-F = 1.593 Å σ = 3
Bond Angles: H-Si-H = 110.43° H-Si-F = 108.50°
Product of the Moments of Inertia: $I_AI_BI_C = 3.4235 \times 10^{-116}\ g^3\ cm^6$

Heat of Formation

There are no reported experimental studies leading to the heat of formation of $SiH_3F(g)$. We estimate this value via a linear interpolation between the established ΔHf°_{298} values of $SiH_4(g)$ and $SiF_4(g)$(1). The reasonableness of this approach has been demonstrated by Lapidus et al. (2), Hunt and Sirtl (3), and Seiter and Sirtl (4). Lapidus et al. (2) examined the trends in the thermodynamic properties of halogenated silanes and methanes. Hunt and Sirtl (3) and Seiter and Sirtl (4) studied the chlorinated silanes and proposed a linear ΔHf relationship within the sequence $SiH_4(g)$ to $SiCl_4(g)$.

Heat Capacity and Entropy

The adopted vibrational frequencies are from the gas phase infrared spectra of SiH_3F and SiD_3F as documented by Robiette et al. (5). Except for ω_4 and ω_5, these values are within ±3 cm^{-1} of those suggested in the compilation by Shimanouchi (6). In particular, based on earlier work, Shimanouchi (6) suggested $\omega_4 = 2196\ cm^{-1}$ and $\omega_5 = 956\ cm^{-1}$. The work of Robiette et al. (5) is judged to yield more accurate frequencies than the earlier work.

The adopted bond angles and bond distances are obtained from the microwave spectra study on SiH_3F and various isotopic derivatives by Kewley et al. (7). This work is deemed more accurate than earlier studies (8-11). The individual moments of inertia are calculated to be $I_A = 0.997 \times 10^{-39}\ g\ cm^2$ and $I_B = I_C = 5.860 \times 10^{-39}\ g\ cm^2$.

References

1. JANAF Thermochemical Tables: $SiH_4(g)$ and $SiF_4(g)$, 6-30-76.
2. I. I. Lapidus, L. A Nisel'son, and A. L. Seifer in "Thermophysical Properties of Gases and Liquids," No. 1, V. A. Rabinovich, Ed., Israel Program for Scientific Translations, Jerusalem, 1970, pp. 102-135 [Translated from Russian].
3. L. P. Hunt and E. Sirtl, J. Electrochem. Soc. 119, 1741 (1972).
4. H. Seiter and E. Sirtl, Z. Naturforsch. 21a, 1956 (1966).
5. A. G. Robiette, G. J. Cartwright, A. R. Hoy, and I. M. Mills, Mol. Phys. 20, 541 (1971).
6. T. Shimanouchi, J. Phys. Chem. Ref. Data 1, 189 (1972).
7. R. Kewley, P. M. McKinney, and A. G. Robiette, J. Mol. Spectrosc. 34, 390 (1970).
8. A. H. Sharbaugh, V. G. Thomas, and B. S. Pritchard, Phys. Rev. 78, 64 (1950).
9. B. Bak, J. Bruhn, and J. Rastrup-Andersen, J. Chem. Phys. 21, 752 (1953).
10. B. Bak, J. Bruhn, and J. Rastrup-Andersen, Acta Chemica Scandanavica 8, 459 (1954).
11. C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

MAGNESIUM MONOFLUORIDE (MGF) FMG
(IDEAL GAS) GFW=43.3034

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	-2.143	-56.492	-56.492	INFINITE
100	6.965	44.914	59.394	-1.448	-56.299	-58.528	127.913
200	7.281	49.811	53.510	-0.740	-56.502	-60.803	66.443
298	7.784	52.814	52.814	0.000	-56.600	-62.794	46.030
300	7.793	52.862	52.814	0.014	-56.604	-62.833	45.774
400	8.173	55.159	53.124	0.814	-56.803	-64.880	35.449
500	8.420	57.012	53.723	1.644	-57.018	-66.874	29.231
600	8.583	58.562	54.403	2.495	-57.252	-68.825	25.069
700	8.695	59.894	55.095	3.359	-57.507	-70.732	22.084
800	8.776	61.061	55.769	4.233	-57.791	-72.604	19.834
900	8.837	62.098	56.416	5.114	-58.109	-74.436	18.076
1000	8.885	63.032	57.032	6.000	-60.584	-76.051	16.621
1100	8.924	63.880	57.616	6.891	-60.942	-77.581	15.414
1200	8.957	64.658	58.171	7.785	-61.323	-79.078	14.402
1300	8.985	65.376	58.698	8.682	-61.731	-80.540	13.540
1400	9.009	66.043	59.199	9.582	-92.528	-81.492	12.721
1500	9.031	66.666	59.675	10.484	-92.579	-80.701	11.758
1600	9.051	67.249	60.132	11.388	-92.629	-79.909	10.915
1700	9.070	67.798	60.567	12.294	-92.679	-79.111	10.170
1800	9.088	68.317	60.983	13.202	-92.729	-78.313	9.508
1900	9.104	68.809	61.382	14.111	-92.778	-77.510	8.916
2000	9.120	69.276	61.765	15.022	-92.827	-76.705	8.382
2100	9.135	69.722	62.134	15.935	-92.876	-75.899	7.899
2200	9.149	70.147	62.488	16.849	-92.926	-75.088	7.459
2300	9.163	70.554	62.830	17.765	-92.974	-74.275	7.058
2400	9.177	70.944	63.160	18.682	-93.023	-73.463	6.690
2500	9.191	71.319	63.479	19.601	-93.073	-72.646	6.351
2600	9.204	71.680	63.788	20.520	-93.123	-71.828	6.038
2700	9.217	72.028	64.086	21.441	-93.174	-71.008	5.748
2800	9.230	72.363	64.376	22.364	-93.224	-70.188	5.478
2900	9.243	72.687	64.657	23.287	-93.275	-69.362	5.227
3000	9.256	73.001	64.930	24.212	-93.329	-68.539	4.993
3100	9.268	73.304	65.195	25.138	-93.383	-67.711	4.774
3200	9.281	73.599	65.453	26.066	-93.439	-66.883	4.566
3300	9.294	73.885	65.704	26.995	-93.496	-66.052	4.374
3400	9.307	74.162	65.949	27.925	-93.557	-65.217	4.192
3500	9.320	74.432	66.188	28.856	-93.620	-64.384	4.020
3600	9.334	74.695	66.420	29.789	-93.687	-63.546	3.858
3700	9.348	74.951	66.647	30.723	-93.758	-62.707	3.704
3800	9.362	75.200	66.869	31.658	-93.833	-61.867	3.558
3900	9.376	75.444	67.086	32.595	-93.912	-61.028	3.420
4000	9.391	75.681	67.298	33.533	-93.997	-60.182	3.288
4100	9.406	75.913	67.505	34.473	-94.089	-59.336	3.163
4200	9.422	76.140	67.708	35.415	-94.186	-58.489	3.043
4300	9.439	76.362	67.907	36.358	-94.290	-57.637	2.929
4400	9.456	76.579	68.101	37.302	-94.401	-56.782	2.820
4500	9.473	76.792	68.292	38.249	-94.520	-55.926	2.716
4600	9.492	77.000	68.479	39.197	-94.647	-55.066	2.616
4700	9.511	77.205	68.663	40.147	-94.783	-54.204	2.521
4800	9.531	77.405	68.843	41.099	-94.929	-53.337	2.429
4900	9.551	77.602	69.020	42.053	-95.084	-52.470	2.340
5000	9.573	77.795	69.193	43.010	-95.248	-51.599	2.255
5100	9.595	77.985	69.364	43.968	-95.424	-50.729	2.174
5200	9.618	78.171	69.531	44.929	-95.610	-49.847	2.095
5300	9.641	78.355	69.696	45.892	-95.807	-48.962	2.019
5400	9.666	78.535	69.858	46.857	-96.017	-48.082	1.946
5500	9.691	78.713	70.017	47.825	-96.238	-47.191	1.875
5600	9.718	78.888	70.174	48.795	-96.472	-46.297	1.807
5700	9.745	79.060	70.329	49.768	-96.718	-45.395	1.741
5800	9.772	79.230	70.481	50.744	-96.977	-44.497	1.677
5900	9.801	79.397	70.630	51.723	-97.251	-43.587	1.615
6000	9.830	79.562	70.778	52.704	-97.538	-42.680	1.555

Dec. 31, 1960; June 30, 1964; March 31, 1967;
Dec. 31, 1975; June 30, 1976

MAGNESIUM MONOFLUORIDE (MgF) (IDEAL GAS) GFW = 43.3034 FMG

Symmetry Number = 1

$S^\circ_{298.15}$ = 52.814 ± 0.02 gibbs/mol

ΔHf°_0 = −56.5 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −56.6 ± 2.0 kcal/mol

Electronic Levels 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}
$X^2\Sigma^+$	0	2	1.7498	0.51630	0.00466	719.56	4.91
$A^2\Pi$	27829.60	4	1.7485	0.51711	0.00324	743.89	3.95
$B^2\Sigma^+$	37187.45	2	1.7183	0.53542	0.00507	759.94	5.57
$C^2\Sigma^+$	42589.64	2	1.6986	0.54792	0.00445	820.77	5.01

Heat of Formation

We adopt D°_{298}(MgF) = 110.7±2.0 kcal/mol from which we calculate ΔHf°_{298} (MgF,g) = −56.6±2.0 kcal/mol. The selected value of D°_{298} is derived from a third law analysis of three sets of mass spectral-equilibrium data reported by Murad et al. (1) and Hildenbrand (2). Our analyses are summarized below. Also included in the analysis are independent mass spectrometer-equilibrium measurements on MgF(g) by Ehlert (3) and Ehlert et al. (4).

Source	Reaction	No. of Points	Temp. Range K	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298} [c] kcal/mol	D°_{298} kcal/mol
Murad et al.(1)	(A)	4	1546-1585	6.2	5.6[b]±1.3	-0.4±26	-57.5±2.0	111.6
Hildenbrand(2) Set 1	(B)	4	1280-1345	22.1	25.87±0.7	2.9±8.7	-56.3±0.8	110.4
Set 2	(B)	7	1413-1493	24.3	26.58±0.2	1.6±3.7	-55.9±0.7	110.0
Ehlert(3)	-(B)	5	1205-1253	-90.0	-31.5±2.1	47±18	-53.5±1.5	107.6
Ehlert et al.(4)	(C)	5	1238-1301	63.0	47.6±2.3	-12.2±26	-53.7±2.0	107.8
Ehlert et al.(4)	(D)	8[a]	1207-1253	-91.9	-126.7±1.8	-28.3±17	-53.4±1.0	107.5

Reactions: (A) $Tl(g) + MgF(g) = TlF(g) + Mg(g)$ (B) $Mg(g) + MgF_2(g) = 2MgF(g)$ (C) $AlF_3(g) + 2Mg(g) = AlF(g) + 2MgF(g)$
(D) $2MgF(g) = Mg(g) + MgF_2(c)$

[a] One point rejected due to failure of a statistical test.

[b] Free-energy functions (FEF) for TlF(g) are calculated from spectral data tabulated by Rosen (5); FEF for Tl(g) are taken from the compilation of Hultgren (6).

[c] Third Law Values; all ancillary ΔHf°_{298} from JANAF Thermochemical Table (8) except for Tl and TlF (7).

We dismiss the measurements of Ehlert (3) and Ehlert et al. (4) since our analyses show that their equilibrium data most likely contain temperature dependent errors. Furthermore, their results (3, 4) yield D° values which are less than that predicted by the Rittner ionic model. Krasnov and Karaseva (9) have applied this potential function to all the alkaline earth monohalides and found that it establishes a lower limit for D°. Recalculation of their results (9) for MgF using a more recent value for the electron affinity of F^- (8) sets D°_{298} (MgF) ≥ 110.4 kcal/mol. Application of this ionic model to MgF is justified since the spin densities calculated from the ESR spectra (10) of matrix-isolated MgF show that the molecule is indeed highly ionic.

Trends in the well-established values of the ratio $D^\circ_{298}(MX)/\Delta Ha^\circ_{298}(MX_2)$ for the majority of the alkaline earth halides (8) suggests a value for MgF/MgF_2 which is less than or equal to 0.45. This sets the upper limit of D°_{298}(MgF) at 111 kcal/mol when $\Delta Ha^\circ_{298}(MgF_2)$ = 246.7 kcal/mol (8). If $MgF_2(g)$ is linear then the maximum D°_{298} value increases to 112.6 kcal/mol, suggesting a possible uncertainty in the adopted D° of ±2 kcal/mol. Our adopted results give $D^\circ_{298}(MgF)/\Delta Ha^\circ_{298}(MgF_2) = 0.44_9$.

Our selected thermochemical D°_{298} value converted to 0 K is 4.76 eV (109.8 kcal/mol). Other values for D°_0 which were considered but believed less reliable are (all in eV) 4.0 (11), 5.0 or 4.7 (11), and 4.2 (12). These spectroscopic values have been derived from linear Birge-Sponer extrapolations of the ground state ($X^2\Sigma^+$) and first excited state ($^2\Pi$) vibrational levels. We obtain $D^\circ_0 = 3.2_2$ eV from a linear Birge-Sponer extrapolation with our adopted ground state vibrational constants. This value adjusts to 3.59 eV when corrected for the ionicity (2) of the Mg-F bond. The corrected D°_0 value is 1.2 eV less than the thermochemical result. This discrepancy is most likely due to the use of an inaccurate value for the anharmonic constant, $\omega_e x_e$, in the Birge-Sponer extrapolation. The use of lower reported values (12, 15) for $\omega_e x_e$ brings the spectroscopic and thermochemical D°_0 values into much better agreement but leaves the thermodynamic functions for MgF unaltered (See Heat Capacity and Entropy section for further discussion). In addition, Singh et al. (13) have employed a method to fit an electronegative potential energy function to the experimental potential energy curves which yields D°_0 = 4.45 eV. This value agrees with our results within probable error limits.

Heat Capacity and Entropy

The electronic levels and vibrational-rotational constants are taken from the compilation of Rosen (5). Values of these constants have been tabulated for $Mg^{24}F$ and are corrected for the natural isotopic abundances of magnesium. The value of α_e listed by Rosen for the $C^2\Sigma^+$ state is incorrect. The rotational constants are based on an analysis (14) of the rotational structure in the bands of the A-X, B-X, and C-X systems. Barrow and Beale (14) used the Pekeris relation (12) to calculate $\omega_e x_e$ values from their spectroscopic α_e's. These $\omega_e x_e$ values were combined with $\Delta G_{1/2}$ values to give ω_e. These estimates of ω_e and $\omega_e x_e$ differ somewhat from those obtained from a vibrational analysis (15) of band head measurements. However, thermodynamic functions calculated with the alternate set of vibrational constants are not significantly different from those adopted here. The uncertainty in the $\omega_e x_e$ values is large, probably near ±1 cm^{-1}. Observed electronic levels (15) above 50000 cm^{-1} are not included since these have a negligible effect. The partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-C_2\varepsilon_i/T)$ is used to calculate the thermodynamic functions with first-order anharmonic corrections included for Qr and Qv.

References

1. E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. 45, 263 (1966).
2. D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).
3. T. C. Ehlert, Ph.D. Thesis, University of Wisconsin, 1963.
4. T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964).
5. B. Rosen, ed., "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, New York, 1970.
6. R. Hultgren et al., "Selected Values of the Thermodynamic Properties of the Elements", Am. Soc. for Metals, Ohio, 1973.
7. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
8. JANAF Thermochemical Tables: Mg(g), 9-30-62; MgF_2(c,g), 6-30-75; AlF_3(g), 6-30-70; AlF(g), 12-31-75; F^-(g), 12-31-75.
9. K. S. Krasnov and N. V. Karaseva, Optics and Spectroscopy 19, 14 (1965).
10. L. B. Knight, Jr., W. C. Easley, and W. Weltner, Jr., J. Chem. Phys. 54, 322 (1971).
11. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1968.
12. G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edition, D. Van Nostrand Company, Inc., New York, 1950.
13. O. N. Singh, B. P. Asthana, and O. N. Singh, Spectrosc. Lett. 7, 175 (1974).
14. R. F. Barrow and J. R. Beale, Proc. Phys. Soc. 91, 483 (1967).
15. M. M. Novikov and L. V. Gurvich, Zh. Prikl. Spectrosk. 14, 820 (1971).

FMG

MAGNESIUM MONOFLUORIDE UNIPOSITIVE ION (MgF^+) FMG+

(IDEAL GAS) GFW=43.3029

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	7.793	51.438	51.438	.000	122.440	115.168	-84.421
300	7.802	51.487	51.438	.014	122.445	115.123	-83.667
400	8.267	53.795	51.750	.818	122.747	112.636	-61.542
500	8.812	55.695	52.354	1.671	123.051	110.075	-48.114
600	9.533	57.363	53.052	2.586	123.379	107.448	-39.138
700	10.374	58.895	53.779	3.581	123.751	104.765	-32.709
800	11.200	60.335	54.509	4.661	124.170	102.024	-27.872
900	11.881	61.695	55.233	5.816	124.623	99.229	-24.096
1000	12.347	62.973	55.944	7.030	122.972	96.564	-21.104
1100	12.593	64.163	56.637	8.278	123.470	93.898	-18.656
1200	12.651	65.262	57.311	9.542	123.954	91.187	-16.607
1300	12.572	66.273	57.962	10.804	124.408	88.438	-14.868
1400	12.405	67.199	58.589	12.053	94.457	86.135	-13.446
1500	12.189	68.047	59.192	13.283	95.232	85.514	-12.459
1600	11.955	68.827	59.770	14.490	95.980	84.840	-11.589
1700	11.720	69.544	60.324	15.674	96.705	84.123	-10.815
1800	11.495	70.208	60.855	16.835	97.405	83.362	-10.121
1900	11.287	70.824	61.364	17.974	98.083	82.563	-9.497
2000	11.098	71.398	61.851	19.093	98.738	81.730	-8.931
2100	10.930	71.935	62.319	20.194	99.373	80.861	-8.415
2200	10.781	72.440	62.767	21.279	99.992	79.967	-7.944
2300	10.650	72.916	63.198	22.351	100.596	79.044	-7.511
2400	10.535	73.367	63.613	23.410	101.186	78.093	-7.111
2500	10.436	73.795	64.012	24.458	101.763	77.118	-6.742
2600	10.350	74.203	64.396	25.498	102.329	76.122	-6.399
2700	10.276	74.592	64.766	26.529	102.886	75.104	-6.079
2800	10.213	74.964	65.124	27.553	103.435	74.063	-5.781
2900	10.159	75.322	65.469	28.572	103.975	73.007	-5.502
3000	10.113	75.665	65.804	29.585	104.507	71.928	-5.240
3100	10.075	75.996	66.127	30.595	105.033	70.833	-4.994
3200	10.043	76.316	66.440	31.600	105.552	69.721	-4.762
3300	10.017	76.624	66.744	32.603	106.065	68.594	-4.543
3400	9.996	76.923	67.039	33.604	106.573	67.453	-4.336
3500	9.980	77.212	67.326	34.603	107.073	66.294	-4.140
3600	9.968	77.493	67.604	35.600	107.567	65.123	-3.954
3700	9.959	77.766	67.875	36.597	108.056	63.938	-3.777
3800	9.954	78.032	68.139	37.592	108.538	62.740	-3.608
3900	9.952	78.290	68.396	38.587	109.014	61.525	-3.448
4000	9.952	78.542	68.647	39.583	109.482	60.302	-3.295
4100	9.955	78.788	68.891	40.578	109.943	59.067	-3.149
4200	9.960	79.028	69.130	41.574	110.397	57.819	-3.009
4300	9.966	79.263	69.363	42.570	110.843	56.563	-2.875
4400	9.975	79.492	69.590	43.567	111.281	55.297	-2.747
4500	9.985	79.716	69.813	44.565	111.710	54.019	-2.624
4600	9.997	79.936	70.030	45.564	112.131	52.733	-2.505
4700	10.010	80.151	70.243	46.564	112.542	51.437	-2.392
4800	10.025	80.362	70.452	47.566	112.943	50.135	-2.283
4900	10.040	80.569	70.656	48.569	113.334	48.822	-2.178
5000	10.057	80.772	70.857	49.574	113.714	47.501	-2.076
5100	10.074	80.971	71.053	50.581	114.084	46.168	-1.978
5200	10.093	81.167	71.246	51.589	114.442	44.837	-1.884
5300	10.112	81.359	71.435	52.599	114.789	43.498	-1.794
5400	10.132	81.548	71.620	53.612	115.124	42.144	-1.706
5500	10.152	81.734	71.802	54.626	115.445	40.791	-1.621
5600	10.174	81.918	71.981	55.642	115.754	39.431	-1.539
5700	10.195	82.098	72.157	56.661	116.050	38.069	-1.460
5800	10.217	82.275	72.330	57.681	116.333	36.694	-1.383
5900	10.240	82.450	72.500	58.704	116.600	35.321	-1.308
6000	10.263	82.622	72.668	59.729	116.853	33.937	-1.236

Dec. 31, 1975

MAGNESIUM MONOFLUORIDE UNIPOSITIVE ION (MgF^+) (IDEAL GAS) GFW = 43.3029

FMG+

Ground State Configuration [$^1\Sigma^+$]

$S^\circ_{298.15}$ = [51.4 ± 2.0] gibbs/mol

ΔHf°_0 = 121.1 ± 11.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 122.4 ± 11.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i	State	ε_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	[1]	$B^1\Sigma^+$	[20000]	[1]
$^3\Pi$	[2600]	[6]	$^3\Pi$	[28000]	[3]
$A^1\Pi$	[3500]	[2]	$^3\Delta$	[29000]	[6]
$^3\Sigma^+$	[15000]	[3]	$D^1\Delta$	[30000]	[2]

ω_e = [718.5] cm^{-1}
$\omega_e x_e$ = [4.80] cm^{-1}
σ = 1
B_e = [0.51621] cm^{-1}
α_e = [0.00463] cm^{-1}
r_e = [1.75]Å

Heat of Formation

MgF^+ ionization-efficiency curves obtained from mass spectral observations on the MgF_2 (1) and MgF_2-Al (2) systems are of the two-process type. Evidence (1, 2) has been presented which shows that the low-energy portion (<13 eV) of the curve arises from the direct ionization (A) of MgF(g). These curves also show an inflection point at higher energies (∿14 eV) which has been interpreted (1-3) as due to the onset of the dissociative ionization (B) of MgF_2(g). The appearance potentials (A) which have been observed for these two processes from measurements on various MgF_2 systems are tabulated below.

Investigator	Year	System	AP, eV (A) Direct Ionization	(B) Dissociative Ionization
Berkowitz and Marquart (4)	1962	MgF_2		13.5±0.4
Green et al. (1)	1964	MgF_2		13.6±0.3
Ehlert et al. (2)	1964	MgF_2-Al	7.8±0.3	13.7±0.4
Murad et al. (5)	1966	MgF_2-Tl-Pd	8.0±0.5	
Hildenbrand (6)	1968	MgF_2-Cu	7.5±0.3	
Hildenbrand (3)	1968	MgF_2	7.5±0.5	13.5±1.0

(A) $MgF(g) + e^- \rightarrow MgF^+(g) + 2e^-$ (B) $MgF_2(g) + e^- \rightarrow MgF^+(g) + F(g) + 2e^-$

Both sets of AP data show the normal scatter (∿0.5 eV) expected for such measurements. The mean value (7.7±0.4 eV) of the four AP's for the direct ionization (A) is supported by the spectroscopic ionization potential of 7.68 eV (7). We adopt $\Delta Hr^\circ_0 = 177.5_6 \pm 9$ kcal/mol (7.7 eV) for process (A), and we obtain ΔHf°_0 (MgF^+,g) = 121.1±11.0 kcal/mol when the ΔHr°_0 value is combined with ΔHf°_0 (MgF,g) = -56.5±2.0 kcal/mol (8). The fragmentation process (B) is likely to involve unknown kinetic energy factors and would not be expected to yield as reliable ΔHf° value as obtained from direct ionization. However, the mean value (13.5_8±0.5 eV) of the four AP's for process (B) leads to ΔHf°_0 (MgF^+,g) = 121.5±13.0 kcal/mol which is in remarkably good with the ΔHf° value from direct ionization (121.1 kcal/mol). This implies that the excess kinetic energy of the fragment MgF^+ is small. ΔHf°_0 corrected to 298.15 K is 122.4_4 kcal/mol.

Heat Capacity and Entropy

The bond dissociation energy for MgF^+ (D°_0 = 108.6 kcal/mol) is nearly the same as that for MgF (D°_0 = 109.8 kcal/mol, 8) which implies that the bonding in these two molecules is quite similar. Thus, it is reasonable to assume that $r_e(MgF^+) = r_e(MgF)$. We adopt the measured r_e value (1.75 Å) for MgF (8). B_e is calculated from the adopted value for r_e. The value of ω_e is obtained from Badger's rule (9) which is written in the form $\omega_e^2 = 3.159 \times 10^6/\mu(r_e-d_{ij})^3$. Molecular data (8) for NaF, MgF, and MgO are used to determine the constant d_{ij}. Barrow and Caunt (10) have shown that the product $x_e\mu^{\frac{1}{2}}$ is fairly constant within a group of similar molecules. We assume $x_e(MgF^+) = x_e(MgF)$ since $\mu^{\frac{1}{2}}(MgF^+) = \mu^{\frac{1}{2}}(MgF)$. These estimates of ω_e and $\omega_e x_e$ are only slightly different from those observed for MgF (8). α_e is obtained from the other constants assuming a Morse potential function. The moment of inertia is 5.4224×10^{-39} g cm^2.

Novikov and Gurvich (11) have observed a band system in the emission spectrum of MgF near 54000 cm^{-1}. An analysis of the vibrational structure showed that the system did not belong to any of those known for MgF, and they (11) assigned it to the $^1\Sigma$-$^1\Sigma$ transition of MgF^+. Band systems have appeared in the absorption spectra (12, 13) of MgF which are now known to arise from AlF. A comparison of the vibrational constants reported by Novikov and Gurvich (11) with those for AlF (8) strongly suggests that this system is the $B^1\Sigma$-$X^1\Sigma$ transition of AlF. Barrow (14) has come to the same conclusion.

MgF^+ (8 valence electrons) is isoelectronic with the alkaline earth monoxides. We estimate the electronic states and levels for MgF^+ by analogy with those for these isoelectronic molecules (8), particularly MgO. The $^1\Pi$-$^3\Pi$ splitting of MgO has recently been reported as 900±200 cm^{-1} (15). We believe that our adopted electronic entropies represent minimal values. Probable upper limits for the electronic contributions can be established by decreasing the two lowest triplet levels to 1000 cm^{-1} ($^3\Pi$) and 5000 cm^{-1} ($^3\Sigma$) and neglecting the other excited states. This increases the entropy to 65.1 and 78.6 gibbs/mol at 1000 K and 4000 K, respectively. The enthalpy is much more uncertain, approaching ±3.0 kcal/mol at temperatures in excess of 2000 K. The enthalpy of the ion between 298.15 K and 0 K is 2.144 kcal/mol.

References

1. J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).
2. T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964).
3. D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).
4. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
5. E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. 45, 263 (1966).
6. D. L. Hildenbrand, J. Chem. Phys. 48, 2458 (1968).
7. R. F. Barrow and J. R. Beale, Proc. Phys. Soc. 91, 483 (1967).
8. JANAF Thermochemical Tables: MgF(g), 12-31-75; NaF(g), 12-31-68; MgO(g), 12-31-74.
9. R. M. Badger, J. Chem. Phys. 2, 128 (1934).
10. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) 219A, 120 (1953).
11. M. M. Novikov and L. V. Gurvich, Zh. Prikl. Spectrosk. 14, 820 (1971).
12. F. A. Jenkins and R. Grinfeld, Phys. Rev. 45, 229 (1934).
13. C. A. Fowler, Jr., Phys. Rev. 59, 645 (1941).
14. R. F. Barrow, ed., "Diatomic Molecules A Critical Bibliography of Spectroscopic Data", Centre National de la Recherche Scientifique, Paris, 1973.
15. G. A. Capelle, H. P. Broida, and R. W. Field, J. Chem. Phys. 62, 3131 (1975).

SULFUR MONOFLUORIDE (SF)
(IDEAL GAS) GFW=51.0584

FS

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	-2.265	2.943	2.943	INFINITE
100	7.170	45.305	60.971	-1.567	3.130	0.931	-2.034
200	7.983	50.539	54.572	-0.807	3.147	-1.282	1.401
298	8.401	53.815	53.815	0.000	3.100	-3.448	2.527
300	8.407	53.867	53.815	0.016	3.099	-3.488	2.541
400	8.617	56.317	54.148	0.868	2.467	-5.649	3.087
500	8.737	58.254	54.782	1.736	1.994	-7.623	3.332
600	8.813	59.854	55.498	2.614	1.598	-9.508	3.463
700	8.864	61.217	56.220	3.498	1.257	-11.307	3.530
800	8.902	62.403	56.920	4.386	-12.113	-14.349	3.920
900	8.931	63.453	57.569	5.278	-12.097	-14.630	3.553
1000	8.955	64.396	58.223	6.172	-12.086	-14.911	3.259
1100	8.974	65.250	58.824	7.069	-12.079	-15.196	3.019
1200	8.991	66.032	59.393	7.967	-12.073	-15.478	2.819
1300	9.007	66.752	59.931	8.867	-12.070	-15.761	2.650
1400	9.020	67.420	60.443	9.768	-12.069	-16.045	2.505
1500	9.033	68.043	60.929	10.671	-12.070	-16.331	2.379
1600	9.045	68.626	61.392	11.575	-12.071	-16.614	2.269
1700	9.056	69.175	61.834	12.480	-12.074	-16.898	2.172
1800	9.067	69.693	62.256	13.386	-12.079	-17.182	2.086
1900	9.077	70.183	62.660	14.293	-12.084	-17.464	2.009
2000	9.087	70.649	63.048	15.201	-12.090	-17.747	1.939
2100	9.097	71.093	63.421	16.111	-12.098	-18.032	1.877
2200	9.107	71.516	63.779	17.021	-12.106	-18.313	1.819
2300	9.116	71.921	64.125	17.932	-12.115	-18.595	1.767
2400	9.126	72.309	64.458	18.844	-12.125	-18.876	1.719
2500	9.135	72.682	64.779	19.757	-12.136	-19.157	1.675
2600	9.144	73.041	65.090	20.671	-12.147	-19.438	1.634
2700	9.153	73.386	65.391	21.586	-12.159	-19.718	1.596
2800	9.162	73.719	65.682	22.502	-12.172	-20.000	1.561
2900	9.172	74.041	65.965	23.419	-12.185	-20.278	1.528
3000	9.181	74.352	66.240	24.336	-12.200	-20.557	1.498
3100	9.190	74.653	66.506	25.255	-12.213	-20.835	1.469
3200	9.200	74.945	66.765	26.174	-12.229	-21.113	1.442
3300	9.209	75.228	67.017	27.095	-12.244	-21.392	1.417
3400	9.219	75.503	67.263	28.016	-12.261	-21.667	1.393
3500	9.229	75.770	67.502	28.938	-12.278	-21.945	1.370
3600	9.239	76.031	67.736	29.862	-12.294	-22.220	1.349
3700	9.250	76.284	67.963	30.786	-12.313	-22.494	1.329
3800	9.261	76.531	68.185	31.712	-12.330	-22.769	1.310
3900	9.272	76.771	68.403	32.638	-12.349	-23.046	1.291
4000	9.284	77.006	68.615	33.566	-12.367	-23.316	1.274
4100	9.296	77.236	68.822	34.495	-12.386	-23.592	1.258
4200	9.308	77.460	69.025	35.425	-12.405	-23.864	1.242
4300	9.321	77.679	69.224	36.357	-12.424	-24.137	1.227
4400	9.334	77.893	69.418	37.290	-12.444	-24.409	1.212
4500	9.348	78.103	69.609	38.224	-12.463	-24.680	1.199
4600	9.362	78.309	69.796	39.159	-12.482	-24.953	1.186
4700	9.377	78.510	69.979	40.096	-12.501	-25.224	1.173
4800	9.392	78.708	70.159	41.034	-12.521	-25.495	1.161
4900	9.407	78.902	70.336	41.974	-12.540	-25.761	1.149
5000	9.423	79.092	70.509	42.916	-12.559	-26.034	1.138
5100	9.439	79.279	70.679	43.859	-12.578	-26.303	1.127
5200	9.456	79.462	70.846	44.804	-12.596	-26.570	1.117
5300	9.473	79.643	71.010	45.750	-12.614	-26.839	1.107
5400	9.491	79.820	71.172	46.698	-12.632	-27.108	1.097
5500	9.509	79.994	71.331	47.648	-12.649	-27.376	1.088
5600	9.527	80.166	71.487	48.600	-12.667	-27.641	1.079
5700	9.546	80.334	71.641	49.554	-12.683	-27.910	1.070
5800	9.565	80.501	71.792	50.510	-12.699	-28.176	1.062
5900	9.585	80.664	71.941	51.467	-12.714	-28.448	1.054
6000	9.604	80.826	72.088	52.427	-12.729	-28.710	1.046

June 30, 1976

SULFUR MONOFLUORIDE (SF) (Ideal Gas) GFW = 51.0584

Ground State Configuration $^2\Pi_{3/2}$
$S^\circ_{298.15}$ = [53.8 ± 0.2] gibbs/mol

ΔHf°_0 = 2.9 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 3.1 ± 1.5 kcal/mol

FS

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
X $^2\Pi_{3/2}$	0	2
X $^2\Pi_{1/2}$	398	2
A $^2\Pi_{3/2}$	24991	2
A $^2\Pi_{1/2}$	25601	2

ω_e = [830 ± 20] cm^{-1} $\omega_e x_e$ = [4.7 ± 0.4] cm^{-1} σ = 1

B_e = 0.55427 ± 0.0005 cm^{-1} α_e = [0.0042] cm^{-1} r_e = 1.5967 ± 0.001 Å

Heat of Formation

Hildenbrand (1) has investigated the isomolecular reaction $CS_2(g) + 2SF(g) = CF_2(g) + 2S_2(g)$ by mass spectrometry. The various molecular species were found to be formed as products of the reaction of gaseous SF_6 with graphite at temperatures in the range 1436-1611 K. This study employed three different effusion cell configurations which were used to optimize the reaction conditions, and ion abundances for each species were measured at 2 eV above their appearance potentials in order to eliminate fragmentation effects. We analyze the reported equilibrium data by the second and third law methods with the results being presented below.

Series	Cell Configuration	No. of Points	Temp Range, K	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	Drift eu	$\Delta Hf^\circ_{298}(SF,g)$[a] kcal/mol
1	Mo cell/C liner/packed with C cloth	2	1529;1611	-11.6	-16.2 ±0.3	-2.9	3.2 ±1.2
2	C cell/wound Pt wire	4	1436-1564	6.8	-16.0 ±1.8	-15.1 ±5.0	3.1 ±2.0
3	C cell/Pt partition/ packed with C cloth and Pt wire	7	1478-1588	-37.2	-15.8 ±1.4	13.9 ±5.0	3.0 ±1.8

[a] Third law values with JANAF auxiliary ΔHf°_{298} data (2).

The three cell configurations used by Hildenbrand (1) yield almost identical third-law ΔHf° values. We adopt the mean value of 3.1±1.5 kcal/mol. This value corresponds to a D°_0 of 81.2±2.0 kcal/mol which is close to the average bond energies (80.0 kcal/mol) for SF_4 and SF_3 (2). Other reported D°_0 values include 96.9 kcal/mol (3) and ≤ 76.1 kcal/mol (4). The former *value is based on Hartree-Foch binding energies (3) which were combined with an estimate of the extra molecular correlation* energy. This estimate now appears to be about 20% too high. The upper limit value for D°_0 was obtained from predissociation observed in the A $^2\Pi$ state by Di Lonardo and Trombetti (4).

Heat Capacity and Entropy

The electronic states and levels (T_o) are taken from the recent compilation of Barrow (5). His results were derived from the spectral measurements of Di Lonardo and Trombetti (4). Further confirmation that the ground state is inverted $^2\Pi$ is provided by the results of an analysis of the gas-phase electron resonance spectra by Carrington et al. (6). The rotational constant (B_e) is calculated from the microwave data (B_{eff}) of Amano and Hirota (7). Other values for B_e determined from EPR (6) measurements and from a rotational analysis (4) of the A $^2\Pi$ - X $^2\Pi$ band system agree with the microwave results but are less precise. The value of r_e is calculated from B_e. The moment of inertia is 5.0499×10^{-39} g cm^2.

The ground state vibrational constants have not been determined experimentally. O'Hare (8) computed Hartree-Fock total energies for the ground states of NF, SiF, PF, and SF and derived spectroscopic constants for each monofluoride by a Dunham analysis. He adjusted the computed values for SF for differences found between calculated and experimental data for the other three monofluorides. We adopt his predicted vibrational constants along with his computed value for α_e. We do not include the rotational and vibrational constants (4, 5) for the A $^2\Pi$ state since they have a negligible effect.

Thermal functions have been previously reported for SF by Wilkins (9) and O'Hare (10). These two sets of functions agree reasonably well, and presumably they are both based on a ground state quantum weight of 2. Our entropies are consistently higher than the literature data (9, 10) at all temperatures by roughly 1.0 - 1.5 gibbs/mol. This increase can be attributed primarily to the entropy contribution from the $X^2\Pi_{1/2}$ state which lies at 398 cm^{-1}.

References

1. D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
2. *JANAF Thermochemical Tables:* $CS_2(g)$, *6-30-61;* $CF_2(g)$, *6-30-70;* $S_2(g)$, 12-31-65; $SF_4(g)$ *and* $SF_3(g)$, 6-30-76.
3. P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 53, 2834 (1970).
4. G. Di Lonardo and A. Trombetti, Trans. Faraday Soc. 66, 2694 (1970).
5. R. F. Barrow, "Diatomic Molecules: A Critical Bibliography of Spectroscopic Data," Centre National De La Recherche Scientifique, Paris, 1973.
6. A. Carrington, G. N. Currie, T. A. Miller, and D. H. Levy, J. Chem. Phys. 50, 2726 (1969).
7. T. Amano and E. Hirota, J. Mol. Spectro. 45, 417 (1973).
8. P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
9. R. L. Wilkins, Aerospace Corporation, Report No. TR-0158 (3240-20)-19, Contract No. FO4695-67-C-0158, July, 1968.
10. P. A. G. O'Hare, Argonne National Laboratory, ANL-7315, Contract W-31-109-Eng-38, July, 1968.

FS

SULFUR MONOFLUORIDE UNIPOS. ION (SF+)   FS$^+$
(IDEAL GAS) GFW=51.0579

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.119	235.578		
100							
200							
298	7.571	53.846	53.846	0.000	237.070	229.026	-167.880
300	7.579	53.893	53.846	0.014	237.076	228.976	-166.809
400	7.970	56.130	54.149	0.792	236.867	226.247	-123.616
500	8.249	57.940	54.732	1.604	236.835	223.596	-97.734
600	8.440	59.462	55.396	2.439	236.894	220.945	-80.479
700	8.574	60.774	56.073	3.290	237.015	218.301	-68.157
800	8.671	61.925	56.734	4.153	224.117	214.349	-58.557
900	8.744	62.951	57.309	5.024	224.609	213.099	-51.748
1000	8.801	63.875	57.974	5.901	225.100	211.794	-46.288
1100	8.848	64.716	58.549	6.784	225.590	210.439	-41.810
1200	8.889	65.488	59.096	7.671	226.081	209.040	-38.071
1300	8.926	66.201	59.615	8.561	226.572	207.602	-34.901
1400	8.961	66.864	60.110	9.456	227.063	206.124	-32.177
1500	8.996	67.483	60.581	10.353	227.554	204.610	-29.812
1600	9.032	68.065	61.031	11.255	228.046	203.064	-27.737
1700	9.068	68.614	61.461	12.160	228.540	201.488	-25.903
1800	9.106	69.133	61.673	13.069	229.035	199.882	-24.269
1900	9.145	69.626	62.268	13.981	229.532	198.251	-22.804
2000	9.185	70.096	62.648	14.898	230.031	196.591	-21.482
2100	9.226	70.546	63.013	15.818	230.531	194.904	-20.284
2200	9.268	70.976	63.365	16.743	231.034	193.198	-19.192
2300	9.310	71.389	63.705	17.672	231.539	191.466	-18.193
2400	9.352	71.786	64.034	18.605	232.047	189.714	-17.276
2500	9.394	72.168	64.351	19.542	232.558	187.940	-16.430
2600	9.436	72.538	64.659	20.484	233.070	186.144	-15.647
2700	9.477	72.894	64.958	21.429	233.586	184.329	-14.920
2800	9.518	73.240	65.247	22.379	234.104	182.494	-14.244
2900	9.558	73.575	65.529	23.333	234.625	180.643	-13.614
3000	9.596	73.899	65.802	24.290	235.147	178.773	-13.024
3100	9.634	74.214	66.069	25.252	235.673	176.884	-12.470
3200	9.671	74.521	66.328	26.217	236.200	174.979	-11.951
3300	9.706	74.819	66.581	27.186	236.730	173.057	-11.461
3400	9.740	75.109	66.827	28.158	237.262	171.122	-11.000
3500	9.773	75.392	67.068	29.134	237.795	169.167	-10.563
3600	9.805	75.668	67.303	30.113	238.330	167.199	-10.150
3700	9.836	75.937	67.533	31.095	238.866	165.217	-9.759
3800	9.866	76.200	67.758	32.080	239.405	163.220	-9.387
3900	9.894	76.456	67.977	33.068	239.945	161.205	-9.034
4000	9.922	76.707	68.192	34.059	240.486	159.183	-8.697
4100	9.948	76.953	68.403	35.052	241.028	157.142	-8.376
4200	9.973	77.193	68.610	36.049	241.572	155.090	-8.070
4300	9.998	77.428	68.612	37.047	242.118	153.025	-7.778
4400	10.022	77.658	69.010	38.048	242.663	150.946	-7.498
4500	10.045	77.883	69.205	39.052	243.209	148.856	-7.229
4600	10.067	78.104	69.396	40.057	243.757	146.752	-6.972
4700	10.089	78.321	69.584	41.065	244.305	144.637	-6.726
4800	10.110	78.534	69.768	42.075	244.855	142.510	-6.489
4900	10.131	78.742	69.949	43.087	245.405	140.377	-6.261
5000	10.151	78.947	70.127	44.101	245.954	138.223	-6.042
5100	10.171	79.148	70.302	45.117	246.505	136.063	-5.831
5200	10.190	79.346	70.474	46.135	247.057	133.895	-5.627
5300	10.210	79.540	70.643	47.155	247.610	131.713	-5.431
5400	10.229	79.731	70.810	48.177	248.163	129.521	-5.242
5500	10.247	79.919	70.973	49.201	248.716	127.318	-5.059
5600	10.266	80.104	71.135	50.227	249.269	125.108	-4.883
5700	10.284	80.286	71.294	51.254	249.823	122.884	-4.712
5800	10.302	80.465	71.450	52.283	250.378	120.654	-4.546
5900	10.320	80.641	71.605	53.315	250.934	118.408	-4.386
6000	10.338	80.815	71.757	54.347	251.488	116.161	-4.231

June 30, 1976

SULFUR MONOFLUORIDE UNIPOSITIVE ION (SF$^+$)   (IDEAL GAS)   GFW = 51.0579

FS$^+$

Ground State Configuration [$^3\Sigma$]

$S^\circ_{298.15}$ = [53.8 ± 2.2] gibbs/mol

ΔHf°_0 = 235.6 ± 4.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 237.1 ± 4.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[$X^3\Sigma$]	0	[3]
[$a^1\Delta$]	[8000]	[2]
[$b^1\Sigma$]	[14500]	[1]
[$B^3\Pi$]	[30000]	[6]

ω_e = [838] cm^{-1} $\omega_e x_e$ = [4.6] cm^{-1} σ = 1

B_e = [0.55686] cm^{-1} α_e = [0.0044] cm^{-1} r_e = [1.593] Å

Heat of Formation

The electron-impact appearance potential (A.P.) of SF$^+$ from SF has been measured by Hildenbrand (1) as 10.09±0.1 eV. Normally, this measured A.P. would be identical to the vertical ionization potential (I.P.) of SF; however, formation of SF$^+$ involves the loss of an antibonding electron which appears to be situated primarily on the sulfur atom (I.P.(S) = 10.36 eV, 2). Thus, the geometrical changes produced upon ionization should be minimal, and therefore, the measured A.P. is *probably very close to the true (adiabatic) ionization potential, as suggested by Hildenbrand (1). We employ the experimental* I.P. value as the heat of reaction, ΔHr° = 232.68±2.3 kcal/mol, for the process $SF(g) + e^- = SF^+(g) + 2e^-$ at 0 K, and we calculate $\Delta Hf^\circ_0(SF^+,g)$ = 235.6±4.0 kcal/mol by combining the value of ΔHr°_0 with $\Delta Hf^\circ_0(SF,g)$ = 2.9±1.5 kcal/mol(3). Independent values of I.P. include 10.0 eV (4) and 9.9 eV (5). Both of these values were obtained from semiempirical molecular orbital calculations and are in excellent agreement with the results adopted here.

Earlier electron-impact studies which can also be used to derive ΔHf° of SF$^+$ have been previously analyzed by O'Hare and Wahl (6). We do not reanalyze these results since their analysis (6) has shown that the data are seriously in error.

Heat Capacity and Entropy

As discussed in the heat of formation section, one would expect that the bonding in SF$^+$ is probably not very different from that in SF, since the ionizing orbital is antibonding. Additional support for this is provided by the fact that the bond dissociation energies (D°_0) for SF$^+$ (87.4 kcal/mol) and SF (81.2 kcal/mol) are very similar. In addition, SF$^+$ is isoelectronic with PF, and one might therefore expect that the molecular characteristics of these two isoelectronic molecules would be quite similar. We estimate the vibrational and rotational constants to be intermediate between those for SF (3) and PF (7). By analogy with other twelve valence electron molecules (7), we predict that the ground state is $^3\Sigma$ and expect several excited states to exist below 35000 cm^{-1}. The two singlet levels are estimated from those observed for NF and O_2 (7). We also include a triplet level at 30000 cm^{-1} based on that observed for PF (7). We assume that the vibrational and rotational constants for the excited states are identical with those for the ground state since a comparison of the constants (7) that are available for the various states of NF and PF shows that they are not significantly different. The uncertainity in our value of S°_{298} is estimated as ±2.2 gibbs/mol and arises primarily from the effect of the ground state quantum weight. If the SF$^+$ ground state is singlet, then our entropy value at 298.15 K should be decreased by 2.18 gibbs/mol. The electronic contribution to the entropy from the estimated excited states is negligible below 2000 K but increases to 0.4 gibbs/mol at 4500 K.

The moment of inertia is 5.0265 x 10^{-39} g cm^2, and the enthalpy between 0 K and 298.15 K is -2.119 kcal/mol.

References

1. D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
2. *U. S. Natl. Bur. Std. NSRDS-NBS 26, June, 1969.*
3. JANAF Thermochemical Tables: SF(g), 6-30-76.
4. A. L. Companion, Theoret. Chim. Acta, 25, 268 (1972).
5. P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
6. P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 53, 2834 (1970).
7. B. Rosen, ed., "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, New York, 1970.

DIFLUOROSILANE (SiH_2F_2) F_2H_2Si

(IDEAL GAS) GFW=68.0988

	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	-2.865	-186.962	-186.962	INFINITE
100	8.386	51.708	72.320	-2.061	-187.676	-186.247	407.043
200	10.271	58.025	63.721	-1.139	-188.338	-184.573	201.692
298	12.970	62.624	62.624	0.000	-189.000	-182.581	133.835
300	13.021	62.704	62.624	0.024	-189.012	-182.542	132.981
400	15.467	66.799	63.166	1.453	-189.554	-180.298	98.510
500	17.346	70.461	64.265	3.098	-189.959	-177.936	77.776
600	18.788	73.757	65.577	4.908	-190.249	-175.502	63.927
700	19.921	76.742	66.962	6.845	-190.450	-173.026	54.021
800	20.826	79.463	68.357	8.884	-190.583	-170.530	46.586
900	21.558	81.960	69.732	11.005	-190.662	-168.016	40.800
1000	22.155	84.263	71.071	13.192	-190.702	-165.498	36.170
1100	22.644	86.398	72.369	15.432	-190.715	-162.977	32.381
1200	23.049	88.386	73.622	17.718	-190.705	-160.455	29.223
1300	23.386	90.245	74.830	20.040	-190.685	-157.935	26.551
1400	23.669	91.989	75.994	22.393	-190.658	-155.417	24.262
1500	23.908	93.630	77.115	24.772	-190.631	-152.898	22.277
1600	24.117	95.180	78.196	27.174	-190.607	-150.386	20.542
1700	24.285	96.647	79.239	29.594	-202.580	-147.765	18.997
1800	24.435	98.039	80.245	32.030	-202.513	-144.545	17.550
1900	24.564	99.364	81.217	34.480	-202.443	-141.326	16.256
2000	24.677	100.627	82.156	36.942	-202.373	-138.109	15.092
2100	24.776	101.833	83.064	39.415	-202.304	-134.899	14.039
2200	24.863	102.988	83.944	41.897	-202.237	-131.692	13.082
2300	24.940	104.095	84.796	44.387	-202.171	-128.486	12.209
2400	25.008	105.158	85.623	46.885	-202.108	-125.282	11.408
2500	25.069	106.180	86.425	49.389	-202.050	-122.086	10.673
2600	25.124	107.164	87.203	51.898	-201.994	-118.886	9.993
2700	25.173	108.114	87.960	54.413	-201.941	-115.691	9.365
2800	25.217	109.030	88.697	56.933	-201.891	-112.498	8.781
2900	25.257	109.915	89.413	59.456	-201.846	-109.302	8.237
3000	25.293	110.772	90.111	61.984	-201.805	-106.118	7.731
3100	25.326	111.602	90.791	64.515	-201.766	-102.929	7.256
3200	25.356	112.407	91.454	67.049	-201.733	-99.738	6.812
3300	25.384	113.187	92.101	69.586	-201.704	-96.551	6.394
3400	25.409	113.946	92.732	72.126	-201.678	-93.366	6.002
3500	25.432	114.682	93.349	74.668	-201.659	-90.179	5.631
3600	25.453	115.399	93.951	77.212	-293.604	-84.736	5.144
3700	25.473	116.097	94.540	79.759	-293.495	-78.936	4.663
3800	25.491	116.776	95.117	82.307	-293.390	-73.136	4.206
3900	25.508	117.439	95.681	84.857	-293.293	-67.346	3.774
4000	25.524	118.085	96.233	87.408	-293.200	-61.551	3.363
4100	25.539	118.715	96.773	89.962	-293.112	-55.765	2.973
4200	25.552	119.331	97.303	92.516	-293.030	-49.975	2.600
4300	25.565	119.932	97.822	95.072	-292.951	-44.188	2.246
4400	25.577	120.520	98.332	97.629	-292.880	-38.406	1.908
4500	25.588	121.095	98.831	100.187	-292.813	-32.623	1.584
4600	25.598	121.658	99.321	102.746	-292.750	-26.840	1.275
4700	25.608	122.208	99.802	105.307	-292.694	-21.058	0.979
4800	25.617	122.747	100.275	107.868	-292.641	-15.279	0.696
4900	25.625	123.276	100.739	110.430	-292.594	-9.499	0.424
5000	25.634	123.793	101.195	112.993	-292.552	-3.729	0.163
5100	25.641	124.301	101.643	115.557	-292.515	2.050	-0.088
5200	25.648	124.799	102.083	118.121	-292.483	7.827	-0.329
5300	25.655	125.288	102.517	120.686	-292.455	13.606	-0.561
5400	25.662	125.767	102.943	123.252	-292.434	19.371	-0.784
5500	25.668	126.238	103.362	125.819	-292.416	25.147	-0.999
5600	25.674	126.701	103.775	128.386	-292.405	30.923	-1.207
5700	25.679	127.155	104.181	130.954	-292.398	36.701	-1.407
5800	25.684	127.602	104.581	133.522	-292.397	42.472	-1.600
5900	25.689	128.041	104.975	136.090	-292.402	48.241	-1.787
6000	25.694	128.473	105.363	138.660	-292.410	54.013	-1.967

Dec. 31, 1960; June 30, 1976

DIFLUOROSILANE (SiH_2F_2) (IDEAL GAS) GFW = 68.0988

Point Group C_{2v}
$S°_{298.15}$ = 62.6 ± 0.5 gibbs/mol
Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = [-187 ± 5] kcal/mol F_2H_2Si
$\Delta Hf°_{298.15}$ = [-189 ± 5] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
2246(1)	322(1)	730(1)
980(1)	730(1)	981(1)
869(1)	2251(1)	903(1)

Bond Distances: Si-H = 1.471 Å Si-F = 1.5767 σ = 2
Bond Angles: H-Si-H = 112.02° F-Si-F = 107.93°
Product of the Moments of Inertia: $I_AI_BI_C = 4.8148 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

There are no reported experimental studies leading to the heat of formation of SiH_2F_2(g). We estimate this value via a linear interpolation between the established $\Delta Hf°_{298}$ values of SiH_4(g) and SiF_4(g) (1). The reasonableness of this approach has been demonstrated by Lapidus et al. (2), Hunt and Sirtl (3), and Seiter and Sirtl (4).

Heat Capacity and Entropy

The adopted vibrational frequencies are from the gas phase infrared study of Cradock et al. (6). Two frequencies (ω_5 and ω_6) were quite uncertain and were discussed in terms of a strong Coriolis interaction.

These frequencies appear quite reasonable when a comparison of the dihalosilanes and dihalomethanes (halogen is fluorine, chlorine, and bromine) is made (1, 5).

The adopted bond distances and bond angles are obtained from the microwave spectrum study by Laurie (7). The individual moments of inertia are: $I_A = 3.4017 \times 10^{-39}\ g\ cm^2$, $I_B = 10.7548 \times 10^{-39}\ g\ cm^2$, and $I_C = 13.1606 \times 10^{-39}\ g\ cm^2$.

References

1. JANAF Thermochemical Tables: SiH_4(g) and SiF_4(g), 6-30-76; CH_2F_2, 12-31-69.
2. I. I. Lapidus, L. A. Nisel'son, and A. L. Seifer in "Thermophysical Properties of Gases and Liquids," No. 1, V. A. Rabinovich, Ed., Israel Program for Scientific Translations, Jerusalem, 1970, pp. 102-135 [translated from Russian].
3. L. P. Hunt and E. Sirtl, J. Electrochem. Soc. 119, 1741 (1972).
4. H. Seiter and E. Sirtl, Z. Naturforsch. 21a, 1956 (1966).
5. T. Shimanouchi, NSRDS-NBS-39, 1972; J. Phys. Chem. Ref. Data 2, 121 (1973).
6. S. Cradock, E. A. V. Ebsworth, and A. G. Robiette, Trans. Faraday Soc. 60, 1502 (1964).
7. V. W. Laurie, J. Chem. Phys. 26, 1359 (1957).

MAGNESIUM DIFLUORIDE (MgF_2) F_2Mg

(CRYSTAL) GFW=62.3018

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.369	- 267.763	- 267.763	INFINITE
100	5.192	2.554	24.477	- 2.192	- 268.435	- 264.394	577.832
200	11.668	8.379	14.950	- 1.314	- 268.819	- 260.280	284.420
298	14.710	13.684	13.684	.000	- 268.700	- 256.006	187.657
300	14.744	13.775	13.685	.027	- 268.698	- 255.927	186.443
400	16.368	18.255	14.284	1.588	- 268.521	- 251.695	137.520
500	17.360	22.020	15.465	3.277	- 268.281	- 247.515	108.188
600	18.002	25.245	16.833	5.047	- 268.012	- 243.387	88.654
700	18.446	28.055	18.240	6.871	- 267.732	- 239.304	74.714
800	18.775	30.540	19.625	8.732	- 267.462	- 235.263	64.271
900	19.031	32.767	20.964	10.623	- 267.208	- 231.253	56.156
1000	19.239	34.783	22.246	12.537	- 269.098	- 227.089	49.630
1100	19.416	36.625	23.471	14.470	- 268.859	- 222.901	44.286
1200	19.569	38.321	24.639	16.419	- 268.634	- 218.733	39.837
1300	19.707	39.893	25.752	18.383	- 268.426	- 214.583	36.075
1400	19.832	41.358	26.815	20.360	- 298.600	- 209.969	32.778
1500	19.949	42.730	27.831	22.349	- 298.019	- 203.658	29.673
1600	20.058	44.021	28.803	24.349	- 297.431	- 197.388	26.962
1700	20.162	45.241	29.734	26.360	- 296.835	- 191.152	24.574
1800	20.262	46.396	30.628	28.382	- 296.232	- 184.954	22.456
1900	20.358	47.494	31.487	30.413	- 295.621	- 178.788	20.565
2000	20.451	48.541	32.314	32.453	- 295.005	- 172.654	18.867

Dec. 31, 1960; June 30, 1964; March 31, 1966;
June 30, 1975

MAGNESIUM DIFLUORIDE (MgF_2) (CRYSTAL) GFW = 62.3018 F_2Mg

$S°_{298.15}$ = 13.68 ± 0.05 gibbs/mol
Tm = 1536 ± 5 K

$\Delta Hf°_0$ = -267.8 ± 0.3 kcal/mol
$\Delta Hf°_{298.15}$ = -268.7 ± 0.3 kcal/mol
ΔHm° = 14.03 ± 0.1 kcal/mol
$\Delta Hs°_{298.15}$ = 95.0 ± 0.5 kcal/mol

Heat of Formation

Rudzitis et al. (1) used fluorine bomb calorimetry to study the heat of combustion of a highly pure (99.91 mole %) sample of magnesium. Six combustion experiments were performed, and the sole combustion product was identified as MgF_2 by x-ray diffraction. Values for the completeness of combustion ranged from 98.4 to 99.99%. Corrections for the unburned magnesium were based on analysis performed by hydrogen evolution. This study gave $\Delta Hf°_{298}(MgF_2, c)$ = -268.7±0.3 kcal/mol which is adopted. The quoted uncertainty is twice the combined standard deviation arising from the scatter in the six results and from the analytical and calibration data.

More uncertain values for ΔHf° derived indirectly from reaction calorimetry (2, 3), high-temperature equilibria (4), and e.m.f.'s of solid electrolyte galvanic cells (5, 6) are tabulated below. The original data are reanalyzed with the use of the most recent auxiliary data. These sources are included in the table.

Reference	Method	Reaction	Temp. Range, K	$\Delta Hr°_{298}$ kcal/mol	$\Delta Hf°_{298}(MgF_2, c)$ kcal/mol	Drift[a] eu
(2)	Reaction Calorimetry	$Mg(OH)_2(c)+2(HF\cdot 4.5H_2O)=MgF_2(c)+H_2O(\ell)$	346.9	-30.85	-268.4±1.0	
(3)	Reaction Calorimetry	$Mg(c)+2(HF\cdot 80H_2O)=MgF_2(c)+H_2(g)$	293	-109.46±0.7	-263.1±1.0	
(4)	Equilibria	$MgF_2(c)+H_2O(g)=MgO(c)+2HF(g)$	1173-1373	51.58±0.9[b]	-268.0±1.5	4.6±0.3
(5)	e.m.f.	$AlF_3(c)+1.5Mg(c)=Al(c)+1.5MgF_2(c)$	720-860	-41.5±0.2[b]	-268.3±1.6	-1.5
(6)	e.m.f.	$AlF_3(c)+1.5Mg(c)=Al(c)+1.5MgF_2(c)$	750-900	-40.6±0.2[b]	-267.7±1.8	1.8

[a] ΔSr°(2nd Law) - ΔSr° (3rd Law)

[b] Third Law Values

[c] ΔHf°(HF, aq.) consistent with JANAF value for HF(g); also, ϕ_c(HF, aq.) taken from reference 9.

Auxiliary $\Delta Hf°_{298}$ Values (kcal/mol): $Mg(OH)_2(c)$, -221.0±0.5 (7); $HF\cdot 4.5\ H_2O$, -76.6±0.1[c]; $H_2O(\ell)$, -68.315 (8); $HF\cdot 80H_2O$, -76.8±0.1[c]; $H_2O(g)$, -57.7979 (7); MgO(c), -143.7+0.15 (7); HF(g), -65.14±0.2 (7); $AlF_3(c)$, -361.0±0.3 (7).

With the exception of the older calorimetric measurements of Wartenberg (3), these results are in reasonable agreement with the directly measured ΔHf° value (1).

Heat Capacity and Entropy

Todd (10) measured the low-temperature heat capacities (54.2-296.5 K) by adiabatic calorimetry. These Cp° data extrapolate to 14.71 gibbs/mol at 298.15 K. Integration of these Cp°'s gives $S°_{298}$=13.68 gibbs/mol when combined with $S°_{51}$ = 0.539 gibbs/mol. The latter value is calculated from a combination of Debye and Einstein functions which fits all the experimental Cp° data with an average deviation of ± 1.0 %.

Relative enthalpies ($H°_T-H°_{298}$) have been measured (411.3-1516 K) by the "drop" method (11) on a portion of the same sample used for the Cp° study (10). Gravimetric analysis for Mg as $MgSO_4$ indicated a MgF_2 purity of 99.87 wt. %. However, premelting effects which appear in the experimental enthalpies about 80° below the melting point suggest that the sample was probably somewhat less pure. Insufficient information is reported to attempt to correct for the impurities. High-temperature heat capacities (300-2000 K) are derived from the measured enthalpies (11) by curve fitting with orthogonal polynomials. The curve is constrained to join smoothly with the low-temperature Cp° data near 298.15 K. Three enthalpy points which appear to involve premelting are not included in the fit. Also, we omit the enthalpy point at 411.3 K which shows an usually large positive deviation (+2.9%) from the adopted curve. The maximum deviation of the seven enthalpy points used in the fit is -0.5% and occurs at 1032.7 K. The older heat capacity measurements (288-1273 K) reported by Krestovnikov and Karetnikov (12) are considered less reliable and are not included in our evaluation.

Melting Data

Tm is the value measured by "drop" calorimetry (11). Melting point determinations (1529 and 1534 K) on two commercially available materials which had been further purified by hydrofluorination (13) suggest an uncertainty in the adopted Tm value (1536 K) of ± 5 K. Other literature values include 1525 K (14) and 1528 K (15).

ΔHm° is calculated as the difference between JANAF enthalpies for the liquid and crystal at Tm. Other reported values for ΔHm° are 13.9 (11) and 13.15 kcal/mol (14).

Sublimation Data

See $MgF_2(g)$ table.

References

See $MgF_2(\ell)$ table.

MAGNESIUM DIFLUORIDE (MgF_2) F_2MG

(LIQUID) GFW=62.3018

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	14.710	21.504	21.504	.000	- 256.297	- 245.934	180.275
300	14.744	21.595	21.504	.027	- 256.295	- 245.870	179.116
400	16.368	26.074	22.104	1.588	- 256.118	- 242.420	132.452
500	17.360	29.840	23.285	3.277	- 255.878	- 239.021	104.476
600	18.002	33.064	24.652	5.047	- 255.609	- 235.676	85.845
700	18.446	35.874	26.059	6.871	- 255.330	- 232.375	72.551
800	18.775	38.360	27.444	8.732	- 255.059	- 229.115	62.591
900	19.031	40.586	28.783	10.623	- 254.805	- 225.887	54.853
1000	22.687	42.603	30.066	12.537	- 256.695	- 222.506	48.629
1100	22.687	44.765	31.305	14.806	- 256.121	- 219.116	43.534
1200	22.687	46.739	32.510	17.074	- 255.576	- 215.777	39.298
1300	22.687	48.555	33.676	19.343	- 255.063	- 212.480	35.721
1400	22.687	50.236	34.799	21.612	- 284.945	- 208.744	32.586
1500	22.687	51.801	35.881	23.880	- 284.085	- 203.330	29.625
1600	22.687	53.266	36.922	26.149	- 283.228	- 197.976	27.042
1700	22.687	54.641	37.925	28.418	- 282.374	- 192.672	24.770
1800	22.687	55.938	38.890	30.686	- 281.525	- 187.422	22.756
1900	22.687	57.164	39.819	32.955	- 280.676	- 182.217	20.960
2000	22.687	58.328	40.716	35.224	- 279.831	- 177.055	19.348
2100	22.687	59.435	41.581	37.493	- 278.990	- 171.940	17.894
2200	22.687	60.490	42.417	39.761	- 278.151	- 166.860	16.576
2300	22.687	61.499	43.225	42.030	- 277.314	- 161.819	15.376
2400	22.687	62.464	44.007	44.299	- 276.480	- 156.817	14.280
2500	22.687	63.390	44.763	46.567	- 275.651	- 151.849	13.275
2600	22.687	64.280	45.497	48.836	- 274.823	- 146.911	12.349
2700	22.687	65.136	46.209	51.105	- 273.998	- 142.007	11.495
2800	22.667	65.962	46.900	53.373	- 273.176	- 137.136	10.704
2900	22.687	66.758	47.571	55.642	- 272.357	- 132.289	9.970
3000	22.687	67.527	48.223	57.911	- 271.543	- 127.477	9.287

Dec. 31, 1960; June 30, 1964; March 31, 1966;
June 30, 1975

MAGNESIUM DIFLUORIDE (MgF_2) (LIQUID) GFW = 62.3018 F_2MG

$S^\circ_{298.15}$ = 21.504 gibbs/mol
Tm = 1536 ± 5 K
Tb = 2536 K (to monomer)
$\Delta Hf^\circ_{298.15}$ = -256.297 kcal/mol
ΔHm° = 14.03 ± 0.1 kcal/mol
ΔHv° = 65.5 kcal/mol

Heat of Formation

The value of ΔHm° and the difference between $(H^\circ_{Tm}-H^\circ_{298})$ for the crystal and liquid are added to ΔHf°(c) to give ΔHf°(ℓ).

Heat Capacity and Entropy

Naylor (1) has measured relative enthalpies (1539-1760 K) for the liquid by "drop" calorimetry. These results give a Cp°(ℓ) equal to 22.687 gibbs/mol. This value is used in the temperature range 1000-3000 K. Below 1000 K, the assumed glass transition temperature, Cp° is that of the crystal. S°_{298} *is obtained in a manner analogous to that of the heat of formation.*

Melting Data

See MgF_2(c) table.

Vaporization Data

Tb is the temperature at which ΔGr° for the process $MgF_2(\ell) = MgF_2(g)$ approaches zero. ΔHv° is the difference between the ΔHf° values for the gas and liquid at Tb. Several methods (2-6) predict an insignificant amount of dimer (∿1%) in the saturated vapor below 2000 K.

References

1. B. F. Naylor, J. Amer. Chem. Soc. 67, 150 (1945).
2. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
3. R. R. Hammer and J. A. Pask, J. Amer. Ceram. Soc. 47, 264 (1964).
4. M. A. Greenbaum, H. C. Ko, M. Wong, and M. Farber, J. Phys. Chem. 68, 965 (1964).
5. D. L. Hildenbrand, W. F. Hall, F. Ju, and N. D. Potter, J. Chem. Phys. 40, 2882 (1964).
6. J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).

MgF_2(c) Table References

1. E. Rudzitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 68, 2978 (1964).
2. D. R. Torgeson and Th. G. Sahama, J. Amer. Chem. Soc. 70, 2156 (1948).
3. H. v. Wartenberg, Z. Anorg. Allgem. Chem. 249, 100 (1942).
4. L. *Domange, Ann. Chim. Phys. 7, 225 (1937).*
5. T. N. Rezukhina, T. F. Sisoeva, L. I. Halokhonova, and E. G. Ippolitor, J. Chem. Thermodynamics 6, 883(1974).
6. W. H. Skelton and J. W. Patterson, J. Less-Common Metals 31, 47 (1973).
7. JANAF Thermochemical Tables: $Mg(OH)_2$(c), 3-31-67; H_2O(g), 3-31-61; HF(g), 12-31-68; AlF_3(c), 6-30-70; MgO(c), 12-31-74.
8. U.S. Natl. Bur. Std. Tech. Note 270-3, 1968.
9. V. B. Parker, NSRDS-NBS 2, April, 1965.
10. S. S. Todd, J. Amer. Chem. Soc. 71, 4115 (1949).
11. B. F. Naylor, J. Amer. Chem. Soc. 67, 150 (1945).
12. A. N. Krestovnikov and G. A. Karetnikov, Legkie Metal. 3, 29 (1934).
13. H. Kojima, S. G. Whiteway, and C. R. Masson, Can. J. Chem. 46, 2968 (1968).
14. G. Petit and F. Delbove, Compt. rend. 254, 1388 (1962).
15. A. Duncanson and R. W. H. Stevenson, Proc. Phys. Soc. 72, 1001 (1958).

MgF_2(g) Table References

1. O. Ruff and L. LeBoucher, Z. Anorg. Allgem. Chem. 219, 376 (1934).
2. K. G. Günther, Glastech. Ber. 31, 9 (1958).
3. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
4. G. Layne, Dow Chemical Co., private communication, May, 1975.
5. R. *R. Hammer, Ph.D. Thesis, University of California, 1961.*
6. R. R. Hammer and J. A. Pask, J. Amer. Ceram. Soc. 47, 264 (1964).
7. M. A. Greenbaum, H. C. Ko, M. Wong, and M. Farber, J. Phys. Chem. 68, 965 (1964).
8. D. L. Hildenbrand, Private Communication, September, 1975.
9. J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).
10. JANAF Thermochemical Tables: BeF_2(g), 6-30-70.
11. P. A. Akishin, V. P. Spiridonov, G. A. Sobolev, and V. A. Naumov, Zhur. Fiz. Khim. 31, 461 (1957).
12. A. Büchler, J. L. Stauffer, and W. Klemperer, J. Amer. Chem. Soc. 86, 4544 (1964).
13. A. Snelson, J. Phys. Chem. 70, 3208 (1966).
14. M. Astier and P. Millie, J. Organometal. Chem. 31, 139 (1971).
15. M. Astier, G. Berthier, and P. Millie, J. Chem. Phys. 57, 5008 (1972).
16. J. L. Gole, A.K.Q. Siu, and E. F. Hayes, J. Chem. Phys. 58, 857 (1973).
17. D. E. Mann, G. V. Calder, K. S. Seshadri, D. White, and M. J. Linevsky, J. Chem. Phys. 46, 1138 (1967).
18. V. Calder, D. E. Mann, K. S. Seshadri, M. Allaveua, and D. White, J. Chem. Phys. 51, 2093 (1969).
19. J. F. Labarre and C. Leibovici, J. Chim. Phys. Physiochim. Biol. 69, 541 (1972).
20. V. I. Baikov, Optics and Spectroscopy 25, 194 (1968).
21. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
22. R. H. Hauge, J. L. Margrave, and A. S. Kana'an, J. Chem. Soc., Faraday Transactions II 71, 1082 (1975).
23. M. L. Lesiecki and J. W. Nibler, to be published.
24. A. Allavena and S. Besnainov, J. Mol. Struct. 11, 439 (1975).

F_2MG

MAGNESIUM DIFLUORIDE (MgF_2) F_2Mg

(IDEAL GAS) GFW=62.3018

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	.000	.000	INFINITE	-2.881	-173.275	-173.275	INFINITE
100	8.967	50.198	70.762	-2.056	-173.299	-174.022	380.326
200	10.452	56.892	62.303	-1.082	-173.587	-174.750	190.958
298	11.534	61.280	61.280	.000	-173.700	-175.196	128.422
300	11.551	61.351	61.280	.021	-173.704	-175.206	127.637
400	12.279	64.782	61.743	1.216	-173.893	-175.678	95.966
500	12.744	67.575	62.638	2.468	-174.090	-176.101	76.974
600	13.045	69.927	63.662	3.759	-174.300	-176.485	64.285
700	13.248	71.954	64.706	5.074	-174.529	-176.830	55.209
800	13.389	73.733	65.725	6.406	-174.788	-177.143	48.393
900	13.490	75.316	66.704	7.751	-175.080	-177.420	43.083
1000	13.565	76.742	67.638	9.104	-177.531	-177.481	38.788
1100	13.622	78.037	68.525	10.463	-177.866	-177.462	35.258
1200	13.666	79.225	69.368	11.828	-178.225	-177.409	32.311
1300	13.701	80.320	70.169	13.196	-178.613	-177.325	29.811
1400	13.729	81.336	70.931	14.568	-209.392	-176.731	27.589
1500	13.752	82.284	71.657	15.942	-209.426	-174.396	25.409
1600	13.770	83.173	72.349	17.318	-209.462	-172.061	23.502
1700	13.786	84.008	73.010	18.696	-209.499	-169.721	21.819
1800	13.799	84.796	73.643	20.075	-209.539	-167.382	20.323
1900	13.810	85.543	74.250	21.455	-209.579	-165.038	18.984
2000	13.820	86.251	74.833	22.837	-209.621	-162.691	17.778
2100	13.828	86.926	75.393	24.219	-209.666	-160.346	16.687
2200	13.835	87.569	75.932	25.602	-209.713	-157.995	15.695
2300	13.842	88.184	76.451	26.986	-209.761	-155.642	14.789
2400	13.847	88.773	76.952	28.371	-209.811	-153.290	13.959
2500	13.852	89.339	77.437	29.756	-209.865	-150.935	13.195
2600	13.856	89.882	77.905	31.141	-209.921	-148.574	12.489
2700	13.860	90.405	78.358	32.527	-209.979	-146.214	11.835
2800	13.864	90.909	78.797	33.913	-210.039	-143.853	11.228
2900	13.867	91.396	79.224	35.300	-210.102	-141.485	10.663
3000	13.870	91.866	79.637	36.687	-210.170	-139.122	10.135
3100	13.872	92.321	80.039	38.074	-210.240	-136.751	9.641
3200	13.875	92.761	80.430	39.461	-210.315	-134.380	9.178
3300	13.877	93.188	80.810	40.849	-210.393	-132.006	8.742
3400	13.879	93.603	81.180	42.236	-210.477	-129.627	8.332
3500	13.880	94.005	81.541	43.624	-210.566	-127.248	7.946
3600	13.882	94.396	81.893	45.012	-210.660	-124.864	7.580
3700	13.883	94.776	82.236	46.401	-210.760	-122.480	7.235
3800	13.885	95.147	82.571	47.789	-210.867	-120.091	6.907
3900	13.886	95.507	82.898	49.178	-210.981	-117.706	6.596
4000	13.887	95.859	83.217	50.566	-211.103	-115.310	6.300
4100	13.888	96.202	83.530	51.955	-211.234	-112.915	6.019
4200	13.889	96.537	83.836	53.344	-211.373	-110.516	5.751
4300	13.890	96.863	84.135	54.733	-211.521	-108.112	5.495
4400	13.891	97.183	84.428	56.122	-211.680	-105.705	5.250
4500	13.892	97.495	84.715	57.511	-211.849	-103.295	5.017
4600	13.893	97.800	84.996	58.901	-212.028	-100.880	4.793
4700	13.894	98.099	85.271	60.290	-212.220	-98.461	4.578
4800	13.894	98.392	85.542	61.679	-212.424	-96.036	4.373
4900	13.895	98.678	85.807	63.069	-212.640	-93.610	4.175
5000	13.896	98.959	86.067	64.458	-212.870	-91.178	3.985
5100	13.896	99.234	86.323	65.848	-213.113	-88.749	3.803
5200	13.897	99.504	86.573	67.237	-213.371	-86.302	3.627
5300	13.897	99.769	86.820	68.627	-213.642	-83.853	3.458
5400	13.898	100.028	87.062	70.017	-213.929	-81.409	3.295
5500	13.898	100.283	87.300	71.407	-214.231	-78.949	3.137
5600	13.898	100.534	87.534	72.796	-214.551	-76.486	2.985
5700	13.899	100.780	87.765	74.186	-214.886	-74.014	2.838
5800	13.899	101.021	87.991	75.576	-215.237	-71.544	2.696
5900	13.900	101.259	88.214	76.966	-215.607	-69.063	2.558
6000	13.900	101.493	88.433	78.356	-215.994	-66.580	2.425

Dec. 31, 1960; June 30, 1964; March 31, 1966;
June 30, 1975

MAGNESIUM DIFLUORIDE (MgF_2) (IDEAL GAS) GFW = 62.3018 F_2Mg

Point Group C_{2v}

$S°_{298.15}$ = 61.3 ± 0.5 (or ± 3) gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -173.3 ± 0.8 (or ± 4) kcal/mol

$\Delta Hf°_{298.15}$ = -173.7 ± 0.8 (or ± 4) kcal/mol

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}

508 (1) 215 (1) 875 (1)

Bond Distance: Mg-F = 1.77 ± 0.02 Å Bond Angle: F-Mg-F = 158° σ = 2

Product of Moments of Inertia: $I_A I_B I_C = 1.0335 \times 10^{-115} g^3 cm^6$

Heat of Formation

The value of $\Delta Hs°_{298}$ is added to $\Delta Hf°_{298}$ (MgF_2, c) = -268.7±0.3 kcal/mol to give $\Delta Hf°_{298}$(g) = -173.7±0.8 kcal/mol. $\Delta Hs°_{298}$ is selected from the results of a third law analysis of twenty sets (1-9) of vapor pressure data for MgF_2(c,ℓ). These measurements cover an extended temperature range (∿1200°) and include the use of manometric (1, 4), Knudsen effusion (2, 5, 6), torsion-effusion (5-8), and mass spectrometric (3, 9) methods. Results of our analysis of these data are tabulated below. The amount of dimer present in the saturated vapor is predicted not to exceed 1% below 2000 K by several methods (3, 6, 7-9).

SOURCE	REACTION	METHOD	Temp. Range K	No. of Points	ΔHs°(or v), kcal/mol 2nd Law	ΔHs°(or v), kcal/mol 3rd Law	Drift eu	$-\Delta Hf°_{298}(MgF_2, g)^d$ kcal/mol
Ruff and LeBoucher (1)	A	Manometric	1934-2129	6	89.2	82.5±1.0	-3.3±3.4	173.8±1.5
Günther(2) Set 1	B	Knudsen Effusion	1337-1480	8	93.7	94.6±0.7	0.6±2.6	174.1±1.0
2	B	"	1440-1530	4	91.3	95.0±0.4	2.5±2.9	173.7±0.7
3	B	"	1284-1357	6	100.3	94.8±0.3	-4.1±1.9	173.9±0.6
Berkowitz and Marquart (3)	B	Mass Spec	1460	1	91.4[a]	93.9		174.8
Layne (4) Set 1	A	Manometric	2155-2327	Equation	82.9	82.40±0.03	-0.2	173.9±0.5
2	A	Manometric	2087-2357	Equation	84.8	82.53±0.2	-1.0	173.8±0.7
Hammer and Set 1	B	Knudsen Effusion	1451-1533	6	98.7	95.3 ±0.5	-2.3±3.5	173.4±0.8
Pask (5, 6) 2	A	"	1568-1613	4	81.9	82.9±0.2	0.6±4.2	173.4±0.7
3	B	Torsion Effusion	1413-1518	11[b]	92.9	95.3±0.6	1.7±2.3	173.4±0.9
4	A	"	1539-1614	11[c]	80.6	82.8±0.3	1.4±1.6	173.5±0.8
Greenbaum Set 1	B	"	1273-1433	21	72.7	90.6±1.4	13.2±1.0	178.1±1.7
et al.(7) 2	B	"	1373-1513	18[b]	76.6	91.0±1.0	10.0±0.8	177.7±1.3
Hilden- Set 1	B	"	1340-1500	Equation	97.7	95.8±0.2	-1.4	172.9±0.5
brand (8) 2	B	"	1348-1482	"	98.3	96.0±0.2	-1.6	172.7±0.5
3	B	"	1324-1465	"	96.7	95.7±0.1	-0.7	173.0±0.4
4	B	"	1376-1517	"	98.9	95.6±0.3	-2.2	173.1±0.7
5	B	"	1345-1515	"	97.9	95.7±0.2	-1.5	173.0±0.5
6	B	"	1341-1520	"	96.9	95.6±0.1	-1.0	173.1±0.4
Green et al.(9)	B	Mass Spec	1241-1492	Equation	93.9	95.4±0.2	1.1	173.3±0.5

Reactions: (A) $MgF_2(\ell) = MgF_2(g)$; (B) $MgF_2(c) = MgF_2(g)$.

[a] Second law value by slope method. [b] One point rejected due to failure of a statistical test.

[c] Two points rejected due to failure of a statistical test. [d] Third law value based on $\Delta Hf°_{298}(MgF_2,c)$ = -268.7±0.3 kcal/mol.

These data are in agreement on $\Delta Hs°_{298}$ = 95.0±0.5 kcal/mol. We adopt this value but assign an alternate uncertainty (±4) to ΔHf° to include the possibility that MgF_2 is linear (see below).

Heat Capacity and Entropy

Considerable confusion exists as to whether MgF_2 is bent or linear. Electron diffraction (11), electric deflection (12), matrix-isolation Raman (23) and infrared (13, 22, 23) spectral studies, and MO calculations (14-16, 24) predict a linear configuration. Other matrix-isolation IR studies (17, 18) and MO calculations (19, 24) favor the nonlinear structure. Isotopic shifts (18) in the matrix frequencies suggest that the most probable value of the apex angle is 158°. An energy minimum has been reported at 140° with a CNDO approximation (19). Unfortunately, the vapor pressure data are not sufficiently precise to be of use in the selection of a structure. The entropies of these two forms differ by only about 1.5 eu at temperatures in the range of the vapor pressure data. We tentatively adopt a bond angle of 158° but assign an alternate uncertainty (±3 eu) to $S°_{298}$ to include the possibility that the angle is 180°. The Mg-F bond length is taken from the electron-diffraction studies of Akishin et al. (11). The individual moments of inertia are: $I_A = 1.9327 \times 10^{-38}$, $I_B = 1.9047 \times 10^{-38}$, and $I_C = 2.807 \times 10^{-40}$ g cm^2

The symmetric stretching frequency is a compromise between the krypton matrix infrared (ν_1 = 478 cm^{-1}, 17) and Raman (ν_1 = 545 cm^{-1}, 23) values. Also, an intermediate value (ν_2 = 215 cm^{-1}) is selected for the bending frequency from the estimated gas-phase value (270 cm^{-1}) of Snelson (13) and that (165 cm^{-1}) which was observed in the high temperature (∿2000 K) infrared spectrum (20) of the vapor. ν_3 is the gas-phase value that was estimated by Snelson (13) from frequencies measured in three matrices. The krypton frequencies for ν_2 and ν_3 reported by Mann et al. (17) and Lesiecki and Nibler (23) agree quite well with those of Snelson (13). Also, the results of Hauge et al. (22) provide further support for the adopted ν_3 value. If MgF_2 is assumed to be linear and ν_2 is reduced to 165 cm^{-1}, then our free energy functions are decreased by 2.1 eu at 298.15 K, 1.6 eu at 1000 K, and 1.0 eu at 2000 K. These alternate functions are also reasonably consistent with the reported vapor pressure data. Previously published free energy functions (21) for MgF_2 (g) which were based on a linear structure are several units (2-5 eu) too low due to the use of an incorrect bending frequency (470 cm^{-1}).

References

See MgF_2 (ℓ) table.

F_2Mg

MAGNESIUM DIFLUORIDE UNIPOSITIVE ION (MgF_2^+) F_2Mg^+

(IDEAL GAS) GFW=62.3013

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	12.535	61.671	61.671	.000	141.487	136.387	- 101.440
300	12.554	61.749	61.671	.023	141.494	138.367	- 100.600
400	13.330	65.476	62.174	1.321	141.905	137.263	- 74.997
500	13.800	68.505	63.147	2.679	142.311	136.056	- 59.470
600	14.095	71.049	64.258	4.075	142.703	134.767	- 49.089
700	14.289	73.237	65.388	5.495	143.075	133.415	- 41.654
800	14.422	75.155	66.491	6.931	143.417	132.011	- 36.064
900	14.517	76.859	67.550	8.378	143.724	130.567	- 31.706
1000	14.587	78.393	68.559	9.833	141.872	129.271	- 28.252
1100	14.640	79.786	69.517	11.295	142.137	127.997	- 25.431
1200	14.681	81.061	70.427	12.761	142.375	126.700	- 23.075
1300	14.713	82.238	71.291	14.231	142.586	125.386	- 21.079
1400	14.736	83.329	72.112	15.703	112.404	124.535	- 19.441
1500	14.759	84.346	72.894	17.178	112.968	125.383	- 18.268
1600	14.776	85.300	73.640	18.655	113.529	126.190	- 17.237
1700	14.791	86.196	74.353	20.133	114.089	126.966	- 16.323
1800	14.803	87.042	75.034	21.613	114.647	127.706	- 15.506
1900	14.813	87.842	75.687	23.094	115.205	128.417	- 14.771
2000	14.822	88.602	76.314	24.576	115.760	129.099	- 14.107
2100	14.830	89.326	76.917	26.058	116.311	129.749	- 13.503
2200	14.836	90.016	77.497	27.542	116.862	130.378	- 12.952
2300	14.843	90.675	78.055	29.026	117.411	130.981	- 12.446
2400	14.848	91.307	78.595	30.510	117.957	131.558	- 11.980
2500	14.854	91.913	79.115	31.995	118.500	132.113	- 11.549
2600	14.859	92.496	79.619	33.481	119.041	132.648	- 11.150
2700	14.864	93.057	80.106	34.967	119.580	133.161	- 10.779
2800	14.869	93.596	80.578	36.454	120.118	133.652	- 10.432
2900	14.875	94.119	81.036	37.941	120.652	134.130	- 10.108
3000	14.880	94.624	81.481	39.429	121.182	134.582	- 9.804
3100	14.886	95.112	81.913	40.917	121.709	135.020	- 9.519
3200	14.893	95.585	82.333	42.406	122.233	135.441	- 9.250
3300	14.900	96.043	82.741	43.896	122.754	135.845	- 8.997
3400	14.908	96.488	83.139	45.386	123.270	136.237	- 8.757
3500	14.916	96.920	83.527	46.877	123.781	136.611	- 8.530
3600	14.926	97.340	83.905	48.369	124.287	136.972	- 8.315
3700	14.936	97.750	84.273	49.862	124.788	137.317	- 8.111
3800	14.946	98.148	84.633	51.356	125.284	137.651	- 7.917
3900	14.958	98.536	84.985	52.852	125.774	137.964	- 7.731
4000	14.970	98.915	85.328	54.348	126.256	138.273	- 7.555
4100	14.983	99.285	85.664	55.846	126.731	138.566	- 7.386
4200	14.997	99.646	85.993	57.345	127.199	138.849	- 7.225
4300	15.012	99.999	86.314	58.845	127.659	139.122	- 7.071
4400	15.028	100.345	86.629	60.347	128.110	139.385	- 6.923
4500	15.044	100.683	86.938	61.851	128.552	139.634	- 6.782
4600	15.061	101.013	87.240	63.356	128.985	139.877	- 6.646
4700	15.079	101.337	87.537	64.863	129.408	140.109	- 6.515
4800	15.097	101.655	87.828	66.372	129.821	140.336	- 6.390
4900	15.116	101.967	88.113	67.882	130.222	140.550	- 6.269
5000	15.136	102.272	88.393	69.395	130.612	140.756	- 6.152
5100	15.156	102.572	88.668	70.909	130.990	140.948	- 6.040
5200	15.176	102.867	88.938	72.426	131.357	141.146	- 5.932
5300	15.197	103.156	89.204	73.945	131.712	141.334	- 5.826
5400	15.219	103.440	89.465	75.466	132.053	141.505	- 5.727
5500	15.241	103.720	89.722	76.989	132.380	141.679	- 5.630
5600	15.263	103.994	89.974	78.514	132.693	141.846	- 5.536
5700	15.285	104.265	90.222	80.041	132.992	142.011	- 5.445
5800	15.307	104.531	90.467	81.571	133.278	142.162	- 5.357
5900	15.330	104.793	90.707	83.103	133.547	142.314	- 5.272
6000	15.352	105.050	90.944	84.637	133.800	142.456	- 5.189

Dec. 31, 1975

MAGNESIUM DIFLUORIDE UNIPOSITIVE ION (MgF_2^+) (IDEAL GAS) GFW = 62.3013

Point Group [$D_{\infty h}$]
$S^\circ_{298.15}$ = [61.7 ± 3.0] gibbs/mol
Ground State Configuration [$^2\Pi$]

ΔHf°_0 = 140.3 ± 5.0(or±9) kcal/mol F_2Mg^+
$\Delta Hf^\circ_{298.15}$ = 141.5 ± 5.0(or±9) kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Pi$	[20000]	4
$^2\Sigma$	[25000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[500](1)
[200](2)
[800](1)

Bond Distance: Mg-F = [1.95] Å
Bond Angle: F-Mg-F = [180]°
Rotational Constant: B_0 = [0.11668] cm^{-1}

σ = 2

Heat of Formation

The MgF_2^+ ion has been identified as an important species in the vapor mass spectra of the MgF_2(1-3), MgF_2-Tℓ-Pd (4), and MgF_2-Cu (5) systems. The observed appearance potentials (AP) for this ion are tabulated below.

Source	Year	AP, eV
Berkowitz and Marquart(1)	1962	13.5±0.4
Green et al.(2)	1964	13.6
Murad et al.(4)	1966	14.0±0.5
Hildenbrand(5)	1968	13.5
Hildenbrand(3)	1968	13.3±0.3

These results show the normal scatter expected for such measurements; the largest deviation is 0.7 eV. We adopt an average value of 13.6±0.2 eV (313.62±4.6 kcal/mol), and we assume that this value refers to the direct ionization process $MgF_2(g) + e^- = MgF_2^+(g) + 2e^-$ occurring at 0 K. Combining the selected AP value with $\Delta Hf^\circ_0(MgF_2,g)$ = -173.3±0.8 kcal/mol (6), we obtain *ΔHf°_0 (MgF_2^+,g) = 140.3±5 kcal/mol. The ΔHf° value at 298.15 K is* 141.5 kcal/mol. An alternate uncertainty of ±9 kcal/mol is included to cover the possibility that the MgF_2 molecule is linear (6).

Heat Capacity and Entropy

A comparison of the atomization energies (ΔHa°_0 in kcal/mol) for MgF_2(245, 6) and MgF_2^+ (107.7) suggests weaker bonding in the ion relative to the neutral molecule. One might therefore expect that the fundamental frequencies of MgF_2^+ would be somewhat less than those for MgF_2. We assume a slight decrease *in the three vibrational frequencies of MgF_2(6). MgF_2^+* (fifteen valence electrons) is isoelectronic with the molecules BO_2, N_3, NCO, and N_2O^+. By analogy with the ground states (6) for these isoelectronic molecules, we assume that the ground state for MgF_2^+ is $^2\Pi$. We also include two excited states ($^2\Pi$ and $^2\Sigma$) which would be expected to exist based on those observed for BO_2(6).

According to the diagram of Walsh (7), MgF_2^+ is predicted to be linear. This prediction is supported by the fact that several other fifteen valence electron molecules (BO_2, NCO, N_2O^+, and N_3) are now known to be linear in their ground states. We adopt a linear configuration. Due to the weaker bonding in MgF_2^+ relative to MgF_2, it is reasonable to assume that $r_e(MgF_2^+) > r_e(MgF_2)$. We assume a 10 % increase in the bond length for MgF_2 (6). The selected structure and bond length corresponds to a moment of inertia of 2.3990×10^{-38} g cm^2. The enthalpy between 298.15 K and 0 K is 2.967 kcal/mol.

References

1. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
2. J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).
3. D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).
4. E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. 45, 263 (1966).
5. D. L. Hildenbrand, J. Chem. Phys. 48, 2457 (1968).
6. JANAF Thermochemical Tables: MgF_2(g), 6-30-75; BO_2(g), 6-30-68; CNO(g), N_2O+(g), and N_3(g), 12-31-70.
7. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

F_2Mg^+

SULFUR DIFLUORIDE (SF_2)
(IDEAL GAS) GFW=70.0568

F_2S

	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	-2.682	-70.419	-70.419	INFINITE
100	8.265	51.442	70.251	-1.881	-70.477	-71.255	155.728
200	9.501	57.535	62.509	-0.995	-70.684	-71.958	78.632
298	10.733	61.565	61.565	0.000	-70.900	-72.536	53.170
300	10.753	61.632	61.566	0.020	-70.904	-72.546	52.850
400	11.686	64.862	62.000	1.145	-71.648	-73.040	39.907
500	12.307	67.541	62.848	2.347	-72.191	-73.325	32.050
600	12.717	69.824	63.825	3.599	-72.628	-73.509	26.776
700	12.995	71.806	64.827	4.886	-72.992	-73.602	22.980
800	13.188	73.555	65.810	6.195	-86.374	-74.936	20.471
900	13.328	75.117	66.759	7.522	-86.361	-73.506	17.850
1000	13.432	76.526	67.667	8.860	-86.349	-72.079	15.753
1100	13.511	77.810	68.531	10.207	-86.337	-70.654	14.038
1200	13.572	78.989	69.354	11.561	-86.324	-69.227	12.608
1300	13.620	80.077	70.138	12.921	-86.312	-67.801	11.398
1400	13.658	81.088	70.884	14.285	-86.302	-66.378	10.362
1500	13.690	82.031	71.596	15.652	-86.294	-64.956	9.464
1600	13.716	82.916	72.276	17.023	-86.286	-63.534	8.678
1700	13.738	83.748	72.927	18.395	-86.281	-62.111	7.985
1800	13.756	84.534	73.550	19.770	-86.278	-60.692	7.369
1900	13.771	85.278	74.148	21.147	-86.275	-59.268	6.817
2000	13.785	85.985	74.722	22.524	-86.276	-57.847	6.321
2100	13.796	86.657	75.275	23.903	-86.279	-56.428	5.873
2200	13.806	87.299	75.807	25.284	-86.283	-55.005	5.464
2300	13.815	87.913	76.320	26.665	-86.290	-53.583	5.092
2400	13.823	88.501	76.815	28.047	-86.299	-52.160	4.750
2500	13.829	89.066	77.294	29.429	-86.311	-50.738	4.435
2600	13.835	89.608	77.757	30.812	-86.325	-49.314	4.145
2700	13.841	90.131	78.206	32.196	-86.340	-47.891	3.876
2800	13.846	90.634	78.641	33.581	-86.357	-46.469	3.627
2900	13.850	91.120	79.063	34.965	-86.378	-45.041	3.394
3000	13.854	91.590	79.473	36.351	-86.401	-43.617	3.178
3100	13.857	92.044	79.871	37.736	-86.425	-42.191	2.974
3200	13.861	92.484	80.258	39.122	-86.453	-40.763	2.784
3300	13.864	92.910	80.635	40.508	-86.482	-39.336	2.605
3400	13.866	93.324	81.002	41.895	-86.513	-37.905	2.436
3500	13.869	93.726	81.360	43.281	-86.549	-36.475	2.278
3600	13.871	94.117	81.709	44.668	-86.584	-35.043	2.127
3700	13.873	94.497	82.050	46.056	-86.623	-33.610	1.985
3800	13.875	94.867	82.382	47.443	-86.664	-32.176	1.851
3900	13.877	95.228	82.707	48.831	-86.708	-30.746	1.723
4000	13.878	95.579	83.024	50.218	-86.754	-29.305	1.601
4100	13.880	95.922	83.335	51.606	-86.802	-27.871	1.486
4200	13.881	96.256	83.638	52.994	-86.853	-26.432	1.375
4300	13.883	96.583	83.936	54.383	-86.904	-24.992	1.270
4400	13.884	96.902	84.227	55.771	-86.961	-23.552	1.170
4500	13.885	97.214	84.512	57.159	-87.019	-22.110	1.074
4600	13.886	97.519	84.791	58.548	-87.078	-20.669	0.982
4700	13.887	97.818	85.065	59.937	-87.140	-19.224	0.894
4800	13.888	98.110	85.334	61.325	-87.205	-17.778	0.809
4900	13.889	98.397	85.598	62.714	-87.272	-16.327	0.728
5000	13.890	98.677	85.857	64.103	-87.342	-14.883	0.651
5100	13.891	98.952	86.111	65.492	-87.414	-13.434	0.576
5200	13.991	99.222	86.360	66.881	-87.488	-11.978	0.503
5300	13.892	99.487	86.605	68.270	-87.564	-10.526	0.434
5400	13.893	99.746	86.846	69.660	-87.643	-9.075	0.367
5500	13.893	100.001	87.083	71.049	-87.724	-7.617	0.303
5600	13.894	100.252	87.316	72.438	-87.809	-6.158	0.240
5700	13.894	100.498	87.545	73.828	-87.895	-4.701	0.180
5800	13.895	100.739	87.771	75.217	-87.983	-3.240	0.122
5900	13.896	100.977	87.992	76.607	-88.073	-1.784	0.066
6000	13.896	101.210	88.211	77.996	-88.167	-0.316	0.011

June 30, 1976

SULFUR DIFLUORIDE (SF_2) (Ideal Gas) GFW = 70.0568

F_2S

Point Group C_{2v}

$S^\circ_{298.15}$ = [61.57 ± 0.02] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[840 ± 20](1)

[357 ± 2](1)

[809 ± 10](1)

ΔHf°_0 = -70.4 ± 4.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -70.9 ± 4.0 kcal/mol

Bond Distance: S-F = 1.59208 ± 0.00008 Å

σ = 2

Bond Angle: F-S-F = 98.197 ± 0.011°

Product of Moments of Inertia: $I_AI_BI_C = 3.51797 \times 10^{-115}$ g^3 cm^6

Heat of Formation

We calculate ΔHf° from a third law analysis of two sets of equilibrium data for the gaseous isomolecular reaction $S + SF_2 = 2SF$. The equilibrium data are obtained from ion currents reported in a mass spectrometric study (1) of the molecular species formed from the reaction of gaseous SF_6 with graphite. We do not include in the equilibrium constants a proportionality constant involving ion multiplier gain and ionization cross sections since Hildenbrand (1) has recently demonstrated that these factors tend to cancel for isomolecular reactions. Results of our analyses are presented below.

Series	Cell Configuration	No. of Points	Temp. Range, K	ΔHr°_{298}, kcal/mol[a] 2nd Law	3rd Law	Drift eu	$-\Delta Hf^\circ_{298}(SF_2,g)$[b] kcal/mol
2	C cell/wound Pt wire	4	1436-1564	3.1	10.68 ±0.7	5.0 ±2.3	70.77 ±4.0
3	C cell/Pt partition/ packed with C cloth and Pt wire	7	1478-1588	7.7	10.87 ±0.9	2.1 ±5.0	70.96 ±4.0

[a] Heats calculated from ion current analogs of the equilibrium constants.

[b] Third law values based on JANAF auxiliary ΔHf° data (2).

The two cell configurations used by Hildenbrand (1) yield nearly identical third law ΔHf° values; thus, we adopt the rounded average of -70.9±4.0 kcal/mol. Our adopted ΔHf° value corresponds to a heat of atomization (ΔHa°_0) and average bond dissociation energy (D°_0) of 172.9 kcal/mol and 86.4 kcal/mol, respectively. In addition, the primary bond dissociation energy of SF_2 is calculated to be $D^\circ_0(SF\text{-}F)$ = 91.7 kcal/mol, suggesting that the individual S-F bonds are somewhat stronger than that in the SF (81.2 kcal/mol, 2) radical. This increase in bond strength is predicted by MO calculations (3) and has been qualitatively accounted for in terms of the valence-state model (1) of covalent bonding.

Two additional pieces of information exist which provide some support for our selected ΔHf° value. Kinetic studies (4) on the dissociation of SF_3 indicate that $D^\circ_0(SF_2\text{-}F) \simeq 72$ kcal/mol. We calculate $D^\circ_0(SF_2\text{-}F)$ = 67.3 kcal/mol from JANAF data (2), indicating that our heats of formation for SF_3 and SF_2 are consistent with these kinetic results. Di Lonardo and Trombetti (5) obtained $D^\circ_0(SF\text{-}F)$ = 92.2±12 kcal/mol from electron-impact threshold measurements on the COS/F and SF_6 systems. This value is to be compared with our calculated value of 91.7 kcal/mol.

Heat Capacity and Entropy

We adopt molecular data which refer to an average ground state structure for SF_2. These results are based on microwave measurements and force field calculations performed by Kirchhoff et al. (6). Earlier microwave spectroscopic observations (7) on the isotopic $^{34}SF_2$ species support the assignment of the spectrum to the difluoride and confirm its angular structure. The individual moments of inertia are: $I_A = 1.2273 \times 10^{-38}$, $I_B = 9.1359 \times 10^{-39}$, and $I_C = 3.1374 \times 10^{-39}$ g cm^2.

A recent review on the chemistry of the lower sulfur fluorides includes a discussion on the vibrational spectrum of SF_2 (8). The only observed vibrational frequency (830 cm^{-1}) which has so far been attributed to the difluoride appeared as a shoulder to a band at 810 cm^{-1} in the infrared spectra of a mixture of S-F compounds. The band at 810 cm^{-1} has been assigned (8) to the S-F equatorial stretching frequency of F_3SSF. We prefer not to adopt the 830 cm^{-1} frequency as a fundamental since the band cannot be positively identified as due to SF_2. Four sets (6, 9-11) of estimated frequencies have been reported. We believe that the best estimates are those of Kirchhoff et al. (6) which we adopt. These frequencies were obtained from force field calculations and include corrections which were made to account for the differences found between predicted and observed fundamentals for the related molecules OF_2, SO_2, SiF_2, and CF_2. By analogy with other even electron S-F species (2), we predict that the ground state is singlet and that there are no low-lying electronic levels which would contribute to the partition function.

Our thermal functions essentially update those reported by Wilkins (10). Another set of functions which cover a rather short (0-2000 K) temperature interval has been reported by O'Hare (11). We believe, however, that his estimate (ν_2 = 523 cm^{-1}, 11) of the bending frequency is too high based on that observed for SO_2(ν_2 = 517.7 cm^{-1}, 2), indicating that his entropies are probably too low by as much as 0.6 - 0.8 gibbs/mol.

References

1. D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
2. JANAF Thermochemical Tables: S(g), 6-30-71; SF_6(g), SF_4(g), SF_3(g), and SF(g), 6-30-76; F(g), 9-30-65; SO_2(g), 6-30-61.
3. A. L. Companion, Theoret. Chim. Acta, 25, 268 (1972).
4. J. F. Bott, J. Chem. Phys. 54, 181 (1971).
5. G. Di Lonardo and A. Trombetti, Trans. Faraday Soc. 66, 2694 (1970).
6. W. H. Kirchhoff, D. R. Johnson, and F. X. Powell, J. Mol. Spectrosc. 48, 157 (1973).
7. D. R. Johnson and F. X. Powell, Science, 164, 950 (1969).
8. F. Seel, in "Advances in Inorganic Chemistry and Radiochemistry", H. J. Emeléus and A. G. Sharpe, eds., Vol. 16, Academic Press, New York, 1974.
9. C. Bliefert and K. P. Wanczek, Z. Naturforsch. 259, 1770 (1970).
10. R. L. Wilkins, Aerospace Corporation, Report No. TR-0158 (3240-20)-19; Contract No. FO4695-67-C-0158, July, 1968.
11. P. A. G. O'Hare, Argonne National Laboratory, ANL-7315, Contract No. W-31-109-Eng-38, July, 1968.

F_2S

DIFLUORODISULFANE (FS_2F)
(IDEAL GAS) GFW=102.1168

F_2S_2

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	-3.488	-79.682	-79.682	INFINITE
100	10.076	56.325	82.640	-2.631	-79.848	-80.819	176.629
200	13.486	64.411	71.638	-1.445	-80.148	-81.673	89.248
298	15.784	70.260	70.260	0.000	-80.410	-82.363	60.374
300	15.817	70.358	70.260	0.029	-80.415	-82.375	60.010
400	17.202	75.116	70.900	1.686	-81.726	-82.950	45.322
500	18.020	79.050	72.148	3.451	-82.644	-83.148	36.344
600	18.525	82.363	73.583	5.280	-83.361	-83.178	30.298
700	18.853	85.265	75.051	7.150	-83.942	-83.052	25.930
800	19.077	87.798	76.489	9.047	-110.561	-85.427	23.338
900	19.236	90.055	77.873	10.963	-110.397	-82.295	19.984
1000	19.351	92.088	79.195	12.893	-110.234	-79.181	17.305
1100	19.439	93.936	80.452	14.833	-110.072	-76.086	15.117
1200	19.506	95.631	81.647	16.780	-109.910	-73.001	13.295
1300	19.559	97.194	82.784	18.733	-109.750	-69.930	11.756
1400	19.601	98.645	83.866	20.691	-109.593	-66.873	10.439
1500	19.635	99.999	84.897	22.653	-109.438	-63.830	9.300
1600	19.663	101.267	85.660	24.618	-109.284	-60.792	8.304
1700	19.687	102.460	86.821	26.586	-109.132	-57.766	7.426
1800	19.706	103.586	87.721	28.555	-108.985	-54.751	6.648
1900	19.723	104.651	88.585	30.527	-108.837	-51.739	5.951
2000	19.738	105.664	89.413	32.500	-108.693	-48.738	5.326
2100	19.750	106.627	90.210	34.474	-108.553	-45.747	4.761
2200	19.761	107.546	90.978	36.450	-108.414	-42.757	4.248
2300	19.770	108.424	91.717	38.426	-108.279	-39.776	3.780
2400	19.778	109.266	92.431	40.404	-108.145	-36.800	3.351
2500	19.785	110.074	93.121	42.382	-108.014	-33.830	2.957
2600	19.792	110.850	93.788	44.361	-107.886	-30.865	2.594
2700	19.798	111.597	94.434	46.340	-107.760	-27.906	2.259
2800	19.803	112.317	95.060	48.320	-107.637	-24.955	1.948
2900	19.808	113.012	95.667	50.301	-107.516	-22.000	1.658
3000	19.812	113.683	96.256	52.282	-107.400	-19.054	1.388
3100	19.815	114.333	96.829	54.263	-107.283	-16.112	1.136
3200	19.819	114.962	97.386	56.245	-107.172	-13.173	0.900
3300	19.822	115.572	97.926	58.227	-107.061	-10.239	0.678
3400	19.825	116.164	98.455	60.209	-106.954	-7.303	0.469
3500	19.828	116.739	98.969	62.192	-106.851	-4.377	0.273
3600	19.830	117.297	99.471	64.175	-106.747	-1.448	0.088
3700	19.832	117.841	99.960	66.158	-106.650	1.477	-0.087
3800	19.834	118.370	100.438	68.141	-106.553	4.398	-0.253
3900	19.836	118.885	100.904	70.125	-106.460	7.312	-0.410
4000	19.838	119.387	101.360	72.109	-106.368	10.236	-0.559
4100	19.839	119.877	101.806	74.092	-106.280	13.146	-0.701
4200	19.841	120.355	102.241	76.076	-106.195	16.059	-0.836
4300	19.842	120.822	102.668	78.061	-106.110	18.969	-0.964
4400	19.844	121.278	103.086	80.045	-106.032	21.876	-1.087
4500	19.845	121.724	103.495	82.029	-105.955	24.784	-1.204
4600	19.846	122.160	103.896	84.014	-105.879	27.686	-1.315
4700	19.847	122.587	104.289	85.999	-105.806	30.588	-1.422
4800	19.848	123.005	104.675	87.983	-105.737	33.488	-1.525
4900	19.849	123.414	105.053	89.968	-105.670	36.395	-1.623
5000	19.850	123.815	105.424	91.953	-105.607	39.288	-1.717
5100	19.851	124.208	105.789	93.938	-105.546	42.185	-1.808
5200	19.852	124.594	106.147	95.923	-105.487	45.086	-1.895
5300	19.852	124.972	106.499	97.909	-105.429	47.980	-1.978
5400	19.853	125.343	106.844	99.894	-105.377	50.872	-2.059
5500	19.854	125.707	107.184	101.879	-105.326	53.766	-2.136
5600	19.854	126.065	107.518	103.865	-105.279	56.662	-2.211
5700	19.855	126.416	107.846	105.850	-105.235	59.550	-2.283
5800	19.856	126.762	108.169	107.836	-105.191	62.442	-2.353
5900	19.856	127.101	108.487	109.821	-105.151	65.323	-2.420
6000	19.857	127.435	108.800	111.807	-105.114	68.221	-2.485

June 30, 1976

DIFLUORODISULFANE (S_2F_2) (IDEAL GAS) GFW = 102.1168

F_2S_2

Point Group C_2

$S^\circ_{298.15}$ = 70.26 ± 0.02 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = [-79.7 ± 10.0] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-80.4 ± 10.0] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
717.0(1)	182.5(1)
614.6(1)	680.8(1)
319.8(1)	301.0(1)

Bond Distances: S-F = 1.635 ± 0.01 Å S-S = 1.888 ± 0.01 Å σ = 2

Bond Angles: F-S-S = 108.3 ± 0.5° Dihedral = 87.9 ± 1.5°

Product of Moments of Inertia: $I_AI_BI_C = 7.33050 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

No direct experimental measurement of ΔHf° is available. We estimate a value from bond energy considerations. From a comparison of bond lengths and force constants for FSSF (1) and SF_4 (2), we expect that the S-F bond energies in FSSF would be quite similar to those for the axial S-F bonds in SF_4. We assume $D^\circ_0(FSS\text{-}F) = D^\circ_0(SF_3\text{-}F)_{axial}$ = 73.6 kcal/mol which leads to the adopted value of $\Delta Hf^\circ_0(S_2F_2,g)$ = -79.7 kcal/mol. We use auxiliary heat of formation data from JANAF (3) and estimate the uncertainty in ΔHf° as ±10.0 kcal/mol. A previous estimate (-83.5 kcal/mol) has been reported by O'Hare (4) who derived this value by a procedure identical with that used here. ΔHf° at 298.15 K corresponds to -80.4 kcal/mol, and the atomization energy is calculated from ΔHf° to be 247.9 kcal/mol.

FSSF is isomeric with SSF_2 (3). Qualitative evidence has been presented (1) which indicates that SSF_2 is the more stable isomer. From our estimated free energy data, we predict a Gibbs energy change for the isomerization reaction $FSSF(g) = SSF_2(g)$ of -15.4 kcal/mol at 298.15 K, indicating that SSF_2 is substantially more stable than FSSF. This conflicts with relative stability predictions based on results from two independent MO studies (5, 6). These semiempirical (CNDO/2) calculations indicate that the instability of FSSF relative to SSF_2 amounts to only about 2.0 kcal/mol. If we assume that these MO calculations are correct, we calculate that $D^\circ_0(FS\text{-}SF) > D^\circ_0(S{=}SF_2)$ by roughly 7.0 kcal/mol. This seems very unlikely in view of what is known (1) about the S-S linkages in the two isomers. Our adopted results give $D^\circ_0(FS\text{-}SF)$ = 85.6 kcal/mol which lies between that for SSF_2(90.4 kcal/mol) and S_2O (79.9 kcal/mol)(3).

Heat Capacity and Entropy

The structural data and vibrational frequencies are taken from the recent review of Seel (1) and are based on reliable experimental measurements. We note that the molecular characteristics of FSSF are unusual in that the S-S bond length (1.888 Å) is much shorter than that in HSSH(2.05 Å, 1) and nearly equal to those in S_2(1.889 Å), SSF_2(1.860 Å), and S_2O (1.884 Å)(3). In contrast, the S-F bonds are longer than those in most S-F species (∿1.58 Å, 3) and nearly as long as the axial S-F bonds (1.646 Å, 3) in SF_4. Rationale (1) has been presented to explain these unique molecular features in terms of double bond ($F^-S{=}S^+\text{-}F$) formation. The individual moments of inertia are: $I_A = 3.2678 \times 10^{-39}$, $I_B = 3.0490 \times 10^{-38}$, and $I_C = 7.3574 \times 10^{-39}\ g\ cm^2$.

We assume that there is no free internal rotation in the molecule, and the contribution from the torsional oscillation ($\nu_4 = 182.5\ cm^{-1}$) is included in the vibrational partition function. Extended Hückel calculations (7) show that the potential barrier to internal rotation is high (∿40 kcal/mol), providing some justification for our treatment. We estimate that the uncertainty in our entropies above 2000 K should not exceed 1.0 gibbs/mol. The UV spectra (1) of FSSF reveal no excited states which would be significant in our calculations. Since S_2F_2 has no unpaired electrons, we predict that the ground state is singlet.

Our thermal functions essentially extend those reported by Brown and Pez (8). Other published functions (4, 9) are based on estimated vibrational frequencies and are considered less reliable.

References

1. F. Seel, in "Advances in Inorganic Chemistry and Radiochemistry," Vol. 16, H. J. Emeléus and A. G. Sharpe, eds., Academic Press, New York, 1974.
2. I. W. Levin, J. Chem. Phys. 55, 5393 (1971).
3. JANAF Thermochemical Tables: $S_2(g)$, 12-31-65; F(g), 9-30-65; $SSF_2(g)$ and $SF_4(g)$, 6-30-76; $S_2O(g)$, 9-30-65.
4. P. A. G. O'Hare, Argonne National Laboratory, ANL-7315, Contract W-31-109-Eng-38, July, 1968.
5. A. L. Companion, Theoret. Chim. Acta, 25, 268 (1972).
6. G. Wagner, H. Bock, R. Budenz, and F. Seel, Chem. Ber. 106, 1285 (1973).
7. R. M. Minyaev, V. I. Minkin, I. I. Zakharov, and I. D. Sadekov, Teor. Eksp. Khim. 9, 816 (1973).
8. R. D. Brown and G. P. Pez, Spectrochimica Acta, 26A, 1375 (1970).
9. B. J. McBride, S. Heimel, J. G. Ehlers, and S. Gordon, NASA Rep. SP-3001, July, 1963.

F_2S_2

THIOTHIONYL FLUORIDE (SSF$_2$) F_2S_2

(IDEAL GAS) GFW=102.1168

	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	-3.279	-95.003	-95.003	INFINITE
100	9.176	57.014	81.580	-2.457	-95.204	-96.242	210.338
200	12.574	64.436	71.267	-1.366	-95.599	-97.129	106.137
298	15.088	69.960	69.960	0.000	-95.940	-97.804	71.692
300	15.125	70.053	69.960	0.028	-95.946	-97.815	71.258
400	16.702	74.640	70.575	1.626	-97.316	-98.350	53.736
500	17.655	78.478	71.782	3.348	-98.277	-98.496	43.052
600	18.252	81.753	73.178	5.145	-99.026	-98.465	35.866
700	18.643	84.598	74.611	6.991	-99.631	-98.274	30.683
800	18.911	87.106	76.019	8.870	-126.268	-100.581	27.478
900	19.101	89.345	77.378	10.771	-126.119	-97.379	23.647
1000	19.241	91.365	78.677	12.688	-125.969	-94.193	20.586
1100	19.346	93.204	79.915	14.618	-125.817	-91.026	18.085
1200	19.428	94.891	81.094	16.557	-125.663	-87.867	16.003
1300	19.491	96.449	82.216	18.503	-125.510	-84.721	14.243
1400	19.543	97.895	83.285	20.455	-125.359	-81.590	12.737
1500	19.584	99.245	84.304	22.411	-125.210	-78.472	11.433
1600	19.618	100.510	85.278	24.371	-125.061	-75.359	10.294
1700	19.647	101.700	86.210	26.334	-124.914	-72.257	9.289
1800	19.671	102.824	87.102	28.300	-124.770	-69.166	8.398
1900	19.691	103.888	87.957	30.268	-124.626	-66.077	7.601
2000	19.708	104.899	88.779	32.238	-124.485	-63.000	6.884
2100	19.723	105.861	89.570	34.210	-124.347	-59.933	6.237
2200	19.736	106.778	90.332	36.183	-124.211	-56.865	5.649
2300	19.748	107.656	91.066	38.157	-124.078	-53.808	5.113
2400	19.758	108.497	91.775	40.133	-123.946	-50.755	4.622
2500	19.767	109.303	92.460	42.109	-123.817	-47.708	4.171
2600	19.775	110.079	93.123	44.086	-123.691	-44.666	3.755
2700	19.782	110.825	93.765	46.064	-123.566	-41.630	3.370
2800	19.788	111.545	94.387	48.042	-123.445	-38.601	3.013
2900	19.794	112.239	94.991	50.021	-123.326	-35.570	2.681
3000	19.799	112.910	95.577	52.001	-123.211	-32.546	2.371
3100	19.803	113.560	96.146	53.981	-123.095	-29.527	2.082
3200	19.808	114.189	96.700	55.962	-122.985	-26.510	1.811
3300	19.811	114.798	97.240	57.943	-122.875	-23.499	1.556
3400	19.815	115.390	97.765	59.924	-122.769	-20.485	1.317
3500	19.818	115.964	98.277	61.906	-122.667	-17.482	1.092
3600	19.821	116.522	98.776	63.888	-122.564	-14.476	0.879
3700	19.824	117.065	99.263	65.870	-122.468	-11.473	0.678
3800	19.827	117.594	99.738	67.852	-122.372	-8.475	0.487
3900	19.829	118.109	100.203	69.835	-122.280	-5.483	0.307
4000	19.832	118.611	100.657	71.818	-122.189	-2.482	0.136
4100	19.834	119.101	101.101	73.802	-122.100	0.506	-0.027
4200	19.837	119.579	101.535	75.785	-122.016	3.497	-0.182
4300	19.839	120.046	101.960	77.769	-121.932	6.484	-0.330
4400	19.841	120.502	102.376	79.753	-121.854	9.469	-0.470
4500	19.844	120.948	102.784	81.737	-121.777	12.455	-0.605
4600	19.846	121.384	103.184	83.722	-121.701	15.434	-0.733
4700	19.848	121.811	103.575	85.706	-121.629	18.414	-0.856
4800	19.851	122.229	103.960	87.691	-121.559	21.392	-0.974
4900	19.853	122.638	104.337	89.676	-121.492	24.376	-1.087
5000	19.856	123.039	104.707	91.662	-121.428	27.346	-1.195
5100	19.859	123.432	105.070	93.648	-121.366	30.321	-1.299
5200	19.862	123.818	105.427	95.634	-121.306	33.300	-1.400
5300	19.865	124.196	105.778	97.620	-121.248	36.271	-1.496
5400	19.868	124.568	106.122	99.607	-121.194	39.241	-1.588
5500	19.871	124.932	106.461	101.594	-121.141	42.212	-1.677
5600	19.875	125.290	106.794	103.581	-121.093	45.186	-1.763
5700	19.879	125.642	107.121	105.569	-121.046	48.151	-1.846
5800	19.883	125.988	107.444	107.557	-121.000	51.121	-1.926
5900	19.887	126.328	107.761	109.545	-120.957	54.079	-2.003
6000	19.891	126.662	108.073	111.534	-120.917	57.054	-2.078

June 30, 1976

THIOTHIONYL FLUORIDE (S_2F_2) (IDEAL GAS) GFW = 102.1168

F_2S_2

Point Group C_s
$S^\circ_{298.15}$ = 69.96 ± 0.10 gibbs/mol

ΔHf°_0 = [-95.0 ± 10.0] kcal/mol
$\Delta Hf^\circ_{298.15}$ = [-95.9 ± 10.0] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[1]
34000	[1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
760.5(1)	330.0(1)
718.5(1)	692.3(1)
411.2(1)	274.0(1)

Bond Distances: S=S = 1.860 ± 0.015 Å S-F = 1.598 ± 0.012 Å σ = 1
Bond Angles: S=S-F = 107.5 ± 1.0° F-S-F = 92.5 ± 1.0°
Product of Moments of Inertia: $I_AI_BI_C$ = 5.9557 x 10^{-114} g^3 cm^6

Heat of Formation

No direct experimental measurement of ΔHf° is available. We estimate two values from bond energy considerations. Seel (1) has presented a detailed discussion on the bonding in S_2, S_2O, and SSF_2 and has shown from bond length and force constant correlations that the S=S linkages in these molecules are very similar. We assume that $D^\circ_0(S{=}SF_2) = (D^\circ_0(S_2) + D^\circ_0(S_2O))/2$ = 90±10 kcal/mol which gives $\Delta Hf^\circ_0(SSF_2,g)$ = -94.7±14 kcal/mol when the value of D°_0 is combined with $\Delta Hf^\circ_0(SF_2,g)$ = -70.4±4 kcal/mol and $\Delta Hf^\circ_0(S,g)$ = 65.75±0.01 kcal/mol (2). From a comparison of bond lengths and force constants (1, 3) for the S-F bonds in SSF_2, OSF_2, and SF_4, we would expect that the mean S-F bond energies for these molecules are probably not too different. Values (2) for OSF_2 and SF_4 are 83.4 kcal/mol and 80.0 kcal/mol, respectively. Using $D^\circ_0(S_2F\text{-}F)$ = 81.5±2.5 kcal/mol, we calculate ΔHr°_0 = 163.0 kcal/mol for the dissociation process $S_2F_2 = S_2+2F$ which leads to $\Delta Hf^\circ_0(SSF_2,g)$ = -95.5±5.0 kcal/mol. These two estimates are in reasonable agreement and we choose to adopt the value of -95.0±10.0 kcal/mol. The heat of atomization (ΔHa°_0) is calculated from our adopted ΔHf° value to be 263.2 kcal/mol which is close to the value of 262.0 kcal/mol predicted by CNDO/2 MO calculations and energy partitioning methods (4).

Published estimates (1, 5, and 6) of ΔHf° based on bond energy schemes similar to those used here include in kcal/mol -92±7, -80.2, and -86.4. Wilkins (6) assumed that the mean S-F bond energy for SSF_2 was 80.0 kcal/mol and obtained ΔHf° = -86.4 kcal/mol. We believe that this estimate is in error. Recalculation of his data gives ΔHf° = -91.6 kcal/mol which is in much better agreement with our results.

Heat Capacity and Entropy

The structural data and vibrational frequencies are taken from the recent review by Seel (1) and are based on reliable experimental measurements. Since SSF_2 has no unpaired electrons, we predict that the ground state is singlet. The ultraviolet spectra (1) show absorption peaks at roughly 34000 cm^{-1} and 42000 cm^{-1}, suggesting the existence of at least two excited states. We do not include the level near 42000 cm^{-1} since its effect is negligible. The individual moments of inertia are: $I_A = 2.7530 \times 10^{-38}$, $I_B = 2.1012 \times 10^{-38}$, and $I_C = 1.0296 \times 10^{-38}$ g cm^2.

Our thermal functions essentially extend those reported by Brown and Pez (7). Other published functions (5, 6) are based on an older set of vibrational frequencies (8) and include a bias due to incorrect analysis of the SSF_2 structure. O'Hare's analysis (5) of the structural data resulted in a value for the product of the moments of inertia which is about 7% lower than our results. In addition, he assigned SSF_2 to point group C_{2v} and used a symmetry number of two rather than the correct value of one. The moments of inertia used by Wilkins (6) are in units of amu Å^2, not g cm^2 as assumed.

References

1. F. Seel, in "Advances in Inorganic Chemistry and Radio Chemistry", Vol. 16, H. J. Emeléus and A. G. Sharpe, eds., Academic Press, New York, 1974.
2. JANAF Thermochemical Tables: $S_2(g)$, 12-31-65; $S_2O(g)$, 6-30-65; $SF_2(g)$ and $SF_4(g)$, 6-30-76; S(g), 6-30-71; $OSF_2(g)$, 6-30-72.
3. I. W. Levin, J. Chem. Phys. 55, 5393 (1971).
4. A. L. Companion, Theoret. Chim. Acta, 25, 268 (1972).
5. P. A. G. O'Hare, Argonne National Laboratory, ANL-7315, Contract W-31-109-Eng-38, July, 1968.
6. R. L. Wilkins, Aerospace Corporation, Report No. TR-0158(3240-20)-19, Contract F04695-67-C-0158, July, 1968.
7. R. D. Brown and G. P. Pez, Spectrochimica Acta, 26A, 1375 (1970).
8. R. D. Brown, G. P. Pez, and M. F. O'Dwyer, Aust. J. Chem. 18, 627 (1965).

SILICON DIFLUORIDE (SiF_2) (IDEAL GAS) GFW=66.0828

F_2SI

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	-2.678	-140.299	-140.299	INFINITE
100	8.298	51.185	69.946	-1.876	-140.256	-141.213	308.622
200	9.476	57.292	62.233	-0.988	-140.349	-142.141	155.325
298	10.638	61.297	61.297	0.000	-140.500	-142.990	104.815
300	10.658	61.363	61.297	0.020	-140.503	-143.006	104.180
400	11.581	64.563	61.727	1.134	-140.666	-143.815	78.577
500	12.214	67.220	62.567	2.326	-140.825	-144.584	63.197
600	12.640	69.487	63.536	3.570	-140.981	-145.321	52.933
700	12.931	71.459	64.530	4.850	-141.137	-146.031	45.593
800	13.137	73.199	65.507	6.154	-141.299	-146.721	40.082
900	13.285	74.756	66.450	7.475	-141.466	-147.388	35.791
1000	13.396	76.162	67.352	8.809	-141.641	-148.037	32.353
1100	13.480	77.442	68.212	10.153	-141.824	-148.668	29.538
1200	13.545	78.618	69.031	11.505	-142.014	-149.282	27.188
1300	13.597	79.705	69.811	12.862	-142.215	-149.879	25.197
1400	13.639	80.714	70.554	14.224	-142.425	-150.461	23.488
1500	13.672	81.656	71.263	15.589	-142.646	-151.026	22.004
1600	13.700	82.539	71.940	16.958	-142.877	-151.578	20.705
1700	13.724	83.371	72.588	18.329	-155.112	-152.008	19.542
1800	13.744	84.156	73.210	19.703	-155.310	-151.821	18.434
1900	13.760	84.899	73.805	21.078	-155.509	-151.622	17.440
2000	13.775	85.605	74.378	22.455	-155.709	-151.410	16.545
2100	13.787	86.278	74.929	23.833	-155.911	-151.192	15.735
2200	13.798	86.919	75.459	25.212	-156.115	-150.963	14.997
2300	13.807	87.533	75.971	26.592	-156.320	-150.723	14.322
2400	13.816	88.121	76.465	27.974	-156.526	-150.475	13.703
2500	13.823	88.685	76.943	29.356	-156.735	-150.220	13.132
2600	13.830	89.227	77.405	30.738	-156.946	-149.954	12.605
2700	13.836	89.749	77.852	32.122	-157.157	-149.681	12.116
2800	13.842	90.252	78.286	33.505	-157.371	-149.400	11.661
2900	13.847	90.738	78.707	34.890	-157.586	-149.110	11.237
3000	13.852	91.208	79.116	36.275	-157.804	-148.818	10.841
3100	13.858	91.662	79.514	37.660	-158.023	-148.515	10.470
3200	13.863	92.102	79.900	39.046	-158.244	-148.202	10.122
3300	13.868	92.529	80.276	40.433	-158.466	-147.885	9.794
3400	13.874	92.943	80.643	41.820	-158.690	-147.561	9.485
3500	13.879	93.345	81.000	43.208	-158.916	-147.230	9.193
3600	13.886	93.736	81.348	44.596	-251.104	-144.635	8.781
3700	13.893	94.117	81.688	45.985	-251.234	-141.676	8.368
3800	13.900	94.487	82.020	47.374	-251.366	-138.712	7.978
3900	13.908	94.849	82.345	48.765	-251.500	-135.750	7.607
4000	13.917	95.201	82.662	50.156	-251.635	-132.778	7.255
4100	13.927	95.545	82.972	51.548	-251.773	-129.808	6.919
4200	13.938	95.880	83.275	52.942	-251.910	-126.831	6.600
4300	13.950	96.208	83.572	54.336	-252.048	-123.849	6.295
4400	13.963	96.529	83.863	55.732	-252.189	-120.868	6.004
4500	13.977	96.843	84.148	57.129	-252.329	-117.879	5.725
4600	13.992	97.151	84.427	58.527	-252.470	-114.891	5.459
4700	14.008	97.452	84.701	59.927	-252.613	-111.898	5.203
4800	14.026	97.747	84.970	61.329	-252.754	-108.901	4.958
4900	14.045	98.036	85.234	62.732	-252.897	-105.902	4.723
5000	14.065	98.320	85.492	64.138	-253.039	-102.904	4.498
5100	14.086	98.599	85.747	65.545	-253.182	-99.900	4.281
5200	14.108	98.873	85.997	66.955	-253.324	-96.890	4.072
5300	14.132	99.141	86.242	68.367	-253.465	-93.879	3.871
5400	14.156	99.406	86.483	69.781	-253.608	-90.872	3.678
5500	14.182	99.666	86.721	71.198	-253.749	-87.857	3.491
5600	14.209	99.922	86.954	72.618	-253.890	-84.835	3.311
5700	14.237	100.173	87.184	74.040	-254.031	-81.813	3.137
5800	14.267	100.421	87.410	75.465	-254.171	-78.791	2.969
5900	14.297	100.665	87.633	76.893	-254.311	-75.772	2.807
6000	14.328	100.906	87.852	78.325	-254.449	-72.744	2.650

Dec. 31, 1960; Sept. 30, 1963; June 30, 1968; Dec. 31, 1968; June 30, 1976

SILICON DIFLUORIDE (SiF_2) (IDEAL GAS) GFW = 66.0828

F_2SI

Point Group = C_{2V}
$S°_{298.15}$ = 61.30 ± 0.10 gibbs/mol

$\Delta Hf°_0$ = -140.3 ± 3 kcal/mol
$\Delta Hf°_{298.15}$ = -140.5 ± 3 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	gi
$^1A_1$	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)

Bond Distance: Si-F = 1.591 Å   σ = 2
Bond Angle: F-Si-F = 100° 59'
Product of the Moments of Inertia: $I_AI_BI_C = 3.20014 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

Margrave, Kanaan, 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 $\Delta Hr°_{298}$ = 92±10 kcal/mol, which gives $\Delta Hf°_{298}$(SiF_2, g) = -147±5 kcal/mol.

Ehlert and Margrave (3) have reported equilibrium constants for three reactions determined mass spectrometrically.

A. CaF_2(c) + Si(g) = Ca(g) + SiF_2(g)
B. CaF_2(g) + Si(g) = Ca(g) + SiF_2(g)
C. 2CaF(g) + Si(g) = 2Ca(g) + SiF_2(g)

M. Farber (13) has determined equilibrium constants mass spectrophotometrically for the reaction

D. SiF_4(g) + Si(g) = 2 SiF_2(g).

A 2nd and 3rd law analysis of the data is shown below.

Reaction	Range K	Points	$\Delta Hr°_{298}$ kcal/mol 2nd law	 3rd law	Drift gibbs/mol	$\Delta Hf°_{298}$(g)* kcal/mol
A	1395 - 1543	12	80.2 ± 14.1	88.0 ± 3.0	4.6 ± 9.7	-140.1 ± 3
B	1395 - 1543	12	-9.2 ± 14.1	-18.0 ± 3.0	-6.6 ± 9.6	-140.7 ± 3
C	1395 - 1543	12	-18.6 ± 7.5	-33.6 ± 1.8	-10.2 ± 5.0	-141. ± 3
D	1590 - 1782	10	-2.1 ± 1.4	-3.2 ± 0.3	0.7 ± 0.8	-140.7 ± 0.3

* *$\Delta Hf°_{298}$(g) is calculated from the third law $\Delta Hr°_{298}$ using auxiliary data (2).*

We adopt $\Delta Hf°_{298}$(SiF_2,g) = -140.5±3 kcal/mol.

Using JANAF values (2), $\Delta Ha°_0$ = 283.68±5 kcal/mol is calculated for the process SiF_2(g) = Si(g) + 2 F(g). The ratio $\Delta Ha°_0$(SiF_2,g)/$\Delta Ha°_0$(SiF_4,g) (2) is 0.502.

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.

References

1. J. L. Margrave, A. S. Kanaan, and D. C. Pease, J. Phys. Chem. 66, 1200 (1962).
2. JANAF Thermochemical Tables: Si(c), 12-31-66; Si(g), 3-31-67; Ca(g), CaF(g), CaF_2(c, g), 12-31-68; SiF_4(g), 6-30-76; F(g), 9-30-65.
3. T. C. Ehlert and J. L. Margrave, J. Chem. Phys. 4, 1066 (1964).
4. V. M. Khanna, G. Besenbruch, and J. L. Margrave, J. Chem. Phys. 46, 2310 (1967).
5. D. R. Rao, J. Mol. Spectrosc. 34, 284 (1970).
6. J. L. Gole, R. H. Hauge, J. L. Margrave, and J. W. Hastie, J. Mol. Spectrosc. 43, 441 (1972).
7. V. M. Khanna, R. Hauge, R. F. Curl, Jr., and J. L. Margrave, J. Chem. Phys. 47, 5031 (1967).
8. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 49, 4269 (1968).
9. J. W. Hastie, R. H. Hauge, and J. L. Margrave, J. Am. Chem. Soc. 91, 2536 (1969).
10. H. Shoji, T. Tanaka, and E. Hirota, J. Mol. Spectrosc. 47, 268 (1973).
11. V. M. Rao and R. F. Curl, Jr., J. Chem. Phys. 45, 2032 (1966).
12. V. M. Rao, R. F. Curl, Jr., P. L. Timms, and J. L. Margrave, J. Chem. Phys. 43, 2557 (1965).
13. M. Farber, private communication, Space Sciences, Inc., October 18, 1976.

F_2SI

TRIFLUOROSILANE ($SiHF_3$) F_3HSi

(IDEAL GAS) GFW=86.0892

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	-3.237	-285.291	-285.291	INFINITE
100	9.085	53.511	77.689	-2.418	-285.958	-283.894	620.449
200	12.259	60.792	67.538	-1.349	-286.522	-281.607	307.726
298	15.173	66.242	66.242	0.000	-287.000	-279.090	204.578
300	15.224	66.336	66.242	0.028	-287.008	-279.041	203.281
400	17.606	71.058	66.870	1.675	-287.370	-276.327	150.978
500	19.340	75.184	68.129	3.527	-287.622	-273.535	119.562
500	20.599	78.827	69.614	5.528	-287.788	-270.701	98.603
700	21.538	82.076	71.167	7.637	-287.891	-267.843	83.624
800	22.257	85.001	72.716	9.828	-287.952	-264.977	72.388
900	22.817	87.656	74.231	12.083	-287.979	-262.101	63.647
1000	23.263	90.084	75.697	14.388	-287.985	-259.227	56.654
1100	23.621	92.319	77.107	16.732	-287.976	-256.351	50.932
1200	23.913	94.387	78.462	19.110	-287.956	-253.476	46.164
1300	24.153	96.311	79.762	21.513	-287.934	-250.604	42.130
1400	24.352	98.108	81.009	23.939	-287.911	-247.733	38.673
1500	24.520	99.794	82.206	26.383	-287.892	-244.862	35.676
1600	24.661	101.381	83.355	28.842	-287.879	-241.996	33.055
1700	24.781	102.880	84.460	31.314	-299.865	-239.021	30.728
1800	24.885	104.300	85.523	33.798	-299.813	-235.445	28.587
1900	24.974	105.647	86.547	36.291	-299.759	-231.870	26.671
2000	25.051	106.930	87.534	38.792	-299.706	-228.296	24.947
2100	25.119	108.154	88.487	41.300	-299.655	-224.729	23.388
2200	25.178	109.324	89.408	43.815	-299.605	-221.164	21.971
2300	25.231	110.445	90.299	46.336	-299.557	-217.598	20.676
2400	25.277	111.520	91.161	48.861	-299.512	-214.034	19.490
2500	25.319	112.552	91.996	51.391	-299.471	-210.476	18.400
2600	25.356	113.546	92.806	53.925	-299.432	-206.916	17.393
2700	25.389	114.504	93.592	56.462	-299.395	-203.358	16.461
2800	25.419	115.427	94.355	59.003	-299.362	-199.802	15.595
2900	25.446	116.320	95.097	61.546	-299.333	-196.243	14.789
3000	25.470	117.183	95.819	64.092	-299.308	-192.696	14.038
3100	25.492	118.018	96.522	66.640	-299.285	-189.142	13.334
3200	25.513	118.828	97.206	69.190	-299.267	-185.586	12.675
3300	25.531	119.614	97.673	71.742	-299.253	-182.034	12.056
3400	25.548	120.376	98.524	74.296	-299.242	-178.482	11.473
3500	25.564	121.117	99.159	76.852	-299.237	-174.928	10.923
3600	25.578	121.837	99.779	79.409	-391.195	-169.119	10.267
3700	25.592	122.538	100.385	81.968	-391.099	-162.952	9.625
3800	25.604	123.221	100.977	84.527	-391.006	-156.785	9.017
3900	25.615	123.886	101.556	87.088	-390.921	-150.628	8.441
4000	25.626	124.535	102.122	89.650	-390.838	-144.464	7.893
4100	25.636	125.168	102.676	92.213	-390.761	-138.310	7.373
4200	25.645	125.785	103.219	94.777	-390.688	-132.152	6.877
4300	25.653	126.389	103.751	97.342	-390.618	-125.995	6.404
4400	25.661	126.979	104.272	99.908	-390.555	-119.844	5.953
4500	25.669	127.556	104.783	102.475	-390.495	-113.692	5.522
4600	25.676	128.120	105.285	105.042	-390.439	-107.540	5.109
4700	25.682	128.672	105.776	107.610	-390.390	-101.390	4.715
4800	25.688	129.213	106.259	110.178	-390.343	-95.240	4.336
4900	25.694	129.743	106.733	112.747	-390.301	-89.091	3.974
5000	25.699	130.262	107.198	115.317	-390.264	-82.950	3.626
5100	25.705	130.771	107.656	117.887	-390.231	-76.804	3.291
5200	25.709	131.270	108.105	120.458	-390.203	-70.654	2.969
5300	25.714	131.760	108.547	123.029	-390.178	-64.506	2.660
5400	25.718	132.240	108.981	125.601	-390.159	-58.371	2.362
5500	25.722	132.712	109.408	128.173	-390.144	-52.225	2.075
5600	25.726	133.176	109.828	130.745	-390.134	-46.077	1.798
5700	25.730	133.631	110.242	133.318	-390.129	-39.930	1.531
5800	25.733	134.079	110.649	135.891	-390.128	-33.788	1.273
5900	25.737	134.519	111.050	138.465	-390.132	-27.651	1.024
6000	25.740	134.951	111.445	141.038	-390.141	-21.508	0.783

Dec. 30, 1960; June 30, 1976

TRIFLUOROSILANE ($SiHF_3$) (IDEAL GAS) GFW = 86.0892

Point Group C_{3v}
$S^\circ_{298.15}$ = 66.24 ± 0.2 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = [-285 ± 5] kcal/mol F_3HSi
$\Delta Hf^\circ_{298.15}$ = [-287 ± 5] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2316(1)	998(2)
858(1)	844(2)
425(1)	306(2)

Bond Distances: Si-H = 1.4468 Å Si-F = 1.5624 Å σ = 3
Bond Angles: H-Si-F = 110.64° F-Si-F = 108.28°
Product of the Moments of Inertia: $I_AI_BI_C = 2.7263 \times 10^{-114}\ g^3\ cm^6$.

Heats of Formation

There are no reported experimental studies leading to the heat of formation of $SiHF_3$(g). We estimate this value via a linear interpolation between the established ΔHf°_{298} values of SiH_4(g) and SiF_4(g)(1). The reasonableness of this approach has been demonstrated by Lapidus et al. (2), Hunt and Sirtl (3), and Seiter and Sirtl (4). Lapidus et al. (2) comparatively examined the thermodynamic properties of halogenated silanes and methanes. Hunt and Sirtl (3) and Seiter and Sirtl (4) studied the chlorinated silanes and proposed a linear ΔHf relationship within the sequence SiH_4(g) to $SiCl_4$(g).

Heat Capacity and Entropy

The adopted vibrational frequencies are from the infrared gas phase studies of Buerger et al. (5, 6). These values are all within ±1 cm^{-1} of the suggested values in the compilation by Shimanouchi (7), as derived from Newman et al. (8).

The adopted bond angles and bond distances are obtained from the microwave spectrum study of six isotopic species of $HSiF_3$(9). Earlier work by Sheridan and Gordy (10) and Heath et al. (11) is in good agreement with these values. The moments of inertia are calculated to be $I_A = I_B = 11.609 \times 10^{-39}$ g cm^2 and $I_C = 20.231 \times 10^{-39}$ g cm^2.

References

1. JANAF Thermochemical Tables: SiH_4(g) and SiF_4(g), 6-30-76.
2. I. I. Lapidus, L. A. Nisel'son, and A. L. Seifer in "Thermophysical Properties of Gases and Liquids," No. 1, V. A. Rabinovich, Ed., Israel Program for Scientific Translations, Jerusalem, 1970, pp 102-135. [Translated from Russian]
3. L. P. Hunt and E. Sirtl, J. Electrochem. Soc. 119, 1741 (1972).
4. H. Seiter and E. Sirtl, Z. Naturforsch. 21a, 1956 (1966).
5. H. Buerger, S. Biedermann, and A. Ruoff, Spectrochim. Acta, Part A 27, 1687 (1971).
6. H. Buerger, S. Biedermann, and A. Ruoff, Spectrochim. Acta, Part A 30, 1655 (1974).
7. T. Shimanouchi, J. Phys. Chem. Ref. Data 1, 189 (1972).
8. C. Newman, S. R. Polo, and M. K. Wilson, Spectrochim. Acta 15, 793 (1959).
9. A. R. Hoy, M. Bertram, and I. M. Mills, J. Mol. Spectrosc. 46, 429 (1973).
10. J. Sheridan and W. Gordy, J. Chem. Phys. 19, 965 (1951).
11. G. A. Heath, L. F. Thomas, and J. Sheridan, Trans. Faraday Soc. 50, 779 (1954).

SULFUR TRIFLUORIDE (SF_3)

(IDEAL GAS) GFW=89.0552

F_3S

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	-3.035	-119.257	-119.257	INFINITE
100	8.558	54.585	76.873	-2.229	-119.657	-118.715	259.451
200	11.333	61.346	67.533	-1.237	-120.109	-117.590	128.497
298	13.773	66.347	66.347	0.000	-120.440	-116.279	85.235
300	13.813	66.432	66.347	0.026	-120.445	-116.254	84.691
400	15.588	70.666	66.912	1.501	-121.224	-114.796	62.722
500	16.769	74.280	68.033	3.123	-121.750	-113.127	49.448
600	17.554	77.411	69.341	4.842	-122.137	-111.364	40.564
700	18.088	80.160	70.695	6.626	-122.429	-109.520	34.194
800	18.463	82.601	72.033	8.454	-135.725	-108.928	29.758
900	18.734	84.792	73.331	10.315	-135.616	-105.585	25.639
1000	18.936	86.777	74.578	12.199	-135.501	-102.254	22.348
1100	19.089	88.589	75.771	14.100	-135.380	-98.937	19.657
1200	19.208	90.256	76.909	16.016	-135.254	-95.628	17.416
1300	19.302	91.797	77.996	17.941	-135.128	-92.329	15.522
1400	19.378	93.230	79.034	19.875	-135.002	-89.042	13.900
1500	19.440	94.569	80.025	21.816	-134.875	-85.764	12.496
1600	19.491	95.826	80.974	23.763	-134.749	-82.494	11.268
1700	19.533	97.009	81.883	25.714	-134.624	-79.231	10.186
1800	19.569	98.126	82.754	27.669	-134.502	-75.979	9.225
1900	19.599	99.185	83.591	29.628	-134.379	-72.729	8.366
2000	19.625	100.191	84.396	31.589	-134.259	-69.486	7.593
2100	19.648	101.149	85.172	33.553	-134.143	-66.254	6.895
2200	19.668	102.064	85.919	35.519	-134.028	-63.022	6.261
2300	19.685	102.938	86.640	37.486	-133.916	-59.797	5.682
2400	19.700	103.776	87.337	39.455	-133.807	-56.577	5.152
2500	19.713	104.581	88.010	41.426	-133.701	-53.362	4.665
2600	19.725	105.354	88.663	43.398	-133.597	-50.150	4.215
2700	19.736	106.099	89.295	45.371	-133.496	-46.942	3.800
2800	19.746	106.817	89.908	47.345	-133.397	-43.741	3.414
2900	19.755	107.510	90.503	49.320	-133.302	-40.537	3.055
3000	19.763	108.180	91.081	51.296	-133.212	-37.343	2.720
3100	19.771	108.828	91.643	53.273	-133.121	-34.149	2.407
3200	19.778	109.456	92.190	55.250	-133.036	-30.957	2.114
3300	19.785	110.064	92.722	57.228	-132.953	-27.770	1.839
3400	19.791	110.655	93.241	59.207	-132.872	-24.581	1.580
3500	19.797	111.229	93.747	61.187	-132.797	-21.397	1.336
3600	19.804	111.787	94.240	63.167	-132.721	-18.213	1.106
3700	19.810	112.329	94.722	65.147	-132.652	-15.034	0.888
3800	19.816	112.858	95.192	67.129	-132.583	-11.854	0.682
3900	19.823	113.373	95.652	69.111	-132.520	-8.683	0.487
4000	19.829	113.875	96.101	71.093	-132.457	-5.503	0.301
4100	19.836	114.364	96.541	73.076	-132.399	-2.333	0.124
4200	19.843	114.842	96.971	75.060	-132.343	0.840	-0.044
4300	19.850	115.309	97.392	77.045	-132.289	4.012	-0.204
4400	19.857	115.766	97.804	79.030	-132.240	7.180	-0.357
4500	19.865	116.212	98.208	81.016	-132.193	10.347	-0.503
4600	19.873	116.649	98.605	83.003	-132.147	13.513	-0.642
4700	19.882	117.076	98.993	84.991	-132.105	16.679	-0.776
4800	19.890	117.495	99.374	86.980	-132.065	19.846	-0.904
4900	19.899	117.905	99.748	88.969	-132.029	23.014	-1.026
5000	19.909	118.307	100.115	90.960	-131.995	26.174	-1.144
5100	19.919	118.702	100.476	92.951	-131.964	29.333	-1.257
5200	19.929	119.088	100.830	94.943	-131.935	32.503	-1.366
5300	19.939	119.468	101.178	96.937	-131.907	35.665	-1.471
5400	19.950	119.841	101.520	98.931	-131.884	38.821	-1.571
5500	19.961	120.207	101.857	100.927	-131.862	41.984	-1.668
5600	19.972	120.567	102.188	102.923	-131.844	45.148	-1.762
5700	19.984	120.921	102.513	104.921	-131.827	48.307	-1.852
5800	19.996	121.268	102.834	106.920	-131.811	51.468	-1.939
5900	20.008	121.610	103.149	108.920	-131.799	54.620	-2.023
6000	20.021	121.947	103.459	110.922	-131.789	57.785	-2.105

June 30, 1976

Point Group [C_{3V}]
$S^\circ_{298.15}$ = [66.3 ± 1.5] gibbs/mol

ΔHf°_0 = -119.3 ± 8.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -120.4 ± 8.0 kcal/mol

F_3S

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}
[900](1)	[890](2)
[500](1)	[375](2)

Bond Distance: S-F = [1.58] Å
$\sigma = 3$
Bond Angle: F-S-F = [97.5]°
Product of Moments of Inertia: $I_AI_BI_C$ = [2.1535 x 10^{-114}] g^3 cm^6

Heat of Formation

Our ΔHf°_0 of -119.3±8.0 kcal/mol is calculated from the primary bond dissociation energy for SF_4 of $D^\circ_0(SF_3\text{-}F)$ = 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 average bond dissociation energy (D°_0) for SF_3 to be 240.1 kcal/mol and 80.0 kcal/mol, respectively.

Several pieces of information are available which are relatively imprecise but do support our assumption that $D^\circ_0(SF_3\text{-}F) = \Delta Ha^\circ_0(SF_4)/4$. 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 $D^\circ_0(SF_3\text{-}F)$ = 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 (A.P.) are in good agreement and indicate A.P.(SF_3^+/SF_4) = 12.67±0.1 eV. Combining this value with an upper limit for the ionization potential of SF_3(I.P. ≤ 9.25 eV, 5), we obtain a lower limit for $D^\circ_0(SF_3\text{-}F)$ of 78.9 kcal/mol.

Two upper limit values for $D^\circ_0(SF_3\text{-}F)$ can be obtained from threshold measurements by Harland and Thynne (5) on dissociative attachment in SF_6 and SF_4. We combine their A.P.(F^-/SF_4) = 0.20±0.05 eV with the electron affinity of F(E.A. = 3.399 eV, 1) to obtain $D^\circ_0(SF_3\text{-}F) \le$ 83.0 kcal/mol. In addition, their A.P.'s (6) for the formation of F^- from SF_6 by two distinct processes are combined directly to give $D^\circ_0(SF_3\text{-}F) \le$ 80.7 kcal/mol.

The A.P. 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 A.P.(SF_3^+/SF_6) = 19.9$_7$±0.1 eV. Assuming the ionization process to be $SF_6(g) + e^- = SF_3^+(g)+3F(g)+2e^-$, we combine the mean A.P. value with I.P.(SF_3) ≤ 9.25 eV (5) to obtain $\Delta Hf^\circ_0(SF_3,g) \le$ -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 involved a large amount of kinetic energy.

Heat Capacity and Entropy

The vibrational spectra and structure of the gaseous SF_3 radical have not been reported. Gibler et al. (9) have determined the crystal structure of the salt $[SF_3]^+[BF_4]^-$ and recorded the solid state Raman spectra. The structural data show that the cation has C_{3v} symmetry with an average bond angle of 97.5°. We adopt this structure and bond angle since they agree with what one might expect based on results for the related PF_3(1) molecule. The x-ray data (9) also show that r_e(S-F) = 1.497 Å for SF_3^+ which is the shortest S-F linkage that has been reported so far. We expect r_e(S-F) for SF_3 to be larger than that for SF_3^+ since the additional unpaired electron should increase the repulsive interactions. Some supporting evidence for this is provided by the trends found in measured S-F bond lengths (1) for the species SF_6, SF_2, and SF. As the number of non-bonding electrons increases in this series, the value of r_e(S-F) also increases. We estimate r_e for SF_3 to be intermediate between those for SF_6 and SF_2. Our adopted value r_e(S-F) = 1.58 Å is close to the average S-F bond length (1.596 Å) in SF_4(1) and an estimate (1.59 Å) made by Wilkins (10). The individual moments of inertia are: I_A = 1.7806 x 10^{-38}, $I_B=I_C$=1.0998x10^{-38} g cm^2.

The vibrational frequencies are estimated to be intermediate between those for SF_3^+(9) and PF_3(1). Our frequencies agree reasonably well with those calculated by Wilkins (10) from estimated force constants. The largest deviation between the two sets of frequencies is 169 cm^{-1} in ν_2. Bott (2) has detected IR radiation in emission at 11.0-12.6μ in SF_4/Ar mixtures which were shock-heated to temperatures above 2050 K. He attributed this radiation to SF_3 which supports the assignment of at least one fundamental in the region 794-909 cm^{-1}. We include an excited level at 25000 cm^{-1} by analogy with those observed for SF_4^+(8). We do not include a level predicted to lie near 40000 cm^{-1} since this would not alter our thermal functions.

Functions for SF_3 have been previously reported by Wilkins (10) over an extended temperature range (0-6000 K). Our entropy values are consistently lower than his data, but not excessively so. The difference in the values of S°_{298} is 0.67 gibbs/mol, and this difference increases to 0.74 gibbs/mol at 1000 K and thereafter remains constant.

References

1. JANAF Thermochemical Tables: F(g), 9-30-65; SF_4(g), SF_6(g), SF_2(g), and SF(g), 6-30-76; F^-(g), 12-31-71; PF_3(g), 12-31-69.
2. J. F. Bott, J. Chem. Phys. 54, 181 (1971).
3. D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
4. O. Glemser, A. Müller, D. Böhler, and B. Krebs, Z. Anorg. Allgem. Chem. 357, 184 (1968).
5. F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).
6. P. W. Harland and J. C. J. Thynne, J. Phys. Chem. 75, 3517 (1971).
7. V. H. Dibeler and F. L. Mohler, J. Res. Natl. Bur. Std. 40, 25 (1948).
8. J. Delwiche, Dynamic Mass Spectrom. 1, 71 (1971).
9. D. D. Gibler, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, Inorg. Chem. 11, 2325 (1972).
10. R. L. Wilkins, Aerospace Corporation, Report No. TR-0158 (3240-20)-19, Contract F04695-67-C-0158, July, 1968.

F_3S

SILICON TRIFLUORIDE (SIF_3) F_3SI
(IDEAL GAS) GFW=85.0812

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	-3.202	-258.768	-258.768	INFINITE
100	9.250	54.836	78.618	-2.378	-259.051	-258.338	564.598
200	12.145	62.195	66.694	-1.300	-259.303	-257.521	281.406
298	14.250	67.454	67.454	0.000	-259.500	-256.604	188.096
300	14.285	67.543	67.455	0.026	-259.504	-256.586	186.923
400	15.856	71.881	68.035	1.538	-259.654	-255.589	139.647
500	16.932	75.542	69.180	3.181	-259.766	-254.559	111.266
600	17.660	78.698	70.510	4.913	-259.850	-253.510	92.341
700	18.162	81.460	71.881	6.705	-259.919	-252.447	78.817
800	18.517	83.910	73.234	8.540	-259.983	-251.377	68.673
900	18.776	86.107	74.545	10.406	-260.043	-250.296	60.780
1000	18.968	88.095	75.802	12.293	-260.107	-249.211	54.465
1100	19.115	89.910	77.003	14.198	-260.176	-248.118	49.297
1200	19.230	91.579	78.149	16.115	-260.249	-247.018	44.988
1300	19.320	93.122	79.242	18.043	-260.330	-245.912	41.342
1400	19.393	94.556	80.285	19.979	-260.420	-244.800	38.215
1500	19.453	95.896	81.282	21.921	-260.519	-243.679	35.504
1600	19.502	97.153	82.235	23.869	-260.629	-242.554	33.131
1700	19.543	98.337	83.148	25.821	-272.742	-241.314	31.023
1800	19.578	99.455	84.023	27.778	-272.818	-239.465	29.075
1900	19.607	100.514	84.863	29.737	-272.895	-237.610	27.331
2000	19.633	101.521	85.671	31.699	-272.974	-235.748	25.761
2100	19.654	102.479	86.449	33.663	-273.054	-233.887	24.341
2200	19.673	103.394	87.198	35.630	-273.137	-232.021	23.049
2300	19.690	104.269	87.922	37.598	-273.222	-230.149	21.869
2400	19.705	105.107	88.620	39.568	-273.309	-228.274	20.787
2500	19.718	105.912	89.296	41.539	-273.399	-226.397	19.792
2600	19.729	106.685	89.950	43.511	-273.491	-224.514	18.872
2700	19.739	107.430	90.584	45.484	-273.586	-222.628	18.021
2800	19.748	108.148	91.198	47.459	-273.682	-220.739	17.229
2900	19.757	108.841	91.795	49.434	-273.781	-218.844	16.493
3000	19.764	109.511	92.374	51.410	-273.885	-216.954	15.805
3100	19.771	110.159	92.938	53.387	-273.989	-215.054	15.161
3200	19.777	110.787	93.486	55.364	-274.097	-213.148	14.557
3300	19.783	111.396	94.019	57.342	-274.208	-211.243	13.990
3400	19.788	111.986	94.539	59.321	-274.321	-209.333	13.456
3500	19.793	112.560	95.046	61.300	-274.438	-207.418	12.952
3600	19.797	113.118	95.540	63.279	-366.517	-203.243	12.339
3700	19.801	113.660	96.022	65.259	-366.540	-198.708	11.737
3800	19.805	114.188	96.494	67.240	-366.565	-194.170	11.167
3900	19.808	114.703	96.954	69.220	-366.596	-189.639	10.627
4000	19.811	115.204	97.404	71.201	-366.628	-185.097	10.113
4100	19.814	115.694	97.844	73.182	-366.666	-180.562	9.625
4200	19.817	116.171	98.275	75.164	-366.705	-176.022	9.159
4300	19.819	116.637	98.696	77.146	-366.745	-171.479	8.715
4400	19.822	117.093	99.109	79.128	-366.792	-166.939	8.292
4500	19.824	117.538	99.514	81.110	-366.839	-162.395	7.887
4600	19.826	117.974	99.911	83.093	-366.889	-157.852	7.500
4700	19.828	118.401	100.299	85.075	-366.944	-153.306	7.129
4800	19.830	118.818	100.661	87.056	-367.000	-148.758	6.773
4900	19.832	119.227	101.055	89.041	-367.060	-144.210	6.432
5000	19.834	119.628	101.423	91.025	-367.122	-139.666	6.105
5100	19.835	120.020	101.784	93.008	-367.188	-135.117	5.790
5200	19.837	120.406	102.138	94.992	-367.256	-130.561	5.487
5300	19.839	120.784	102.486	96.975	-367.327	-126.007	5.196
5400	19.840	121.154	102.828	98.959	-367.402	-121.461	4.916
5500	19.842	121.518	103.165	100.944	-367.479	-116.904	4.645
5600	19.844	121.876	103.496	102.928	-367.560	-112.343	4.384
5700	19.845	122.227	103.821	104.912	-367.644	-107.782	4.133
5800	19.847	122.572	104.142	106.897	-367.731	-103.223	3.890
5900	19.849	122.912	104.457	108.882	-367.821	-98.670	3.655
6000	19.850	123.245	104.767	110.867	-367.915	-94.106	3.426

Sept. 30, 1963; Dec. 31, 1969; June 30, 1970, June 30, 1976

SILICON TRIFLUORIDE (SiF_3) (IDEAL GAS) GFW = 85.0812

Point Group = C_{3v}
$S^\circ_{298.15}$ = [67.45 ± 0.05] gibbs/mol

ΔHf°_0 = -258.77 ± 2 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -259.5 ± 2 kcal/mol

F_3SI

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
[X $^2A_1$]	0	[2]
[$^2B_1$]	44120	[2]

Vibational Frequencies and Degeneracies

ω, cm^{-1}
832 (1)
406 (1)
954 (2)
290 (2)

Bond Distance: Si-F = [1.56] Å
σ = 3
Bond Angle: F-Si-F = [109° 28']
Product of the Moments of Inertia: $I_AI_BI_C = 2.51354 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

The adopted ΔHf°_{298} (SiF_3,g) = -259.5±2 kcal/mole is derived from the mass spectrophotometric 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 ΔHr°_{298} = 7.48±0.18 kcal/mol (second law) and ΔHr°_{298} = 7.58±0.04 kcal/mol with a drift of 0.06±0.11 gibbs/mol (third law). The third law heat of reaction leads to the adopted heat of formation. The average of ΔHf°_{298} (SiF_2,g) and ΔHf°_{298} (SiF_4, g) (1) is -263.2 kcal/mol; this is in reasonable agreement with the adopted value in view of the trends shown in the ΔHf°_{298} values of MX_n molecules: C-H, C-Cl, C-F, Al-Cl, and Al-F (1). The adopted value is also consistent with the total pressure data above the silicon-magnesium fluoride system observed by Layne (2). The value of ΔHf° = -235±20 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.

ΔHf°_0 = -258.77 kcal/mol corresponds to ΔHa°_0 - 420.51 kcal/mol, using auxiliary data (1).

Heat Capacity and Entropy

The electronic levels are those tentatively assigned by Wang, Krishnan, and Margrave (5) from emission spectral observations. The vibrational frequencies are from Milligan, Jacox, and Guillory (6) derived from matrix-isolation UV and IR spectra. 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) indicate that the F-S-F bond angle should be somewhat less than the tetrahedral angle. Calculations based on a bond angle of 108° decreases S°_{298} by 0.029 gibbs/mol. As suggested in Milligan et al. (6), the bond length is assumed to be the Si-F bond length in $SiHF_3$ (1).

The principal moments of inertia are $I_A = I_B = 1.10806 \times 10^{-38}$ g cm^2 and $I_C = 2.04718 \times 10^{-38}$ g cm^2.

References

1. JANAF Thermochemical Tables: SiF_2(g), SiF_4(g), 6-30-76; CH(g), 12-31-67; CH_2(g), 12-31-72; CH_3(g), 6-30-69; CH_4(g), 3-31-61; CCl(g), 12-31-69; CCl_2(g), CCl_4(g) 12-31-68; CCl_3(g), CF(g), CF_2(g), 6-30-70; CF_3(g), CF_4(g), 6-30-69; AlCl(g), $AlCl_3$(g), 6-30-70; $AlCl_2$(g), 6-30-76; AlF(g), 12-31-75; AlF_2(g), 6-30-76; AlF_3(g), 6-30-70; F(g), 9-30-65; Li(g), 3-31-67; $SiHF_3$, 6-30-76.
2. G. S. Layne, private communication, The Dow Chemical Company, Midland, Michigan, Aug., 1969.
3. J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, Advan. Chem. Ser. No. 72, 261 (1968).
4. J. Ling-Fai Wang, J. L. Margrave, and J. L. Franklin, J. Chem. Phys. 58, 5417 (1973).
5. J. Ling-Fai Wang, C. N. Krishnan, and J. L. Margrave, J. Mol. Spectrosc. 48, 346 (1973).
6. D. E. Milligan, M. E. Jacox, and W. A. Guillory, J. Chem. Phys. 49, 5330 (1968).
7. L. J. Aarons, I. H. Hillier, and M. F. Guest, J. Chem. Soc. Faraday Trans. II 70, 167 (1974).
8. Y. I. Gorlov, I. I. Ukrainskii, and V. V. Pen'kovskii, Theor. Chim. Acta 34, 31 (1974).
9. M. Farber, private communication, Space Sciences, Inc., October 18, 1976.
10. J. L. Franklin, Science 193, 725 (1976).

MAGNESIUM DIFLUORIDE, DIMERIC (Mg_2F_4) F_4Mg_2

(IDEAL GAS) GFW=124.6036

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 5.053	- 409.141	- 409.141	INFINITE
100	13.305	59.118	100.199	- 4.108	- 409.894	- 407.212	889.961
200	21.428	71.075	82.754	- 2.336	- 410.646	- 404.430	441.940
298	25.693	80.521	80.521	.000	- 410.700	- 401.159	294.057
300	25.749	80.680	80.521	.048	- 410.702	- 401.100	292.201
400	27.969	88.425	81.562	2.745	- 410.773	- 397.887	217.395
500	29.195	94.810	83.593	5.609	- 410.807	- 394.660	172.506
600	29.926	100.203	85.923	8.568	- 410.850	- 391.429	142.578
700	30.392	104.854	88.303	11.586	- 410.920	- 388.184	121.197
800	30.706	108.934	90.632	14.641	- 411.047	- 384.931	105.158
900	30.926	112.564	92.871	17.724	- 411.238	- 381.656	92.679
1000	31.086	115.831	95.007	20.825	- 415.745	- 377.993	82.610
1100	31.206	118.800	97.037	23.939	- 416.019	- 374.207	74.348
1200	31.298	121.519	98.965	27.065	- 416.341	- 370.392	67.458
1300	31.370	124.027	100.798	30.198	- 416.720	- 366.547	61.622
1400	31.428	126.354	102.541	33.338	- 477.882	- 361.713	56.466
1500	31.474	128.524	104.202	36.484	- 477.552	- 353.425	51.494
1600	31.513	130.557	105.786	39.633	- 477.227	- 345.164	47.147
1700	31.544	132.468	107.300	42.786	- 476.904	- 336.916	43.314
1800	31.571	134.272	108.749	45.942	- 476.586	- 328.695	39.909
1900	31.594	135.980	110.138	49.100	- 476.268	- 320.486	36.864
2000	31.613	137.601	111.471	52.260	- 475.956	- 312.293	34.126
2100	31.630	139.144	112.752	55.422	- 475.648	- 304.123	31.650
2200	31.645	140.615	113.985	58.586	- 475.344	- 295.959	29.401
2300	31.657	142.022	115.174	61.751	- 475.043	- 287.809	27.348
2400	31.668	143.370	116.321	64.918	- 474.746	- 279.679	25.468
2500	31.678	144.663	117.429	68.085	- 474.457	- 271.559	23.740
2600	31.687	145.905	118.500	71.253	- 474.171	- 263.444	22.145
2700	31.695	147.101	119.538	74.422	- 473.890	- 255.345	20.669
2800	31.702	148.254	120.543	77.592	- 473.612	- 247.260	19.300
2900	31.708	149.367	121.518	80.763	- 473.341	- 239.174	18.025
3000	31.714	150.442	122.464	83.934	- 473.080	- 231.112	16.836
3100	31.719	151.482	123.383	87.105	- 472.823	- 223.049	15.725
3200	31.723	152.489	124.277	90.278	- 472.574	- 214.997	14.684
3300	31.728	153.465	125.147	93.450	- 472.334	- 206.952	13.706
3400	31.732	154.412	125.994	96.623	- 472.103	- 198.908	12.786
3500	31.735	155.332	126.819	99.796	- 471.884	- 190.877	11.919
3600	31.738	156.226	127.624	102.970	- 471.674	- 182.847	11.100
3700	31.741	157.096	128.408	106.144	- 471.478	- 174.827	10.327
3800	31.744	157.943	129.175	109.318	- 471.294	- 166.809	9.594
3900	31.747	158.767	129.923	112.493	- 471.125	- 158.810	8.899
4000	31.749	159.571	130.654	115.668	- 470.970	- 150.798	8.239
4100	31.751	160.355	131.369	118.843	- 470.835	- 142.798	7.612
4200	31.753	161.120	132.068	122.018	- 470.716	- 134.800	7.014
4300	31.755	161.867	132.752	125.193	- 470.615	- 126.801	6.445
4400	31.757	162.597	133.423	128.369	- 470.535	- 118.805	5.901
4500	31.759	163.311	134.079	131.545	- 470.475	- 110.813	5.382
4600	31.760	164.009	134.722	134.721	- 470.437	- 102.819	4.885
4700	31.762	164.692	135.352	137.897	- 470.423	- 94.828	4.409
4800	31.763	165.361	135.971	141.073	- 470.433	- 86.830	3.953
4900	31.764	166.016	136.577	144.249	- 470.469	- 78.840	3.516
5000	31.765	166.658	137.172	147.426	- 470.530	- 70.847	3.097
5100	31.767	167.287	137.757	150.602	- 470.620	- 62.867	2.694
5200	31.768	167.903	138.330	153.779	- 470.737	- 54.858	2.306
5300	31.769	168.509	138.894	156.956	- 470.882	- 46.853	1.932
5400	31.770	169.102	139.448	160.133	- 471.059	- 38.866	1.573
5500	31.771	169.685	139.993	163.310	- 471.266	- 30.855	1.226
5600	31.771	170.258	140.528	166.487	- 471.507	- 22.845	.892
5700	31.772	170.820	141.054	169.664	- 471.780	- 14.823	.568
5800	31.773	171.373	141.572	172.841	- 472.085	- 6.812	.257
5900	31.774	171.916	142.082	176.019	- 472.427	1.214	- .045
6000	31.774	172.450	142.584	179.196	- 472.804	9.237	- .336

Dec. 31, 1960; June 30, 1964; March 31, 1966;
Dec. 31, 1975

Point Group [D_{2h}]
$S^\circ_{298.15}$ = [80.5 ± 5.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -409.1 ± 5.0(or±9) kcal/mol
$\Delta Hf^\circ_{298.15}$ = -410.7 ± 5.0(or±9) kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
585 (1)	[235](1)	487 (1)
353 (1)	[220](1)	[220](1)
[400](1)	[240](1)	747 (1)
[508](1)	[200](1)	450 (1)

Bond Distances: Mg-F = [1.77] Å Mg-F' = [1.96] Å
Bond Angles: Mg-F'-Mg = [90]° F'-Mg-F' = [90]°
F-Mg-F' = [135]° (F' = Ring Fluorine)

σ = 4

Product of Moments of Inertia: $I_AI_BI_C$ = [$8.5873X10^{-113}$] g^3cm^6

Heat of Formation

Berkowitz and Marquart (1) have found approximately 1% dimer in the equilibrium vapor over $MgF_2(c)$ at about 1400 K by mass spectrometry. Independent measurements which are discussed elsewhere (See $MgF_2(g)$ table) support their results. Berkowitz and Marquart (1) reported a second law ΔHr_{1440} of 30 kcal/mol for the reaction $MgF_2(c) + MgF_2(g) = Mg_2F_4(g)$. This value corrected to 298.15 K gives ΔHr° = 31.7 kcal/mol which leads to $\Delta Hf^\circ_{298}(Mg_2F_4,g)$ = -410.7 kcal/mol. The corresponding heat of dimerization at 298.15 K is -63.3 kcal/mol. Berkowitz and Marquart (1) also reported approximate absolute pressures for $MgF_2(g)$ and $Mg_2F_4(g)$ at 1429 K. A third law analysis of these reported pressures gives ΔHr°_{298} of -69.5 kcal/mol for the process $2MgF_2(g) = Mg_2F_4(g)$, or $\Delta Hf^\circ_{298}(Mg_2F_4,g)$ = -416.9 kcal/mol. We prefer the second law result (ΔHf°=-410.7 kcal/mol) since the less negative (-63.3 kcal/mol) heat of dimerization is more consistent with the dimerization energies for the alkali metal fluorides (2). The uncertainty in ΔHf° is estimated as ± 5.0 kcal/mol; however, we also include an alternate uncertainty (±9 kcal/mol) to cover the possibility that $MgF_2(g)$ is linear (2).

Heat Capacity and Entropy

The dimer is assumed to have a bridge-bond structure of D_{2h} symmetry similar to that suggested by Thompson and Carlson (3) for the dimers of several transition metal dichlorides. The two outer Mg-F bond lengths are assumed to be the same as that for MgF_2(2). The four ring Mg-F' bond lengths are assumed to be 10% longer. The four atoms which lie in the ring form a square. The F'-Mg-F bond angle is estimated as 135°. The individual moments of inertia are: $I_A = 9.0458X10^{-38}$, $I_B = 7.8340x10^{-38}$, and $I_C = 1.2118x10^{-38}$ g cm^2.

This planar bridge-bond structure will have six Raman ($3A_g + 2B_{1g} + 2B_{2g}$) and six infrared ($2B_{1u} + 2B_{2u} + 2B_{3u}$) active fundamentals. The Raman spectra of MgF_2 isolated in an argon matrix has been recorded by Lesiecki and Nibler (4). They assigned two bands observed at 585 and 353 cm^{-1} to ν_1 and ν_2, respectively, of Mg_2F_4. Lesiecki and Nibler (4), using a standard high-low frequency separation method and a diagonal force field, calculated ν_4 as 508 cm^{-1}. The other three Raman active frequencies (ν_3, ν_5, and ν_6) are estimated by analogy with those for MgF_2 and Na_2F_2 (2). Four of the six infrared active fundamentals have been observed and assigned by Lesiecki and Nibler (4). These frequencies were recorded in an argon matrix. Results of three independent infrared studies (5-7) conducted with various matrices support these assignments. The other two infrared active fundamentals (ν_8 and ν_{10}) are estimated from the bending frequency (ν_2 = 215 cm^{-1}) for MgF_2 (2). Following the observations made by Thompson and Carlson (3), all the estimated frequencies are taken to lie above the bending frequency of the monomer.

References

1. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
2. JANAF Thermochemical Tables: $MgF_2(g)$, 6-30-75; $Li_2F_2(g)$ and $Na_2F_2(g)$, 12-31-68; $K_2F_2(g)$, 6-30-69.
3. K. R. Thompson and K. D. Carlson, J. Chem. Phys. 49, 4379 (1968).
4. M. L. Lesiecki and J. W. Nibler, to be published.
5. R. H. Hauge, J. L. Margrave, and A. S. Kana'an, J. Chem. Soc., Faraday Transactions II 71, 1082 (1975).
6. A. Snelson, J. Phys. Chem. 70, 3208 (1966).
7. D. E. Mann, G. V. Calder, K. S. Seshadri, D. White, and M. J. Linevsky, J. Chem. Phys. 46, 1138 (1967).

SULFUR TETRAFLUORIDE (SF_4) F_4S

(IDEAL GAS) GFW=108.0536

	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	-3.772	-180.899	-180.899	INFINITE
100	10.185	56.343	85.527	-2.918	-181.599	-178.798	390.763
200	14.969	64.899	73.181	-1.656	-182.130	-175.768	192.070
298	18.546	71.590	71.589	0.000	-182.400	-172.580	126.505
300	18.600	71.704	71.590	0.034	-182.404	-172.520	125.680
400	20.912	77.398	72.350	2.019	-183.058	-169.182	92.437
500	22.348	82.231	73.856	4.188	-183.441	-165.668	72.413
600	23.265	86.393	75.607	6.472	-183.678	-162.088	59.040
700	23.874	90.028	77.413	8.831	-183.821	-158.453	49.471
800	24.295	93.245	79.195	11.240	-196.969	-156.092	42.642
900	24.597	96.125	80.919	13.686	-196.713	-150.997	36.667
1000	24.819	98.729	82.572	16.157	-196.453	-145.932	31.893
1100	24.987	101.102	84.150	18.648	-196.189	-140.894	27.993
1200	25.117	103.282	85.655	21.153	-195.922	-135.877	24.747
1300	25.219	105.297	87.089	23.670	-195.656	-130.882	22.003
1400	25.302	107.169	88.457	26.196	-195.391	-125.910	19.655
1500	25.368	108.917	89.764	28.730	-195.127	-120.957	17.623
1600	25.423	110.556	91.013	31.270	-194.865	-116.021	15.848
1700	25.469	112.099	92.208	33.814	-194.606	-111.100	14.283
1800	25.508	113.556	93.354	36.363	-194.351	-106.199	12.894
1900	25.541	114.936	94.454	38.916	-194.096	-101.305	11.653
2000	25.569	116.246	95.511	41.471	-193.846	-96.427	10.537
2100	25.593	117.495	96.528	44.029	-193.600	-91.566	9.529
2200	25.614	118.686	97.509	46.590	-193.357	-86.712	8.614
2300	25.633	119.825	98.454	49.152	-193.118	-81.868	7.779
2400	25.649	120.916	99.368	51.716	-192.883	-77.037	7.015
2500	25.663	121.963	100.251	54.282	-192.652	-72.215	6.313
2600	25.676	122.970	101.105	56.849	-192.425	-67.402	5.666
2700	25.687	123.939	101.933	59.417	-192.201	-62.596	5.067
2800	25.697	124.874	102.736	61.986	-191.981	-57.804	4.512
2900	25.706	125.776	103.515	64.556	-191.766	-53.011	3.995
3000	25.715	126.647	104.271	67.127	-191.557	-48.235	3.514
3100	25.722	127.491	105.007	69.699	-191.348	-43.461	3.064
3200	25.729	128.307	105.722	72.272	-191.146	-38.693	2.643
3300	25.735	129.099	106.419	74.845	-190.947	-33.933	2.247
3400	25.741	129.867	107.097	77.419	-190.752	-29.175	1.875
3500	25.746	130.614	107.758	79.993	-190.564	-24.425	1.525
3600	25.751	131.339	108.403	82.568	-190.376	-19.678	1.195
3700	25.755	132.045	109.033	85.143	-190.196	-14.940	0.882
3800	25.759	132.732	109.648	87.719	-190.018	-10.204	0.587
3900	25.763	133.401	110.248	90.295	-189.847	-5.481	0.307
4000	25.766	134.053	110.835	92.872	-189.677	-0.749	0.041
4100	25.770	134.689	111.409	95.448	-189.514	3.968	-0.212
4200	25.773	135.310	111.971	98.025	-189.355	8.687	-0.452
4300	25.775	135.917	112.521	100.603	-189.197	13.403	-0.681
4400	25.778	136.509	113.059	103.181	-189.048	18.111	-0.900
4500	25.780	137.089	113.587	105.758	-188.902	22.816	-1.108
4600	25.783	137.655	114.104	108.337	-188.758	27.518	-1.307
4700	25.785	138.210	114.611	110.915	-188.621	32.219	-1.498
4800	25.787	138.753	115.108	113.494	-188.486	36.918	-1.681
4900	25.789	139.284	115.596	116.072	-188.358	41.617	-1.856
5000	25.790	139.805	116.075	118.651	-188.234	46.304	-2.024
5100	25.792	140.316	116.546	121.230	-188.114	50.989	-2.185
5200	25.794	140.817	117.007	123.810	-187.997	55.685	-2.340
5300	25.795	141.308	117.461	126.389	-187.885	60.371	-2.489
5400	25.796	141.791	117.907	128.969	-187.779	65.046	-2.633
5500	25.798	142.264	118.346	131.548	-187.676	69.730	-2.771
5600	25.799	142.729	118.777	134.128	-187.579	74.413	-2.904
5700	25.800	143.185	119.201	136.708	-187.486	79.090	-3.032
5800	25.801	143.634	119.619	139.288	-187.395	83.766	-3.156
5900	25.802	144.075	120.030	141.868	-187.310	88.432	-3.276
6000	25.803	144.509	120.434	144.449	-187.229	93.110	-3.392

Sept. 30, 1965; Dec. 31, 1969; June 30, 1976

SULFUR TETRAFLUORIDE (SF_4) (IDEAL GAS) GFW = 108.0536

F_4S

Point Group C_{2v}

$S°_{298.15}$ = 71.6 ± 0.1 gibbs/mol

Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -180.9 ± 5.0 kcal/mol

$\Delta Hf°_{298.15}$ = -182.4 ± 5.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
891.5(1)	228.0(1)	532.5(1)
558.4(1)	475.0(1)	867.0(1)
353.0(1)	728.0(1)	233.0(1)

Bond Distances: S-F* = 1.545±0.003 Å S-F** = 1.646±0.003 Å

Bond Angles: F*-S-F* = 101.55 ± 0.5° F*-S-F** = 87.81 ± 0.5°

F**-S-F** = 173.07 ± 0.5° (* - equatorial ** - axial)

Product of Moments of Inertia: $I_AI_BI_C = 6.7227 \times 10^{-114}\ g^3\ cm^6$

σ = 2

Heat of Formation

Data on ΔHf° published prior to 1970 have been reviewed by O'Hare et al. (1). We reanalyze this earlier work together with more recent studies; our results are presented below. Unless otherwise indicated, all auxiliary data are taken from JANAF tables (2). We also include in the table for those reactions involving the formation of HF ΔHf° values which have been derived in previous analyses (11, 12, 13).

Source	Method	Reaction	ΔHr°(T,K) kcal/mol	$-\Delta Hf°_{298}(SF_4,g)$, kcal/mol From (Ref.)	This Work
(3)	Calorimetric	$SF_4(g)+2H_2(g)=4HF(\ell)+S(c)$	-104.8(298)[b] ±4.0	185.2(11, 12) 188.5(13)	184.7[a] ±6.0
(4)	Calorimetric	$SF_4(g)+3H_2O(\ell)=4HF(aq)+H_2SO_3(aq)$	c	179.0(11)	180.6
(5 - 8)	Appearance Potentials[d]	$SF_6(g)=SF_4(g)+2F(g)$	145.0±4.6(0)		181.6±5.0
(8)	Appearance Potentials[e]	$NSF_3(g)+F(g)=SF_4(g)+N(g)$	17.5(0)		161.8
(9)	Appearance Potentials[f]	$SF_6(g)=SF_4(g)+2F(g)$	116.2(0)		210.4

[a] Auxiliary $\Delta Hf°_{298}$ data in kcal/mol: $NSF_3(g)$, -85.2±0.5(1); HF(ℓ), -72.37(2, 10).

[b] Results reduced with HF PVT and calorimetric data from (10).

[c] Hydrolysis data unavailable; ΔHr° value from (11) adjusted for changes in ΔHf° of HF(aq).

[d] Ion Processes: $SF_6(g)+e^-=SF_4^+(g)+2F(g)+2e^-$ $SF_4(g)+e^-=SF_4^+(g)+2e^-$

[e] Ion Processes: $SF_4(g)+e^-=SF_3^+(g)+F(g)+2e^-$ $NSF_3(g)+e^-=SF_3^+(g)+N(g)+2e^-$

[f] Ion Processes: $SF_5(g)+e^-=SF_4(g)+F^-(g)$ $SF_5(g)+e^-=SF_5^-(g)$ $SF_6(g)+e^-=SF_5^-(g)+F(g)$

All of these studies are relatively imprecise, suggesting the need for an unequivocal redetermination of ΔHf°. Both calorimetric results (3, 4) are based on measurements made with impure samples (∿ 98% SF_4) and suffer from the additional uncertainties introduced by the formation of HF. The ionization processes involve unknown kinetic and excitation energies, as evidenced by the widely scattered results. The first three ΔHf° values listed above are reasonably consistent; thus, we are led to adopt their mean value of $\Delta Hf°_{298}(SF_4,g)$ = -182.4 kcal/mol. The estimated uncertainty is ±5.0 kcal/mol. Our ΔHf° value corresponds to a heat of atomization ($\Delta Ha°_0$) and average bond dissociation energy ($D°_0$) of 320.1 kcal/mol and 80.0 kcal/mol, respectively.

Heat Capacity and Entropy

Detailed structural data determined by electron diffraction (14) and microwave spectroscopy (15) show good agreement. We arbitrarily adopt the microwave data which indicate that the SF_4 structure is a trigonal bipyramid with two inequivalent sets of fluorine atoms. The inequivalence of the fluorines is also supported by nuclear resonance (16, 17) and x-ray photoelectron spectroscopic (18, 19) studies. The individual moments of inertia are: $I_A = 2.6069 \times 10^{-38}$, $I_B = 2.0545 \times 10^{-38}$, and $I_C = 1.2552 \times 10^{-38}\ g\ cm^2$.

Various spectroscopic methods have been used to study the vibrational spectrum of SF_4. These studies include crystal (20), liquid (21), and gas (22) phase Raman and gas (21 - 23) phase and argon matrix-isolation (24) infrared spectra. The measured frequencies show good agreement but various interpretations of the observed spectra have been presented. We choose to adopt the results of the latest interpretation by Levin (20). It should be noted that the vibrational assignments are immaterial for the purpose of evaluating the thermal functions since none of the fundamentals are degenerate. MO calculations (25) predict a singlet ground state with no excited states lying at energies which would be significant in the statistical calculations.

Our thermal functions essentially extend and update those reported by O'Hare (11) but are in disagreement with other literature data (26, 27). The functions reported by Radhakrishnan (26) are based on an incorrect structure and older vibrational frequencies (21). The set of frequencies used by Wilkins (27) are very similar to ours but his moments of inertia appear unrealistic. We conclude that his thermal functions (27) are erroneous.

References

1. P. A. G. O'Hare, W. N. Hubbard, O. Glemser, and J. Wegener, J. Chem. Thermodynamics, 2, 71 (1970).
2. JANAF Thermochemical Tables: HF(g), 12-31-68; F(g), 9-30-65; SF_6(g), 6-30-76; F^-(g), 12-31-71; N(g), 3-31-61.
3. J. D. Vaugh and E. L. Muetterties, J. Phys. Chem. 64, 1787 (1960).
4. M. J. Nichols, Ph.D. Thesis, University of Durham, England, 1958.
5. D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
6. V. H. Dibeler and F. L. Mohler, J. Res. Natl. Bur. Std. 40, 25 (1948).
7. J. Delwiche, Dynamic Mass Spectrom. 1, 71 (1970).
8. O. Glemser, A. Müller, D. Böhler, and B. Krebs, Z. Anorg. Allgem. Chem. 357, 184 (1968).
9. J. Kay and F. M. Page, Trans. Faraday Soc. 60, 1042 (1964).
10. C. E. Vanderzee and W. Wm. Rodenburg, J. Chem. Thermodynamics, 2, 461 (1970).
11. P. A. G. O'Hare, Argonne National Laboratory, Report ANL-7315, Contract W-31-109-Eng-38, July, 1968.
12. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
13. V. B. Parker, D. D. Wagman, and D. Garvin, NBSIR 75-968, January, 1976.
14. K. Kimura and S. H. Bauer, J. Chem. Phys. 39, 3172 (1963).
15. W. M. Tolles and W. D. Gwinn, J. Chem. Phys. 36, 1119 (1962).
16. F. A. Cotton, J. W. George, and J. S. Waugh, J. Chem. Phys. 28, 944 (1958).
17. J. Bacon, R. J. Gillespie, and J. W. Quail, Can. J. Chem. 41, 1016 (1963).
18. R. W. Shaw, Jr., T. X. Carroll, T. D. Thomas, J. Amer. Chem. Soc. 95, 2033 (1973).
19. R. W. Shaw, Jr., T. X. Carroll, and T. D. Thomas, J. Amer. Chem. Soc. 95, 5870 (1973).
20. I. W. Levin, J. Chem. Phys. 55, 5393 (1971).
21. R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc. 52, 1052 (1956).
22. K. O. Christe and W. Sawodny, J. Chem. Phys. 52, 6320 (1970).
23. I. W. Levin and C. V. Berney, J. Chem. Phys. 44, 2557 (1966).
24. R. L. Redington and C. V. Berney, J. Chem. Phys. 43, 2020 (1965).
25. R. D. Brown and J. B. Peel, Aust. J. Chem. 21, 2617 (1968).
26. M. Radhakrishnan, Z. Naturforsch. 18a, 103 (1963).
27. R. L. Wilkins, Aerospace Corporation, Report No. TR-0158 (3240-20) - 19, Contract No. F04695-67-C-0158, July, 1968.

F_4S

SILICON TETRAFLUORIDE (SiF_4) F_4Si
(IDEAL GAS) GFW=104.0796

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	-3.670	-384.661	-384.661	INFINITE
100	9.994	52.714	80.995	-2.828	-385.273	-382.314	835.546
200	14.550	61.144	69.072	-1.585	-385.711	-379.165	414.332
298	17.596	67.554	67.554	0.000	-385.980	-375.891	275.535
300	17.644	67.663	67.554	0.033	-385.984	-375.829	273.791
400	19.871	73.062	68.275	1.915	-386.149	-372.415	203.478
500	21.421	77.673	69.705	3.984	-386.238	-368.971	161.277
600	22.488	81.679	71.374	6.183	-386.271	-365.514	133.138
700	23.233	85.205	73.103	8.471	-386.270	-362.053	113.038
800	23.765	88.344	74.816	10.822	-386.251	-358.597	97.964
900	24.154	91.167	76.478	13.219	-386.218	-355.140	86.240
1000	24.446	93.727	78.077	15.650	-386.181	-351.690	76.862
1100	24.670	96.068	79.608	18.106	-386.144	-348.243	69.190
1200	24.845	98.223	81.071	20.582	-386.107	-344.799	62.796
1300	24.983	100.217	82.468	23.074	-386.076	-341.357	57.387
1400	25.095	102.073	83.802	25.578	-386.051	-337.918	52.751
1500	25.187	103.807	85.079	28.093	-386.033	-334.479	48.734
1600	25.262	105.435	86.301	30.615	-386.026	-331.044	45.218
1700	25.325	106.969	87.472	33.145	-398.020	-327.501	42.103
1800	25.379	108.418	88.596	35.680	-397.979	-323.356	39.261
1900	25.424	109.791	89.675	38.220	-397.937	-319.211	36.718
2000	25.463	111.096	90.714	40.764	-397.897	-315.065	34.429
2100	25.497	112.340	91.715	43.313	-397.858	-310.928	32.359
2200	25.526	113.526	92.679	45.864	-397.823	-306.790	30.477
2300	25.552	114.662	93.611	48.418	-397.789	-302.651	28.758
2400	25.575	115.750	94.510	50.974	-397.759	-298.516	27.184
2500	25.594	116.794	95.381	53.532	-397.733	-294.383	25.735
2600	25.612	117.798	96.224	56.093	-397.708	-290.248	24.398
2700	25.628	118.765	97.041	58.655	-397.686	-286.114	23.159
2800	25.642	119.697	97.834	61.218	-397.667	-281.983	22.010
2900	25.655	120.598	98.603	63.783	-397.652	-277.848	20.939
3000	25.667	121.467	99.354	66.349	-397.642	-273.725	19.941
3100	25.677	122.309	100.078	68.917	-397.632	-269.594	19.006
3200	25.687	123.125	100.786	71.485	-397.628	-265.461	18.130
3300	25.695	123.915	101.475	74.054	-397.627	-261.331	17.307
3400	25.703	124.682	102.146	76.624	-397.629	-257.200	16.533
3500	25.711	125.428	102.801	79.195	-397.636	-253.067	15.802
3600	25.717	126.152	103.439	81.766	-489.606	-246.678	14.975
3700	25.723	126.857	104.063	84.338	-489.521	-239.932	14.172
3800	25.729	127.543	104.671	86.911	-489.439	-233.185	13.411
3900	25.734	128.211	105.267	89.484	-489.364	-226.450	12.690
4000	25.739	128.863	105.848	92.057	-489.291	-219.705	12.004
4100	25.744	129.498	106.417	94.632	-489.223	-212.971	11.352
4200	25.748	130.119	106.974	97.206	-489.159	-206.233	10.731
4300	25.752	130.725	107.520	99.781	-489.096	-199.494	10.139
4400	25.755	131.317	108.054	102.356	-489.042	-192.762	9.575
4500	25.759	131.896	108.577	104.932	-488.988	-186.028	9.035
4600	25.762	132.462	109.090	107.508	-488.938	-179.297	8.519
4700	25.765	133.016	109.594	110.085	-488.894	-172.565	8.024
4800	25.768	133.558	110.087	112.661	-488.852	-165.832	7.551
4900	25.770	134.090	110.572	115.238	-488.815	-159.102	7.096
5000	25.773	134.610	111.047	117.815	-488.782	-152.378	6.660
5100	25.775	135.121	111.514	120.393	-488.752	-145.653	6.242
5200	25.777	135.621	111.973	122.970	-488.727	-138.918	5.839
5300	25.779	136.112	112.424	125.548	-488.704	-132.190	5.451
5400	25.781	136.594	112.667	128.126	-488.688	-125.474	5.078
5500	25.783	137.067	113.303	130.704	-488.674	-118.745	4.718
5600	25.785	137.532	113.731	133.283	-488.665	-112.013	4.372
5700	25.787	137.988	114.153	135.861	-488.661	-105.285	4.037
5800	25.788	138.437	114.568	138.440	-488.659	-98.560	3.714
5900	25.790	138.878	114.976	141.019	-488.663	-91.844	3.402
6000	25.791	139.311	115.378	143.598	-488.671	-85.117	3.100

Dec. 31, 1960; Sept. 30, 1963; June 30, 1976

SILICON TETRAFLUORIDE (SiF_4) (IDEAL GAS) GFW = 104.0796

Point Group = T_d
$S^\circ_{298.15}$ = 67.55 ± 0.10 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -384.66 ± 0.20 kcal/mol F_4Si
$\Delta Hf^\circ_{298.15}$ = -385.98 ± 0.20 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
800.8(1)	1029.6(3)
264.2(2)	388.7(3)

Bond Distance: Si-F = 1.552 ± 0.002 Å σ = 12
Bond Angle: F-Si-F = 109° 28'
Product of the Moments of Inertia: $I_AI_BI_C = 8.31638 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

The adopted $\Delta Hf^\circ_{298}(SiF_4, g)$ = -385.98±0.20 kcal/mol is the result of measurement of the direct combination of the elements in a bomb calorimeter by Wise et al. (1) and is the value recommended by CODATA (2). Bousquet et al. (3) determined ΔHf°_{298} = -385±4 kcal/mol, also by fluorine combustion calorimetry, which is less precise but is in agreement with the adopted value. An average result, ΔHf°_{298} = -372.4±0.4 kcal/mol, by Vorob'ev et al. (4) from the reaction of SiF_4(g) and Na(c) and from two rather involved heat of solution schemes, is not used.

Using *JANAF auxiliary values* (5), ΔHa°_0 = *564.76±3 kcal/mol* is calculated for the process $SiF_4(g) = Si(g) + 4F(g)$.

Heat Capacity and Entropy

The four fundamental vibrational frequencies are adopted from the vapor-phase Raman spectral investigation of Clark and Rippon (6). Jones et al. (7) photographed the Raman spectrum of the liquid and assigned values of 800, 268, 1010, and 390 cm^{-1} to the four fundamental vibrational frequencies. Yost et al. (8) determined only ν_1 at 800 cm^{-1}. Shimanouchi (9) references four articles including that of Jones et al. (7) and has selected 800, 268, 1032, and 389 cm^{-1}. All of these assignments are in good agreement.

The interatomic distances *from electron diffraction studies* were found to be 1.555±0.002 and 2.534±0.003 Å for Si-F and F...F, respectively, by Beagley et al. (10) and 1.552±0.002 and 2.534±0.003 Å by Hagen and Hedberg (11). The value of Si-F = 1.552±0.002 Å is adopted because it is in agreement with the F...F distance and the tetrahedral bond angle. The three principal moments of inertia are: $I_A = I_B = I_C = 2.02602 \times 10^{-38}\ g\ cm^2$.

Our calculation of S°_{298} = 67.55±0.10 gibbs/mol agrees with the value recommended by CODATA (2).

References

1. S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 67, 815 (1963).
2. ICSU-CODATA Task Group, "*CODATA Recommended Key Values for 1975*," CODATA Bulletin No. 17, 1976.
3. J. Bousquet, J. Carre, P. Claudy, J. Etienne, P. Provencal, J. Thourey, and P. Barberi, J. Chim. Phys. Physicochim. Biol. 69, 1065 (1972).
4. A. F. Vorob'ev, V. P. Kolesov, and S. M. Skuratov, Zh. Neorgan. Khim. 5, 1402 (1960).
5. JANAF Thermochemical Tables: F(g), 9-30-65; Si(g), 3-31-67.
6. R. J. H. Clark and D. M. Rippon, J. Mol. Spectrosc. 44, 479 (1972).
7. E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz, and A. H. Nielsen, J. Chem. Phys. 19, 242 (1951).
8. D. M. Yost, E. N. Lassettre, and S. T. Gross, J. Chem. Phys. 4, 325 (1936).
9. T. Shimanouchi, NSRDS-NBS 39, 1972.
10. B. Beagley, D. P. Brown, and J. M. Freeman, J. Mol. Struct. 18, 337 (1973).
11. K. Hagen and K. Hedberg, J. Chem. Phys. 59, 1549 (1973).

ZIRCONIUM TETRAFLUORIDE (ZrF_4)

(CRYSTAL) GFW=167.2136

F_4Zr

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.182	- 455.441	- 455.441	INFINITE
100	10.060	5.481	43.591	- 3.811	- 456.672	- 448.746	980.733
200	20.210	15.991	27.166	- 2.235	- 457.022	- 440.613	481.480
298	24.760	25.024	25.024	.000	- 456.800	- 432.595	317.101
300	24.810	25.177	25.024	.046	- 456.793	- 432.445	315.036
400	27.120	32.663	26.029	2.653	- 456.349	- 424.391	231.876
500	28.610	38.883	27.996	5.444	- 455.823	- 416.463	182.036
600	29.630	44.195	30.264	8.359	- 455.250	- 408.644	148.848
700	30.350	48.820	32.591	11.360	- 454.657	- 400.922	125.174
800	30.930	52.911	34.881	14.424	- 454.058	- 393.288	107.441
900	31.510	56.587	37.092	17.546	- 453.450	- 385.728	93.668
1000	32.050	59.936	39.211	20.725	- 452.830	- 378.237	82.664
1100	32.560	63.014	41.237	23.955	- 452.201	- 370.809	73.673
1200	33.050	65.868	43.172	27.235	- 452.411	- 363.385	66.181
1300	33.550	68.533	45.021	30.565	- 451.581	- 355.999	59.849
1400	34.060	71.039	46.791	33.946	- 450.719	- 348.679	54.431

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963;
June 30, 1969; June 30, 1975

ZIRCONIUM TETRAFLUORIDE (ZrF_4) (CRYSTAL) GFW= 167.2136

F_4ZR

$S^\circ_{298.15}$ = 25.024 ± 0.05 gibbs/mol
Tt ($\alpha \rightarrow \beta$) = 723K
Tm = 1205 ± 2K
Ts = 1179K

ΔHf°_0 = -455.44 ± 0.25 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -456.80 ± 0.25 kcal/mol
ΔHt° = Unavailable
ΔHm° = 15.35 ± 0.10 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 56.80 kcal/mol

Heat of Formation

The heat of formation of zirconium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter by Greenberg, Settle, Feder, and Hubbard (1). The reported value $\Delta Hf^\circ_{298}(ZrF_4, c)$ = *-456.80 ± 0.25* kcal/mol is adopted.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range 5 to 307 K were determined by adiabatic calorimetry by Westrum (2). Using these low temperature Cp° data the value of S°_{298} is derived as 25.024 ± 0.05 gibbs/mol based on S°_{10} = 0.0074 gibbs/mol.

McDonald, Sinke, and Stull (3) measured the high temperature enthalpies of ZrF_4(c) at temperatures 283.9 - 1225.8 K in a copper block drop calorimeter. Smith, Miller, and Taylor (4) used a Bunsen ice calorimeter for the enthalpy measurements in the temperature range 273-1150 K. These two sets of enthalpy data are not in good agreement. It is possible that the discrepancies are due to the difference in crystal structure of the samples used (see "Transition Data" for more information). In order to join smoothly with the low temperature heat capacities at 298 K, the high temperature heat capacities derived from the enthalpy data of McDonald, Sinke, and Stull (3) are adopted. The Cp° values above 1200 K are obtained by smooth extrapolation.

Fontana and Winand (8) also measured the enthalpy of ZrF_4 in the range 773-1350 K. Their reported average heat capacity in this range and their reported enthalpies are considerably lower than those adopted.

Transition Data

Gaudreau (5) presented evidence that ZrF_4 has three crystal structures (α, β, and σ) and one amorphous form. Chrétien and Gaudreau (6) found that ZrF_4 (c) has an α (tetragonal) and β (monoclinic) form with a transition temperature of T_t=723K. The crystal data compilation of Donnay and Ondik (7) tabulated two monoclinic structures for ZrF_4; one of which was specified as the β form while no mention was made of a tetragonal form.

The ZrF_4 sample employed by McDonald, Sinke, and Stull (3) for enthalpy measurement was prepared by dissolving hafnium-free zirconium metal in 48% aqueous HF, and the resulting solution was evaporated to dryness. The crystalline product was heated slowly to 773K in a platinum boat in a slow current of anhydrous HF. X-ray diffraction showed only crystalline ZrF_4. Wet analysis indicated 54.6% Zr (theory 54.55) and 44.9% F (theory 45.45). Due to the above facts we are uncertain whether the sample prepared is a mixture of α and β forms or a pure $ZrF_4(\beta)$. Smith, Miller, and Taylor (4) obtained their ZrF_4 sample from the Oak Ridge National Laboratories, Oak Ridge, Tenn. Since the method of preparation of the compound is unavailable from the report, we do not know what kind of sample they used for measurement.

Because of the above unresolved situation, we emphasize that this ZrF_4(c) table is not strictly a α, β-combined phase table. However, the differences in the calculated functions are probably not significant.

Melting Data

Tm and ΔHm° are taken from McDonald, Sinke, and Stull (3). The values were obtained under conditions greater than one atmosphere. Fontana and Winand (8) reported a heat of melting of 11.81±2.40 kcal/mol (under pressure).

Sublimation Data

The sublimation temperature (Ts) is calculated as the temperature at which the Gibbs free energy change of the process $ZrF_4(c) = ZrF_4(g)$ approaches zero. The difference between ΔHf°_{298} for ZrF_4(g) and ZrF_4(c) at 1179 and 298.15 K is ΔHs° and ΔHs°_{298}, respectively. Since the sublimation temperature is lower than the melting point, the ZrF_4 sublimes before it melts.

References

1. E. Greenberg, J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 65, 1168 (1961).
2. E. F. Westrum, Jr., J. Chem. Eng. Data 10, 140 (1965).
3. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).
4. D. F. Smith, W. C. Miller, and A. R. Taylor, Jr., U. S. Bur. Mines RI 5964, 1962.
5. B. Gaudreau, Rev. Chim. Minerale 2, 1 (1965) [Chem. Abstr. 63, 17245d (1965)].
6. A. Chrétien and B. Gaudreau, Compt. Rend. 246, 2266 (1958); Compt. Rend. 248, 2878 (1959).
7. J. D. H. Donnay and H. M. Ondik, "Crystal Data, Determinative Tables," 3rd edition, Vol. 2, National Bureau of Standards and Joint Committee on Powder Diffraction Standards, 1973.
8. A. Fontana and R. Winand J. Nucl. Mat. 3, 295 (1972).

ZIRCONIUM TETRAFLUORIDE (ZrF_4)

F_4Zr

(IDEAL GAS) GFW=167.2136

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 4.527	- 398.986	- 398.986	INFINITE
100	13.653	57.560	92.910	- 3.535	- 399.596	- 396.878	867.375
200	18.119	68.546	78.169	- 1.925	- 399.912	- 394.014	430.559
298	20.887	76.339	76.339	.000	- 400.000	- 391.095	286.680
300	20.927	76.468	76.339	.039	- 400.000	- 391.039	284.872
400	22.603	82.740	77.183	2.223	- 399.979	- 388.053	212.022
500	23.593	87.899	78.826	4.537	- 399.930	- 385.078	168.318
600	24.205	92.259	80.711	6.929	- 399.880	- 382.112	139.184
700	24.603	96.022	82.635	9.371	- 399.846	- 379.153	118.377
800	24.873	99.326	84.519	11.845	- 399.837	- 376.199	102.773
900	25.065	102.267	86.331	14.343	- 399.853	- 373.244	90.636
1000	25.205	104.916	88.059	16.856	- 399.899	- 370.286	80.926
1100	25.310	107.323	89.703	19.382	- 399.974	- 367.321	72.980
1200	25.391	109.529	91.264	21.918	- 400.928	- 364.296	66.347
1300	25.455	111.564	92.749	24.460	- 400.886	- 361.244	60.731
1400	25.506	113.453	94.161	27.008	- 400.857	- 358.196	55.917
1500	25.548	115.214	95.506	29.561	- 400.842	- 355.148	51.745
1600	25.582	116.864	96.790	32.118	- 400.843	- 352.104	48.095
1700	25.610	118.415	98.017	34.677	- 400.858	- 349.055	44.874
1800	25.634	119.880	99.191	37.239	- 400.890	- 346.011	42.011
1900	25.654	121.266	100.317	39.804	- 400.934	- 342.959	39.449
2000	25.671	122.583	101.398	42.370	- 400.994	- 339.905	37.143
2100	25.686	123.836	102.437	44.938	- 401.069	- 336.852	35.057
2200	25.699	125.031	103.437	47.507	- 406.163	- 333.615	33.142
2300	25.710	126.174	104.401	50.078	- 406.262	- 330.313	31.387
2400	25.720	127.268	105.331	52.649	- 406.367	- 327.010	29.778
2500	25.729	128.318	106.229	55.222	- 406.476	- 323.702	28.298
2600	25.737	129.327	107.098	57.795	- 406.589	- 320.387	26.931
2700	25.744	130.299	107.940	60.369	- 406.705	- 317.068	25.665
2800	25.750	131.235	108.755	62.944	- 406.824	- 313.748	24.489
2900	25.756	132.139	109.546	65.519	- 406.949	- 310.418	23.394
3000	25.761	133.012	110.314	68.095	- 407.079	- 307.094	22.372
3100	25.765	133.857	111.060	70.671	- 407.211	- 303.758	21.415
3200	25.770	134.675	111.785	73.248	- 407.348	- 300.417	20.518
3300	25.773	135.468	112.491	75.825	- 407.489	- 297.074	19.674
3400	25.777	136.237	113.178	78.403	- 407.633	- 293.725	18.880
3500	25.780	136.985	113.847	80.981	- 407.783	- 290.369	18.131
3600	25.783	137.711	114.500	83.559	- 407.935	- 287.011	17.424
3700	25.785	138.417	115.137	86.137	- 408.093	- 283.652	16.755
3800	25.788	139.105	115.759	88.716	- 408.254	- 280.284	16.120
3900	25.790	139.775	116.366	91.295	- 408.421	- 276.920	15.518
4000	25.792	140.428	116.960	93.874	- 408.590	- 273.542	14.946
4100	25.794	141.065	117.540	96.453	- 408.765	- 270.166	14.401
4200	25.796	141.687	118.107	99.033	- 408.943	- 266.782	13.882
4300	25.798	142.294	118.663	101.612	- 409.124	- 263.392	13.387
4400	25.799	142.887	119.207	104.192	- 409.312	- 260.003	12.914
4500	25.801	143.466	119.739	106.772	- 409.502	- 256.611	12.463
4600	25.802	144.034	120.261	109.352	- 409.696	- 253.210	12.030
4700	25.804	144.588	120.773	111.933	- 409.895	- 249.805	11.616
4800	25.805	145.132	121.275	114.513	- 551.254	- 245.711	11.188
4900	25.806	145.664	121.767	117.094	- 551.565	- 239.341	10.675
5000	25.807	146.185	122.250	119.674	- 551.887	- 232.968	10.183
5100	25.808	146.696	122.725	122.255	- 552.217	- 226.594	9.710
5200	25.809	147.197	123.190	124.836	- 552.555	- 220.197	9.255
5300	25.810	147.669	123.648	127.417	- 552.901	- 213.801	8.816
5400	25.811	148.171	124.098	129.998	- 553.257	- 207.408	8.394
5500	25.812	148.645	124.540	132.579	- 553.619	- 200.997	7.987
5600	25.812	149.110	124.974	135.160	- 553.989	- 194.579	7.594
5700	25.813	149.567	125.402	137.742	- 554.366	- 188.157	7.214
5800	25.814	150.016	125.822	140.323	- 554.748	- 181.729	6.848
5900	25.814	150.457	126.236	142.904	- 555.138	- 175.300	6.494
6000	25.815	150.891	126.643	145.486	- 555.534	- 168.859	6.151

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963;

June 30, 1969; June 30, 1975

ZIRCONIUM TETRAFLUORIDE (ZrF_4) (IDEAL GAS) GFW = 167.2136

F_4Zr

Point Group = T_d

$S^\circ_{298.15}$ = [76.3±1.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -399.0±0.8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -400.0±0.8 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[630] (1)	668 (3)
[180] (2)	190 (3)

Bond Distance: Zr-F = 1.94±0.02 Å

σ = 12

Bond Angle: F-Zr-F = 109° 28'

Products of the Moments of Inertia: $I_AI_BI_C = 3.17347\times10^{-113}\ g^3\ cm^6$

Heat of Formation

The vapor pressures of ZrF_4(c) in the temperature range 617-1150 K were determined by many investigators using various methods. Based on the reported vapor pressure data, the corresponding heats of sublimation are evaluated by the second and third law methods. Using the third law ΔHs°_{298} and $\Delta Hf^\circ_{298}(ZrF_4, c)$ = -456.8 kcal/mol, the heats of formation at 298.15 K for ZrF_4 (g) are evaluated. The results are presented in the table below. The values of $\Delta Hf^\circ_{298}(ZrF_4, g)$ listed in the last column of this table are in excellent agreement which indicate that the estimated missing vibrational frequencies ν_1 and ν_2 are reasonable. The heat of formation at 298.15 K for ZrF_4(g) is adopted as -400.0 kcal/mol.

Investigator	Method	Temperature, K	No. of Points	ΔHs°_{298}, kcal/mol 2nd law	3rd law	drift gibbs/mol	ΔHf°_{298} kcal/mol
1. Lauter (1948)	unavailable	950-1150	eqn	56.49±0.12	56.83	0.3	-399.97
2. Sense et al. (1954)	transpiration	617-881	14	60.57±0.09	57.13	-3.4±0.1	-399.67
3. Sense et al. (1957)	transpiration	900-1150	6	60.64±0.13	57.24	-3.3±0.1	-399.56
4. Cantor (1958)	quasistatic	710-808	29	56.11±0.62	56.65	0.5±0.6	-400.15
5. *Hildenbrand-Theard (1961)*	*torsion/effusion*	748-849	15	55.81±1.44	57.05	1.5±1.8	-399.75
6. Hildenbrand-Theard (1961)	torsion/effusion	735-825	10	52.59±0.39	57.09	5.7±0.5	-399.71
7. Galkin et al. (1963)	Knudsen-effusion	720-825	5	51.53±0.05	54.79	4.1±0.1	-402.01
8. *Akishin et al. (1963)*	*mass spectrometry*	700-900	5	59.25±2.34	57.30	-2.4±2.9	-399.50
9. Fischer et al. (1964)	"bell method"	1000-1150	eqn	57.38±0.12	56.89	-0.5	-399.91
10. Sidorov et al. (1965)	mass spectrometry	769	1	---	57.58	--	-399.22

Heat Capacity and Entropy

The molecular structure of ZrF_4(g) has been studied by electron diffraction by Spiridonov (11). The configuration was found to be a regular tetrahedron with interatomic distance Zr-F = 1.94 ± 0.02 Å and F-Zr-F bond angle = 109.47° which are adopted.

Employing the estimated interaction coefficients and interatomic distance Zr-F = 1.85 Å, Godnev, Aleksandrovskaia, and Rigina (12) calculated three vibrational frequencies for ZrF_4(g) as ν_2 = 150 - 200, and ν_4 = 180 ± 230 cm^{-1}. Büchler, *Berkowitz, and Dugre (13) observed the infrared spectra of some group IV halides and assigned* ν_3 = 668 and ν_4 = 190 ± 20 cm^{-1} for ZrF_4(g). The frequency ν_3 has also been reported as 670 cm^{-1} (14). In studying matrix isolated ZrF_4, Hauge et al. (15) found a strong infrared band at 668.0 cm^{-1} in an argon matrix and 677.0 cm^{-1} in a neon matrix; both of which were attributed to the ν_3 stretch frequency. The values of ν_3 and ν_4 adopted here are those reported by Büchler, Berkowitz, and Dugre (13). The adopted ν_1 is obtained by correlating the corresponding frequencies of the tetrafluorides of C, Pb, Si, Ti and Ge with their respective interatomic distances. ν_2 is calculated from ν_1, ν_3 and ν_4 using the relationship (15) $\frac{\nu_3\nu_4}{\nu_1\nu_2} = \frac{2}{3}(1+\frac{4F}{Zr})$ where F and Zr are gram atomic weights of fluorine and zirconium, respectively. Vibrational frequencies (635, 178, 668, and 190 cm^{-1}) were suggested by Godnev et al. (17) who also critically examined the sublimation data in order to achieve internal consistency. These values are in good agreement with our adopted values. The three principal moments of inertia are $I_A = I_B = I_C = 3.166 \times 10^{-38}\ g\ cm^2$.

References

1. S. Lauter, Dissertation Technische Hohschule Hannover, 1948. (Cited in reference 9)
2. K. A. Sense, M. Snyder, and R. B. Filbert, Jr., J. Phys. Chem. 58, 995 (1954).
3. K. A. Sense, C. A. Alexander, R. E. Bowman, and R. B. Filbert, Jr., J. Phys. Chem. 61, 337 (1957).
4. S. Cantor, R. F. Newton, W. R. Grimes, and F. F. Blankenship, J. Phys. Chem. 62, 96 (1958).
5. D. L. Hildenbrand and L. P. Theard, Aeronutronic, U-1187, Ford Motor Company, 15 Mar. 1961.
6. D. L. Hildenbrand and L. P. Thread, Aeronutronic, U-1274, Ford Motor Company, 15 June 1961.
7. N. P. Galkin, Y. N. Tumanov, V. I. Tarasov, and Y. D. Shishhov, Russ. J. Inorg. Chem. 8, 1054 (1963).
8. P. A. Akishin, V. I. Belousov, and L. N. Sidorov, Russ. J. Inorg. Chem. 8, 1520 (1963).
9. W. Fischer, T. Petzel, and S. Lauter, Z. Anorg. Allgem. Chem. 333, 226 (1964).
10. L. N. Sidorov, P. A. Akishim, V. B. Shol'ts, and Y. M. Korenev, Russ. J. Phys. Chem. 39, 1146 (1965).
11. V. P. Spiridonov, *Vestn. Mosk. Univ. Ser. II, Khim.* 23, 113 (1968).
12. I. N. Godnev, A. M. Aleksandrovskaia, and I. V. Rigina, Opt. Spectry, USSR 7, 172 (1959).
13. A. Büchler, J. B. Berkowitz-Mattuck, and D. H. Dugre, J. Chem. Phys. 34, 2202 (1961).
14. M. Blander and H. W. Morgan, presented at the 138th Meeting, American Chemical Society, New York, September 1960.
15. R. H. Hauge, J. L. Margrave, and J. W. Hastie, High Temp. Sci 5, 89 (1973).
16. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945, P. 182.
17. I. N. Godnev, A. M. Aleksandrcoskaya, and A. S. Sverdlin, Opt. Spektrosk. 29, 676 (1970).

SULFUR PENTAFLUORIDE (SF_5) F_5S
(IDEAL GAS) GFW=127.0520

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	-4.627	-231.719	-231.719	INFINITE
100	11.355	57.707	95.216	-3.751	-232.744	-228.045	498.391
200	19.571	68.230	79.153	-2.185	-233.321	-223.071	243.760
298	24.444	77.053	77.053	0.000	-233.420	-218.007	159.803
300	24.510	77.204	77.053	0.045	-233.420	-217.912	158.748
400	27.138	84.653	78.051	2.641	-233.848	-212.733	116.232
500	28.612	90.882	80.012	5.435	-234.009	-207.435	90.670
600	29.500	96.183	82.277	8.344	-234.037	-202.115	73.620
700	30.069	100.777	84.599	11.324	-233.985	-196.773	61.435
800	30.452	104.818	86.879	14.352	-246.947	-192.733	52.652
900	30.723	108.422	89.076	17.411	-246.516	-185.982	45.163
1000	30.920	111.669	91.175	20.494	-246.087	-179.279	39.181
1100	31.068	114.623	93.175	23.594	-245.660	-172.621	34.297
1200	31.182	117.332	95.077	26.706	-245.234	-165.997	30.232
1300	31.273	119.831	96.886	29.829	-244.813	-159.410	26.799
1400	31.348	122.152	98.609	32.960	-244.397	-152.857	23.862
1500	31.411	124.317	100.251	36.098	-243.984	-146.332	21.321
1600	31.466	126.346	101.819	39.242	-243.576	-139.836	19.101
1700	31.515	128.255	103.319	42.391	-243.171	-133.363	17.145
1800	31.561	130.058	104.755	45.545	-242.772	-126.920	15.410
1900	31.605	131.765	106.132	48.704	-242.373	-120.492	13.860
2000	31.648	133.387	107.454	51.866	-241.979	-114.085	12.467
2100	31.690	134.933	108.726	55.033	-241.589	-107.705	11.209
2200	31.732	136.408	109.951	58.204	-241.203	-101.337	10.067
2300	31.775	137.819	111.132	61.379	-240.818	-94.987	9.026
2400	31.817	139.172	112.273	64.559	-240.436	-88.655	8.073
2500	31.861	140.472	113.375	67.743	-240.058	-82.340	7.198
2600	31.904	141.723	114.441	70.931	-239.681	-76.037	6.392
2700	31.948	142.927	115.474	74.124	-239.305	-69.749	5.646
2800	31.992	144.090	116.476	77.321	-238.931	-63.480	4.955
2900	32.036	145.214	117.447	80.522	-238.559	-57.215	4.312
3000	32.080	146.300	118.391	83.728	-238.192	-50.975	3.714
3100	32.124	147.353	119.308	86.938	-237.822	-44.740	3.154
3200	32.168	148.374	120.201	90.153	-237.457	-38.516	2.631
3300	32.211	149.364	121.070	93.372	-237.091	-32.307	2.140
3400	32.254	150.326	121.916	96.595	-236.727	-26.104	1.678
3500	32.297	151.262	122.741	99.823	-236.368	-19.912	1.243
3600	32.339	152.172	123.546	103.054	-236.006	-13.730	0.834
3700	32.381	153.059	124.332	106.290	-235.649	-7.562	0.447
3800	32.422	153.923	125.099	109.530	-235.292	-1.400	0.081
3900	32.462	154.766	125.849	112.775	-234.939	4.743	-0.266
4000	32.502	155.588	126.582	116.023	-234.585	10.891	-0.595
4100	32.541	156.391	127.300	119.275	-234.234	17.020	-0.907
4200	32.579	157.176	128.002	122.531	-233.885	23.145	-1.204
4300	32.617	157.943	128.689	125.791	-233.536	29.264	-1.487
4400	32.655	158.693	129.363	129.054	-233.193	35.369	-1.757
4500	32.691	159.427	130.022	132.322	-232.849	41.467	-2.014
4600	32.727	160.146	130.670	135.593	-232.507	47.558	-2.260
4700	32.762	160.850	131.304	138.867	-232.168	53.644	-2.494
4800	32.797	161.541	131.927	142.145	-231.830	59.724	-2.719
4900	32.831	162.217	132.538	145.426	-231.496	65.799	-2.935
5000	32.864	162.881	133.139	148.711	-231.164	71.857	-3.141
5100	32.897	163.532	133.728	151.999	-230.834	77.908	-3.339
5200	32.929	164.171	134.307	155.291	-230.505	83.970	-3.529
5300	32.960	164.799	134.677	158.585	-230.179	90.015	-3.712
5400	32.991	165.415	135.437	161.882	-229.858	96.043	-3.887
5500	33.020	166.021	135.987	165.183	-229.536	102.080	-4.056
5600	33.050	166.616	136.529	168.487	-229.220	108.111	-4.219
5700	33.078	167.201	137.062	171.793	-228.907	114.131	-4.376
5800	33.106	167.777	137.586	175.102	-228.592	120.147	-4.527
5900	33.133	168.343	138.103	178.414	-228.283	126.147	-4.673
6000	33.159	168.900	138.612	181.729	-227.977	132.157	-4.814

June 30, 1976

SULFUR PENTAFLUORIDE (SF_5) (IDEAL GAS) GFW = 127.0520

F_5S

Point Group [C_{4v}]

$S^\circ_{298.15}$ = [77.1 ± 2.0] gibbs/mol

ΔHf°_0 = -231.7 ± 5.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -233.4 ± 5.0 kcal/mol

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]		

Bond Distances:
S-F* = [1.56] Å S-F** = [1.46] Å

Bond Angle:
F*-S-F* = [90]° F**-S-F* = [85]°
(* - equatorial ** - axial)

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[795](1)	[434](1)	[596](2)
[530](1)	[269](1)	[388](2)
[467](1)	[348](1)	[242](2)

Product of Moments of Inertia: $I_AI_BI_C$ = [1.2559 x 10^{-113}] g^3 cm^6 σ = 4

Heat of Formation

No direct determination of ΔHf° has been made. Several studies have been reported, however, which permit the primary bond dissociation energy of SF_6 to be established *within reasonable limits of uncertainty.*

Bott and Jacobs (1) used an ultraviolet absorption technique to monitor SF_4 concentrations in shock-heated (1650-2050 K) SF_6/Ar mixtures. They interpreted their dissociation data in terms of classical unimolecular reaction kinetics and found $D^\circ_0(SF_5-F)$ = 75.9 kcal/mol. More recently, Modica (2) performed similar shock experiments and analyzed equilibrium data for SF_6/Ar, SF_5Cl/Ar, and SF_6/H_2 systems with a thermochemical equilibrium computer program. With $\Delta Hf^\circ_0(SF_4, g)$ = -172.2 kcal/mol, Modica (2) adjusted the value of ΔHf° for SF_5 to bring the calculated and experimental SF_4/HF concentrations into good agree*ment. The results suggest* $\Delta Hf^\circ_0(SF_5, g)$ = -241.7 kcal/mol which corresponds to $D^\circ_0(SF_5-F)$ = 65.2 kcal/mol. We are not able to analyze these shock tube equilibrium data but presumably the D°_0 value should be adjusted for the changes in ΔHf° of SF_4(3).

The electron-impact appearance potential (A.P.) of F^- from SF_6 has been reported as approximately zero by Harland and Thynne (4) and Curran (5). In addition, Curran (5) 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 (E.A.) of F of 3.399 eV(3), we obtain an upper limit value for $D^\circ_0(SF_5-F)$ of $\leq$ 3.2 eV (73.1 kcal/mol). Another upper limit value is suggested from the results obtained by electron-impact (4, 6) and dissociative electron transfer (7) measurements. These studies have shown that the A.P. for SF_5^- from SF_6 is 0.5 eV. We use an E.A. value of 3.4 eV (7, 8) for SF_5, and we obtain $D^\circ_0(SF_5-F) \leq$ 3.9 eV (89.9 kcal/mol) from the measured A.P. by assuming that the kinetic and excitation energies of the products are zero.

The A.P. of SF_5^+ from SF_6 has been extensively studied by electron-impact (9-11), photoionization (12), and photoelectron (P.E.) spectrometric (13-15) methods. The A.P. values show considerable scatter (>1 eV) with the electron-impact results (9-11) being consistently higher (∿0.5 eV) than those determined by photoionization (12) and P.E.(13, 15). We assume that the latter measurements are more accurate and adopt A.P. (SF_5^+) equal to 15.12 eV. Using the ionization potential for SF_5 as $\leq$ 12.5 eV (16), we calculate a lower limit for the primary bond dissociation energy of $D^\circ_0(SF_5-F) \geq$ 70.8 kcal/mol.

All of the derived D°_0 values are subject to an uncertainty of several kcal/mol. We choose to adopt $D^\circ_0(SF_5-F)$ = 75.0± 5.0 kcal/mol from which we calculate $\Delta Hf^\circ_0(SF_5, g)$ = -231.7±5.0 kcal/mol with JANAF auxiliary data for SF_6 and F (3). We note that the average bond dissociation energy for SF_6 is 77.4 kcal/mol (3) which suggests that the primary bond dissociation energy is close to the value that we have selected. ΔHf°_{298} is equal to -233.4 kcal/mol. The heat of atomization (ΔHa°_0) and average bond dissociation energy (D°_0) for SF_5 are 389.3 kcal/mol and 77.9 kcal/mol, respectively.

Heat Capacity and Entropy

Two plausible structures exist for the SF_5 free radical. Wilkins (17) proposed a structure similar to that found for PF_5 (D_{3h} symmetry). O'Hare (18) preferred a strucure which consists of a regular tetragonal pyramid (C_{4v} symmetry), similar to that assumed for the halogen pentafluorides (3). Infrared and Raman spectra (19, 20) for salts of SF_5^- favor a slightly distorted tetragonal pyramidal structure for this anion. We adopt this structure and assume that the axial S-F bond length is 0.1 Å shorter than the equatorial S-F bond. The latter bond length is taken equal to that found for SF_6 (3). The bond angles are those proposed by Drullinger and Griffiths (20) for the SF_5^- anion. The individual moments of inertia are: I_A = 3.0475 x 10^{-38} and $I_B = I_C$ = 2.0301 x 10^{-38} g cm^2.

The vibrational frequencies are those observed by Drullinger and Griffiths (20) for SF_5^-. An independent set (19) of frequencies show good agreement with those adopted here except for the assignment of ν_8. Christe et al. (19) assumed a double coincidence between ν_4 (435 cm^{-1}) and ν_8 as found in the case of ClF_5. We estimate four upper electronic levels by analogy with those observed for SF_6^+ (14). We assume that the ground state and upper levels are all doublets.

Our thermal functions essentially extend those reported for SF_5^- (20) but are significantly *different from literature data* (17, 18) for SF_5. We believe that our statistical calculations are based on more reliable estimates, particularly the vibrational frequencies. If SF_5 has D_{3h} symmetry, then our value of S°_{298} should be decreased by roughly 0.47 gibbs/mol. The electronic entropy contribution due to the estimated excited levels is insignificant below 3000 K. At 4500 K, this entropy contribution is 0.36 gibbs/mol.

References

1. J. F. Bott and T. A. Jacobs, J. Chem. Phys. 50, 3850 (1969).
2. A. P. Modica, J. Phys. Chem. 77, 2713 (1973).
3. JANAF Thermochemical Tables: SF_4(g), SF_6(g), 6-30-76; F^-(g), 12-31-71; F(g), BrF_5(g), 9-30-65; ClF_5(g), 6-30-66; IF_5(g), 12-31-69.
4. P. Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).
5. R. K. Curran, J. Chem. Phys. 34, 1069 (1961).
6. W. M. Hickam and R. E. Cox, J. Chem. Phys. 25, 642 (1956).
7. C. Lifshitz, T. O. Tiernan, and B. M. Hughes, J. Chem. Phys. 59, 3182 (1973).
8. J. Kay and F. M. Page, Trans. Faraday Soc. 60, 1042 (1964).
9. D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
10. R. E. Fox and R. K. Curran, J. Chem. Phys. 34, 1595 (1961).
11. V. H. Dibeler and F. L. Mohler, J. Res. Natl. Bur. Std. 40, 25 (1948).
12. V. H. Dibeler and J. A. Walker, J. Chem. Phys. 44, 4405 (1966).
13. B. P. Pullen, Ph.D. Thesis, University of Tennessee, 1970.
14. J. Delwiche, Dynamic Mass Spectrom. 1, 71 (1971).
15. D. C. Frost, C. A. McDowell, J. S. Sandhu, and D. A. Vroom, Advan. Mass Spectrom. 4, 781 (1968).
16. F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).
17. R. L. Wilkins, Aerospace Corporation, Report No. TR-0158 (3240-20)-19, Contract No. F04695-66-C-0158, July, 1968.
18. P. A. G. O'Hare, Argonne National Laboratory, Report No. ANL-7315, Contract No. W-31-109-Eng-38, July, 1968.
19. K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, Inorg. Chem. 11, 1679 (1972).
20. L. F. Drullinger and J. E. Griffiths, Spectrochimica Acta, 27A, 1793 (1971).

F_5S

SULFUR HEXAFLUORIDE (SF_6) F_6S

(IDEAL GAS) GFW=146.0504

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	-4.043	-288.360	-288.360	INFINITE
100	9.254	53.303	85.543	-3.224	-289.790	-282.615	617.655
200	16.448	61.758	71.570	-1.962	-291.021	-274.922	300.421
298	23.174	69.651	69.651	0.000	-291.700	-266.858	195.612
300	23.278	69.795	69.652	0.043	-291.709	-266.704	194.294
400	27.813	77.162	70.625	2.615	-292.546	-258.293	141.125
500	30.676	83.700	72.600	5.550	-292.970	-249.679	109.134
600	32.521	89.468	74.941	8.716	-293.157	-240.998	87.783
700	33.754	94.580	77.388	12.034	-293.192	-232.276	72.520
800	34.609	99.146	79.628	15.455	-306.194	-224.847	61.425
900	35.223	103.260	82.207	18.948	-305.767	-214.703	52.137
1000	35.676	106.996	84.502	22.494	-305.317	-204.610	44.717
1100	36.020	110.413	86.704	26.080	-304.850	-194.563	38.656
1200	36.286	113.559	88.813	29.695	-304.370	-184.555	33.612
1300	36.496	116.472	90.830	33.335	-303.884	-174.589	29.351
1400	36.664	119.183	92.759	36.993	-303.394	-164.662	25.705
1500	36.801	121.717	94.606	40.667	-302.901	-154.769	22.550
1600	36.914	124.096	96.376	44.353	-302.408	-144.911	19.794
1700	37.008	126.337	98.073	48.049	-301.915	-135.080	17.366
1800	37.087	128.455	99.702	51.754	-301.426	-125.286	15.212
1900	37.155	130.462	101.269	55.466	-300.936	-115.510	13.287
2000	37.213	132.369	102.777	59.184	-300.450	-105.761	11.557
2100	37.262	134.186	104.229	62.908	-299.968	-96.045	9.995
2200	37.306	135.920	105.631	66.637	-299.490	-86.344	8.577
2300	37.344	137.579	106.984	70.369	-299.016	-76.664	7.285
2400	37.377	139.169	108.292	74.105	-298.547	-67.008	6.102
2500	37.406	140.696	109.558	77.844	-298.084	-57.371	5.015
2600	37.433	142.163	110.784	81.586	-297.625	-47.750	4.014
2700	37.456	143.577	111.973	85.331	-297.169	-38.146	3.088
2800	37.477	144.939	113.126	89.077	-296.719	-28.566	2.230
2900	37.496	146.255	114.246	92.826	-296.275	-18.990	1.431
3000	37.513	147.526	115.334	96.576	-295.840	-9.445	0.688
3100	37.528	148.756	116.392	100.329	-295.404	0.096	-0.007
3200	37.542	149.948	117.422	104.082	-294.979	9.623	-0.657
3300	37.555	151.103	118.426	107.837	-294.557	19.133	-1.267
3400	37.566	152.225	119.403	111.593	-294.141	28.635	-1.841
3500	37.577	153.314	120.357	115.350	-293.734	38.126	-2.381
3600	37.587	154.373	121.287	119.108	-293.328	47.605	-2.890
3700	37.596	155.403	122.195	122.867	-292.932	57.068	-3.371
3800	37.604	156.405	123.082	126.627	-292.540	66.525	-3.826
3900	37.612	157.382	123.949	130.388	-292.157	75.960	-4.257
4000	37.619	158.334	124.797	134.150	-291.776	85.402	-4.666
4100	37.625	159.263	125.626	137.912	-291.404	94.822	-5.054
4200	37.631	160.170	126.438	141.675	-291.038	104.240	-5.424
4300	37.637	161.056	127.233	145.438	-290.675	113.651	-5.776
4400	37.642	161.921	128.011	149.202	-290.324	123.047	-6.112
4500	37.647	162.767	128.774	152.967	-289.975	132.435	-6.432
4600	37.652	163.595	129.522	156.732	-289.632	141.817	-6.738
4700	37.656	164.404	130.256	160.497	-289.298	151.194	-7.031
4800	37.661	165.197	130.976	164.263	-288.967	160.566	-7.311
4900	37.664	165.974	131.682	168.029	-288.645	169.933	-7.579
5000	37.668	166.735	132.376	171.796	-288.329	179.282	-7.836
5100	37.671	167.481	133.057	175.563	-288.019	188.623	-8.083
5200	37.675	168.212	133.726	179.330	-287.715	197.979	-8.321
5300	37.678	168.930	134.383	183.098	-287.416	207.318	-8.549
5400	37.681	169.634	135.029	186.866	-287.127	216.638	-8.768
5500	37.683	170.326	135.665	190.634	-286.841	225.970	-8.979
5600	37.686	171.005	136.290	194.402	-286.565	235.296	-9.183
5700	37.688	171.672	136.905	196.171	-286.294	244.611	-9.379
5800	37.691	172.327	137.510	201.940	-286.026	253.924	-9.568
5900	37.693	172.972	138.106	205.709	-285.767	263.219	-9.750
6000	37.695	173.605	138.692	209.478	-285.515	272.527	-9.927

Dec. 31, 1960; Sept. 30, 1965; June 30, 1976

SULFUR HEXAFLUORIDE (SF_6) (IDEAL GAS) GFW = 146.0504 F_6S

Point Group O_h

$S°_{298.15}$ = 69.7 ± 0.1 gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
773.5(1)	947.5(3)	525.0(3)
641.7(2)	615.5(3)	347.0(3)

$\Delta Hf°_0$ = -288.4 ± 0.2 kcal/mol

$\Delta Hf°_{298.15}$ = -291.7 ± 0.2 kcal/mol

Bond Distance: S-F = 1.564 ± 0.01 Å

Bond Angle: F-S-F = 90°

Product of Moments of Inertia:

$I_AI_BI_C = 2.9405 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

The calorimetric measurement of ΔHf° by direct combination of the elements has been the subject of numerous investigations (1-6). O'Hare et al. (1) performed six combustion experiments on a sample of rhombic sulfur which contained 60 ppm oxygen as the major impurity. The sulfur (∼0.5 gram) was burned in 5-6 atmospheres of fluorine which had a purity of 99.97%. Spectrometric and gas chromatographic analyses of the product gases indicated that the sole combustion product was SF_6. We adjust their result ($\Delta Hf°_{298} = -291.7_7 \pm 0.24$ kcal/mol) to correspond to an atomic weight of sulfur equal to 32.06, and we obtain $\Delta Hf°_{298}(SF_6, g) = -291.7_3 \pm 0.24$ kcal/mol. The rounded value of -291.7±0.2 kcal/mol is adopted in this tabulation. Less extensive measurements (3 determinations) by Schröder and Sieben (2) on a portion of the same sample used by O'Hare et al. (1) gave $\Delta Hf°_{298}(SF_6, g)$ = -291.4 kcal/mol which provides confirmation for our selected value.

Other reported ΔHf° values which are consistently less negative than the value selected here include (in kcal/mol) -291.0±0.3 (3), -288.9±0.7 (4), -288.5±0.7 (5) and -262.0 (6). The fluorine used by Leonidov et al. (3) contained 0.13 wt. % oxygen, and this impurity may be responsible for their low results. Gross et al. (4) studied the sulfur fluorination reaction in a glass apparatus and also applied their technique to titanium. Their reported ΔHf° value for TiF_4 is in satisfactory agreement (±0.8 kcal/mol) with JANAF data (7). Insufficient information has been reported (4) to resolve the discrepancy in the case of SF_6.

Our adopted ΔHf° value is essentially the same as that recently selected by NBS (8). The earlier NBS selection (9) of -289.0 kcal/mol based on the work of Gross et al. (4, 5) is unreliable. The heat of atomization ($\Delta H\text{å}_0$) and average bond dissocation energy ($D°_0$) for SF_6 are 464.3 kcal/mol and 77.4 kcal/mol, respectively.

Heat Capacity and Entropy

The product of the moments of inertia is calculated for a structure in which the fluorine atoms lie at the corners of a regular octahedran. This structure belongs to the highest symmetry point group O_h (σ = 24) and is consistant with observations made from electron diffraction (10-12), Raman (13-15) and infrared (16-18) studies. The bond length and angle are from the electron diffraction work of Ewing and Sutton (10). Earlier and less precise work (11, 12) led to r_e(S-F) values which are only slightly different from the adopted value. The individual moments of inertia are: $I_A = I_B = I_C = 3.0865 \times 10^{-38}$ g cm^2.

The SF_6 molecule has been extensively characterized by vibrational spectroscopy. Weinstock and Goodman (19) reviewed work prior to 1965. More recent studies include gas-phase Raman (13, 14), matrix-isolation Raman (15), and gas-phase infrared (16-18). These spectrometric results are in good agreement; the largest deviation arising in the Raman and infrared inactive fundamental ν_6. Weinstock and Goodman (19) obtained ν_6 = 349 cm^{-1} from the combination (2 + 6) band. Claassen et al. (13) reported ν_6 = 347 cm^{-1} from the overtone $2\nu_6$ band, and Holzer and Ouillon (14) have directly observed this forbidden fundamental in the collision-induced *Raman spectra* at 336 cm^{-1}. *Rosenberg and Birnbaum* (20) recorded the far-infrared absorption spectrum of gaseous SF_6 and assigned a band centered at 173 cm^{-1} to $\nu_5-\nu_6$. This difference band gives ν_6 = 352 cm^{-1} with ν_5 = 525 cm^{-1} (13) and supports the higher value for ν_6. All frequencies used in this tabulation except for the two infrared active (ν_3 and ν_4) fundamentals are taken from the work of Claassen et al. (13). Values for the infrared active frequencies are from Abramowitz and Levin (16). Recent MO calculations (21) predict a singlet ground state with no low-lying electronic levels. These predictions are supported by the x-ray emission (22) and absorption (22, 23) spectra of gaseous SF_6. *A detailed description of the electronic properties* has been presented by Gianturco (28).

Kelley and King (24) analyzed Cp° data (13-230 K) reported by Eucken and Schröder (25) and obtained $S°_{298}$ = 70.3±0.7 gibbs/mol for the gas phase. This value is in reasonable agreement with the spectroscopic result (69.7±0.1 gibbs/mol). Our thermal functions essentially extend and update those reported in the literature (1, 26, 27).

References

1. P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard, Trans. Faraday Soc. 62, 558 (1966).
2. J. Schröder and F. J. Sieben, Chem. Ber. 103, 76 (1970).
3. V. Ya. *Leonidov, V. S. Pervov, O. M. Gaisinskaya*, and L. I. Klyuev, Dokl. Akad. Nauk SSSR, 211 901 (1973).
4. P. Gross, C. Haymann, and D. L. Levi, 17th Int. Congr. Pure Appl. Chem., Abstr. 1959, 1, 90.
5. P. Gross, Bull. Chem. Thermodynamics, No. 3, 14 (1960).
6. D. M. Yost and W. H. Claussen, J. Amer. Chem. Soc. 55, 885 (1933).
7. JANAF Thermochemical Tables: TiF_4 (c), 9-30-67.
8. V. B. Parker, D. D. Wagman, and D. Garvin, NBSIR 75-968, January, 1976.
9. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
10. V. C. Ewing and L. E. Sutton, Trans. Faraday Soc. 59, 1241 (1963).
11. L. O. Brockway and L. Pauling, Proc. Natl. Acad. Sci. 19, 68 (1933).
12. H. Braune and S. Knobe, Z. Physik. Chem. 21, 297 (1933).
13. H. H. Claassen, G. L. Goodman, J. H. Holloway, and H. Selig, J. Chem. Phys. 53, 341 (1970).
14. W. Holzer and R. Ouillon, Chem. Phys. Letters, 24, 589 (1974).
15. J. S. Shirk and H. H. Claassen, J. Chem. Phys. 54, 3237 (1971).
16. S. Abramowitz and I. W. Levin, J. Chem. Phys. 44, 3353 (1966).
17. H. Brunet and M. Perez, J. Mol. Spectrosc. 29, 472 (1969).
18. V. D. Klimov and E. A. Lobikov, Opt. Spektrosk. 30, 25 (1971).
19. B. Weinstock and G. L. Goodman, in "Advances in Chemical Physics," Vol. 9, Ed. by I. Prigogine, Interscience, 1965.
20. A. Rosenberg and G. Birnbaum, J. Chem. Phys. 52, 683 (1970).
21. E. L. Rozenberg and M. E. Dyatkina, Zhur. Strukt. Khim. 11, 299 (1970).
22. R. E. LaVilla, J. Chem. Phys. 57, 899 (1972).
23. J. L. Dehmer, J. Chem. Phys. 56, 4496 (1972).
24. K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 1961.
25. A. Eucken and E. Schröder, Z. Physik. Chem. 41B, 307 (1938).
26. G. Nagarajin and D. C. Brinkley, Z. Naturforsch. 26a, 1658 (1971).
27. R. L. Wilkins, Aerospace Corporation, Report No. TR-0158(3240-20)-19, Air Force Contract F04695-67-C-0158, July, 1968.
28. F. A. Gianturco, Chem. Phys. Letters 17, 127 (1972).

F_6S

MAGNESIUM MONOHYDROXIDE (MgOH) HMgO

(IDEAL GAS) GFW=41.3124

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.428	-38.560	-38.560	INFINITE
100	7.130	44.885	62.193	-1.731	-38.743	-39.715	86.797
200	8.794	50.287	54.995	-.942	-39.166	-40.642	44.412
298	10.286	54.098	54.098	.000	-39.377	-41.219	30.214
300	10.307	54.162	54.098	.019	-39.382	-41.231	30.037
400	11.209	57.262	54.515	1.099	-39.619	-41.811	22.844
500	11.742	59.825	55.328	2.249	-39.826	-42.333	18.504
600	12.084	61.999	56.263	3.441	-40.030	-42.817	15.596
700	12.332	63.881	57.220	4.662	-40.242	-43.264	13.507
800	12.534	65.541	58.158	5.906	-40.475	-43.681	11.933
900	12.712	67.028	59.063	7.168	-40.737	-44.066	10.701
1000	12.877	68.376	59.928	8.448	-43.149	-44.238	9.668
1100	13.031	69.610	60.753	9.744	-43.438	-44.335	8.809
1200	13.176	70.750	61.539	11.054	-43.745	-44.403	8.087
1300	13.310	71.810	62.289	12.378	-44.074	-44.445	7.472
1400	13.434	72.801	63.005	13.716	-74.790	-43.981	6.866
1500	13.548	73.732	63.689	15.065	-74.757	-41.781	6.087
1600	13.652	74.610	64.344	16.425	-74.721	-39.586	5.407
1700	13.748	75.441	64.973	17.795	-74.682	-37.389	4.807
1800	13.834	76.229	65.576	19.174	-74.643	-35.197	4.273
1900	13.913	76.979	66.157	20.562	-74.602	-33.006	3.797
2000	13.984	77.694	66.716	21.956	-74.562	-30.819	3.368
2100	14.049	78.378	67.255	23.358	-74.522	-28.633	2.980
2200	14.108	79.033	67.776	24.766	-74.483	-26.447	2.627
2300	14.162	79.662	68.279	26.180	-74.444	-24.265	2.306
2400	14.211	80.265	68.766	27.598	-74.406	-22.084	2.011
2500	14.256	80.846	69.238	29.022	-74.373	-19.907	1.740
2600	14.296	81.406	69.695	30.449	-74.339	-17.726	1.490
2700	14.334	81.947	70.139	31.881	-74.309	-15.550	1.259
2800	14.368	82.469	70.570	33.316	-74.281	-13.377	1.044
2900	14.400	82.973	70.989	34.754	-74.255	-11.198	.844
3000	14.429	83.462	71.397	36.196	-74.234	-9.026	.658
3100	14.456	83.936	71.793	37.640	-74.216	-6.853	.483
3200	14.482	84.395	72.180	39.087	-74.202	-4.681	.320
3300	14.505	84.841	72.557	40.536	-74.192	-2.509	.166
3400	14.528	85.274	72.925	41.988	-74.187	-.335	.022
3500	14.549	85.696	73.284	43.442	-74.188	1.835	-.115
3600	14.569	86.106	73.634	44.898	-74.194	4.009	-.243
3700	14.588	86.505	73.977	46.356	-74.208	6.183	-.365
3800	14.607	86.895	74.311	47.815	-74.227	8.357	-.481
3900	14.625	87.274	74.639	49.277	-74.253	10.526	-.590
4000	14.643	87.645	74.960	50.740	-74.288	12.701	-.694
4100	14.660	88.006	75.273	52.206	-74.331	14.877	-.793
4200	14.677	88.360	75.581	53.672	-74.382	17.052	-.887
4300	14.694	88.706	75.882	55.141	-74.443	19.230	-.977
4400	14.711	89.044	76.177	56.611	-74.513	21.409	-1.063
4500	14.729	89.374	76.467	58.083	-74.593	23.591	-1.146
4600	14.746	89.698	76.751	59.557	-74.684	25.777	-1.225
4700	14.764	90.016	77.030	61.033	-74.785	27.961	-1.300
4800	14.781	90.327	77.304	62.510	-74.898	30.150	-1.373
4900	14.800	90.632	77.573	63.989	-75.022	32.337	-1.442
5000	14.818	90.931	77.837	65.470	-75.158	34.529	-1.509
5100	14.837	91.224	78.096	66.952	-75.307	36.723	-1.574
5200	14.857	91.513	78.352	68.437	-75.469	38.920	-1.636
5300	14.876	91.796	78.603	69.924	-75.642	41.128	-1.696
5400	14.897	92.074	78.850	71.412	-75.830	43.326	-1.753
5500	14.917	92.348	79.092	72.903	-76.032	45.537	-1.809
5600	14.938	92.617	79.332	74.396	-76.248	47.747	-1.863
5700	14.960	92.881	79.567	75.891	-76.478	49.967	-1.916
5800	14.982	93.142	79.799	77.388	-76.724	52.184	-1.966
5900	15.005	93.398	80.027	78.887	-76.985	54.412	-2.016
6000	15.027	93.650	80.252	80.389	-77.261	56.637	-2.063

Dec. 31, 1960; June 30, 1967; June 30, 1975; Dec. 31, 1975

MAGNESIUM MONOHYDROXIDE (MgOH) (IDEAL GAS) GFW = 41.3124

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [54.10 ± 2] gibbs/mol

ΔHf°_0 = [-38.56 ± 9] kcal/mol HMgO

$\Delta Hf^\circ_{298.15}$ = [-39.38 ± 9] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	2
[27000]	[4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[718] (1)
[492] (2)
[3650] (1)

Bond Distance: Mg-O = [1.77] Å O-H = [0.96] Å

Bond Angle: Mg-O-H = [180°] σ = 1

Rotational Constant: B_0 = [0.49192] cm^{-1}

Heat of Formation

From observations made during a flame spectra study of the bond dissociation energy of magnesium oxide, Cotton and Jenkins (1) concluded that D°_0 (Mg-OH) is less than 90 kcal/mol. The analogy between gaseous monohydroxides and monohalides has been recognized (2-5). Hildenbrand (6) has found that the ratio of D°_0 (Mg-F)/D°_0(F-Mg-F) is 0.45; current JANAF values (7) give 0.448. From the latter ratio and current JANAF data (7), D°_0(Mg-OH) = 84.49 kcal/mol is derived. Adding the difference, -16.1 kcal/mol, between D°_0(Mg-F) and D°_0(Ca-F) (7) to D°_0(Ca-OH) = 97.5 kcal/mole (7) gives D°_0(Mg-OH) = 81.4 kcal/mol. The average D°_0(Mg-OH) = 82.9±5 kcal/mol is adopted from which ΔHf°_0(MgOH, g) -38.56±9 kcal/mol is derived.

The value of D°_0(Mg-OH) = 56±5 kcal/mol derived by Bulewicz and Sugden (8) from flame spectra studies appears to be too low.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh (9), the evidence that the alkali metal monohydroxides are linear (10-13), and the ESR spectrum study of MgOH in argon and neon matrices from which Brom and Weltner (13) concluded that MgOH is probably linear with a $^2\Sigma$ ground state. The analogy with MgF and MgCl (7) also indicates a $^2\Sigma^+$ ground state, which is assumed.

Ultraviolet emission spectra near 3800 Å were observed for MgOH and MgOD by Pesic and Gaydon (14) and by Brewer and Trajmar (15). Brom and Weltner (13) observed absorption spectra of MgOH in an argon matrix in the 3100-3700 Å range. From these observations and from the comparison with MgF and MgCl, the first excited state at 27000 cm^{-1} is estimated.

The Mg-O bond distance is estimated to be slightly larger, 0.02 Å, than the MgF bond distances (7) after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is that in water (7). The moment of inertia is 5.6901×10^{-39} g cm^2.

The Mg-O stretching frequency, 718 cm^{-1}, is estimated to be the same as in MgF (5, 7). The O-H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 492 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz (5, 12).

The entropy in the present table is lower by 0.20 gibbs/mol at 298 K and 0.25 gibbs/mol at 1000 K than that proposed by Jackson (5); the data relevant to the calculation are nearly the same.

References

1. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 65, 376 (1969).
2. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
3. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
4. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
5. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif. Report UCRL-51137, Contract No. W-7405-Eng-48, Dec. 8, 1971.
6. D. L. Hildenbrand, private communication, Stanford Research Institute, July 2, 1974.
7. JANAF Thermochemical Tables: $Mg(OH)_2$(g), CaOH(g), MgF(g), 12-31-75; MgF_2(g), 6-30-75; Mg(g), 9-30-62; OH(g), 12-31-70; CaF(g), 12-31-68; H_2O(g), 3-31-61.
8. E. M. Bulewicz and T. M. Sugden, Trans. Faraday Soc. 55, 720(1959).
9. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
10. N. Acquista, S. Abramowitz, and R. Lide, J. Chem. Phys. 49, 780 (1968).
11. R. L. Kuczkowski and R. Lide, J. Chem. Phys. 44, 3131 (1966).
12. N. Acquista and S. Abramowitz, U. S. Natl. Bur. Std. Report 9905, July, 1968.
13. J. M. Brom, Jr., and W. Weltner, Jr., J. Chem. Phys. 58, 5322 (1973).
14. D. Pesic and A. G. Gaydon, Proc. Phys. Soc. (London) 73, 244 (1959).
15. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).

MAGNESIUM MONOHYDROXIDE UNIPOSITIVE ION ($MgOH^+$) $HMgO^+$
(IDEAL GAS) GFW=41.3119

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	10.329	52.751	52.751	.000	139.680	136.752	-100.242
300	10.350	52.815	52.752	.019	139.684	136.734	-99.610
400	11.245	55.927	53.170	1.103	139.949	135.711	-74.149
500	11.770	58.498	53.986	2.256	140.241	134.620	-58.842
600	12.106	60.675	54.924	3.451	140.537	133.466	-48.615
700	12.349	62.561	55.883	4.674	140.823	132.265	-41.295
800	12.547	64.223	56.824	5.919	141.088	131.024	-35.794
900	12.723	65.711	57.730	7.183	141.325	129.752	-31.508
1000	12.886	67.060	58.597	8.463	139.411	128.636	-28.113
1100	13.039	68.295	59.423	9.760	139.620	127.547	-25.341
1200	13.182	69.436	60.210	11.071	139.809	126.440	-23.028
1300	13.316	70.497	60.961	12.396	139.977	125.320	-21.068
1400	13.439	71.488	61.678	13.734	109.759	124.666	-19.461
1500	13.552	72.419	62.364	15.083	110.290	125.713	-18.316
1600	13.656	73.297	63.020	16.444	110.822	126.721	-17.309
1700	13.751	74.128	63.649	17.814	111.358	127.701	-16.417
1800	13.837	74.916	64.253	19.194	111.895	128.646	-15.620
1900	13.916	75.667	64.834	20.581	112.433	129.563	-14.903
2000	13.987	76.382	65.394	21.977	112.971	130.450	-14.255
2100	14.051	77.066	65.934	23.379	113.507	131.309	-13.666
2200	14.110	77.721	66.455	24.787	114.043	132.146	-13.127
2300	14.164	78.350	66.958	26.200	114.579	132.957	-12.634
2400	14.212	78.954	67.446	27.619	115.114	133.745	-12.179
2500	14.257	79.535	67.918	29.043	115.645	134.508	-11.759
2600	14.298	80.095	68.375	30.470	116.174	135.254	-11.369
2700	14.335	80.635	68.819	31.902	116.702	135.977	-11.007
2800	14.369	81.157	69.251	33.337	117.227	136.680	-10.668
2900	14.400	81.662	69.670	34.776	117.749	137.369	-10.352
3000	14.429	82.150	70.078	36.217	118.267	138.035	-10.056
3100	14.455	82.624	70.475	37.661	118.782	138.685	-9.777
3200	14.480	83.083	70.862	39.108	119.293	139.317	-9.515
3300	14.502	83.529	71.239	40.557	119.799	139.936	-9.268
3400	14.523	83.962	71.607	42.009	120.301	140.540	-9.034
3500	14.542	84.384	71.966	43.462	120.796	141.126	-8.812
3600	14.560	84.794	72.317	44.917	121.265	141.702	-8.602
3700	14.577	85.193	72.659	46.374	121.767	142.263	-8.403
3800	14.593	85.582	72.994	47.832	122.244	142.812	-8.214
3900	14.607	85.961	73.322	49.292	122.713	143.343	-8.033
4000	14.621	86.331	73.643	50.754	123.173	143.866	-7.860
4100	14.633	86.692	73.956	52.216	123.624	144.379	-7.696
4200	14.645	87.045	74.264	53.680	124.067	144.879	-7.539
4300	14.656	87.390	74.565	55.145	124.499	145.370	-7.388
4400	14.667	87.727	74.860	56.612	124.923	145.850	-7.244
4500	14.676	88.056	75.150	58.079	125.333	146.321	-7.106
4600	14.686	88.379	75.434	59.547	125.734	146.786	-6.974
4700	14.694	88.695	75.713	61.016	126.123	147.239	-6.847
4800	14.702	89.005	75.987	62.486	126.500	147.686	-6.724
4900	14.710	89.308	76.255	63.956	126.865	148.121	-6.607
5000	14.717	89.605	76.519	65.428	127.215	148.550	-6.493
5100	14.724	89.897	76.779	66.900	127.552	148.972	-6.384
5200	14.731	90.183	77.034	68.373	127.876	149.389	-6.279
5300	14.737	90.463	77.285	69.846	128.186	149.806	-6.177
5400	14.743	90.739	77.531	71.320	128.480	150.204	-6.079
5500	14.748	91.009	77.774	72.794	128.759	150.606	-5.985
5600	14.754	91.275	78.013	74.270	129.022	150.998	-5.893
5700	14.759	91.536	78.248	75.745	129.269	151.392	-5.805
5800	14.763	91.793	78.479	77.221	129.500	151.775	-5.719
5900	14.768	92.045	78.707	78.698	129.713	152.161	-5.636
6000	14.772	92.294	78.931	80.175	129.908	152.535	-5.556

June 30, 1968; Dec. 31, 1975

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [52.75 ± 2.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = [139.01 ± 15.0] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [139.68 ± 15.0] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[700](1)
[490](2)
[3650](1)

Bond Distance: Mg-O = [1.77] Å O-H = [0.96] Å
Bond Angle: Mg-O-H = [180°] σ = 1
Rotational Constant: B_o = [0.4918] cm^{-1}

Heat of Formation

The heat of formation of $MgOH^+(g)$ is estimated based on trends suggested by the alkaline earth monohydroxide unipositive ions. The estimate is based on the close agreement of the appearance potentials of the alkaline earth monohydroxides and the corresponding monofluoride (1). In addition, the ionization potentials of the alkaline earth elements are fairly close to the appearance potential of the monohydroxide. We adopt, as the ionization potential for MgOH(g), a value of 7.7 ev (177.57 kcal/mol). This value is identical to the appearance potential of MgF(g,1). The ionization potential of Mg(g) is 7.65 ev (1), which is very close to our adopted value.

The adopted ionization potential of 7.7 ev refers to the process $MgOH(g) + e^- = MgOH^+(g) + 2e^-$. Using auxiliary data (1), we calculate ΔHf°_0 = 139.01±15.0 kcal/mol for $MgOH^+(g)$. This leads to ΔHf°_{298} = 139.68±15.0 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear (1,2,3,4). In addition, Walsh (5) had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons ($MgOH^+$ has 8 valence electrons) will be linear in their ground state. The molecule $MgOH^+$ is isoelectronic with NaOH.

The bond dissociation energy for $MgOH^+$ (D°_0 = 81.7 kcal/mol, 1) for the process $MgOH^+(g) = Mg^+(g) + OH(g)$ is essentially identical to that for MgOH (D°_0 = 82.0 kcal/mol, 1). This suggests a similar bonding in these two molecules. Thus, the bond distances are assumed to be the same as those adopted for MgOH(g,1). The moment of inertia is 5.690×10^{-39} g cm^2. The vibrational frequencies are assumed to be similar to those adopted for MgOH(g,1). The ground state quantum weight is assumed to be the same as that of NaOH(g,1). The enthalpy change between 0 and 298.15 K is -2.435 kcal/mol.

References

1. JANAF Thermochemical Tables: e^-, 3-31-65; NaOH(g) and $Mg^+(g)$, 12-31-70; MgOH(g) and $MgF^+(g)$, 12-31-75.
2. N. Acquista, S. Abramowitz, and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
3. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. 44, 313 (1966).
4. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9905, July, 1968.
5. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

STRONTIUM MONOHYDROXIDE (SROH) HOSR
(IDEAL GAS) GFW=104.6274

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.559	-48.110	-48.110	INFINITE
100	7.324	49.030	67.611	-1.858	-48.456	-49.469	108.115
200	9.549	54.778	59.856	-1.016	-48.852	-50.334	55.003
298	10.984	58.891	58.891	.000	-49.120	-50.994	37.380
300	11.003	58.959	58.891	.020	-49.125	-51.006	37.158
400	11.732	62.235	59.333	1.161	-49.346	-51.599	28.192
500	12.128	64.900	60.188	2.356	-49.565	-52.137	22.789
600	12.374	67.134	61.165	3.582	-49.809	-52.629	19.170
700	12.556	69.056	62.158	4.829	-50.093	-53.077	16.571
800	12.711	70.743	63.128	6.092	-50.429	-53.482	14.611
900	12.855	72.248	64.059	7.370	-50.991	-53.825	13.070
1000	12.995	73.610	64.947	8.663	-51.371	-54.119	11.828
1100	13.130	74.855	65.792	9.969	-53.671	-54.265	10.782
1200	13.259	76.003	66.596	11.289	-53.983	-54.305	9.890
1300	13.382	77.069	67.361	12.621	-54.291	-54.320	9.132
1400	13.496	78.065	68.090	13.965	-54.596	-54.311	8.478
1500	13.603	79.000	68.787	15.320	-54.900	-54.279	7.908
1600	13.702	79.881	69.453	16.685	-55.202	-54.229	7.407
1700	13.793	80.714	70.091	18.060	-88.075	-53.253	6.846
1800	13.877	81.505	70.703	19.444	-88.033	-51.206	6.217
1900	13.955	82.258	71.292	20.835	-87.992	-49.161	5.655
2000	14.028	82.975	71.858	22.234	-87.952	-47.119	5.149
2100	14.097	83.661	72.404	23.641	-87.915	-45.078	4.691
2200	14.162	84.319	72.931	25.054	-87.883	-43.039	4.276
2300	14.225	84.950	73.440	26.473	-87.855	-41.002	3.896
2400	14.287	85.556	73.932	27.899	-87.835	-38.964	3.548
2500	14.347	86.141	74.409	29.330	-87.825	-36.930	3.228
2600	14.408	86.705	74.871	30.768	-87.823	-34.892	2.933
2700	14.468	87.250	75.319	32.212	-87.836	-32.857	2.660
2800	14.530	87.777	75.755	33.662	-87.863	-30.820	2.406
2900	14.592	88.288	76.178	35.118	-87.908	-28.781	2.169
3000	14.655	88.784	76.590	36.580	-87.972	-26.742	1.948
3100	14.720	89.265	76.991	38.049	-88.057	-24.699	1.741
3200	14.786	89.734	77.382	39.524	-88.168	-22.655	1.547
3300	14.854	90.190	77.763	41.006	-88.304	-20.605	1.365
3400	14.923	90.634	78.135	42.495	-88.470	-18.552	1.193
3500	14.993	91.068	78.499	43.991	-88.667	-16.492	1.030
3600	15.064	91.491	78.854	45.494	-88.897	-14.427	.876
3700	15.136	91.905	79.201	47.004	-89.161	-12.354	.730
3800	15.209	92.309	79.541	48.521	-89.461	-10.273	.591
3900	15.282	92.705	79.873	50.045	-89.800	-8.186	.459
4000	15.355	93.093	80.199	51.577	-90.177	-6.090	.333
4100	15.428	93.473	80.518	53.117	-90.592	-3.981	.212
4200	15.501	93.846	80.831	54.663	-91.047	-1.864	.097
4300	15.574	94.211	81.138	56.217	-91.541	.266	-.014
4400	15.645	94.570	81.439	57.778	-92.073	2.406	-.120
4500	15.716	94.923	81.735	59.346	-92.643	4.559	-.221
4600	15.785	95.269	82.025	60.921	-93.250	6.728	-.320
4700	15.853	95.609	82.311	62.503	-93.893	8.909	-.414
4800	15.919	95.944	82.591	64.091	-94.569	11.103	-.506
4900	15.984	96.272	82.867	65.687	-95.278	13.309	-.594
5000	16.047	96.596	83.138	67.288	-96.017	15.532	-.679
5100	16.107	96.914	83.405	68.896	-96.785	17.773	-.762
5200	16.165	97.228	83.668	70.509	-97.578	20.025	-.842
5300	16.221	97.536	83.927	72.129	-98.396	22.298	-.919
5400	16.275	97.840	84.182	73.754	-99.235	24.579	-.995
5500	16.326	98.139	84.433	75.384	-100.094	26.882	-1.066
5600	16.375	98.434	84.680	77.019	-100.971	29.196	-1.139
5700	16.421	98.724	84.924	78.659	-101.862	31.529	-1.209
5800	16.465	99.010	85.164	80.303	-102.766	33.878	-1.277
5900	16.506	99.292	85.402	81.952	-103.681	36.242	-1.342
6000	16.545	99.569	85.635	83.604	-104.605	38.621	-1.407

June 30, 1975; Dec. 31, 1975

STRONTIUM MONOHYDROXIDE (SrOH) (IDEAL GAS) GFW = 104.6274

Point Group $[C_{\infty v}]$

$S°_{298.15}$ = [58.89 ± 2] gibbs/mol

$\Delta Hf°_0$ = -48.11 ± 5 kcal/mol HOSR

$\Delta Hf°_{298.15}$ = -49.12 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[14700]	[2]
[15100]	[2]
[16000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[498](1)
[438](2)
[3650](1)

Bond Distance: Sr-O = [2.10] Å O-H = [0.96] Å

Bond Angle: Sr-O-H = [180°] σ = 1

Rotational Constant: B_o = [0.25110] cm^{-1}

Heat of Formation

The adopted $\Delta Hf°_0(SrOH,g)$ = -48.11±5 kcal/mol is based on an assessment of $D°_0$ values derived from flame spectra of CaOH, SrOH, and BaOH. Cotton and Jenkins (1) found both the alkaline earth monohydroxides and dihydroxides to be present in significant amounts in fuel-rich hydrogen-oxygen-nitrogen flames. They determined equilibrium constants for the reactions $M(g) + H_2O(g) = MOH(g) + H(g)$ and $M(g) + 2H_2O(g) = M(OH)_2(g) + 2H(g)$ and derived $D°_0$ values. For $D°_0$(Sr-OH), Cotton and Jenkins (1) gave 103±5 kcal/mol. Ryabova and Gurvich (2) considered SrOH to be the dominant compound and reported $D°_0$ = 95±8 kcal/mol. Sugden and Schofield (3) interpreted $Sr(OH)_2$ as dominant. Cotton and Jenkins (1) have recalculated the work of Ryabova and Gurvich (2) and of Sugden and Schofield (3) considering both SrOH and $Sr(OH)_2$ to be present and have obtained the recalculated $D°_0$ (Sr-OH) values of 96 and 101 kcal/mol, respectively. Gurvich et al. (4) made further measurements, interpreted SrOH as dominant, and reported $D°_0$(Sr-OH) = 93±3 kcal/mol. Kalff and Alkemade (5) chose flame conditions to minimize the dihydroxide formation and determined $D°_0$(Sr-OH) = 100.1 kcal/mol.

A third law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins (1) using current JANAF auxiliary data (7) leads to $D°_0$ (Sr-OH) = 103.7 kcal/mol which is 0.7 kcal/mol higher than the 103 kcal/mol given by Cotton and Jenkins (1). Applying the correction to the value of Ryabova and Gurvich (2) and Sugden and Schofield (3) as recalculated by Cotton and Jenkins (1) gives $D°_0$(Sr-OH) = 96.7 and 101.7 kcal/mol, respectively.

Because the corrected dissociation energy of Ryabova and Gurvich was near the adopted value for $Ba(OH)_2(g)$(7), their corrected value was adopted for $Sr(OH)_2(g)$(7). While their corrected value for BaOH(g)(7) is not as close to the adopted value as is the dihydroxide case, it is nevertheless the nearest one, and therefore $D°_0$(Sr-OH) = 96.7 kcal/mol is adopted.

The ratio of the dissociation energies of the alkaline earth monohalides to those of the corresponding dihalides range from 0.40 to 0.51 with the ratio for the strontium fluorides being 0.49 (7). The similarity between the halides and hydroxides has been established (8-11). The ratio of the adopted values for the dissociation energies of SrOH(g) and $Sr(OH)_2(g)$ is 0.49 where $D°_0$ of the dihydroxide is defined by the reaction $Sr(OH)_2(g) = Sr(g) + 2\ OH(g)$ and is 198.6 kcal/mol (7).

$\Delta Hf°_0(SrOH,g)$ = -48.11±5 kcal/mol is calculated from the adopted dissociation energy.

Heat Capacity and Entropy

The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides has been recognized (8-11). The molecular configuration is assumed to be linear in accordance with the prediction of Walsh (12) and the evidence that the gaseous alkali metal hydroxide are linear (13-15). The ground state is assumed to be $^2\Sigma^+$ by analogy with SrF and SrCl (7). The electronic levels are estimated from the band spectra observed by James and Sugden (16), Lagerqvist and Huldt (17), Charton and Gaydon (18), Zhitkevich et al (19), and Van der Hurk et al. (20), and the comparison with SrF and SrCl (7).

The Sr-O bond distance is estimated to be slightly larger, 0.02 Å, than the Sr-F distance (7) after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is that in water (7). The moment of inertia is 11.1472×10^{-39} g cm^2.

The Sr-O stretching frequency, 498 cm^{-1}, is estimated to be the same as the Sr-F stretching frequency (7, 11). The O-H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 438 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz (11, 15).

The entropy in the present table is lower by 0.06 gibbs/mol at 298 K and 0.10 gibbs/mol at 1000 K than that proposed by Jackson (11); the data relevant to the calculation are nearly the same.

References

1. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 64, 2988 (1968).
2. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 3, 318 (1965).
3. T. M. Sugden and K. Schofield, Trans. Faraday Soc. 62, 566 (1966).
4. L. V. Gurvich, V. G. Ryabova, A. N. Khitrov, and E. M. Starovoitov, Teplofiz. Vys. Temp. 9, 250 (1971).
5. P. J. Kalff and C. Th. J. Alkemade, J. Chem. Phys. 59, 2572 (1973).
6. V. G. Ryabova, A. N. Khitrov, and L. V. Gurvich, Teplofiz. Vys. Temp. 10, 744(1972).
7. JANAF Thermochemical Tables: Sr(g), 12-31-70; $H_2O(g)$, 3-31-61; H(g), 6-30-74; SrCl(g), SrF(g), 12-31-72; $Sr(OH)_2$, BaOH, $Ba(OH)_2$, 12-31-75.
8. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
9. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
10. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
11. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Contract No. W-7405-Eng.-48, Dec 8, 1971.
12. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
13. N. Acquista, S. Abramowitz, and R. Lide, J. Chem. Phys. 49, 780 (1968).
14. R. L. Kuczkowski and R. Lide, J. Chem. Phys. 44, 3131 (1966).
15. N. Acquista and S. Abramowitz, U. S. Natl. Bur. Std. Report 9905, July, 1968.
16. C. G. James and T. M. Sugden, Nature 175, 333 (1955).
17. A. Lagerqvist and L. Huldt, Naturwissenschaften 42, 365 (1955).
18. M. Charton and A. G. Gaydon, Proc. Phys. Soc. (London) 69A, 520 (1952).
19. V. F. Zhitkevich, A. I. Lyutyi, N. A. Nesterko, V. S. Rossikhin, and I. L. Tsikora, Optika i Spektroskopiya 14, 35 (1963).
20. J. Van der Hurk, Tj. Hollander, and C. Th J. Alkemade, J. Quant. Spectrosc. Radiat. Transfer 13, 273 (1973).

HOSR

STRONTIUM MONOHYDROXIDE UNIPOS. ION ($SrOH^+$) $HOSr^+$
(IDEAL GAS) GFW=104.6269

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0				-2.572	76.190		
100							
200							
298	11.037	57.585	57.585	0.000	76.673	73.701	-54.025
300	11.055	57.653	57.585	0.020	76.678	73.683	-53.678
400	11.768	60.943	58.029	1.166	76.958	72.643	-39.690
500	12.153	63.614	58.887	2.363	77.239	71.532	-31.266
600	12.393	65.852	59.867	3.591	77.495	70.366	-25.631
700	12.570	67.777	60.862	4.840	77.708	69.159	-21.592
800	12.722	69.465	61.834	6.105	77.870	67.925	-18.556
900	12.864	70.972	62.767	7.384	77.806	66.692	-16.195
1000	13.002	72.334	63.657	8.677	77.924	65.451	-14.304
1100	13.136	73.580	64.503	9.984	76.121	64.308	-12.777
1200	13.264	74.728	65.308	11.304	76.307	63.226	-11.515
1300	13.386	75.795	66.074	12.637	76.496	62.128	-10.445
1400	13.500	76.791	66.805	13.981	76.688	61.016	-9.525
1500	13.606	77.726	67.502	15.336	76.882	59.890	-6.726
1600	13.703	78.607	68.169	16.702	77.076	58.750	-8.025
1700	13.793	79.441	68.807	18.077	44.699	58.504	-7.521
1800	13.875	80.232	69.420	19.460	45.239	59.301	-7.200
1900	13.949	80.984	70.009	20.852	45.776	60.068	-6.909
2000	14.017	81.701	70.576	22.250	46.312	60.806	-6.645
2100	14.079	82.387	71.122	23.655	46.844	61.517	-6.402
2200	14.135	83.043	71.649	25.066	47.370	62.203	-6.179
2300	14.187	83.672	72.158	26.482	47.892	62.865	-5.974
2400	14.234	84.277	72.651	27.903	48.405	63.507	-5.783
2500	14.276	84.859	73.128	29.328	48.906	64.124	-5.606
2600	14.316	85.420	73.590	30.758	49.395	64.724	-5.441
2700	14.351	85.961	74.038	32.191	49.869	65.304	-5.286
2800	14.384	86.483	74.473	33.628	50.326	65.867	-5.141
2900	14.415	86.989	74.896	35.068	50.762	66.416	-5.005
3000	14.442	87.478	75.307	36.511	51.175	66.948	-4.877
3100	14.468	87.952	75.708	37.956	51.563	67.467	-4.756
3200	14.492	88.411	76.097	39.404	51.922	67.973	-4.642
3300	14.513	88.858	76.477	40.855	52.251	68.471	-4.535
3400	14.534	89.291	76.848	42.307	52.545	68.957	-4.432
3500	14.552	89.713	77.209	43.761	52.804	69.436	-4.336
3600	14.570	90.123	77.563	45.218	53.024	69.908	-4.244
3700	14.586	90.522	77.907	46.675	53.204	70.375	-4.157
3800	14.601	90.912	78.245	48.135	53.343	70.839	-4.074
3900	14.615	91.291	78.574	49.595	53.438	71.296	-3.995
4000	14.628	91.661	78.897	51.058	53.487	71.752	-3.920
4100	14.641	92.023	79.213	52.521	53.493	72.210	-3.849
4200	14.652	92.376	79.522	53.986	53.454	72.667	-3.781
4300	14.663	92.720	79.825	55.451	53.369	73.126	-3.717
4400	14.673	93.058	80.122	56.918	53.240	73.586	-3.655
4500	14.682	93.387	80.413	58.386	53.065	74.048	-3.596
4600	14.691	93.710	80.698	59.855	52.849	74.520	-3.541
4700	14.700	94.026	80.979	61.324	52.590	74.994	-3.487
4800	14.708	94.336	81.254	62.795	52.293	75.474	-3.436
4900	14.715	94.639	81.524	64.266	51.957	75.958	-3.388
5000	14.722	94.937	81.789	65.738	51.585	76.450	-3.342
5100	14.729	95.228	82.050	67.210	51.178	76.954	-3.298
5200	14.735	95.514	82.306	68.684	50.741	77.461	-3.256
5300	14.741	95.795	82.558	70.157	50.276	77.984	-3.216
5400	14.747	96.071	82.805	71.632	49.783	78.508	-3.177
5500	14.752	96.341	83.049	73.107	49.265	79.045	-3.141
5600	14.758	96.607	83.289	74.582	48.726	79.590	-3.106
5700	14.763	96.868	83.525	76.058	48.168	80.146	-3.073
5800	14.767	97.125	83.757	77.535	47.593	80.713	-3.041
5900	14.772	97.378	83.986	79.012	47.003	81.290	-3.011
6000	14.776	97.626	84.211	80.489	46.400	81.875	-2.982

Dec. 31, 1975; June 30, 1976

STRONTIUM MONOHYDROXIDE UNIPOSITIVE ION ($SrOH^+$) (IDEAL GAS) GFW = 104.6269

Point Group $[C_{\infty v}]$

$S^\circ_{298.15}$ = [57.59 ± 2.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = 76.19 ± 15.0 kcal/mol $HOSr^+$

$\Delta Hf^\circ_{298.15}$ = 76.67 ± 15.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[490](1)
[430](2)
[3650](1)

Bond Distances: Sr-O = [2.1] Å O-H = [0.96] Å
Bond Angle: Sr-O-H = [180°] σ = 1
Rotational Constant: B_o = [0.2511] cm^{-1}

Heat of Formation

The ionization potential of SrOH(g) was deduced by Kelly and Padley (1) to be 5.55±0.1 ev. Using a rotating single probe, these authors quantitatively examined the total positive ion concentrations produced from Sr aqueous salt solutions in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data (2), we recalculate the ionization potential to be 5.75 ev.

Jensen (3) determined the heat of reaction ΔHr°_0 = 25±8kcal/mol for Sr(g) + OH(g) = $SrOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ *flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for* $SrOH^+$; the value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data (2), we derive an ionization potential of 5.28 ev, which is in fair agreement with the value derived from the data of Kelly and Padley (1).

We adopt an ionization potential of 5.39 ev (124.30 kcal/mol) which is an average of the above two studies (1,3). This leads to ΔHf°_0 = 76.19 kcal/mol and ΔHf°_{298} = 76.67 kcal/mol for $SrOH^+(g)$. We assign an uncertainty of ±15 kcal/mol.

In comparison, the ionization potential of SrF(g) is 5.03 ev (2) while that of Sr(g) is 5.692 ev (4). Note that the average of these two values is very close to our adopted ionization potential.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear (2,5,6,7). In addition, Walsh (8) had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons ($SrOH^+$ has eight valence electrons) will be linear in their ground state. The molecule $SrOH^+$ is isoelectronic with RbOH.

The bond dissociation energy for $SrOH^+$ (D°_0 = 103.7 kcal/mol, 2, 4) for the process $SrOH^+(g) = Sr^+(g)$ + OH(g) is fairly close to that for SrOH (D°_0 = 96.7 kcal/mol, 2). This suggests that the bonding in these two molecules may be quite similar. Thus bond distances are assumed to be the same as those adopted for SrOH(g,2). The *moment of inertia* is 11.1472 x 10^{-39} g cm^2. The vibrational frequencies are assumed to be similar to those adopted for SrOH(g,2). The ground state quantum weight is assumed to be the same as that of KOH(g,2). The enthalpy change between 0 and 298.15 K is -2.572 kcal/mol.

References

1. R. Kelly and P. J. Padley, Trans. Faraday Soc. 67, 1384 (1971).
2. JANAF Thermochemical Tables: e^-, 3-31-65; $H_2(g)$ and $H_2O(g)$, 3-31-61; Sr(g), 12-31-70; OH(g), 12-31-70; H(g), 6-30-74; SrOH(g) and $Sr(OH)_2(g)$, 12-31-75.
3. D. E. Jensen, Combustion and Flame 12, 261 (1968).
4. C. E. Moore, Natl. Bur. Stds., Circ. 467, Vol. II (1958).
5. N. Acquista, S. Abramowitz, and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
6. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. 44, 3131 (1966).
7. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9905, July, 1968.
8. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

MAGNESIUM DIHYDROXIDE (MG(OH)$_2$) H_2MgO_2

(CRYSTAL) GFW=58.3198

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.137	-218.842	-218.842	INFINITE
100	5.167	2.335	27.948	-2.561	-219.873	-213.301	466.169
200	13.592	8.686	16.667	-1.596	-220.769	-206.452	225.600
298	18.463	15.115	15.115	.000	-221.000	-199.262	146.063
300	18.536	15.230	15.116	.034	-221.003	-199.127	145.064
400	21.918	21.061	15.888	2.069	-220.987	-191.831	104.811
500	23.809	26.177	17.446	4.366	-220.762	-184.563	80.673
600	24.962	30.627	19.280	6.808	-220.444	-177.354	64.601
700	25.784	34.540	21.186	9.347	-220.078	-170.199	53.138
800	26.429	38.026	23.077	11.959	-219.695	-163.102	44.557
900	26.971	41.171	24.916	14.630	-219.311	-156.050	37.894
1000	27.450	44.038	26.687	17.351	-221.054	-148.859	32.533

Dec. 31, 1960; Dec. 31, 1966; March 31, 1967
Dec. 31, 1975

MAGNESIUM DIHYDROXIDE (Mg(OH)$_2$) (CRYSTAL) GFW = 58.3198 H_2MgO_2

$S°_{298.15}$ = 15.11 gibbs/mol
Td = 542.2 K

$\Delta Hf°_0$ = -218.84 ± 0.5 kcal/mol
$\Delta Hf°_{298.15}$ = -221.0 ± 0.5 kcal/mol

Heat of Formation

The adopted value is an average of -221.10 and -220.86 kcal/mol obtained from $\Delta Hr°_{298}$ = 9.08 and 8.84 kcal/mol for the dehydration reaction $Mg(OH)_2(c) = MgO(c) + H_2O(\ell)$. Auxiliary data are from JANAF (13) and Natl. Bur. Standards (14) Tables. The two values correspond to naturally occurring brucite and to synthetic $Mg(OH)_2$ prepared from MgO by hydration at 177°C under a steam pressure of about 9 atm. The enthalpies of reaction are derived from studies of Taylor and Wells (1) on the heats of solution of various samples of $Mg(OH)_2$ and MgO in aqueous HCl. These studies show that the heat of dehydration is quite dependent on the nature of the MgO sample; e.g., values for synthetic $Mg(OH)_2$ vary monotonically from 9.79 to 8.84 kcal/mol for MgO ignited at temperatures from 450 to 1425°C, respectively. The authors ascribe this difference primarily to increase in particle size at the higher ignition temperatures. More recent work (15) suggests that the difference is caused by crystalline disorder rather than particle size alone. We have adopted the results at 1425°C since they are reasonably consistent with the high temperature samples on which the JANAF heat of formation for MgO is based. The uncertainty is estimated as ±0.5 kcal/mol.

Shomate and Huffman (2) have confirmed the heat of solution of MgO (ignited at 1000°C) within about 0.3 kcal. Their value may be combined with the heat of solution for synthetic $Mg(OH)_2$, determined under similar conditions by Torgeson and Sahama (3), to obtain ΔHr° = 8.85 kcal/mol for the dehydration reaction. At the other extreme, the heat of solution data of Giauque and Archibald (4) lead to ΔHr° = 9.74 kcal/mol; however, this value corresponds to MgO ignited at 350°C. The MgO sample was microcrystalline and had significant excess Cp°, as suggested by Giauque and Archibald (4) and later confirmed by data of T. H. K. Barron et al. (5). Giauque and Archibald (4) intentionally used the microcrystalline form which would be similar to the product in their decomposition pressure measurements (190 and 212°C). Thus, it is not surprising that third law analysis of their decomposition pressures yields essentially the same heat of formation as their solution data (see summary below). Decomposition data at higher pressures have been reported by W. S. Fyfe (6), D. M. Roy and R. Roy (7), G. C. Kennedy (8), G. M. Zhabrova and B. M. Kadenatsi (9), and L. G. Berg and I. S. Rassonskaya (10). These data do not significantly affect the heat of formation, however, because of uncertainties in the attainment of equilibrium and in reduction to standard state values.

Source	$Mg(OH)_2$ Sample	Temp. of MgO Formation, °C	Heat of Dehydration $\Delta Hr°_{298.15}$ (kcal/mol)	$\Delta Hf°_{298.15}$
1. Taylor & Wells (1)	Brucite	1425	9.08	-221.10
	Synthetic	1425	8.84	-220.86
	Synthetic	1000	9.18	-221.20
	Synthetic	450	9.79	>-221.81
2. Torgeson (3) - Shomate (2)	Synthetic	1000	8.85	-220.87
3. Giauque & Archibald (4)	Synthetic*	350	9.74	>-221.74
Kp data	Synthetic*	190, 212	20.10**	>-221.59

*Prepared by reaction of KOH with $MgCl_2(aq)$ at 210°C, rather than by hydration of MgO.

**For $Mg(OH)(c) = MgO(c) + H_2O(g)$ rather than $Mg(OH)_2(c) = MgO(c) + H_2O(\ell)$.

Heat Capacity and Entropy

The low temperature heat capacities are from the measurements (22-321 K) of Giauque and Archibald (4) who used a synthetic, macrocrystalline sample of magnesium dihydroxide prepared by reacting KOH with aqueous $MgCl_2$ at 210°C. The entropy is derived from the heat capacities starting with $S°_{20}$ = 0.027 gibbs/mol from a T^3 extrapolation. $S°_{298}$ = 15.11 gibbs/mol compares favorably with 15.09 gibbs/mol given by Giauque and Archibald (4). The drop calorimeter enthalpy measurements (350-699 K) of King et al. (11) are used to derive heat capacities above 298.15 K. They used a ground sample of natural brucite, which analyzed 98.77% $Mg(OH)_2$. Their published data are corrected for impurities and to one atmosphere total pressure. The low and high temperature heat capacities were joined smoothly by mathematical curve fitting techniques. Heat capacities above 700 K are obtained by extrapolation.

The reference temperature for the enthalpy measurements (393-667 K) of Lashchenko and Kompanskii (12) is uncertain. Their values appear to be near those of King et al. (11) up to around 550 K; above 550 K their values average about 5% lower than those of King et al. (11).

Decomposition Data

Td = 542.2 K is calculated as the temperature at which ΔGr° = 0 for the reaction $Mg(OH)_2(c) = MgO(c) + H_2O(g)$. Auxiliary data are from the JANAF Tables (13).

References

1. K. Taylor and L. S. Wells, J. Res. Natl. Bur. Std. 21, 133 (1938).
2. C. H. Shomate and E. H. Huffman, J. Am. Chem. Soc. 65, 1625 (1943).
3. D. R. Torgeson and Th. G. Sahama, J. Am. Chem. Soc. 70, 2156 (1948).
4. W. F. Giauque and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937).
5. T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) A250, 70 (1959).
6. W. S. Fyfe, Am. J. Sci. 256, 729 (1958).
7. D. M. Roy and R. Roy, Am. J. Sci. 255, 573 (1957).
8. G. C. Kennedy, Am. J. Sci. 254, 567 (1956).
9. G. M. Zhabrova and B. M. Kadenatsi, J. Gen. Chem. U.S.S.R. 24, 1129 (1954).
10. L. G. Berg and I. S. Rassonskaya, Dokl. Akad. Nauk S.S.S.R. 81, 855 (1951).
11. E. G. King, M. J. Ferrante, and L. B. Pankratz, U. S. Bur. Mines RI 8041, 1975.
12. P. N. Lashchenko and D. I. Kompanskii, Zh. Prikl. Khim. 8, 628 (1935).
13. JANAF Thermochemical Tables: MgO(c) 12-31-74, $H_2O(g)$ 3-31-61.
14. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968: $H_2O(\ell)$.
15. M. Natarajan, T. S. Sarma, J. C. Ahluwalia, and C. N. R. Rao, Trans. Faraday Soc. 65, 3088 (1969).

MAGNESIUM DIHYDROXIDE $(MG(OH)_2)$ H_2MGO_2

(IDEAL GAS) GFW=58.3198

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.459	-134.964	-134.964	INFINITE
100	9.303	50.113	76.404	-2.629	-135.741	-133.947	292.741
200	13.519	57.828	65.285	-1.491	-136.464	-131.976	144.216
298	16.605	63.854	63.854	.000	-136.800	-129.593	94.994
300	16.649	63.957	63.854	.031	-136.806	-129.549	94.376
400	18.443	69.016	64.532	1.794	-137.062	-127.088	69.438
500	19.500	73.254	65.864	3.695	-137.233	-124.573	54.451
600	20.181	76.874	67.405	5.681	-137.371	-122.029	44.449
700	20.676	80.024	68.988	7.725	-137.500	-119.460	37.297
800	21.081	82.812	70.545	9.814	-137.640	-116.875	31.929
900	21.440	85.316	72.049	11.940	-137.801	-114.269	27.748
1000	21.771	87.592	73.491	14.100	-140.105	-111.463	24.360
1100	22.080	89.681	74.869	16.293	-140.279	-108.593	21.575
1200	22.370	91.615	76.185	18.516	-140.465	-105.704	19.251
1300	22.639	93.417	77.442	20.766	-140.669	-102.799	17.282
1400	22.888	95.103	78.644	23.043	-171.254	-99.398	15.517
1500	23.117	96.691	79.795	25.343	-171.088	-94.270	13.735
1600	23.326	98.189	80.898	27.666	-170.917	-89.158	12.178
1700	23.517	99.609	81.957	30.008	-170.741	-84.050	10.805
1800	23.690	100.958	82.976	32.368	-170.564	-78.957	9.587
1900	23.848	102.243	83.956	34.746	-170.383	-73.872	8.497
2000	23.991	103.470	84.902	37.138	-170.203	-68.798	7.518
2100	24.121	104.644	85.814	39.543	-170.024	-63.732	6.633
2200	24.239	105.769	86.696	41.961	-169.847	-58.674	5.829
2300	24.347	106.849	87.549	44.391	-169.669	-53.625	5.096
2400	24.445	107.887	88.374	46.831	-169.495	-48.582	4.424
2500	24.534	108.887	89.175	49.280	-169.327	-43.552	3.807
2600	24.616	109.851	89.952	51.737	-169.160	-38.520	3.238
2700	24.691	110.781	90.706	54.202	-168.999	-33.500	2.712
2800	24.759	111.680	91.439	56.675	-168.841	-28.487	2.223
2900	24.822	112.550	92.152	59.154	-168.688	-23.471	1.769
3000	24.879	113.393	92.846	61.639	-168.542	-18.469	1.345
3100	24.933	114.210	93.522	64.130	-168.399	-13.469	.950
3200	24.982	115.002	94.181	66.626	-168.264	-8.475	.579
3300	25.027	115.771	94.824	69.126	-168.136	-3.483	.231
3400	25.069	116.519	95.451	71.631	-168.015	1.505	-.097
3500	25.108	117.246	96.064	74.140	-167.902	6.488	-.405
3600	25.144	117.954	96.662	76.652	-167.798	11.471	-.696
3700	25.177	118.644	97.247	79.168	-167.704	16.451	-.972
3800	25.208	119.315	97.819	81.688	-167.616	21.429	-1.232
3900	25.238	119.971	98.378	84.210	-167.540	26.397	-1.479
4000	25.265	120.610	98.926	86.735	-167.475	31.370	-1.714
4100	25.290	121.234	99.463	89.263	-167.421	36.341	-1.937
4200	25.314	121.844	99.988	91.793	-167.378	41.309	-2.150
4300	25.336	122.440	100.503	94.326	-167.347	46.278	-2.352
4400	25.357	123.022	101.009	96.860	-167.329	51.244	-2.545
4500	25.377	123.592	101.504	99.397	-167.324	56.212	-2.730
4600	25.395	124.150	101.990	101.936	-167.331	61.186	-2.907
4700	25.413	124.697	102.468	104.476	-167.354	66.153	-3.076
4800	25.429	125.232	102.936	107.018	-167.390	71.123	-3.238
4900	25.445	125.756	103.397	109.562	-167.440	76.088	-3.394
5000	25.459	126.271	103.849	112.107	-167.506	81.056	-3.543
5100	25.473	126.775	104.294	114.654	-167.588	86.030	-3.687
5200	25.486	127.270	104.731	117.202	-167.685	91.001	-3.825
5300	25.499	127.755	105.161	119.751	-167.798	95.987	-3.958
5400	25.510	128.232	105.584	122.301	-167.929	100.954	-4.086
5500	25.521	128.700	106.000	124.853	-168.075	105.939	-4.210
5600	25.532	129.160	106.409	127.406	-168.241	110.918	-4.329
5700	25.542	129.612	106.812	129.959	-168.424	115.909	-4.444
5800	25.552	130.056	107.209	132.514	-168.625	120.897	-4.556
5900	25.561	130.493	107.600	135.070	-168.845	125.893	-4.663
6000	25.569	130.923	107.985	137.626	-169.084	130.886	-4.768

June 30, 1967; Dec. 31, 1975

MAGNESIUM DIHYDROXIDE $(Mg(OH)_2)$ (IDEAL GAS) GFW = 58.3198 H_2MGO_2

Point Group $[C_{2v}]$

$S^\circ_{298.15}$ = [63.9 ± 3.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -134.96 ± 8.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -136.80 ± 8.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[508] (1)
[215] (1)
[875] (1)
[3650] (2)
[492] (4)

Bond Distances: Mg-O = [1.79] Å O-H = [0.96] Å
Bond Angles: O-Mg-O = [158°] Mg-O-H = [180°] $\sigma = 2$
Product of the Moments of Inertia : $I_AI_BI_C = [109.5024] \times 10^{-117}\ g^3cm^6$

Heat of Formation

Alexander, Ogden, and Levy (1) determined the temperature dependence of the equilibrium constant for the reaction MgO(c) + $H_2O(g) = Mg(OH)_2(g)$ in the range of 1650 to 2020 K by measuring vapor densities using a transpiration technique. The data are presented graphically and are represented by a linear equation. With auxiliary data from the JANAF Thermochemical Tables (2), analysis of the equation yields a second law ΔHr°_{298} = 67.1 kcal/mol and a third law ΔHr°_{298} = 64.70 kcal/mol with a drift of -1.3 gibbs/mol. From the third law heat of reaction, the adopted ΔHf°_{298} = -136.80 kcal/mol is calculated. An uncertainty of ±8.0 kcal is assigned to allow for the uncertainty shown in the vapor density measurements and for the uncertainty in the entropy.

The heat of dissociation listed by Jackson (6) leads to ΔHf°_{298} $(Mg(OH)_2,g)$ = -140.74 kcal/mol. Another recent compilation (7) lists ΔHf°_{298} = -134 kcal/mol.

Based on the adopted ΔHf°_{298} = -136.80±8 kcal/mol, D°_0 = 188.6 kcal/mol is calculated for the reaction $Mg(OH)_2(g) = Mg(g) + 2OH(g)$.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized (3-6). The O-Mg-O bond angle is assumed to be the same as the F-Mg-F bond angle (2); the Mg-O-H bond is considered to be linear as in MgOH (2). The Mg-O bond distance is estimated to be slightly larger, 0.02Å, than the Mg-F distance in MgF_2 (2) after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is taken to be the same as in water (2).

The vibrational frequencies are estimated to be the same as in MgF_2 (2) (O-Mg-O symmetrical and asymmetrical stretch, and bend) and as in MgOH (2) (O-H stretch and Mg-O-H bend). The three principal moments of inertia are $I_A = 19.1441 \times 10^{-39}$, $I_B = 18.8406 \times 10^{-39}$, and $I_C = 0.3036 \times 10^{-39}\ g\ cm^2$.

Jackson (6) has used a different molecular configuration and different vibrational frequencies to estimate S°_{298} = 63.829 gibbs/mol. We assign an uncertainty of ±3.0 gibbs/mol to the adopted entropy.

References

1. C. A. Alexander, J. S. Ogden, and A. Levy, J. Chem. Phys. 39, 3057 (1963).
2. JANAF Thermochemical Tables: MgO(c), 12-31-74; $H_2O(g)$, 3-31-61; $Mg(OH)_2(g)$, MgOH(g), 12-31-75, $MgF_2(g)$, 6-30-75.
3. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
4. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
5. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
6. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Contract No. W-7405-Eng.-48, Dec. 8, 1971.
7. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.

STRONTIUM DIHYDROXIDE ($SR(OH)_2$) H_2O_2SR

(CRYSTAL) GFW=121.6348

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.900	23.200	23.200	.000	- 231.570	- 210.845	154.553
300	17.960	23.311	23.200	.033	- 231.575	- 210.717	153.507
400	21.140	28.913	23.943	1.988	- 231.684	- 203.740	111.319
500	24.320	33.972	25.450	4.261	- 231.540	- 196.766	86.006
600	27.490	38.685	27.267	6.851	- 231.147	- 189.844	69.151
700	30.670	43.162	29.220	9.759	- 230.510	- 183.007	57.137
800	33.850	47.465	31.233	12.985	- 229.636	- 176.279	48.157
900	37.030	51.635	33.269	16.529	- 228.695	- 169.657	41.198
1000	40.210	55.701	35.310	20.391	- 227.278	- 163.170	35.661

Dec. 31, 1975

STRONTIUM DIHYDROXIDE ($Sr(OH)_2$) (CRYSTAL) GFW = 121.6348

H_2O_2SR

$S°_{298.15}$ = [23.2 ± 2] gibbs/mol
Tm = 783.15 ± 15 K

$\Delta Hf°_0$ = unknown
$\Delta Hf°_{298.15}$ = -231.57 ± 2.2 kcal/mol
ΔHm° = 5.024 ± 0.50 kcal/mol

Heat of Formation

The adopted $\Delta Hf°_{298}$ = -231.57±2.2 kcal/mol is obtained from the heat of formation adopted for the liquid (1) minus the heat of melting and the enthalpy difference of the liquid and the crystal between the melting point and 298.15 K. The dissociation pressure measurements by Johnston (2) and by Tamaru and Shiomi (3) span the melting point, but there is not a definite break in the log P vs 1/T curve at the melting point. The temperatures of the dissociation pressures determined by Sano (4) are all below the melting point. For second and third law analysis, using auxiliary data from the JANAF Thermochemical Tables (1), the dissociation pressures below the melting point are considered to pertain to the equilibrium $Sr(OH)_2(c) = SrO(c) + H_2O(g)$.

	No. of	Temp.	$\Delta Hr°_{298}$, kcal/mol		Drift	$\Delta Hf°_{298}(c)$*
Investigator	Points	Range, K	2nd Law	3rd Law	gibbs/mol	kcal/mol
Johnston (2)	4	703-776	18.7	31.65±1.06	17.5±1.4	-230.9±1.9
Tamaru and Shiomi (3)	10	667-782	28.0	31.50±0.42	4.9±0.3	-230.8±1.2
Sano (4)	5	613-743	26.0	31.27±0.75	7.6±0.2	-230.6±1.6

*$\Delta Hf°_{298}$ is calculated from the third law $\Delta Hr°_{298}$ value.

These three third law values for $\Delta Hf°_{298}$ (c) are in excellent agreement, are in reasonable agreement with the adopted value, and are closer to another recent evaluation of -229.2 kcal/mol (5) than is the adopted value. The route taken to derive the adopted value is presently preferred because dissociation pressure measurements of the liquid are judged to be better than those of the solid.

Heat Capacity and Entropy

The heat capacities are derived from a curve fit of the drop ice calorimeter enthalpy measurements of Powers and Blalock (6, 545-783 K), extrapolated and forced through zero relative enthalpy at 273.15 K. The change in heat capacity with temperature is larger than it is for the other alkaline earth dihydroxides (1). There appears to be no definite explanation for this. The purity of the $Sr(OH)_2$ sample, as indicated by total alkalinity, did change more during the enthalpy measurement than other samples in the same report (6). The total alkalinity of the $Sr(OH)_2$ sample changed from 99.80 to 94.1% while for $Ba(OH)_2$ the change was 100.4 to 99.81%, for NaOH the change was 99.97 to 99.46%, and for KOH the change was 100.00 to 98.68% (6). The known existence of crystalline allotropy in some of the alkaline earth halides and hydroxides suggests this possibility for $Sr(OH)_2$ crystal also.

The adopted entropy, $S°_{298}$ = [23.2±2] kcal/mol, is calculated from Kelley's additive entropy constants for cations and anions (7).

Melting Data

From their drop calorimetry, Powers and Blalock (6) selected a melting point of 783.15 K where they derived ΔHm° = 5.23 kcal/mol. *Our smoothing of their data leads to the adopted ΔHm° = 5.024±0.50 kcal/mol. Brcic and Jernejcic (8) determined a* melting point of 771 K and Berggren and Brown (9), 723 K. The latter dihydroxide sample contained 5 mole percent $SrCO_3$. Tm = 783.15±15 K is adopted.

References

1. JANAF Thermochemical Tables: SrO(c), 12-31-72; $H_2O(g)$, 3-31-61; $Be(OH)_2$ (β-c), $Mg(OH)_2(c)$, $Ca(OH)_2(c)$, $Ba(OH)_2(c)$, *$Sr(OH)_2(\ell)$*, 12-31-75.
2. J. Johnston, Z. physik. Chem. 62, 330 (1908).
3. S. Tamaru and K. Shiomi, Z. physik. Chem. A171, 221 (1935).
4. K. Sano, J. Chem. Soc. Japan 60, 758 (1939).
5. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.
6. W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm., ORNL-1653 (1954).
7. K. K. Kelley in Chap. 13, D. R. Stull and H. Prophet, "The Characterization of High Temperature Vapors," J. L. Margrave, ed., John Wiley and Sons, New York, 1967.
8. B. S. Brcic and J. Jernejcic, Vestn. Sloven. Kem. Drustva 9, 65 (1962).
9. G. Berggren and A. Brown, Acta Chem. Scand. 25, 1377 (1971).

STRONTIUM DIHYDROXIDE ($Sr(OH)_2$) H_2O_2SR

(LIQUID) GFW=121.6348

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.900	25.989	25.989	.000	− 228.800	− 208.907	153.133
300	17.960	26.100	25.990	.033	− 228.805	− 208.784	152.099
400	21.140	31.702	26.732	1.988	− 228.914	− 202.086	110.415
500	24.320	36.761	28.239	4.261	− 228.770	− 195.390	85.405
600	37.700	43.122	30.172	7.770	− 227.458	− 188.817	68.777
700	37.700	48.933	32.448	11.540	− 225.959	− 182.496	56.976
800	37.700	53.968	34.830	15.310	− 224.541	− 176.387	48.187
900	37.700	58.408	37.208	19.080	− 223.374	− 170.432	41.387
1000	37.700	62.380	39.530	22.850	− 222.049	− 164.621	35.976
1100	37.700	65.973	41.773	26.620	− 222.668	− 158.631	31.557
1200	37.700	69.254	43.929	30.390	− 221.320	− 153.086	27.881
1300	37.700	72.271	45.994	34.160	− 219.991	− 147.455	24.789
1400	37.700	75.065	47.972	37.930	− 218.679	− 141.924	22.155
1500	37.700	77.666	49.866	41.700	− 217.386	− 136.486	19.886
1600	37.700	80.099	51.681	45.470	− 216.111	− 131.136	17.912

Dec. 31, 1975

STRONTIUM DIHYDROXIDE ($Sr(OH)_2$) (LIQUID) GFW = 121.6348

S°_{298} = [25.989] gibbs/mol
Tm = 783.15 ± 15 K
Td = 1017 K

$\Delta Hf^\circ_{298.15}$ = −228.8 ± 1.7
ΔHm° = 5.024 ± 0.50 kcal/mol

H_2O_2SR

Heat of Formation

The adopted ΔHf°_{298} = −228.8±1.7 kcal/mol is the average of values derived from the third law analysis of the dissociation pressure measurements of Johnston (1) and of Tamaru and Shiomi (2). The data from both sources (1, 2) span the melting point; only those data above the melting point are used for the second and third law analysis of the reaction $Sr(OH)_2(\ell) = SrO(c) + H_2O(g)$.

Investigator	No. of Points	Temp. Range, K	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	ΔHf°_{298}, $(\ell)^b$ kcal/mol
Johnston (1)	11[a]	806-1038	28.5	30.06±0.28[c]	1.6±0.4	−229.36±1.1
Tamaru and Shiomi (2)	6	880-942	30.9	28.93±0.26[c]	−2.3±0.2	−228.23±1.1

[a] One point rejected due to failure of a statistical test.

[b] ΔHf°_{298} (ℓ) is calculated from the third law ΔHr° value using auxiliary data from the JANAF Thermochemical Tables(3).

[c] Considering all of the data as liquid state data (733-1038 K, 1; 667-942 K, 2) yields third-law heats of reaction of 29.97±0.48 kcal/mol for (1) and 29.08±0.16 kcal/mol for (2) leading to standard state heats of formation at 298.15 K of −229.27±1.3 and −228.38±1.0 kcal/mol, respectively.

Heat Capacity and Entropy

Cp° is derived from the drop ice calorimeter measurements of Powers and Blalock (4, 788-1187 K) and is assumed constant at 27.7 gibbs/mol over the range of 520 to 1600 K. A glass transition is assumed at 520 K below which Cp° is that of the crystal. The entropy of 298.15 K is derived from the value adopted for the crystal (3).

Decomposition Data

Td = 1017 K is calculated as the temperature at which $\Delta Gr^\circ = 0$ for the reaction $Sr(OH)_2(\ell) = SrO(c) + H_2O(g)$. Auxiliary data used in the calculations are from the JANAF Thermochemical Tables (3).

References

1. J. Johnston, Z. physik. Chem. 62, 330 (1908).
2. S. Tamaru and K. Shiomi, Z. physik. Chem. A171, 221 (1935).
3. JANAF Thermochemical Tables: SrO(c), 12-31-72, $H_2O(g)$, 3-31-61; $Sr(OH)_2(c)$, 12-31-75.
4. W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm., ORNL-1653 (1954).

STRONTIUM DIHYDROXIDE ($Sr(OH)_2$) H_2O_2SR

(IDEAL GAS) GFW=121.6348

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.880	-140.660	-140.660	INFINITE
100	10.579	57.312	86.990	-2.968	-141.521	-140.074	306.130
200	15.384	66.143	74.469	-1.665	-142.107	-138.388	151.223
298	18.214	72.880	72.880	.000	-142.399	-136.486	100.047
300	18.250	72.993	72.880	.034	-142.403	-136.450	99.403
400	19.645	78.457	73.616	1.936	-142.564	-134.438	73.454
500	20.392	82.928	75.045	3.942	-142.688	-132.392	57.869
600	20.856	86.690	76.680	6.005	-142.821	-130.321	47.469
700	21.199	89.931	78.347	8.109	-142.989	-128.225	40.033
800	21.495	92.782	79.977	10.244	-143.206	-126.103	34.450
900	21.775	95.330	81.544	12.407	-143.645	-123.933	30.095
1000	22.047	97.638	83.039	14.599	-143.899	-121.729	26.604
1100	22.312	99.752	84.464	16.817	-146.070	-119.389	23.720
1200	22.567	101.704	85.820	19.061	-146.248	-116.955	21.300
1300	22.808	103.520	87.113	21.329	-146.420	-114.508	19.250
1400	23.035	105.219	88.346	23.622	-146.586	-112.047	17.491
1500	23.245	106.815	89.525	25.936	-146.749	-109.573	15.965
1600	23.439	108.322	90.653	28.270	-146.910	-107.091	14.626
1700	23.617	109.748	91.735	30.623	-179.640	-103.690	13.330
1800	23.780	111.103	92.773	32.993	-179.454	-99.229	12.048
1900	23.929	112.393	93.772	35.379	-179.269	-94.776	10.902
2000	24.064	113.624	94.734	37.779	-179.086	-90.335	9.871
2100	24.188	114.801	95.662	40.191	-178.908	-85.902	8.940
2200	24.300	115.929	96.558	42.616	-178.736	-81.478	8.094
2300	24.403	117.011	97.424	45.051	-178.570	-77.061	7.322
2400	24.496	118.052	98.262	47.496	-178.415	-72.648	6.616
2500	24.582	119.053	99.073	49.950	-178.274	-68.249	5.966
2600	24.660	120.019	99.860	52.412	-178.144	-63.847	5.367
2700	24.731	120.951	100.624	54.882	-178.033	-59.454	4.812
2800	24.797	121.852	101.367	57.358	-177.942	-55.065	4.298
2900	24.857	122.723	102.088	59.841	-177.873	-50.674	3.819
3000	24.912	123.566	102.790	62.329	-177.829	-46.291	3.372
3100	24.963	124.384	103.473	64.823	-177.812	-41.906	2.954
3200	25.011	125.178	104.139	67.322	-177.827	-37.523	2.563
3300	25.054	125.948	104.789	69.825	-177.875	-33.138	2.195
3400	25.095	126.696	105.422	72.333	-177.959	-28.752	1.848
3500	25.132	127.424	106.040	74.844	-178.082	-24.361	1.521
3600	25.167	128.133	106.644	77.359	-178.245	-19.966	1.212
3700	25.199	128.823	107.234	79.877	-178.452	-15.566	.919
3800	25.229	129.495	107.811	82.399	-178.701	-11.158	.642
3900	25.257	130.151	108.376	84.923	-178.998	-6.748	.378
4000	25.283	130.791	108.928	87.450	-179.342	-2.328	.127
4100	25.308	131.415	109.469	89.980	-179.732	2.103	-.112
4200	25.331	132.025	109.999	92.512	-180.170	6.543	-.340
4300	25.352	132.622	110.518	95.046	-180.656	10.995	-.559
4400	25.373	133.205	111.027	97.582	-181.189	15.456	-.768
4500	25.392	133.775	111.526	100.120	-181.769	19.930	-.968
4600	25.409	134.334	112.016	102.660	-182.393	24.425	-1.160
4700	25.426	134.880	112.497	105.202	-183.062	28.928	-1.345
4800	25.442	135.416	112.969	107.745	-183.771	33.445	-1.523
4900	25.457	135.940	113.432	110.290	-184.521	37.975	-1.694
5000	25.471	136.455	113.887	112.837	-185.309	42.521	-1.859
5100	25.484	136.959	114.335	115.385	-186.134	47.091	-2.018
5200	25.497	137.454	114.775	117.934	-186.991	51.668	-2.172
5300	25.509	137.940	115.207	120.484	-187.879	56.274	-2.320
5400	25.520	138.417	115.633	123.035	-188.796	60.881	-2.464
5500	25.531	138.885	116.051	125.588	-189.739	65.517	-2.603
5600	25.542	139.346	116.463	128.142	-190.706	70.162	-2.738
5700	25.551	139.798	116.869	130.696	-191.693	74.830	-2.869
5800	25.561	140.242	117.268	133.252	-192.700	79.517	-2.996
5900	25.569	140.679	117.661	135.808	-193.722	84.219	-3.120
6000	25.578	141.109	118.048	138.366	-194.759	88.938	-3.240

Dec. 31, 1975

STRONTIUM DIHYDROXIDE ($Sr(OH)_2$) (IDEAL GAS) GFW = 121.6348 H_2O_2SR

Point Group [C_{2v}]
$S^\circ_{298.15}$ = [72.9 ± 2.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -140.66 ± 10.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -142.40 ± 10.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[442](1)
[82](1)
[443](1)
[3650](2)
[438](4)

Bond Distances: Sr-O = [2.22] Å O-H = [0.96] Å
Bond Angles: O-Sr-O = [108°] Sr-O-H = [180°] σ = 2
Product of the Moments of Inertia: $I_AI_BI_C$ = [3.8243] x 10^{-114} g^3cm^6

Heat of Formation

Dissociation energies, D°_0 for the reaction $Sr(OH)_2(g) = Sr(g) + 2OH(g)$ have been derived from flame spectral measurements (1-3). Ryabova and Gurvich (1) believed the dominant reaction to be $Sr(g) + H_2O(g) = SrOH(g) + H(g)$, but they also considered the possibility that the reaction $Sr(g) + 2H_2O(g) = Sr(OH)_2 + 2H(g)$ was dominant and derived D°_0 = 180±20 kcal/mol. Sugden and Schofield (2) considered the dihydroxide to be the dominant product and derived D°_0 = 215 ± 12 kcal/mol. Cotton and Jenkins (3) found both SrOH and $Sr(OH)_2$ to be present in significant amounts in fuel-rich hydrogen-oxygen-nitrogen flames and derived D°_0 = 202.2 ± 5 kcal/mol. Cotton and Jenkins (3) recalculated the work of Ryabova and Gurvich (1) and of Sugden and Schofield (2) considering both SrOH and $Sr(OH)_2$ to be present and obtained the recalculated D°_0 values of 196 and 200 kcal/mol, respectively.

A third law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins (3) using current JANAF auxiliary data (4) leads to D°_0 = 204.8 kcal/mol which is 2.6 kcal/mol higher than the 202.2 kcal/mol derived by Cotton and Jenkins (3). Applying this difference to the data of Ryabova and Gurvich (1) and of Sugden and Schofield (2) as recalculated by Cotton and Jenkins (3) gives D°_0 = 198.6 and 202.6 kcal/mol, respectively.

For $Ba(OH)_2(g)$ (4), the corrected dissociation energy of Ryabova and Gurvich (4), D°_0 = 208.8 kcal/mol, is in better agreement with the "adopted" value of 209.6 kcal/mol, based on good Knudsen cell mass spectrometric measurements, than are the corrected dissociation energies of Sugden and Schofield or Cotton and Jenkins (4). We adopt D°_0 = 198.6 kcal/mol for the dissociation of $Sr(OH)_2$ from which $\Delta Hf^\circ_0(Sr(OH)_2,g)$ = -140.66±6.0 kcal/mol is calculated.

The heat of dissociation listed by Jackson (8) leads to $\Delta Hf^\circ_{298}(Sr(OH)_2,g)$ = -143.82 kcal/mol. Another recent compilation (9) lists ΔHf°_{298} = -135 kcal/mol.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized (5-8). The O-Sr-O bond angle is assumed to be the same as the F-Sr-F bond angle (4); the Sr-O-H bond angle is considered to be linear as in SrOH (4). The Sr-O bond distance is estimated to be slightly larger, 0.02 Å, than the Sr-F distance in SrF_2 (4) after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is taken to be the same as in water (4).

The vibrational frequencies are assumed to be the same as in SrF_2 (4) (O-Sr-O symmetrical and asymmetrical stretch, and bend) and as in SrOH (4) (O-H stretch and Sr-O-H bend). The three principal moments of inertia are $I_A = 26.7429 \times 10^{-39}$, $I_B = 19.3544 \times 10^{-39}$, and $I_C = 7.3884 \times 10^{-39}$ g cm^2.

Jackson (8) has used a different molecular configuration and different vibrational frequencies to estimate S°_{298} = 74.057 gibbs/mol. We assign an uncertainty of ±2.0 gibbs/mol to the adopted entropy.

References

1. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 3, 318 (1965).
2. T. M. Sugden and K. Schofield, Trans. Faraday Soc. 62, 566 (1966).
3. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 64, 2988 (1968).
4. JANAF Thermochemical Tables: Sr(g), HO(g), 12-31-70; $H_2O(g)$, 3-31-61; H(g), 6-30-74; SrOH(g), $Sr(OH)_2(g)$, $Ba(OH)_2(g)$, 12-31-75; $SrF_2(g)$, 3-31-72.
5. R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959).
6. J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. 33, 533 (1960).
7. F. E. Stafford and J. Berkowitz, J. Chem. Phys. 40, 2963 (1964).
8. D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCRL-51137, Contract No. W-7405-Eng.-48, Dec. 8, 1971.
9. U. S. Natl. Bur. Std. Tech. Note 270-6, 1971.

SILANE (SiH_4) H_4Si
(IDEAL GAS) GFW=32.1180

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	-2.519	10.498	10.498	INFINITE
100	7.951	39.594	56.832	-1.724	9.711	10.721	-23.430
200	8.489	45.196	49.761	-0.913	9.035	11.961	-13.071
298	10.236	48.887	48.886	0.000	8.200	13.575	-9.951
300	10.274	48.950	48.887	0.019	8.184	13.608	-9.913
400	12.302	52.186	49.314	1.149	7.419	15.535	-8.488
500	14.136	55.132	50.187	2.473	6.801	17.639	-7.710
600	15.745	57.855	51.241	3.968	6.328	19.852	-7.231
700	17.140	60.390	52.369	5.614	5.985	22.137	-6.911
800	18.335	62.759	53.521	7.390	5.749	24.459	-6.682
900	19.347	64.978	54.672	9.275	5.598	26.810	-6.510
1000	20.199	67.062	55.808	11.254	5.517	29.171	-6.375
1100	20.914	69.022	56.921	13.310	5.486	31.538	-6.266
1200	21.516	70.868	58.007	15.433	5.496	33.907	-6.175
1300	22.023	72.611	59.064	17.610	5.530	36.272	-6.098
1400	22.452	74.259	60.091	19.835	5.582	38.636	-6.031
1500	22.818	75.821	61.088	22.099	5.639	40.997	-5.973
1600	23.130	77.304	62.056	24.397	5.696	43.349	-5.921
1700	23.399	78.714	62.995	26.723	-6.240	45.809	-5.889
1800	23.631	80.059	63.906	29.075	-6.132	48.866	-5.933
1900	23.822	81.342	64.790	31.449	-6.020	51.919	-5.972
2000	24.009	82.569	65.648	33.841	-5.908	54.966	-6.006
2100	24.163	83.744	66.482	36.250	-5.797	58.007	-6.037
2200	24.300	84.871	67.293	38.673	-5.688	61.042	-6.064
2300	24.420	85.954	68.081	41.109	-5.580	64.073	-6.088
2400	24.528	86.996	68.847	43.556	-5.477	67.103	-6.111
2500	24.624	87.999	69.593	46.014	-5.379	70.119	-6.130
2600	24.709	88.966	70.320	48.481	-5.282	73.141	-6.148
2700	24.787	89.900	71.028	50.956	-5.191	76.153	-6.164
2800	24.856	90.803	71.718	53.438	-5.105	79.163	-6.179
2900	24.919	91.677	72.391	55.927	-5.022	82.176	-6.193
3000	24.976	92.522	73.048	58.422	-4.945	85.177	-6.205
3100	25.029	93.342	73.690	60.922	-4.871	88.178	-6.217
3200	25.076	94.138	74.316	63.427	-4.804	91.182	-6.227
3300	25.120	94.910	74.929	65.937	-4.742	94.183	-6.237
3400	25.159	95.660	75.528	68.451	-4.684	97.176	-6.246
3500	25.196	96.390	76.113	70.969	-4.634	100.173	-6.255
3600	25.230	97.100	76.686	73.490	-96.550	105.423	-6.400
3700	25.261	97.792	77.248	76.015	-96.414	111.033	-6.558
3800	25.290	98.466	77.797	78.542	-96.282	116.639	-6.708
3900	25.317	99.123	78.336	81.073	-96.159	122.239	-6.850
4000	25.342	99.765	78.863	83.605	-96.043	127.839	-6.985
4100	25.365	100.391	79.381	86.141	-95.932	133.431	-7.113
4200	25.386	101.002	79.888	88.678	-95.829	139.026	-7.234
4300	25.406	101.600	80.386	91.218	-95.731	144.614	-7.350
4400	25.425	102.184	80.875	93.760	-95.640	150.200	-7.461
4500	25.443	102.756	81.355	96.303	-95.557	155.787	-7.566
4600	25.459	103.315	81.826	98.848	-95.478	161.377	-7.667
4700	25.475	103.863	82.289	101.395	-95.408	166.961	-7.764
4800	25.489	104.399	82.744	103.943	-95.342	172.540	-7.856
4900	25.503	104.925	83.192	106.493	-95.282	178.123	-7.945
5000	25.516	105.440	83.632	109.043	-95.230	183.694	-8.029
5100	25.528	105.946	84.064	111.596	-95.183	189.281	-8.111
5200	25.539	106.442	84.490	114.149	-95.142	194.854	-8.189
5300	25.550	106.928	84.909	116.703	-95.107	200.437	-8.265
5400	25.560	107.406	85.321	119.259	-95.079	206.005	-8.337
5500	25.570	107.875	85.727	121.816	-95.056	211.580	-8.407
5600	25.579	108.336	86.126	124.373	-95.041	217.155	-8.475
5700	25.588	108.789	86.520	126.931	-95.031	222.736	-8.540
5800	25.596	109.234	86.908	129.491	-95.028	228.306	-8.603
5900	25.604	109.671	87.290	132.051	-95.031	233.880	-8.663
6000	25.612	110.102	87.666	134.611	-95.040	239.451	-8.722

Dec. 31, 1960; June 30, 1976

SILANE (SiH_4) (IDEAL GAS) GFW = 32.1180

Point Group = T_d
$S^\circ_{298.15}$ = 48.89 ± 0.01 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = 10.5 ± 0.5 kcal/mol H_4Si
$\Delta Hf^\circ_{298.15}$ = 8.2 ± 0.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
2185.7 (1)
972.1 (2)
2189.08 (3)
913.28 (3)

Bond Distance: Si-H = 1.4806 ± 0.001 Å σ = 12
Bond Angle: H-Si-H = 109.47122 °
Product of Moments of Inertia: $I_AI_BI_C = 9.366 \times 10^{-118}\ g^3\ cm^6$

Heat of Formation

The adopted ΔHf°_{298} (SiH_4,g) = 8.2±0.5 kcal/mol is derived from the heat of decomposition measurements by Gunn and Green (1). We have taken the average of the three measurements, ΔE = -7.83 kcal/mol, to obtain ΔH = -7.24 kcal/mol for the decomposition. Some question exists about the final state of the silicon; we choose to consider it as amorphous and apply a correction of 1 kcal/mol to convert to the crystalline state (2) (the authors chose to neglect this correction). The results of Gunn and Green (1) are in good agreement with the value of ΔHf°_{298} (SiH_4,g) = 7.8 ± 3.5 kcal/mol determined by Brimm and Humphreys (3) from high temperature (680°C) heat of decomposition measurements. We question the earlier negative values for the heat of formation of SiH_4(g) (4-6) which range from -8.7 to -14.8 kcal/mol and the later result of Feher, Jansen, and Rohmer (7), -11.3 kcal/mol, because of suspected uncertainty in the final states and/or corrections for the final states.

Heat Capacity and Entropy

The four fundamental vibrational frequencies and the Si-H bond distance are the result of gas-phase infrared and Raman spectral studies by Kattenberg and Oskam (8). They are in excellent agreement with values selected from earlier work as given in the compilations of Janz and Mikawa (9) and Shimanouchi (10). The heat capacity and entropy calculations are based on a tetrahedral structure. The S°_{298} = 48.89±0.01 gibbs/mol is in good agreement with another evaluation (2).

The three principal moments of inertia are $I_A=I_B=I_C = 9.784 \times 10^{-40}\ g\ cm^2$.

References

1. S. R. Gunn and L. H. Green, J. Phys. Chem. 65, 779 (1961).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. E. O. Brimm and H. M. Humphreys, J. Phys. Chem. 61, 829 (1957).
4. H. Von Wartenberg, Z. Anorg. Allgem. Chem. 79, 71 (1913).
5. F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold, New York, 1936.
6. U. S. Natl. Bur. Std. Circ. 500, 1952.
7. F. Feher, G. Jansen, and H. Rohmer, Z. Anorg. Allgem. Chem. 329, 31 (1964).
8. H. W. Kattenberg and A. Oskam, J. Mol. Spectrosc. 49, 52 (1974).
9. G. J. Janz and Y. Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961).
10. T. Shimanouchi, NSRDS-NBS 39, 1972.

Magnesium Monoiodide (MgI) IMg

(Ideal Gas) GFW = 151.2095

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.347	6.309	6.309	INFINITE
100	7.447	56.127	72.533	-1.641	6.497	1.841	-4.023
200	8.377	61.618	65.833	-.843	6.143	-2.804	3.064
298	8.751	65.042	65.042	.000	5.883	-7.042	5.162
300	8.755	65.096	65.042	.016	5.876	-7.122	5.188
400	8.942	67.643	65.388	.902	3.562	-11.330	6.190
500	9.059	69.652	66.047	1.802	-1.941	-14.524	6.349
600	9.146	71.311	66.790	2.713	-2.148	-17.023	6.201
700	9.219	72.727	67.540	3.631	-2.372	-19.484	6.083
800	9.283	73.962	68.267	4.556	-2.623	-21.912	5.986
900	9.343	75.059	68.962	5.488	-2.904	-24.307	5.903
1000	9.400	76.046	69.622	6.425	-5.339	-26.487	5.789
1100	9.454	76.945	70.247	7.367	-5.652	-28.588	5.680
1200	9.508	77.770	70.840	8.316	-5.985	-30.659	5.584
1300	9.560	78.533	71.403	9.269	-6.339	-32.700	5.497
1400	9.612	79.243	71.938	10.228	-37.080	-34.235	5.344
1500	9.663	79.908	72.447	11.191	-37.070	-34.032	4.958
1600	9.714	80.534	72.933	12.160	-37.055	-33.830	4.621
1700	9.765	81.124	73.398	13.134	-37.036	-33.629	4.323
1800	9.815	81.684	73.843	14.113	-37.013	-33.429	4.059
1900	9.865	82.216	74.270	15.097	-36.984	-33.231	3.822
2000	9.915	82.723	74.680	16.086	-36.952	-33.035	3.610
2100	9.965	83.208	75.074	17.080	-36.916	-32.840	3.418
2200	10.015	83.672	75.455	18.079	-36.875	-32.646	3.243
2300	10.064	84.119	75.822	19.083	-36.831	-32.454	3.084
2400	10.114	84.548	76.176	20.092	-36.781	-32.266	2.938
2500	10.164	84.962	76.520	21.106	-36.729	-32.080	2.804
2600	10.213	85.362	76.852	22.125	-36.672	-31.893	2.681
2700	10.263	85.748	77.174	23.148	-36.612	-31.711	2.567
2800	10.313	86.122	77.487	24.177	-36.548	-31.532	2.461
2900	10.363	86.485	77.791	25.211	-36.480	-31.352	2.363
3000	10.414	86.837	78.087	26.250	-36.410	-31.178	2.271
3100	10.465	87.179	78.375	27.294	-36.337	-31.004	2.186
3200	10.516	87.512	78.655	28.343	-36.261	-30.835	2.106
3300	10.567	87.837	78.929	29.397	-36.182	-30.666	2.031
3400	10.619	88.153	79.195	30.456	-36.103	-30.498	1.960
3500	10.672	88.462	79.456	31.521	-36.021	-30.336	1.894
3600	10.725	88.763	79.710	32.591	-35.939	-30.174	1.832
3700	10.779	89.058	79.959	33.666	-35.857	-30.014	1.773
3800	10.833	89.346	80.202	34.747	-35.773	-29.857	1.717
3900	10.889	89.628	80.440	35.833	-35.690	-29.705	1.665
4000	10.945	89.904	80.673	36.924	-35.608	-29.552	1.615
4100	11.002	90.175	80.902	38.022	-35.527	-29.401	1.567
4200	11.059	90.441	81.126	39.125	-35.448	-29.253	1.522
4300	11.118	90.702	81.345	40.233	-35.372	-29.108	1.479
4400	11.178	90.958	81.561	41.348	-35.298	-28.962	1.439
4500	11.238	91.210	81.772	42.469	-35.227	-28.817	1.400
4600	11.299	91.458	81.980	43.596	-35.160	-28.674	1.362
4700	11.362	91.701	82.185	44.729	-35.096	-28.536	1.327
4800	11.425	91.941	82.385	45.868	-35.037	-28.395	1.293
4900	11.489	92.177	82.583	47.014	-34.983	-28.258	1.260
5000	11.554	92.410	82.777	48.166	-34.934	-28.120	1.229
5100	11.620	92.640	82.968	49.325	-34.891	-27.989	1.199
5200	11.687	92.866	83.156	50.490	-34.855	-27.853	1.171
5300	11.755	93.089	83.342	51.662	-34.824	-27.715	1.143
5400	11.823	93.310	83.524	52.841	-34.800	-27.583	1.116
5500	11.892	93.527	83.704	54.027	-34.784	-27.450	1.091
5600	11.962	93.742	83.881	55.220	-34.775	-27.319	1.066
5700	12.033	93.954	84.056	56.419	-34.775	-27.182	1.042
5800	12.104	94.164	84.229	57.626	-34.782	-27.053	1.019
5900	12.176	94.372	84.399	58.840	-34.799	-26.916	.997
6000	12.248	94.577	84.567	60.062	-34.825	-26.785	.976

Dec. 31, 1974

MAGNESIUM MONOIODIDE (MgI) (IDEAL GAS) GFW = 151.2095

Ground State Configuration $^2\Sigma^+$

$S°_{298.15}$ = 65.04 ± 0.05 gibbs/mol

$\Delta Hf°_0$ = [6.3 ± 10] kcal/mol IMG

$\Delta Hf°_{298.15}$ = [5.9 ± 10] kcal/mol

Electronic Levels and Quantum Weight

State	ε_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A[^2\Pi]$	24319	2
	25294	2

ω_e = 312 cm^{-1} $\omega_e x_e$ = [1.09] cm^{-1} σ = 1

B_e = [0.0130] cm^{-1} α_e = [0.00062] cm^{-1} r_e = [2.52] Å

Heat of Formation

The adopted $\Delta Hf°_0$ = 6.309 ± 10 kcal/mol is calculated from a D_0° value of 54.3 kcal/mol (2.35 eV). An approximate value of 312 cm^{-1} has been given for ω_e (1). A value of $\omega_e x_e$, 1.09 cm^{-1}, is calculated from an average value of $x_e \mu^{1/2}$ calculated from data for CaI, SrI, BaI, MgBr, and MgCl (1, 2). A linear Birge-Sponer extrapolation of these ω_e and $\omega_e x_e$ data is corrected for the ionic character of the molecule as described by Hildenbrand (3) to give the adopted value of D_0° = 54.3 kcal/mol.

From a consideration of ionic bonding forces, Krasnov and Karaseva (4) calculated $D_0^\circ \geq 55 \pm 10$ kcal/mol.

Using JANAF data, D_0° (MgI)/D_0° (MgI_2) = 0.44, in reasonable agreement with the ratios found by Blue et al. (5) for the alkaline earth fluorides and by Hildenbrand (6) for the alkaline with fluorides and chlorides.

$\Delta Hf°_{298.15}$ = 5.883 ± 10 kcal/mol is calculated from the adopted $\Delta Hf°_0$ = 6.309 kcal/mol.

Heat Capacity and Entropy

The ground state vibrational constants are as given in the Heat of Formation section above. The adopted value of r_e = 2.52 Å is the bond distance in MgI_2 (7); Margrave (8) has estimated 2.72 Å from additive ionic radii. B_e is calculated from the adopted r_e, and α_e is calculated assuming a Morse potential function.

The electronic levels and their designation are those given by Rosen (1). The possibility of additional electronic levels near 15000 cm^{-1} is suggested by a comparison with CaI, SrI, and BaI (2). Including these levels does not change the entropy at 298 K and increases the entropy at 6000 K by only 0.69 gibbs/mol.

References

1. B. Rosen, Ed. "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.
2. JANAF Thermochemical Tables: CaI(g), SrI(g), BaI(g), 6-30-74; MgBr(g), 6-30-66; MgCl(g) 3-31-66.
3. D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, L. Eyring, Ed., Academic Press, New York, 1967, pp 193-215.
4. K. S. Krasnov and N. V. Karaseva, Optics and Spectrosc. 19, 14 (1965).
5. G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, Nature 199, 804 (1963).
6. D. L. Hildenbrand, private communication, Stanford Research Institute, July 2, 1974.
7. P. A. Akishin and V. P. Spiridinov, Zhur. Fiz. Khim. 32, 1682 (1958).
8. J. L. Margrave, J. Phys. Chem. 58, 258 (1954).

Magnesium Diiodide (MgI_2) (Crystal) GWF = 278.1140

I_2Mg

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.880	31.000	31.000	.000	- 87.700	- 86.337	63.287
300	17.920	31.111	31.000	.033	- 87.702	- 86.328	62.890
400	18.740	36.384	31.714	1.868	- 91.653	- 85.720	46.835
500	19.340	40.632	33.086	3.773	- 101.913	- 83.267	36.396
600	19.840	44.203	34.649	5.733	- 101.519	- 79.576	28.986
700	20.250	47.293	36.240	7.737	- 101.107	- 75.951	23.713
800	20.620	50.022	37.795	9.781	- 100.689	- 72.385	19.775
900	20.950	52.462	39.291	11.854	- 100.281	- 68.872	16.724
1000	21.270	54.687	40.721	13.966	- 101.993	- 65.222	14.254
1100	21.570	56.729	42.085	16.108	- 101.560	- 61.568	12.232
1200	21.860	58.618	43.385	18.280	- 101.124	- 57.952	10.555
1300	22.140	60.379	44.625	20.480	- 100.686	- 54.371	9.141
1400	22.410	62.030	45.810	22.707	- 130.615	- 50.345	7.859
1500	22.670	63.585	46.944	24.961	- 129.771	- 44.642	6.504

Dec. 31, 1974

MAGNESIUM DIIODIDE (MgI_2) (CRYSTAL)

GFW = 278.1140
ΔHf°_0 = unknown
$\Delta Hf^\circ_{298.15} = -87.7 \pm 1.5$ kcal/mol
$\Delta Hm^\circ = 7.0 \pm 2.0$ kcal/mol
$\Delta Hs^\circ_{298.15} = 49.4 \pm 0.8$ kcal/mol

I_2MG

$S^\circ_{298.15} = [31.0 \pm 1.0]$ gibbs/mol
Tm = 907 ± 15 K

Heat of Formation

Finch et al. (1) measured the heat of solution of MgO(c) in aqueous HI and of MgI_2(c) in the same solvent. Combining and correcting for a concentration change gives $\Delta Hr^\circ_{298} = 14.53$ kcal/mol for the process $MgO(c) + 2HI\ (0.5m) = MgI_2(c) + H_2O(\ell)$ from which ΔHf°_{298} (MgI_2,c) = -87.70 ± 1.5 kcal/mol is calculated. The auxiliary data used are ΔHf°_{298}(MgO,c) = -143.7 kcal/mol (2), $\Delta Hf^\circ_{298}(H_2O,\ell)$ = -68.315 kcal/mol (3), and ΔHf°_{298}(HI, 0.5m) = -13.42 kcal/mol. This last value was calculated from the CODATA value of -13.60 for $\Delta Hf^\circ_{298}(I^-$, aq, std. state) (3) = ΔHf°_{298} (HI, aq, std. state) and the heat of dilution of HI (4).

Combination of $\Delta Hf^\circ_{298}(Mg^{+2}$, aq, std. state) = -111.58 kcal/mol selected by Parker (4, 5) with the CODATA value of ΔHf°_{298} (I^- , aq, std., state) = -13.60 kcal/mol gives ΔHf°_{298} (MgI_2, aq, std. state) = -138.78 kcal/mol. Further combination with the heat of solution, -50.96 kcal/mol (4), gives ΔHf°_{298} (MgI_2c) = -87.82 kcal/mol. We adopt ΔHf°_{298}(MgI_2,c) = -87.7 ± 1.5 kcal/mol to retain internal consistency.

Heat Capacity and Entropy

Cp°_{298} = 17.88 gibbs/mol is calculated from the reaction $MgCl_2(c) + 2NaI(c) = MgI_2(c) + 2NaCl(c)$ assuming no net change in heat capacity. Cp = 21.0 gibbs/mol at Tm = 907 K estimated from a Kopp's rule value of 7.0 cal/g atom appears reasonable in comparison with a Cp vs. T plot for $MgBr_2$(c), $MgCl_2$(c), and CaI_2(c) (2). Values of Cp between 298.15 and 907 K are read from the graphical comparison curve. The adopted values lead to $H_{500} - H_{298}$ = 3.77 kcal/mol, in reasonable agreement with the estimate of 4.0 by Brewer et al. (6).

$S^\circ_{298} = 31.0 \pm 1.0$ gibbs/mol is adopted from Kelly and King (7).

Melting Data

The melting point of 650°C (923 K) quoted in the literature appears to be based on the assumed value of Devoto and Jeny (8). In a study of molten electrolytes, Bockris et al. (9), found MgI_2 to be molten at 910 K; a graph in the same paper infers that a Tm = 907 K was chosen. We adopt Tm = 907 ± 15 K.

From the KI/MgI_2 phase diagram by Klemm et al. (10), values of ΔHm° (MgI_2) ranging from 7 to 9 kcal are calculated. Brewer (11) earlier estimated 5.3 kcal/mol. We adopt 7.0 ± 2.0 kcal/mol.

Sublimation Data

By a mass spectrometric - Knudsen cell technique, Berkowitz and Marguart (12) found the sublimation pressure of MgI_2(c) to be 5.18×10^{-6} atm at 734 K and 2.02×10^{-5} atm at 757 K. A third law analysis of these two points gives $\Delta Hs^\circ_{298} = 49.4 \pm 0.8$ kcal/mol. The second law analysis of these two points gives 67.5 kcal/mol but other data covering an approximate range of 550 to 750 K are shown graphically by Berkowitz and Marguardt (12) from which they calculate $\Delta Hs^\circ_{550-750}$ = 45 kcal/mol. We adopt $\Delta Hs^\circ_{298} = 49.4 \pm 0.8$ kcal/mol.

References

1. A. Finch, P. J. Gardner, and C. J. Steadman, Can. J. Chem. 46, 3447 (1968).
2. JANAF Thermochemical Tables: MgO(c), 12-31-74; $MgBr_2$(c), 6-30-74; $MgCl_2$(c), 12-31-65; $CaCl_2$(c), 6-30-70.
3. ICSU - CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
4. U.S. Natl. Bur. Std. Tech. Note 270-3, 1968.
5. V. B. Parker, U.S. Natl. Bur. Std. Report 9803, 1968.
6. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren in "The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics," L. L. Quill, Ed, McGraw-Hill, New York, 1950.
7. K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 1961.
8. G. Devoto and G. Jeny, Gazz. chim., ital. 61, 305 (1931).
9. J. O'M. Bockris, E. H. Crook, H. Bloom, and N. E. Richards, *Proc. Roy. Soc. (London)* A255, 558 (1960).
10. W. Klemm, K. Beyersdorfer, and J. Oryschkewitsch, Z. Anorg. Allgem. Chem. 256, 34 (1948).
11. L. Brewer in "The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics," L. L. Quill, Ed., McGraw-Hill, New York, 1950.
12. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).

Magnesium Diiodide (MgI_2) I_2Mg

(Liquid) GFW = 278.1140

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.880	37.222	37.222	.000	-81.800	-82.292	60.322
300	17.920	37.333	37.222	.033	-81.802	-82.295	59.952
400	18.740	42.605	37.936	1.868	-85.753	-82.309	44.972
500	19.340	46.854	39.308	3.773	-96.013	-80.478	35.177
600	24.000	50.425	40.871	5.733	-95.619	-77.410	28.196
700	24.000	54.125	42.507	8.133	-94.811	-74.438	23.241
800	24.000	57.330	44.164	10.533	-94.037	-71.580	19.555
900	24.000	60.157	45.787	12.933	-93.302	-68.818	16.711
1000	24.000	62.685	47.352	15.333	-94.726	-65.953	14.414
1100	24.000	64.973	48.852	17.733	-94.035	-63.112	12.539
1200	24.000	67.061	50.284	20.133	-93.371	-60.330	10.968
1300	24.000	68.982	51.649	22.533	-92.733	-57.602	9.684
1400	24.000	70.761	52.951	24.933	-122.489	-54.443	8.499
1500	24.000	72.416	54.195	27.333	-121.499	-49.618	7.229
1600	24.000	73.965	55.382	29.733	-120.510	-44.858	6.127
1700	24.000	75.420	56.519	32.133	-119.523	-40.159	5.163
1800	24.000	76.792	57.607	34.533	-118.537	-35.520	4.313
1900	24.000	78.090	58.651	36.933	-117.552	-30.934	3.558
2000	24.000	79.321	59.654	39.333	-116.569	-26.403	2.885

Dec. 31, 1974

MAGNESIUM DIIODIDE (MgI_2) (LIQUID) GFW = 278.1140

$S^\circ_{298.15}$ = [37.222] gibbs/mol

Tm = 907 ± 15 K

Tb = 1255 K

$\Delta Hf^\circ_{298.15}$ = -81.800 kcal/mol

ΔHm° = 7.0 ± 2.0 kcal/mol

ΔHv° = 36.126 kcal/mol

I_2MG

Heat of Formation

ΔHf°_{298} (MgI_2, ℓ) = -81.800 kcal/mol is obtained from the sum of the heat of formation of the crystal, the heat of melting, and the enthalpy difference of the crystal and the liquid between the melting point and 298.15 K.

Heat Capacity and Entropy

The liquid heat capacity of 24.0 gibbs/mol (8 cal/g atom) follows the trend of the liquid heat capacities of the alkaline earth chlorides and bromides and the other alkaline earth iodides. This value is adopted and assumed constant over a 600 - 2000 K range. A glass transition is assumed at 600 K below which the heat capacity is that of the crystal.

S°_{298}(MgI_2, ℓ) = 37.222 gibbs/mol is calculated from the crystal entropy in a manner similar to the heat of formation calculation.

Melting Data

See MgI_2(c) table.

Vaporization Data

The temperature at which $\Delta Gr^\circ = 0$ for the reaction MgI_2(ℓ) = MgI_2(g) is 1255 K, the adopted Tb.

ΔHv° = 36.126 kcal/mol is the calculated difference between the heats of formation of the ideal gas and the liquid at Tb.

Magnesium Diiodide (MgI_2)
(Ideal Gas) GFW = 278.1140

I_2Mg

T, °K	Cp°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.707	- 37.657	- 37.657	INFINITE
100	12.368	61.220	88.100	- 2.688	- 37.521	- 41.958	91.698
200	13.694	70.268	77.143	- 1.375	- 37.948	- 46.356	50.655
298	14.250	75.854	75.854	.000	- 38.300	- 50.310	36.878
300	14.257	75.943	75.855	.026	- 38.309	- 50.384	36.705
400	14.512	80.083	76.417	1.466	- 42.655	- 54.202	29.615
500	14.644	83.337	77.488	2.925	- 53.361	- 56.068	24.507
600	14.720	86.015	78.692	4.393	- 53.459	- 56.602	20.617
700	14.767	88.288	79.905	5.868	- 53.576	- 57.116	17.833
800	14.798	90.262	81.079	7.346	- 53.724	- 57.612	15.739
900	14.820	92.006	82.198	8.827	- 53.908	- 58.088	14.106
1000	14.836	93.568	83.258	10.310	- 56.249	- 58.359	12.754
1100	14.847	94.983	84.261	11.794	- 56.474	- 58.561	11.635
1200	14.856	96.275	85.209	13.280	- 56.724	- 58.741	10.698
1300	14.863	97.465	86.106	14.765	- 57.001	- 58.897	9.901
1400	14.869	98.566	86.958	16.252	- 87.670	- 58.552	9.140
1500	14.873	99.592	87.766	17.739	- 87.593	- 56.476	8.228
1600	14.877	100.552	88.535	19.227	- 87.516	- 54.403	7.431
1700	14.880	101.454	89.269	20.715	- 87.441	- 52.335	6.728
1800	14.883	102.305	89.970	22.203	- 87.367	- 50.273	6.104
1900	14.885	103.110	90.641	23.691	- 87.294	- 48.214	5.546
2000	14.887	103.873	91.283	25.180	- 87.222	- 46.160	5.044
2100	14.888	104.599	91.900	26.668	- 87.152	- 44.109	4.590
2200	14.889	105.292	92.493	28.157	- 87.083	- 42.060	4.178
2300	14.891	105.954	93.064	29.646	- 87.015	- 40.014	3.802
2400	14.892	106.588	93.615	31.135	- 86.948	- 37.972	3.458
2500	14.893	107.196	94.146	32.625	- 86.883	- 35.935	3.141
2600	14.894	107.780	94.659	34.114	- 86.820	- 33.896	2.849
2700	14.894	108.342	95.155	35.603	- 86.760	- 31.863	2.579
2800	14.895	108.884	95.636	37.093	- 86.700	- 29.831	2.328
2900	14.896	109.406	96.102	38.582	- 86.643	- 27.799	2.095
3000	14.896	109.911	96.554	40.072	- 86.589	- 25.774	1.878
3100	14.897	110.400	96.993	41.561	- 86.538	- 23.746	1.674
3200	14.897	110.873	97.419	43.051	- 86.489	- 21.723	1.484
3300	14.897	111.331	97.834	44.541	- 86.444	- 19.696	1.305
3400	14.898	111.776	98.237	46.031	- 86.403	- 17.675	1.136
3500	14.898	112.208	98.630	47.520	- 86.367	- 15.655	.976
3600	14.898	112.627	99.013	49.010	- 86.336	- 13.635	.828
3700	14.899	113.036	99.387	50.500	- 86.310	- 11.616	.686
3800	14.899	113.433	99.751	51.990	- 86.289	- 9.597	.552
3900	14.899	113.820	100.107	53.480	- 86.275	- 7.580	.425
4000	14.899	114.197	100.455	54.970	- 86.268	- 5.564	.304
4100	14.900	114.565	100.794	56.460	- 86.269	- 3.543	.189
4200	14.900	114.924	101.126	57.950	- 86.278	- 1.526	.079
4300	14.900	115.275	101.451	59.440	- 86.296	.488	- .025
4400	14.900	115.617	101.769	60.930	- 86.323	2.508	- .125
4500	14.900	115.952	102.081	62.420	- 86.360	4.531	- .220
4600	14.900	116.280	102.386	63.910	- 86.407	6.552	- .311
4700	14.901	116.600	102.685	65.400	- 86.464	8.570	- .399
4800	14.901	116.914	102.978	66.890	- 86.534	10.596	- .482
4900	14.901	117.221	103.266	68.380	- 86.615	12.620	- .563
5000	14.901	117.522	103.548	69.870	- 86.709	14.646	- .640
5100	14.901	117.817	103.825	71.360	- 86.815	16.669	- .714
5200	14.901	118.106	104.097	72.850	- 86.936	18.700	- .786
5300	14.901	118.390	104.364	74.340	- 87.069	20.738	- .855
5400	14.901	118.669	104.626	75.831	- 87.216	22.772	- .922
5500	14.901	118.942	104.884	77.321	- 87.379	24.809	- .986
5600	14.902	119.211	105.137	78.811	- 87.556	26.846	- 1.048
5700	14.902	119.474	105.387	80.301	- 87.752	28.896	- 1.108
5800	14.902	119.734	105.632	81.791	- 87.962	30.941	- 1.166
5900	14.902	119.988	105.873	83.281	- 88.189	32.995	- 1.222
6000	14.902	120.239	106.110	84.772	- 88.432	35.049	- 1.277

Dec. 31, 1974

MAGNESIUM DIIODIDE (MgI_2) (IDEAL GAS) GFW = 278.1140 I_2MG

Point Group = $D_{\infty h}$
$S^\circ_{298.15}$ = 75.85 ± 2.0 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -37.7 ± 2.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -38.3 ± 2.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}

[125] (1)
[60] (2)
[423] (1)

Bond Distance: Mg-I = 2.52 ± 0.03 Å
Bond Angle: I-Mg-I = 180° $\sigma = 2$
Rotational Constant: B_0 = [0.010459] cm^{-1}

Heat of Formation

ΔHf°_{298} (MgI_2,g) is obtained from that of the crystal by addition of ΔHs°_{298} = 49.4 ± 0.8 kcal/mol. The heat of sublimation is derived from the sublimation pressure measurements of Berkowitz and Marquart (1). See MgI_2(c) table.

Heat Capacity and Entropy

The bond distance is taken from the electron diffraction study of Akishin and Spiridonov (2). From an electric deflection study of mass spectrometrically detected molecular beams, Buechler et al. (3) concluded that MgI_2 is linear. The moment of inertia is 2.676×10^{-37} g cm^2.

The equality of the stretching force constant of the alkaline earth monohalide and the stretching force constant of the alkaline earth dihalide has been indicated as a reasonable assumption (4, 5). The stretching force constant for MgI(g) is calculated, using the valence force model, from the ground state vibrational frequency given by Rosen (6). The bending force constant for MgI_2(g) is taken as 0.01 of the stretching force constant. Brewer et al. (4) used a factor of 0.1 for MgI_2; however, a factor of 0.01 appears more reasonable (7). The adopted vibrational frequencies are calculated from the estimated force constants. Other estimates for ν_1, ν_2, and ν_3 are 132, 199, 446 (4) and 137, 140, 464 (8).

We assign an uncertainty of ± 2 gibbs/mol to the entropy to allow for error in estimating the vibrational frequencies.

References

1. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
2. P. A. Akishin and V. P. Spiridonov, Zhur. Fiz. Khim. 32, 1682 (1958).
3. A. Buechler, J. L. Stauffer, and W. Klemperer, J. Amer. Chem. Soc. 86, 4544 (1964).
4. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev. 63, 111 (1963).
5. JANAF Thermochemical Tables: BeF_2(g), 6-30-70; MgF_2(g), 3-31-66; CaF_2(g), 12-31-68; SrF_2(g), 12-31-72; BaF_2(g), 12-31-72; CaI_2(g), 6-30-74; SrI_2(g), 6-30-74; BaI_2(g), 6-30-74.
6. B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970.
7. JANAF Thermochemical Table: $MgBr_2$(g), 6-30-74.
8. K. S. Krasnov and V. I. Svettsov, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 6, 167 (1963).

SILICON TETRAIODIDE (SiI_4) I_4Si
(CRYSTAL) GFW=535.7040

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	25.821	61.700	61.700	0.000	-45.300	-45.803	33.574
300	25.860	61.860	61.700	0.048	-45.309	-45.805	33.369
400	27.950	69.586	62.740	2.738	-53.470	-45.629	24.931
500	33.040	76.047	64.771	5.638	-74.160	-41.708	18.231

June 30, 1976

SILICON TETRAIODIDE (SiI_4) (CRYSTAL) GFW = 535.7040

ΔHf°_0 = unknown
$\Delta Hf^\circ_{298.15}$ = -45.3 ± 4.0 kcal/mol I_4Si
ΔHm° = 4.7 ± 0.5 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 18.9 ± 5.0 kcal/mol

$S^\circ_{298.15}$ = [61.7 ± 0.8] gibbs/mol
Tm = 393.65 ± 3.0 K (120.5°C)

Heat of Formation

Schäfer and Heine (1) measured the heats of solution of Si(c) and SiI_4(c) in an HF solution containing AgF. For the overall reaction $SiI_4(c)+4Ag(c)=Si(c)+4AgI(c)$, they reported $\Delta Hr^\circ_{298}=-13.80\pm0.44$ kcal/mol. Using auxiliary data for AgI(2), we calculate $\Delta Hf^\circ_{298}=-45.3$ kcal/mol for SiI_4(c). We adopt this value and assign an uncertainity of ±4.0kcal/mol due to the overall inconsistency in the SiI_4 thermochemical data. Refer to the SiI_4(g) table for more details.

Wolf (3) studied the heats of solution of SiI_4(c) and Na_2SiO_3(c) in caustic solution. The net reaction of interest $SiI_4(c)+6NaOH(c)=Na_2SiO_3(c)+4NaI(c)+3H_2O(\ell)$ yielded a heat of reaction of ΔHr°_{298} = -191.5±1.5 kcal/mol based on the appropriate combination of results from five solution studies. Using current auxiliary data (4,5), we calculate ΔHf°_{298}= -51.0 kcal/mol for SiI_4(c). This data is suspect due to uncertainities in how Wolf converted his data from Na_2SiO_3 (calorimetric solution) to Na_2SiO_3(c).

Heat Capacity and Entropy

The adopted heat capacity values are from the study of Kurosawa, et al. (6). The data was obtained from an adiabatic calorimeter of a type used for specific heat measurements and differential thermal analysis. Similar studies on Cr(c) and Si(c) would suggest uncertainties of the order of 3% near room temperature and 0-10% at 600-70 K.

There is no low temperature heat capacity data for T<298.15 K. The entropy at 298.15 K is chosen from a consideration of the sublimation and vaporization data. Refer to the SiI_4(g) table for additional information. However, the discrepancies in the various vapor pressure studies are such that a precise estimate of the entropy is not possible.

Melting Data

Kurosawa et al. (6), using differential thermal analysis (DTA) techniques, determined ΔHm°=4.7 kcal/mol, an average of eight measurements with a standard deviation of 0.08 kcal/mol. The same study reported Tm=120.5°C as determined from the cooling curve. McCarty et al. (7) reported Tm=123.68±0.06°C for 99.998%(mole) pure SiI_4. Other studies have listed melting points in the range 120-127°C as reported by Kurosawa et al. (6). The sublimation and vaporization studies of Bartsch and Wolf (8) suggest a melting point of 123.5°C and a heat of melting of 4.1±0.6 kcal/mol. Due to the short temperature range of measurement in each condensed phase, precise melting data is not expected. In general, the vapor pressure studies as discussed in the SiI_4(g) table (5), show poor agreement in the vicinity of Tm.

We adopt Tm=120.5°C and ΔHm°=4.7 kcal/mol as derived from Kurosawa et al (6). We assign respective uncertainties of ±3.0K and 0.5 kcal/mol due to the variances among the various studies.

Sublimation Data

The heat of sublimation, ΔHs°_{298}, is the difference between the ΔHf°_{298} values for SiI_4(g) and SiI_4(c). Three sublimination studies are summarized in the SiI_4(g) table.

References

1. H. Schäfer and H. Heine, Z. Anorg. Alleg. Chem. 332, 25 (1964).
2. U. S. Natl. Bur. Std. Tech. Note 270-4, 1969.
3. E. Wolf, Z. Chem. 7, 283 (1967).
4. ICSU-COMDATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
5. JANAF Thermochemical Tables: NaI(c), 9-30-63; NaOH(c), 12-31-70; Na_2SiO_3(c), 9-30-67; $SiCl_4$(g), 12-31-70; SiI_4(g), 6-30-76.
6. T. Kurosawa, R. Hasegawa, and T. Yagihashi, Trans. Japan Inst. Metals 6, 229 (1965); Trans. Natl. Res. Inst. Metals (Tokyo) 7, 222 (1965).
7. L. V. McCarty, L. C. Landauer, and J. M. Binkowski, J. Chem. Eng. Data 5, 365-6 (1960).
8. K. Bartsch and E. Wolf, Z. Anorg. Allg. Chem 383, 66 (1971).

I_4Si

SILICON TETRAIODIDE (SiI_4) I_4Si
(LIQUID) GFW=535.7040

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	25.821	72.048	72.048	0.000	-41.173	-44.761	32.811
300	25.860	72.208	72.048	0.048	-41.182	-44.783	32.624
400	39.198	81.828	73.235	3.437	-48.644	-45.700	24.969
500	40.185	90.559	75.854	7.352	-68.319	-43.123	18.849
600	41.172	97.972	78.939	11.420	-66.613	-38.245	13.931
700	42.159	104.393	82.127	15.587	-64.829	-33.656	10.508

June 30, 1976

SILICON TETRAIODIDE (SiI_4) (Liquid) GFW = 535.7040

$S°_{298.15}$ = 72.048 gibbs/mol
Tm = 393.65 ± 3.0 K (120.5°C)
Tb = 575.8 K

$\Delta Hf°_{298.15}$ = -41.173 kcal/mol I_4Si
ΔHm° = 4.7 ± 0.5 kcal/mol
ΔHv° = 11.244 kcal/mol

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 ($H°_{393.65}-H°_{298}$) 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 an assumed glass transition at Tg = 340K. Below 340K, the heat capacity values are those of the crystal. $S°_{298}$ is obtained in a manner analogous to that used for $\Delta Hf°_{298}$.

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 discussed in the $SiI_4(g)$ table which approached closely the normal boiling point yielded normal boiling points (p = 760 mm) 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.

Reference

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)

(IDEAL GAS) GFW=535.7040

I_4SI

	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	124.256	-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	25.825	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	172.861	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	-7.245
6000	25.828	176.085	151.629	146.732	-154.465	201.535	-7.341

June 30, 1976

SILICON TETRAIODIDE (SiI_4) (IDEAL GAS) GFW = 535.7040

I_4SI

Point Group = T_d
$S^\circ_{298.15}$ = 99.51 ± 0.05 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -25.1 ± 4.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -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)

Bond Distance: Si-I = 2.43 ± 0.02 Å   σ = 12
Bond Angle: I-Si-I = 109.47122°
Product 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 = 850K and Pc = 42.1 atm as suggested by Lapidus et al. (1) are used to calculate B.

ref/eqn	no. of data pts.	range, K	ΔHr°_{298}, kcal/mol 2nd law	3rd law	drift gibbs/mol	$\Delta Hf^\circ_{298}(g)$* kcal/mol
2A	13	343-396	16.24±0.32	18.82±0.28	6.9±0.9	-26.48
3A	eqn (flow)	373-392	18.76	19.08	0.8	-26.22
3A	eqn (static)	370-395	18.34	19.08	1.9	-26.22
3B	eqn (static)	398-425	15.15	14.94	-0.6	-26.23
4B	10	399-572	14.95±0.06	14.82±0.05	-0.3±0.1	-26.35
5B	eqn	393-573	14.28	14.72	0.9	-26.45
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.

A $SiI_4(c) = SiI_4(g)$ B $SiI_4(l) = SiI_4(g)$ 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). Primary weight on the Andersen and Belz (4) study also determined an approximate $S^\circ_{298}(c)$ value. 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 individual 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 $SiI_4(g)$.

References

1. I. I. Lapidus, L. A. Nisel'son and A. L. Seifer in "Thermophysical Properties of Gases and Liquids," Vol. 1, V. A. Rabinovick, Ed., Israel Program for Scientific Translations, Jerusalem, 1970, pp. 102-135.
2. I. R. Krichevskii, G. F. Ivanovskii, and E. K. Safronov, Zh. Fiz. Khim. 39, 2594 (1965).
3. K. Bartsch and E. Wolf, Z. Anorg. Allg. Chem. 383, 66 (1971).
4. H. C. Andersen and L. H. Belz, J. Am. Chem. Soc. 75, 4828 (1953).
5. K. Uchimura, T. Takuma, M. Yuizumi, and T. Kunugi, Denki Kagaku 35, 876 (1967).
6. H. Schäfer and B. Morcher, Z. Anorg. Allg. Chem. 352, 122 (1967).
7. E. Wolf and C. Herbst, Z. Chem. 7, 34 (1967).
8. R. J. H. Clark and D. M. Rippon, J. Mol. Spectrosc. 44, 479 (1972).
9. M. W. Liston and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941).
10. T. Shimanouchi, NSRDS-NBS 39, June 1972.
11. M. L. Delwaulle, J. Phys. Chem. 56, 355 (1952).
12. M. L. Delwaulle and F. Francois, J. Phys. Radium 15, 206 (1954).

I_4SI

ZIRCONIUM TETRAIODIDE (ZrI_4) I_4ZR

(CRYSTAL) GFW=598.8380

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 7.275	- 116.446	- 116.446	INFINITE
100	24.906	31.440	88.210	- 5.677	- 116.518	- 116.411	254.415
200	29.058	50.293	64.958	- 2.933	- 116.656	- 116.247	127.029
298	30.545	62.206	62.206	.000	- 116.800	- 116.018	85.043
300	30.564	62.395	62.207	.057	- 116.802	- 116.012	84.515
400	31.310	71.296	63.415	3.152	- 124.674	- 115.453	63.081
500	31.790	78.336	65.720	6.308	- 145.215	- 111.210	48.610
600	32.170	84.167	68.322	9.507	- 144.488	- 104.478	38.056
700	32.490	89.150	70.950	12.740	- 143.759	- 97.867	30.556
800	32.780	93.508	73.503	16.004	- 143.030	- 91.359	24.958
900	33.070	97.385	75.945	19.296	- 142.308	- 84.946	20.628
1000	33.360	100.885	78.267	22.618	- 141.585	- 78.609	17.180

March 31, 1962; June 30, 1964; June 30, 1975

ZIRCONIUM TETRAIODIDE (ZrI_4) (CRYSTAL) GFW = 598.8380 I_4ZR

$S°_{298.15}$ = [62.21±1.0] gibbs/mol
Tm = 772±2 K
Ts = 705.6 K

$\Delta Hf°_0$ = [-116.4±2.0] kcal/mol
$\Delta Hf°_{298.15}$ = -116.8±1.5 kcal/mol
ΔHm° = unknown
$\Delta Hs°_{298.15}$ = 30.2±0.5 kcal/mol

Heat of Formation

Turnbull (1) measured the heats of reaction for the dissolution of the zirconium tetrahalides in caustic and in water. The reported heats of reaction and the corresponding reactions may be combined to yield the following:

$ZrI_4(c) + 4NaCl(aq) = ZrCl_4(c) + 4NaI(aq)$, $\Delta Hr°_{298}$ = -12.50 kcal/mol
$ZrI_4(c) + 4Cl^-(aq) = ZrCl_4(c) + 4I^-(aq)$, $\Delta Hr°_{298}$ = -11.97 kcal/mol

Using auxiliary data (2, 4), we calculate $\Delta Hf°_{298}$ = -116.52 and -117.05 kcal/mol for $ZrI_4(c)$ from these two reactions. We adopt a mean of these two values, $\Delta Hf°_{298}$ = -116.8 kcal/mol, and assign an uncertainty of ± 1.5 kcal/mol. The value suggested by NBS(3) is 1.7 kcal/mol more positive.

Baev and Shelton (5) referenced a heat of formation value for $ZrI_4(c)$. They reported $\Delta Hf°_{298}$ = -105.9 kcal/mol as supposedly extracted from Karapet'yants and Karapet'yants (6). We tentatively discard this value due to the large number of inconsistencies in the reported tabular results of Baev and Shelton (5).

Heat Capacity and Entropy

There is no heat capacity and enthalpy data reported in the literature for $ZrI_4(c)$. The adopted heat capacity values are estimated such that they parallel those adopted for $ZrCl_4(c)$ and $ZrBr_4(c)$ (7) and are consistent with the sublimation data.

The crystal data compilation of Donnay and Ondik (9) does not list the crystal structure of $ZrI_4(c)$ but does tabulate both $ZrCl_4$ and $ZrBr_4$ as cubic structures. The literature data related to the crystal structure of ZrI_4 is not definitive. Assuming $ZrI_4(c)$ also has a cubic structure, the adopted heat capacity value are estimated so as to parallel those for $ZrCl_4$ and $ZrBr_4$. The values below 300K are calculated in the same manner as for $ZrBr_4(c)$ (7). The high temperature heat capacities are obtained graphically.

Melting Data

The melting point was observed by Rahlfs and Fischer (10) to be 772±2 K and by Nisel'son (11) to be 773 K.

Sublimation Data

The sublimation data is treated in the $ZrI_4(g)$ table (7). The sublimation temperature, Ts, is calculated from the Gibbs free energy crossover between the crystal and gas. Since Ts is less than Tm, the liquid phase is thermodynamically unstable at one atmosphere pressure.

References

1. A. G. Turnbull, J. Phys. Chem. 65, 1652 (1961).
2. JANAF Thermochemical Tables: $ZrCl_4(c)$, 6-30-75.
3. U. S. Natl. Bur. Std. Tech. Note 270-5, 1971.
4. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
5. A. K. Baev and R. A. J. Shelton, Russ. J. Phys. Chem. 47, 1340 (1973).
6. M. K. Karapet'yants and M. L. Karapet'yants, "*Osnovnye Termokhimicheskie Konstanty Neorganisheskekh i Organicheskikh* Veshchestv," Izd. Khimiya, Moscow, 1968 (as referenced by Baev and Shelton [5]).
7. JANAF Thermochemical Tables: $ZrCl_4(c)$, $ZrBr_4(c)$, and $ZrI_4(g)$, 6-30-75.
8. F. R. Sale and R. A. J. Shelton, J. *Less-Common Metals* 9, 54 (1965).
9. J. D. H. Donnay and H. M. Ondik, "Crystal Data, Determinative Tables", 3rd edition, Vol. 2, National Bureau of Standards and Joint Committee on Powder Diffraction Standards, 1973.
10. O. Rahlfs and W. Fischer, Z anorg. allgem. Chem. 211, 349 (1933).
11. L. A. Nisel'son, Russ. J. Inorg. Chem 7, 354 (1962).

ZIRCONIUM TETRAIODIDE (ZrI_4) I_4ZR

(IDEAL GAS) GFW=598.8380

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	.000	.000	INFINITE	- 6.288	- 85.259	- 85.259	INFINITE
100	20.944	81.145	128.202	- 4.706	- 85.347	- 90.210	197.153
200	24.109	96.881	108.968	- 2.417	- 85.940	- 94.849	103.646
298	24.997	106.703	106.703	.000	- 86.600	- 99.085	72.631
300	25.007	106.858	106.704	.046	- 86.613	- 99.161	72.239
400	25.355	114.107	107.690	2.567	- 95.059	- 102.963	56.257
500	25.523	119.784	109.561	5.112	- 116.211	- 102.930	44.991
600	25.616	124.447	111.665	7.669	- 116.126	- 100.284	36.528
700	25.673	128.400	113.781	10.234	- 116.065	- 97.649	30.487
800	25.710	131.831	115.827	12.803	- 116.031	- 95.018	25.958
900	25.736	134.861	117.777	15.375	- 116.029	- 92.394	22.436
1000	25.754	137.573	119.624	17.950	- 116.053	- 89.766	19.618
1100	25.768	140.029	121.369	20.526	- 116.108	- 87.136	17.312
1200	25.778	142.271	123.018	23.103	- 117.045	- 84.447	15.380
1300	25.786	144.335	124.580	25.682	- 116.978	- 81.732	13.740
1400	25.793	146.246	126.060	28.261	- 116.928	- 79.022	12.336
1500	25.798	148.026	127.466	30.840	- 116.891	- 76.318	11.119
1600	25.802	149.691	128.803	33.420	- 116.867	- 73.611	10.055
1700	25.806	151.255	130.079	36.001	- 116.856	- 70.908	9.116
1800	25.809	152.731	131.256	38.581	- 116.860	- 68.206	8.281
1900	25.811	154.126	132.462	41.162	- 116.878	- 65.503	7.535
2000	25.813	155.450	133.578	43.744	- 116.908	- 62.802	6.863
2100	25.815	156.709	134.650	46.325	- 116.952	- 60.093	6.254
2200	25.817	157.910	135.680	48.907	- 122.013	- 57.208	5.683
2300	25.818	159.058	136.672	51.488	- 122.080	- 54.260	5.156
2400	25.819	160.157	137.628	54.070	- 122.148	- 51.308	4.672
2500	25.820	161.211	138.550	56.652	- 122.220	- 48.357	4.227
2600	25.821	162.224	139.441	59.234	- 122.294	- 45.401	3.816
2700	25.822	163.198	140.303	61.816	- 122.372	- 42.442	3.435
2800	25.823	164.137	141.138	64.399	- 122.451	- 39.478	3.081
2900	25.824	165.043	141.946	66.981	- 122.533	- 36.513	2.752
3000	25.824	165.919	142.731	69.563	- 122.619	- 33.550	2.444
3100	25.825	166.766	143.493	72.146	- 122.706	- 30.577	2.156
3200	25.825	167.586	144.233	74.728	- 122.796	- 27.604	1.885
3300	25.826	168.380	144.953	77.311	- 122.889	- 24.626	1.631
3400	25.826	169.151	145.653	79.894	- 122.984	- 21.649	1.392
3500	25.827	169.900	146.335	82.476	- 123.082	- 18.663	1.165
3600	25.827	170.628	147.000	85.059	- 123.183	- 15.681	.952
3700	25.827	171.335	147.648	87.642	- 123.286	- 12.697	.750
3800	25.828	172.024	148.281	90.224	- 123.392	- 9.704	.558
3900	25.828	172.695	148.898	92.807	- 123.501	- 6.709	.376
4000	25.828	173.349	149.501	95.390	- 123.612	- 3.719	.203
4100	25.828	173.987	150.091	97.973	- 123.725	- .713	.038
4200	25.829	174.609	150.667	100.556	- 123.842	2.290	- .119
4300	25.829	175.217	151.231	103.139	- 123.961	5.287	- .269
4400	25.829	175.810	151.783	105.721	- 124.085	8.294	- .412
4500	25.829	176.391	152.323	108.304	- 124.210	11.309	- .549
4600	25.829	176.959	152.853	110.887	- 124.337	14.323	- .681
4700	25.830	177.514	153.371	113.470	- 124.466	17.333	- .806
4800	25.830	178.058	153.880	116.053	- 265.756	21.038	- .958
4900	25.830	178.591	154.379	118.636	- 265.995	27.018	- 1.205
5000	25.830	179.112	154.868	121.219	- 266.244	32.999	- 1.442
5100	25.830	179.624	155.349	123.802	- 266.498	38.983	- 1.671
5200	25.830	180.125	155.821	126.385	- 266.762	44.973	- 1.890
5300	25.830	180.617	156.284	128.968	- 267.030	50.975	- 2.102
5400	25.830	181.100	156.739	131.551	- 267.306	56.982	- 2.306
5500	25.831	181.574	157.186	134.134	- 267.588	62.984	- 2.503
5600	25.831	182.040	157.626	136.717	- 267.876	68.992	- 2.693
5700	25.831	182.497	158.058	139.300	- 268.170	75.013	- 2.876
5800	25.831	182.946	158.483	141.884	- 268.467	81.038	- 3.054
5900	25.831	183.388	158.902	144.467	- 268.769	87.065	- 3.225
6000	25.831	183.822	159.313	147.050	- 269.078	93.101	- 3.391

March 31, 1962; June 30, 1964; June 30, 1975

ZIRCONIUM TETRAIODIDE (ZrI_4) (IDEAL GAS) GFW = 598.8380 I_4ZR

Point Group = T_d

$S°_{298}$ = 106.70 ± 0.03 gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -85.3 ± 2.0 kcal/mol

$\Delta Hf°_{298.15}$ = -86.6 ± 2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
158 (1)
43 (2)
254 (3)
55 (3)

Bond Distance: ZrI = 2.660±0.005 Å σ = 12

Bond Angle: I-Zr-I = 109° 28'

Product of the Moments of Inertia: $I_AI_BI_C$ = 6.2848X10^{-110} g^3cm^6

Heat of Formation

The heat of formation for $ZrI_4(g)$ is calculated from the heats of formation and sublimation at 298.15 K. The adopted value for the heat of sublimation, $\Delta Hs°_{298}$ = 30.2 ± 0.5 kcal/mol, is based on the 2nd and 3rd law analyses of the sublimation data of Sale and Shelton (1) and Rahlfs and Fischer (2). Using Knudsen effusion techniques, Sale and Shelton (1) studied effusion in a nickel effusion cell for three different orifice areas. The results were then extrapolated to zero orifice area (refer to last line in the following table). Other sublimation studies have been conducted by Rahlfs and Fischer (2), using a liquid tin tensimeter, and by Gerlach et al. (3), using the oscillating quartz fiber method. It should be noted that the work of Rahlfs and Fischer (2) covered an observed pressure range of 4.0 - 272 mm Hg, which is much wider than range covered by Sale and Shelton (1). The adopted $\Delta Hs°_{298}$ is based on the mean of the third law results of Sale and Shelton (30.01 kcal/mol, 1) and Rahlfs and Fischer (30.32 kcal/mol, 2).

The effusion studies (membrane method) by Baev and Shelton (4) are discarded due to the large number of discrepancies in their tabulated results.

In analyzing the vapor pressures for the three sublimation studies (1, 2, 3), corrections were made for non-ideality by means of the equation $\Delta G°/T = -R\ln p - Bp/T$. The Bertholet equation of state and the critical constants Tc = 959 K and pc = 40.7 atm as determined by Nisel'son and Sokolova (5) are used to calculate B.

	range, K	no. pts	$\Delta Hs°_{298}$, kcal/mol 2nd law	3rd law	drift gibbs/mol
Rahlfs and Fischer (2)	558-671	15*	31.33±0.24	30.32±0.12	-1.62±0.38
Gerlach et al (3)	393-453	eqn	26.91	29.98	7.25
Sale and Shelton (1)	426-474A**	12*	29.84±1.28	31.22±0.30	3.09±2.84
	432-500B**	14*	30.81±0.57	30.86±0.15	0.10±1.24
	436-480C**	12	30.24±0.76	30.51±0.17	0.61±1.66
	423-503	eqn	29.97	30.01	0.08

*One point rejected due to a statistical test

**Orifice area (cm^2 10^2) A = 0.5364 B = 0.2041 C = 0.0935

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark et al. (6, 7), who recorded the Raman spectra of ZrI_4 in the vapor phase (380-420°C). These studies indicated that ZrI_4 is a tetrahedral monomer in the vapor phase. Shimanouchi, in his compilation of molecular vibrational frequencies (8), also adopted the values of Clark et al. (6, 7) for $ZrI_4(g)$. Rahlfs and Fischer (2), through vapor density measurements, had earlier concluded that ZrI_4 was monomeric in the vapor phase.

An electron diffraction study of $ZrI_4(g)$ at 250-270°C was conducted by Zasorin et al. (9). This study confirmed the tetrahedral structure and determined the Zr-I bond length to be 2.660±0.005 Å. We adopt this value. Other interatomic distances reported in the literature are estimates. The individual moments of inertia are $I_A = I_B = I_C = 3.9756 \times 10^{-37}$ g cm^2.

Much literature has been published on the inter-relationships between force constants and vibrational frequencies. Since the majority of these are based on estimated frequencies, they will not be further discussed or referenced. The same situation is true for thermodynamic tabulations of $ZrI_4(g)$. One exception is that Clark et al. (6) calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is very similar to ours; the difference in the entropy being 0.04 gibbs/mol in the range 100-1000K.

References

1. F. R. Sale and R. A. J. Shelton, J. Less Common Metals 9, 54 (1965).
2. O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).
3. J. Gerlach, J. P. Krumme, F. Pawlek, and H. Probst, Z. Phys. Chem. (Frankfurt am Main) 53, 135 (1967).
4. A. K. Baev and R. A. J. Shelton, Russ. J. Phys. Chem. 47, 1340 (1973).
5. L. A. Nisel'son and T. D. Sokolova, Russ. J. Inorg. Chem. 7, 1382 (1962).
6. R. J. H. Clark, B. K. Hunter, and D. M. Rippon, Chem. Ind. (London) 1971, 787 (1971); Inorg. Chem. 11 56 (1972).
7. R. J. H. Clark and D. M. Rippon, J. Mol. Spectrosc. 44, 479 (1972); Advan. Raman Spectrosc. 1, 443 (1972).
8. T. Shimanouchi, J. Phys. Chem. Ref. Data 3, 269 (1971).
9. E. Z. Zasoren, G. V. Girichev, V. P. Spiridonov, K. S. Krasnov, and V. I. Tsirel'nikov, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 16, 802 (1973).

Magnesium Oxide (MgO) MgO
(Crystal) GFW = 40.3044

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.233	- 142.699	- 142.699	INFINITE
100	1.865	.609	12.479	- 1.187	- 143.154	- 140.918	307.977
200	6.377	3.369	7.179	- .762	- 143.639	- 138.585	151.438
298	8.869	6.435	6.435	.000	- 143.700	- 135.984	99.679
300	8.902	6.490	6.435	.016	- 143.701	- 135.936	99.029
400	10.172	9.244	6.802	.977	- 143.710	- 133.344	72.856
500	10.885	11.597	7.532	2.033	- 143.662	- 130.756	57.154
600	11.336	13.625	8.382	3.145	- 143.596	- 128.183	46.690
700	11.651	15.397	9.261	4.295	- 143.528	- 125.618	39.220
800	11.888	16.969	10.128	5.473	- 143.474	- 123.065	33.620
900	12.079	18.380	10.968	6.671	- 143.444	- 120.515	29.265
1000	12.239	19.661	11.774	7.887	- 145.560	- 117.786	25.742
1100	12.379	20.834	12.545	9.118	- 145.551	- 115.011	22.851
1200	12.506	21.917	13.281	10.363	- 145.557	- 112.235	20.441
1300	12.622	22.923	13.985	11.619	- 145.582	- 109.457	18.401
1400	12.730	23.862	14.657	12.887	- 175.991	- 106.197	16.578
1500	12.833	24.744	15.300	14.165	- 175.645	- 101.224	14.748
1600	12.932	25.575	15.917	15.453	- 175.292	- 96.275	13.151
1700	13.028	26.362	16.508	16.751	- 174.932	- 91.346	11.743
1800	13.121	27.109	17.077	18.059	- 174.566	- 86.440	10.495
1900	13.212	27.821	17.624	19.375	- 174.193	- 81.554	9.381
2000	13.301	28.501	18.151	20.701	- 173.814	- 76.689	8.380
2100	13.389	29.152	18.659	22.036	- 173.429	- 71.843	7.477
2200	13.475	29.777	19.150	23.379	- 173.039	- 67.013	6.657
2300	13.561	30.378	19.626	24.730	- 172.643	- 62.202	5.911
2400	13.646	30.957	20.086	26.091	- 172.240	- 57.410	5.228
2500	13.730	31.516	20.532	27.460	- 171.833	- 52.635	4.601
2600	13.814	32.056	20.965	28.837	- 171.420	- 47.873	4.024
2700	13.897	32.579	21.385	30.222	- 171.003	- 43.130	3.491
2800	13.980	33.086	21.794	31.616	- 170.579	- 38.403	2.997
2900	14.062	33.578	22.192	33.018	- 170.151	- 33.688	2.539
3000	14.144	34.056	22.580	34.428	- 169.720	- 28.990	2.112
3100	14.225	34.521	22.957	35.847	- 169.283	- 24.306	1.714
3200	14.307	34.974	23.326	37.274	- 168.842	- 19.638	1.341
3300	14.388	35.415	23.685	38.708	- 168.397	- 14.983	.992
3400	14.470	35.846	24.037	40.151	- 167.950	- 10.338	.664
3500	14.550	36.267	24.380	41.602	- 167.499	- 5.711	.357
3600	14.631	36.678	24.716	43.061	- 167.046	- 1.093	.066
3700	14.711	37.080	25.045	44.528	- 166.591	3.511	- .207
3800	14.792	37.473	25.367	46.003	- 166.133	8.103	- .466
3900	14.872	37.858	25.682	47.487	- 165.674	12.678	- .710
4000	14.953	38.236	25.991	48.978	- 165.215	17.247	- .942

Dec. 31, 1960; Dec. 31, 1965; Dec. 31, 1974

MAGNESIUM OXIDE (MgO) (CRYSTAL) GFW = 40.3044 MgO

$S^\circ_{298.15}$ = 6.435 ± 0.02 gibbs/mol
Tm = 3105 ± 30 K

ΔHf°_0 = -142.70 ± 0.15 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -143.70 ± 0.15 kcal/mol
ΔHm° = [18.6±4] kcal/mol

Heat of Formation

ΔHf° is based on oxygen-bomb calorimetry of Holley and Huber (1) and HCl-solution calorimetry of Shomate and Huffman (2). The reported values of -143.70 ± 0.12 (1) and -143.84 ± 0.05 (2) kcal/mol become ΔHf°_{298} = -143.61 ± 0.12 and -143.78 ± 0.08 kcal/mol when adjusted to 1969 atomic weights. We adopt the median value of -143.70 ± 0.15 kcal/mol.

NBS (3) adopted -143.81 kcal/mol for macrocrystalline periclase, based on the data of Shomate and Huffman (2) converted to 1961 atomic weights. Parker (3) preferred the data of Shomate and Huffman because of the inference that their sample corresponded more closely to the macrocrystalline standard state. New ΔHsoln data (4) suggest that excess energy of up to ~1.1 kcal/mol arises mainly from disorder (defects) in MgO rather than from high surface area and small particle size. Since the excess energy is eliminated at T>~1000°C(4), it is unlikely that this effect would bias the combustion data of Holley and Huber (1).

Other data for ΔHf° were reviewed by Parker (3). New measurements exist for ΔHsoln of MgO (4) and Mg (5), but we have not attempted to derive ΔHf° because of differences in the final states of the solutions.

Heat Capacity and Entropy

Cp° below 270 K is based on data (3-270 K) for single crystals measured by Barron et al. (6). Values above 270 K are from a constrained fit of Cp° (6) and enthalpies (373-1173 K) of fused MgO measured in a Bunsen ice calorimeter by Victor & Douglas (7). S° is obtained from Cp° based on a negligible extrapolation to absolute zero.

Maximum deviations of the Cp° data (6) from the adopted curve are ±1.7% near 15 K, ±1.0% near 20 K, ±0.4% near 40 K, and ~0.2% at higher temperatures. Gmelin (8) later reported smoothed Cp° values (2-320 K) derived from data for MgO sintered at high temperature. These values are in good agreement with the adopted curve except from 70 to 140 K, where deviations are all positive and reach a maximum of almost 7% at 90 K. Gmelin's values gave S_{298} = 6.50, i.e., higher by ~0.06 gibbs/mol. Larger positive deviations in Cp exist at all temperatures (20-301 K) for the non-standard state MgO used by Giauque and Archibald (9). Their sample was prepared from hydroxide in vacuo at ~350°C and was not annealed at high temperature. The microcrystalline product presumably was disordered, leading to excess Cp and S_{298} = 6.66 gibbs/mol. Limited data of Parks and Kelley (10) for fused MgO tend to confirm the adopted curve.

Deviations of the enthalpy data from the adopted curve are ±0.15% (7, 373-1173 K), -0.3 ± 0.3% (11, 402-1799 K), +0.8 ± 0.9% (12, 370-1591 K) and -2.8 to +1.0% (13, equation for 1200-2500 K). Microcalorimetric Cp data (14, 305-455 K) agree with the adopted curve at the mid-temperature but have a temperature derivative which is too small.

Melting Data

See MgO(ℓ).

References

1. C. E. Holley and E. J. Huber, J. Amer. Chem. Soc. 73, 5577 (1951).
2. C. H. Shomate and E. H. Huffman, J. Amer. Chem. Soc. 65, 1625 (1943).
3. U.S. Natl. Bur. Std. Tech. Note 270-6, 1971; V. B. Parker, U.S. Natl. Bur. Std. Rept. 9803, pp. 91-2 (1968).
4. M. Natarajan, T. S. Sarma, J. C. Ahluwalia and C. N. R. Rao, Trans. Faraday Soc. 65, 3088 (1969), and references cited therein.
5. A. S. Monaenkova, E. B. Pashlova and A. F. Vorob'ev, Dokl. Akad. Nauk SSSR 199, 1332 (1971).
6. T. H. K. Barron, W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) 250 A, 70 (1959).
7. A. C. Victor and T. B. Douglas, J. Res. Natl. Bur. Std. 67 A, 325 (1963).
8. E. Gmelin, Z. Naturforsch. 24a, 1794 (1969); Cryogenics 7, 225 (1967).
9. W. F. Giauque and R. C. Archibald, J. Amer. Chem. Soc. 59, 561 (1937).
10. G. S. Parks and K. K. Kelley, J. Phys. Chem. 30, 47 (1926).
11. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6295, (1963).
12. D. S. Tsagareishvili and G. G. Gvelesiani, Teplofiz. Vys. Temp. 12, 208 (1974).
13. V. P. Bondarenko, E. N. Fomichev and V. V. Kandyba, High Temp. High Press. 5, 5 (1973).
14. L. Malaspino, R. Gigli and G. Bardi, Calore 42, 317 (1971).

Magnesium Oxide (MgO) MgO
(Liquid) GFW = 40.3044

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.869	11.560	11.559	.000	-127.297	-121.109	88.775
300	8.902	11.615	11.560	.016	-127.298	-121.070	88.200
400	10.172	14.369	11.927	.977	-127.308	-118.992	65.014
500	10.885	16.722	12.656	2.033	-127.259	-116.916	51.104
600	11.336	18.749	13.507	3.145	-127.193	-114.855	41.836
700	11.651	20.521	14.385	4.295	-127.125	-112.803	35.219
800	11.888	22.093	15.252	5.473	-127.072	-110.762	30.259
900	12.079	23.505	16.092	6.671	-127.041	-108.725	26.402
1000	12.239	24.786	16.898	7.887	-129.158	-106.508	23.277
1100	12.379	25.959	17.669	9.118	-129.148	-104.246	20.712
1200	12.506	27.042	18.406	10.363	-129.155	-101.982	18.573
1300	12.622	28.047	19.109	11.619	-129.180	-99.716	16.764
1400	12.730	28.987	19.782	12.887	-159.588	-96.969	15.138
1500	12.833	29.868	20.425	14.165	-159.242	-92.508	13.478
1600	12.932	30.700	21.041	15.453	-158.890	-88.072	12.030
1700	13.028	31.487	21.633	16.751	-158.530	-83.655	10.755
1800	13.121	32.234	22.201	18.059	-158.164	-79.261	9.624
1900	13.212	32.946	22.748	19.375	-157.791	-74.888	8.614
2000	13.301	33.626	23.275	20.701	-157.412	-70.535	7.708
2100	13.389	34.277	23.784	22.035	-157.027	-66.201	6.890
2200	16.000	35.021	24.278	23.635	-156.380	-61.890	6.148
2300	16.000	35.732	24.760	25.235	-155.735	-57.610	5.474
2400	16.000	36.413	25.232	26.835	-155.093	-53.358	4.859
2500	16.000	37.066	25.692	28.435	-154.455	-49.133	4.295
2600	16.000	37.694	26.142	30.035	-153.819	-44.931	3.777
2700	16.000	38.298	26.581	31.635	-153.187	-40.756	3.299
2800	16.000	38.880	27.010	33.235	-152.557	-36.604	2.857
2900	16.000	39.441	27.429	34.835	-151.931	-32.472	2.447
3000	16.000	39.984	27.838	36.435	-151.310	-28.364	2.066
3100	16.000	40.508	28.239	38.035	-150.691	-24.276	1.711
3200	16.000	41.016	28.630	39.635	-150.077	-20.209	1.380
3300	16.000	41.509	29.013	41.235	-149.467	-16.161	1.070
3400	16.000	41.986	29.387	42.835	-148.863	-12.127	.780
3500	16.000	42.450	29.754	44.435	-148.263	-8.118	.507
3600	16.000	42.901	30.113	46.035	-147.669	-4.120	.250
3700	16.000	43.339	30.465	47.635	-147.081	-.139	.008
3800	16.000	43.766	30.809	49.235	-146.498	3.825	-.220
3900	16.000	44.181	31.147	50.835	-145.922	7.769	-.435
4000	16.000	44.587	31.478	52.435	-145.354	11.704	-.639
4100	16.000	44.982	31.802	54.035	-144.795	15.624	-.833
4200	16.000	45.367	32.121	55.635	-144.242	19.528	-1.016
4300	16.000	45.744	32.433	57.235	-143.699	23.422	-1.190
4400	16.000	46.111	32.740	58.835	-143.165	27.302	-1.356
4500	16.000	46.471	33.041	60.435	-142.640	31.172	-1.514
4600	16.000	46.823	33.337	62.035	-142.126	35.031	-1.664
4700	16.000	47.167	33.627	63.635	-141.622	38.876	-1.808
4800	16.000	47.504	33.913	65.235	-141.129	42.712	-1.945
4900	16.000	47.834	34.194	66.835	-140.648	46.534	-2.076
5000	16.000	48.157	34.470	68.435	-140.178	50.350	-2.201

Dec. 31, 1965; Dec. 31, 1974

MAGNESIUM OXIDE (MgO) (LIQUID) GFW = 40.3044

$S^\circ_{298.15}$ = [11.560] gibbs/mol

Tm = 3105 ± 30 K

$\Delta Hf^\circ_{298.15}$ = [-127.297] kcal/mol MgO

ΔHm° = [18.6±4] kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by adding ΔHm° and the difference in ($H^\circ_{3105}-H^\circ_{298}$) between crystal and liquid.

Heat Capacity and Entropy

Cp° is assumed to be 16 gibbs/mol except below the glass transition (2100 K) where Cp°(ℓ) is taken equal to Cp°(c). Enthalpy data yield Cp° ≥ 19 gibbs/mol for liquid BeO (1), but there may be a positive bias due to volatilization. S° is calculated in a manner analogous to that of ΔHf°.

Melting Data

Documented values for Tm (in °C, IPTS-48) include 2800 ± 20 (2), 2827 ± 20 (3) and 2852 (4, 5). We adopt the median value (3) which becomes 2832°C = 3105 K on IPTS-68.

Calorimetric data for ΔHm° are not available. Kelley (6) derived an apparent ΔHm = 18.5 kcal/mol at Tm = 2915 K from liquidus data for the $MgO-ZrO_2$ binary (7). The old (7) and new (8, 9) data for $MgO-ZrO_2$ imply gross non-ideality which makes the system unsuitable for obtaining ΔHm. Apparent ΔHm values ranging from 8 to 30 kcal/mol are obtained from more suitable binary systems (9, 10) involving CaO, Al_2O_3, Cr_2O_3, PuO_2 and UO_2. These values are so uncertain that we assume ΔHm° = 18.6 kcal/mol based on ΔSm° = 6 gibbs/mol. ΔHm = 20 kcal/mol was measured calorimetrically for BeO (1), but the crystal is hexagonal or tetragonal rather than cubic as in the case of MgO.

Vaporization Data

Vaporization rates based on weight loss at Tm were reported by Noguchi (8) for MgO and six other refractory oxides. Vaporization of MgO near 2000 K has been studied by Langmuir-torsion (11), Langmuir-weight-loss (12, 13), Knudsen-mass-spectrometric (14), Knudsen-effusion (15) and transpiration (15, 16) methods. Vaporization near 2000 K is primarily to the elements (14), Mg(g) and presumably O(g) and O_2(g), rather than to MgO(g). Quantitative interpretation of the vaporization species is uncertain. The adopted tables (1) predict that MgO(g) is insignificant near 2000 K but should become one of the significant components of the vapor near Tm.

References

1. JANAF Thermochemical Tables: BeO(c,ℓ) and MgO(c,g) 12-31-74.
2. B. Riley, Rev. Int. Hautes Temp. Refract. 3, 327 (1966).
3. R. N. McNally, F. I. Peters and P. H. Ribbe, J. Amer. Ceram. Soc. 44, 491 (1961).
4. C. W. Kanolt, Bull. Bur. Std. 10, 295 (1914); J. Wash. Acad. Sci. 3, 315 (1913).
5. S. J. Schneider, U.S. Natl. Bur. Std. Monograph 68, 1963.
6. K. K. Kelley, U.S. Bur. Mines Bull. 393, 1936.
7. F. Ebert and E. Cohn, Z. Anorg. Allgem. Chem. 213, 321 (1933).
8. T. Noguchi, Advan. High Temp. Chem. 2, 235 (1969).
9. N. A. Toropov, V. P. Barzakovskii, V. A. Lapin and N. N. Kurtseva, "Handbook of Phase Diagrams of Silicate Systems, Vol. I, Binary Systems," Second revised edition (1969), English transl. (avail. NTIS), Israel Program for Scientific Translations, Jerusalem, 1972.
10. E. M. Levin, C. R. Robbins and H. F. McMurdie, "Phase Diagrams for Ceramists," Third edition and 1969 Supplement, The American Ceramic Society, Columbus, Ohio, 1964 and 1969.
11. C. B. Alcock and M. Peleg, Trans. Brit. Ceram. Soc. 66, 217 (1967); High Temp. Sci. 6, 52 (1974); Bull. Soc. Fr. Ceram. 72, 25 (1966).
12. W. Kroenert, Glas-Email-Keramo-Tech. 23, 319 (1972).
13. A. G. Karaulov et al., Refractories (USSR) 1971, No. 2, 121.
14. R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 23, 1347 (1955).
15. R. L. Altman, J. Phys. Chem. 67, 366 (1963).
16. C. A. Alexander, J. S. Ogden and A. Levy, J. Chem. Phys. 39, 3057 (1963).

Magnesium Oxide (MgO) MgO

(Ideal Gas) GFW = 40.3044

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.129	14.004	14.004	INFINITE
100	6.961	43.110	57.452	-1.434	14.198	12.184	-26.629
200	7.198	47.983	51.632	-.730	13.993	10.124	-11.063
298	7.689	50.946	50.946	.000	13.900	8.346	-6.117
300	7.699	50.993	50.946	.014	13.897	8.311	-6.055
400	8.313	53.288	51.255	.813	13.726	6.475	-3.538
500	9.186	55.231	51.859	1.686	13.591	4.680	-2.046
600	10.296	57.002	52.571	2.659	13.518	2.904	-1.058
700	11.421	58.675	53.324	3.745	13.522	1.137	-.355
800	12.323	60.262	54.093	4.935	13.588	-.637	.174
900	12.880	61.749	54.862	6.198	13.683	-2.421	.588
1000	13.096	63.120	55.620	7.500	11.652	-4.033	.881
1100	13.051	64.368	56.360	8.809	11.740	-5.608	1.114
1200	12.841	65.496	57.075	10.105	11.785	-7.187	1.309
1300	12.547	66.512	57.763	11.374	11.773	-8.768	1.474
1400	12.222	67.430	58.421	12.613	-18.665	-9.866	1.540
1500	11.903	68.262	59.050	13.819	-18.391	-9.247	1.347
1600	11.605	69.021	59.649	14.994	-18.151	-8.647	1.181
1700	11.338	69.716	60.221	16.141	-17.942	-8.058	1.036
1800	11.103	70.358	60.767	17.263	-17.762	-7.482	.908
1900	10.898	70.952	61.288	18.363	-17.606	-6.916	.795
2000	10.722	71.507	61.785	19.444	-17.472	-6.357	.695
2100	10.571	72.026	62.260	20.508	-17.357	-5.805	.604
2200	10.442	72.515	62.715	21.558	-17.260	-5.256	.522
2300	10.332	72.976	63.152	22.597	-17.176	-4.712	.448
2400	10.239	73.414	63.570	23.625	-17.106	-4.172	.380
2500	10.160	73.830	63.972	24.645	-17.048	-3.636	.318
2600	10.093	74.228	64.359	25.658	-16.999	-3.098	.260
2700	10.036	74.607	64.732	26.664	-16.961	-2.565	.208
2800	9.989	74.972	65.091	27.665	-16.930	-2.034	.159
2900	9.950	75.321	65.438	28.662	-16.907	-1.500	.113
3000	9.917	75.658	65.773	29.656	-16.892	-.970	.071
3100	9.890	75.983	66.097	30.646	-16.884	-.439	.031
3200	9.869	76.296	66.411	31.634	-16.882	.090	-.006
3300	9.852	76.600	66.715	32.620	-16.886	.620	-.041
3400	9.839	76.894	67.010	33.604	-16.897	1.153	-.074
3500	9.830	77.179	67.297	34.588	-16.913	1.681	-.105
3600	9.824	77.456	67.575	35.570	-16.937	2.215	-.134
3700	9.821	77.725	67.846	36.553	-16.966	2.748	-.162
3800	9.821	77.987	68.109	37.535	-17.002	3.282	-.189
3900	9.823	78.242	68.366	38.517	-17.044	3.812	-.214
4000	9.827	78.491	68.616	39.499	-17.093	4.349	-.238
4100	9.834	78.733	68.860	40.482	-17.151	4.886	-.260
4200	9.842	78.970	69.097	41.466	-17.215	5.422	-.282
4300	9.852	79.202	69.330	42.451	-17.287	5.963	-.303
4400	9.864	79.429	69.557	43.436	-17.367	6.505	-.323
4500	9.878	79.650	69.779	44.424	-17.455	7.050	-.342
4600	9.893	79.868	69.996	45.412	-17.552	7.598	-.361
4700	9.910	80.081	70.208	46.402	-17.658	8.145	-.379
4800	9.928	80.290	70.416	47.394	-17.773	8.696	-.396
4900	9.948	80.494	70.619	48.388	-17.898	9.246	-.412
5000	9.969	80.696	70.819	49.384	-18.033	9.802	-.428
5100	9.991	80.893	71.014	50.382	-18.178	10.358	-.444
5200	10.014	81.087	71.206	51.382	-18.334	10.919	-.459
5300	10.039	81.278	71.395	52.385	-18.500	11.488	-.474
5400	10.065	81.466	71.579	53.390	-18.677	12.050	-.488
5500	10.092	81.651	71.761	54.398	-18.866	12.623	-.502
5600	10.120	81.833	71.939	55.408	-19.067	13.195	-.515
5700	10.150	82.013	72.114	56.422	-19.280	13.776	-.528
5800	10.180	82.190	72.286	57.438	-19.505	14.356	-.541
5900	10.211	82.364	72.456	58.458	-19.743	14.944	-.554
6000	10.244	82.536	72.622	59.481	-19.994	15.531	-.566

Dec. 31, 1960; Dec. 31, 1965; Dec. 31, 1974

MAGNESIUM OXIDE (MgO) (IDEAL GAS) GFW = 40.3044

Symmetry Number = 1

$S^\circ_{298.15}$ = 50.946 ± 0.8 gibbs/mol

ΔHf°_0 = 14.0 ± 6 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 13.9 ± 6 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	1.749	0.5743	0.0050	785.1	5.18
(2-7)	$^3\Pi$	[2300]	6	[1.864]	[0.5050]	[0.0040]	[664.4]	[3.9]
(1)	$A^1\Pi$	3503.3	2	1.864	0.5050	0.0040	664.4	3.9
(2-5)	$^3\Sigma^+$	[14000]	3	[1.737]	[0.5822]	[0.0045]	[824.1]	[4.8]
(1)	$B^1\Sigma^+$	20004.	1	1.737	0.5822	0.0045	824.1	4.76
(4, 3)	$^3\Sigma^+$	[28000]	3	[1.872]	[0.501]	[0.0048]	[632.5]	[5.3]
(4, 3)	$^3\Delta$	[29000]	6	[1.872]	[0.501]	[0.0048]	[632.5]	[5.3]
(1, 8, 9)	$D^1\Delta$	29775.	2	1.872	0.5014	0.0048	632.5	5.3
(4, 3)	$^3\Sigma^-$	[30000]	3	[1.872]	[0.501]	[0.0048]	[632.5]	[5.3]
(1)	$C^1\Sigma^-$	30004.	1	1.873	0.5008	0.0048	632.4	5.2
(10, 3, 4)	$E^1\Sigma^+$	37684.	1	1.825	0.5273	[0.0048]	[632.4]	[5.2]
(4, 3)	$^3\Pi$	[37000]	6	[1.768]	[0.5615]	[0.005]	[710]	[5.]
(10, 3, 4)	$F^1\Pi$	37879.	2	1.768	0.5615	[0.005]	710	[5.]
(4, 3)	$^3\Pi$	[39000]	6	[1.83]	[0.5249]	[0.005]	[790]	[5.]
(10, 3, 4)	$G^1\Pi$	39868.	2	1.83	0.5249	[0.005]	790	[5.]

Heat of Formation

We adopt D°_0 = 80 ± 6 kcal/mol and ΔHf°_{298} = 13.9 ± 6 kcal/mol based on equilibria analyzed below. Greatest weight is given to mass-spectrometric data (11) for reactions A and B. We give "<" or ">" for ΔH° and D°_0 values which may have a systematic bias. The JANAF difference in ΔHf°_{298} for WO_3-WO_2 (3) may be biased by as much as -3.5 kcal/mol, leading to a positive bias in D°_0 from reaction B. Mass spectra (12) and transpiration data (13) yield an upper limit to D°_0; we neglect $Mg(OH)_2$ and MgOH which probably are important in (13). Cotton and Jenkins (15) concluded that hydroxides were negligible in their H_2-O_2-N_2 flames; we doubt this conclusion and presume that reaction D yields an upper limit to D°_0. Our adopted value is comparable with those of Richards et al. (7, 1) and Brewer & Rosenblatt (16), considering the difference in functions for MgO.

Other published values of D°_0 are dismissed for reasons cited in critical reviews (17, 18, 11). Schofield's criticism (17) of flame studies is supported by new evidence for importance of hydroxides (3, CaO, g). Inadequate allowance for hydroxides *may bias a recent flame result of* D°_0 *= 88 ± 2.3 kcal/mol (19); furthermore, we cannot confirm this* D°_0 *from the published information.* D°_0 = 83 kcal/mol was derived (20) by fitting an electronegativity potential function to $X^1\Sigma$. This state is predicted *(18, 4, 11) to dissociate to excited state* $O(^1D)$ *at 45.4 kcal/mol. Theoretical calculations (21)* support this prediction. Linear Birge-Sponer extrapolation yields a very low estimate for D°_0, just as it does for the alkali halides (18), unless $X^1\Sigma$ fails to dissociate to $O(^1D)$ as predicted.

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} kcal/mol	D°_0 kcal/mol
(11)Drowart(1964)	Knudsen mass spec.	A	2026-2274	8	-13±5	12±11	39.5±3	15.3	78.6±3
	Knudsen mass spec.	B	2106-2225	6	-18±8	23±16	63.1±3	≥10.1	≤83.8±5
(12)Porter(1955)	Knudsen mass spec.	C	1950	1	-	-	>148.7	>5.0	<88.9±5
(13)Alexander(1963)	Transpiration	C	1780-2010	7	-8±3	132±5	>148.3±2	>4.7	<89.2±2
(14)Altman(1963)	Transpiration	C	2033-2175	8	-52±32	53±68	162.8±8	19.1	74.7±8
(15)Cotton(1969)	Flame spec.	D	1570-2370	4	-9±1	-11±2	>5.7±6	>-1.6	<95.4±6

[a] Reactions: *A)* $Mg(g)+O_2(g) = MgO(g)+O(g)$; *B)* $Mg(g)+WO_3(g) = MgO(g)+WO_2(g)$; *C)* $MgO(c) = MgO(g)$; *D)* $Mg(g)+OH(g) = MgO(g)+H(g)$.

[b] $\delta S = \Delta Sr^\circ$(2nd Law) − ΔSr°(3rd Law).

Heat Capacity and Entropy

Electronic levels (T_o) and vibrational-rotational constants of observed states are from Rosen (1) and other recent sources (8-10). States are listed in the isoconfigurational order given by Schamps and Lefebvre-Brion (4). Designations (3) of the new E, F and G states are based on theoretical calculations (4). Field (2) concluded that calculations (4-6) of the isoconfigurational $A^1\Pi$-$^3\Pi$ separation should be adequate for estimating the low-lying $^3\Pi$ state. The other potentially low-lying state ($^3\Sigma^+$) is estimated (4) similarly from isoconfigurational $B^1\Sigma^+$. Higher estimated levels are also based on calculations (4). Vibrational-rotational constants are estimated in isoconfigurational groups by comparison with BeO, CaO, SrO and BaO (3). Low-lying levels and their vibrational-rotational constants cause marked changes in the thermodynamic functions, which are calculated using first-order anharmonic corrections to Q^i_r and Q^i_v in the partition function $Q = Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2\varepsilon_i/T)$.

References

1. B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970, p. 255.
2. R. W. Field, J. Chem. Phys. 60, 2400 (1974).
3. JANAF Thermochemical Tables: MgO(g), BeO(g), CaO(g) 12-31-74; SrO(g), BaO(g) 6-30-74; WO_2(g), WO_3(g) 9-30-66.
4. J. Schamps and H. Lefebvre-Brion, J. Chem. Phys. 56, 573 (1972).
5. B. Huron and P. Rancurel, Chem. Phys. Lett. 13, 515 (1972).
6. W. M. Huo, K. F. Freed and W. Klemperer, J. Chem. Phys. 46, 3556 (1967).
7. W. G. Richards, G. Verhaegen and C. M. Moser, J. Chem. Phys. 45, 3226 (1966).
8. D. W. Green, Ph.D. Thesis, Univ. California, Berkeley, UCRL-17878-Rev., 1968.
9. J. Schamps, G. Gandara and M. Becart, Can. Spectrosc. 14, 13 (1969).
10. M. Singh, J. Phys. B4, 565 (1971); B6, 1339, 1917 (1973).
11. J. Drowart, G. Exsteen and G. Verhaegen, Trans. Faraday Soc. 60, 1920 (1964).
12. R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 23, 1347 (1955).
13. C. A. Alexander, J. S. Ogden and A. Levy, J. Chem. Phys. 39, 3057 (1963).
14. R. L. Altman, J. Phys. Chem. 67, 366 (1963).
15. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 65, 376 (1969).
16. L. Brewer and G. Rosenblatt, Advan. High Temp. Chem. 2, 1 (1969).
17. K. Schofield, Chem. Rev. 67, 707 (1967).
18. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall Ltd., London, 1968, pp. 236-244, 109.
19. P. J. T. Zeegers, W. P. Townsend and J. D. Winefordner, Spectrochim. Acta 24B, 243 (1969).
20. B. Rai and S. N. Rai, Indian J. Pure Appl. Phys. 10, 401 (1972).
21. N. J. Stag and W. G. Richards, Mol. Phys. 27, 787 (1974).

Dimagnesium (Mg_2)

(Ideal Gas) GFW = 48.610

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	.000	.000	INFINITE	- 2.466	68.836	68.836	INFINITE
100	8.860	49.139	65.483	- 1.634	69.360	64.900	- 141.839
200	8.206	55.120	58.998	- .776	69.094	60.284	- 65.875
298	7.658	58.282	58.282	.000	68.910	56.193	- 41.190
300	7.651	58.330	58.282	.014	68.902	56.114	- 40.879
400	7.376	60.489	58.579	.764	68.424	51.919	- 28.367
500	7.233	62.118	59.130	1.494	67.870	47.858	- 20.919
600	7.151	63.428	59.741	2.212	67.250	43.910	- 15.994
700	7.100	64.527	60.348	2.925	66.577	40.075	- 12.512
800	7.066	65.472	60.931	3.633	65.835	36.337	- 9.927
900	7.043	66.303	61.483	4.338	65.018	32.698	- 7.940
1000	7.026	67.044	62.002	5.042	59.884	29.518	- 6.451
1100	7.014	67.713	62.492	5.744	58.982	26.522	- 5.269
1200	7.005	68.323	62.953	6.445	58.029	23.611	- 4.300
1300	6.997	68.884	63.387	7.145	57.023	20.785	- 3.494
1400	6.991	69.402	63.799	7.844	- 4.766	18.995	- 2.965
1500	6.987	69.884	64.189	8.543	- 5.061	20.703	- 3.016
1600	6.983	70.335	64.559	9.242	- 5.356	22.428	- 3.064
1700	6.980	70.758	64.911	9.940	- 5.652	24.176	- 3.108
1800	6.977	71.157	65.247	10.638	- 5.948	25.939	- 3.149
1900	6.975	71.534	65.568	11.335	- 6.243	27.718	- 3.188
2000	6.973	71.892	65.875	12.032	- 6.540	29.513	- 3.225
2100	6.971	72.232	66.170	12.730	- 6.836	31.321	- 3.260
2200	6.970	72.556	66.453	13.427	- 7.133	33.148	- 3.293
2300	6.969	72.866	66.725	14.124	- 7.430	34.986	- 3.324
2400	6.967	73.163	66.987	14.820	- 7.728	36.834	- 3.354
2500	6.967	73.447	67.240	15.517	- 8.027	38.696	- 3.383
2600	6.966	73.720	67.484	16.214	- 8.326	40.574	- 3.411
2700	6.965	73.983	67.720	16.910	- 8.628	42.459	- 3.437
2800	6.965	74.236	67.948	17.607	- 8.929	44.354	- 3.462
2900	6.964	74.481	68.169	18.303	- 9.233	46.265	- 3.487
3000	6.964	74.717	68.384	19.000	- 9.540	48.183	- 3.510
3100	6.964	74.945	68.592	19.696	- 9.850	50.113	- 3.533
3200	6.964	75.166	68.794	20.392	- 10.164	52.050	- 3.555
3300	6.965	75.381	68.990	21.089	- 10.481	53.999	- 3.576
3400	6.965	75.589	69.181	21.785	- 10.805	55.963	- 3.597
3500	6.966	75.790	69.367	22.482	- 11.134	57.927	- 3.617
3600	6.967	75.987	69.548	23.179	- 11.471	59.907	- 3.637
3700	6.968	76.178	69.725	23.875	- 11.817	61.896	- 3.656
3800	6.970	76.363	69.897	24.572	- 12.170	63.893	- 3.675
3900	6.972	76.545	70.065	25.269	- 12.533	65.894	- 3.693
4000	6.974	76.721	70.229	25.967	- 12.907	67.913	- 3.711
4100	6.977	76.893	70.390	26.664	- 13.296	69.937	- 3.728
4200	6.980	77.061	70.547	27.362	- 13.696	71.970	- 3.745
4300	6.984	77.226	70.700	28.060	- 14.112	74.014	- 3.762
4400	6.987	77.386	70.850	28.759	- 14.541	76.071	- 3.778
4500	6.992	77.543	70.997	29.458	- 14.988	78.138	- 3.795
4600	6.996	77.697	71.141	30.157	- 15.453	80.213	- 3.811
4700	7.002	77.848	71.282	30.857	- 15.935	82.297	- 3.827
4800	7.007	77.995	71.421	31.557	- 16.439	84.395	- 3.843
4900	7.013	78.140	71.556	32.258	- 16.962	86.499	- 3.858
5000	7.020	78.281	71.689	32.960	- 17.506	88.617	- 3.873
5100	7.027	78.421	71.820	33.662	- 18.074	90.738	- 3.888
5200	7.034	78.557	71.948	34.365	- 18.665	92.881	- 3.904
5300	7.042	78.691	72.074	35.069	- 19.279	95.037	- 3.919
5400	7.050	78.823	72.198	35.774	- 19.918	97.193	- 3.934
5500	7.059	78.952	72.320	36.479	- 20.585	99.369	- 3.949
5600	7.068	79.080	72.439	37.186	- 21.278	101.555	- 3.963
5700	7.077	79.205	72.557	37.893	- 21.999	103.762	- 3.978
5800	7.087	79.328	72.672	38.601	- 22.749	105.966	- 3.993
5900	7.097	79.449	72.786	39.310	- 23.530	106.199	- 4.008
6000	7.108	79.568	72.898	40.021	- 24.339	110.430	- 4.022

Dec. 31, 1974

DIMAGNESIUM (Mg_2) (IDEAL GAS) GFW = 48.610

Ground State Configuration $^1\Sigma_g^+$

$S^\circ_{298.15}$ = 58.28 ± 0.1 gibbs/mol

ΔHf°_0 = 68.84 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 68.91 ± 0.5 kcal/mol

Energy Levels and Quantum Weight

State	ε_i, cm^{-1}	g_i
X $^1\Sigma_g^+$	0	1
A $^1\Sigma_u^+$	26068	1

The contribution of the ground state vibrational levels is approximated by direct summation of the following levels (in cm^{-1}): 24.97, 72.56, 117.02, 158.55, 197.26, 233.31, 266.87, 298.10, 327.21, 354.42, 379.93, and 404.00.

ω_e = 50.75 cm^{-1} $\omega_e x_e$ = 1.62 cm^{-1} σ = 2

B_e = 0.091619 cm^{-1} α_e = 0.003702 cm^{-1} r_e = 3.8915 Å

Heat of Formation

Balfour and Douglas (10) have examined the absorption spectrum of the Mg_2 molecule. The dissociation energy, D_0°, was determined to be 399 cm^{-1} (1.14 kcal/mol) by extrapolating the ground state vibrational levels to the dissociation limit. The vibrational levels were observed to within 25 cm^{-1} of the limit. Balfour and Douglas (10) stated that they believed the dissociation energy was in error by less than ± 5 cm^{-1}. Using an accurate RKR potential (Rydberg-Klein-Rhee) and a calculated van der Waals constant C_6 for the ground state of Mg_2, Stwalley (11) calculated an improved dissociation energy, D_0° = 403.7 ± 0.7 cm^{-1} (1.154±0.002 kcal/mol). We adopt this latter value, D_0° = 1.154 ± 0.002 kcal/mol, which corresponds to ΔHf°_{298}(Mg_2, g) = 69.360 ± 0.020 kcal/mol, using auxiliary JANAF data (20).

A linear Birge-Sponer extrapolation using the ω_e and $\omega_e x_e$ values tabulated above yields D_0° = 1.064 kcal/mol. As expected this is in good agreement with the adopted value. The Mg_2 gas phase spectrum had been reported previously in emission by Hamada (1, 2) and Strukov (3) and in absorption by Sthapitanonda (4), Soulen et al. (5), and Weniger (8). Based on their spectroscopic studies, Hamada (1, 2) and Soulen et al. (5) reported rough dissociation energy values of 6.92 kcal/mol and 72 ± 0.2 kcal/mol, respectively. The latter value was quoted by Verhaegen et al (7). Balfour and Douglas (10) postulate that Soulen et al (5) were observing transitions from the ground state to a $^1\pi_u$ state.

Brewer (6) tabulated a value of ΔHs°_{298} = 63.4 ± 7 kcal/mol for the process 2 Mg(c) = Mg_2(g). Mellor (9) calculated a *value of 59.2 ± 4.4 kcal/mol for the same process. This latter calculation was based on Lennard-Jones potential parameters* which were estimated via approximate relations based on pVT data for gases. These ΔHs°_{298} values are actually ΔHf°_{298} values for Mg_2(g). Additional comments on this work are given by Ewing and Mellor (12), Brett and Balfour (13), and Mellor (14).

Additional comments on the RKR potential calculations or the van der Waals nature of Mg_2 are given by Stwalley (15), Brett and Chan (17), and Balfour and Whitlock (18).

Heat Capacity and Entropy

The molecular data are from Balfour and Douglas (10) with adjustments being made for the natural abundances of the isotopes. They measured the absorption spectrum of the $^{24}Mg_2$ molecule in a furnace containing Mg vapor at 700-850°C. The observed bands corresponded to a $^1\Sigma$-$^1\Sigma$ transition between a very weakly bound ground state and a more stable excited state. The original value of r_e as reported by Balfour and Douglas (10) was in error. The corrected value is given by Stwalley (11). Treatment of Mg_2(g) as an harmonic oscillator or an anharmonic oscillator gives heat capacity values which appear unreasonably large (~50 gibbs/mol at 6000 K). Thus the heat capacity values are generated using a summation over thirteen vibrational levels of the ground state.

Brewer and Wang (16) synthesized the Mg_2 *molecule in solid rare-gas (Kr, Ar) matrices at 20 K. Their results are* consistent with those of Balfour and Douglas (10). Jensen (19) also studied matrix-isolated Mg_2 and presented comments on the study by Brewer and Wang (16).

References

1. H. Hamada, Nature 127, 555 (1931)
2. H. Hamada, Phil. Mag. 12, 50 (1931)
3. V. S. Strukov, Opt. Spectrosc. (USSR) 14, 184 (1963).
4. P. Sthapitanonda, Ph.D. Thesis, University of Wisconsin, 1955.
5. J. R. Soulen, P. Sthapitanonda, and J. L. Margrave, J. Phys. Chem. 59, 132 (1955).
6. L. Brewer, UCRL-2854, February, 1955.
7. G. Verhaegen, F. E. Stafford, P. Goldfinger, and M. Ackerman, Trans. Faraday Soc. 58, 1926 (1962).
8. S. Weniger, J. Phys. (Paris) 25, 946 (1964).
9. A. M. Mellor, J. Chem. Phys. 51, 1678 (1969).
10. W. J. Balfour and A. E. Douglas, Can. J. Phys. 48, 901 (1970).
11. W. C. Stwalley, Chem. Phys. Letters 7, 600 (1970).
12. R. H. Ewing and A. M. Mellor, J. Chem. Phys. 53, 2983 (1970).
13. A. C. Brett and W. J. Balfour, J. Chem. Phys. 54, 3240 (1971).
14. A. M. Mellor, J. Chem. Phys. 54, 3241 (1971).
15. W. C. Stwalley, J. Chem. Phys. 54, 4517 (1971).
16. L. Brewer and J. L. F. Wang, J. Mol. Spectrosc. 40, 95 (1971).
17. A. C. Brett and C. Chan, Can. J. Phys. 50, 1587 (1972).
18. W. J. Balfour and R. F. Whitlock, Can. J. Phys. 50, 1648 (1972).
19. D. D. Jensen, J. Mol. Spectrosc. 43, 472 (1972).
20. JANAF Thermochemical Tables: Mg(g), 9-30-62.