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M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker

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JANAF Thermochemical Tables, 1974 Supplement

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The thermodynamic tabulations previously published as NSRDS-NBS-37 are extended by 154 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.

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1. Introduction

The Joint-Army-Navy-Air Force (JANAF) Thermochemical Tables project has been conducted at The Dow Chemical Company since late 1959. Since the inception of this JANAF project, the tables have been collected together to form five publications [1-5]. NSRDS-NBS-37 [1], which supercedes the four earlier publications [2-5], includes all work through June 30, 1970. The earlier publications [2-5] are now out of print. Tables generated in the period June 30, 1970 to June 30, 1972 are combined in this article to provide 154 additional tables of data which may be used in conjunction with NSRDS-NBS-37 [1].

As of June 30, 1972, there are 1154 tabulations involving 31 elements and their simple compounds. The compounds are principally those with the halogens, oxygen, and hydrogen. The 31 elements include H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, Co, Cu, Br, Sr, Zr, Mo, I, Cs, Ba, W, Hg, and Pb.

The JANAF Thermochemical Tables are prepared following the procedures outlined in NSRDS-NBS-37. Note that 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. Even with internal and external reviews however, some minor discrepancies do arise. In addition, changes in the nomenclature as adopted by Chemical Abstracts leave the tables with some outdated chemical names. Changes in the atomic weights and the temperature scale also cause minor internal inconsistencies. At present we are maintaining the nomenclature within the tables while gradually converting 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. Unfortunately, some of the tables in this article were prepared prior to our adoption of these newer scales. 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 calorie per degree-mole. These units can be converted to SI units of joules per degree-mole by multiplying the tabulated value by 4.184. Similarly, values in kilocalories per mole can be converted to kilojoules per mole by multiplying by the same factor. In addition, vibrational frequencies are expressed in their wavenumber (cm^{-1}) equivalents; frequencies in Hz can be obtained by multiplying by c expressed in centimeters per second.

Two indices are provided in this article. The index in section 4 lists the tables which appear in this article. The list is alphabetical by name. Where applicable, the appropriate cross reference for the currently accepted Chemical Abstracts name is also included. The index in section 5 is the complete index for the JANAF Thermochemical Tables. This complete index lists tables which are in NSRDS-NBS-37 [1] and tables which are in this article (the latter indicated by an ' * ' or ' * * '). It should be emphasized that the tables in this article may be new (in which case there is no corresponding entry in NSRDS-NBS-37) or revised (in which case the table in this article supercedes the corresponding table in NSRDS-NBS-37). In both in-

* Deceased.

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dices, new tables are indicated by '* * *'. 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

Under the sponsorship of the U. S. Air Force Office of Scientific Research (Contract F44620-70-C-0104), the JANAF project has been monitored by Dr. Joseph F. Masi. His cooperation and direction is 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 is currently the project director with the principal contributors being Alan N. Syverud, Jerry L. Curnutt and Richard A. McDonald. We thank the staff of DIG Computation Research of The Dow Chemical Company for their assistance in the production of these tables, with special thanks to Mary Jane Walter and Joan Weldon.

3. References

[1] JANAF Thermochemical Tables, 2nd Edition, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37, 1141 pages (June 1971).
[2] JANAF Thermochemical Tables, PB 168370, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1965.
[3] JANAF Thermochemical Tables, PB 168370-1, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1966.
[4] JANAF Thermochemical Tables, PB 168370-2, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1967.
[5] JANAF Thermochemical Tables, PB 16870-3, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1968.

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5. Complete List of JANAF Thermochemical Tables

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Al	Aluminum (ℓ)
Al	Aluminum, Monatomic (g)
Al^+	Aluminum Unipositive Ion (g)
$AlBO_2$	Aluminum Boron Dioxide (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 Unipositive Ion (g)
AlClF	Aluminum Chlorofluoride (g)
$AlClF_2$	Aluminum Chlorodifluoride (g)
AlClO	Aluminum Oxychloride (c)
AlClO	Aluminum Oxychloride (g)
$AlCl_2$	*Aluminum Dichloride (g)
$AlCl_2^+$	*Aluminum Dichloride Unipositive Ion (g)
$AlCl_2^-$	*Aluminum Dichloride Uninegative Ion (g)
$AlCl_2F$	Aluminum Dichlorofluoride (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 Unipositive Ion (g)
AlFO	Aluminum Oxyfluoride (g)
AlF_2	*Aluminum Difluoride (g)
AlF_2^+	*Aluminum Difluoride Unipositive Ion (g)
AlF_2^-	*Aluminum Difluoride Uninegative Ion (g)
AlF_3	Aluminum Trifluoride (c)
AlF_3	Aluminum Trifluoride (g)
AlF_4Li	Lithium Tetrafluoroaluminate (g)
AlF_4Na	Sodium Tetrafluoroaluminate (g)
AlF_6K_3	Tripotassium Hexafluoroaluminate (c)
AlF_6Li_3	Trilithium Hexafluoroaluminate (c)
AlF_6Li_3	Trilithium Hexafluoroaluminate (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 Monohydroxide Unipositive Ion (g)
$AlHO^-$	Aluminum Monohydroxide Uninegative Ion (g)
$AlHO_2$	Aluminum Dioxyhydride (g)
AlH_4Li	Lithium Aluminum Hydride (c)
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 Unipositive Ion (g)
AlO_2	Aluminum Dioxide (g)
AlO_2^-	Aluminum Dioxide Uninegative 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, Dimer (g)
$Al_2Cl_9K_3$	Potassium Nonachloroaluminate (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^+	*Dialuminum Monoxide Unipositive Ion (g)
Al_2O_2	Aluminum Monoxide, Dimeric (g)
$Al_2O_2^+$	Dialuminum Dioxide Unipositive Ion (g)
Al_2O_3	*Aluminum Oxide (c, alpha)
Al_2O_3	*Aluminum Oxide (c, gamma)
Al_2O_3	*Aluminum Oxide (ℓ)
Al_2O_5Si	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 Unipositive Ion (g)
$BBeO_2$	Beryllium Boron Dioxide (g)
BBr	Boron Monobromide (g)
BBrCl	Boron Bromide Chloride (g)
$BBrCl_2$	Boron Bromide Dichloride (g)
BBrF	Boron Bromide Fluoride (g)
$BBrF_2$	Boron Bromide Difluoride (g)
BBrO	Boron Oxide Bromide (g)
BBr_2	Boron Dibromide (g)

Filing Order	Table Title
BBr_2Cl	Boron Dibromide Chloride (g)
BBr_2F	Boron Dibromide Fluoride (g)
BBr_2H	Boron Dibromide Hydride (g)
BBr_3	Boron Tribromide (ℓ)
BBr_3	Boron Tribromide (g)
BCl	Boron Monochloride (g)
BCl^+	Boron Monochloride Unipositive Ion (g)
BClF	Boron Chloride Fluoride (g)
$BClF_2$	Boron Chloride Difluoride (g)
BClO	Boron Oxide Chloride (g)
BCl_2	*Boron Dichloride (g)
BCl_2^+	*Boron Dichloride Unipositive Ion (g)
BCl_2^-	*Boron Dichloride Uninegative Ion (g)
BCl_2F	Boron Dichloride Fluoride (g)
BCl_2H	Boron Dichloride Hydride (g)
BCl_3	Boron Trichloride (g)
BF	Boron Monofluoride (g)
BFO	Boron Oxide Fluoride (g)
BF_2	*Boron Difluoride (g)
BF_2^+	*Boron Difluoride Unipositive Ion (g)
BF_2^-	*Boron Difluoride Uninegative Ion (g)
BF_2H	Difluoroborane (g)
BF_2HO	Boron Hydroxide Difluoride (g)
BF_2O	Boron Oxide Difluoride (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 Oxide Hydride (g)
BHO^+	Boron Oxide Hydride Unipositive Ion (g)
BHO_2	Metaboric Acid (c)
BHO_2	Metaboric Acid (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 Tetrahydroborate (c)
BH_4Li	Lithium Tetrahydroborate (c)
BH_4Na	Sodium Tetrahydroborate (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)
BN	Boron Nitride (g)
$BNaO_2$	*Sodium Metaborate (c)
$BNaO_2$	*Sodium Metaborate (ℓ)
$BNaO_2$	*Sodium Metaborate (g)
BO	Boron Monoxide (g)
BO_2	Boron Dioxide (g)
BO_2^-	Boron Dioxide Uninegative Ion (g)
BS	*Boron Monosulfide (g)
BTi	Titanium Monoboride (c)
B_2	Boron, Diatomic (g)
B_2BeO_4	Beryllium Diborate (g)
$B_2Be_3O_6$	Triberyllium Diborate (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 Oxide Chloride, Trimeric (g)
$B_3FH_2O_3$	Monofluoroboroxin (g)
$B_3F_2HO_3$	Difluoroboroxin (g)
$B_3F_3O_3$	Boron Oxide Fluoride, Trimeric (c)
$B_3F_3O_3$	Boron Oxide Fluoride, Trimeric (g)
$B_3H_3O_3$	Boroxin (c)
$B_3H_3O_3$	Boroxin (g)
$B_3H_3O_6$	Metaboric Acid, Trimeric (g)
$B_3H_6N_3$	Borazine (g)
$B_4K_2O_7$	Dipotassium Tetraboron Heptaoxide (c)
$B_4K_2O_7$	Dipotassium Tetraboron Heptaoxide (ℓ)
$B_4Li_2O_7$	Dilithium Tetraborate (c)
$B_4Li_2O_7$	Dilithium Tetraborate (ℓ)
B_4Mg	Magnesium Tetraboride (c)
$B_4Na_2O_7$	Disodium Tetraborate (c)
$B_4Na_2O_7$	Disodium Tetraborate (ℓ)
B_4O_7Pb	Lead Tetraborate (c)
B_5H_9	Pentaborane (ℓ)
B_5H_9	Pentaborane (g)
$B_6K_2O_{10}$	Dipotassium Hexaborate (c)

Filing Order	Table Title
$B_6Li_2O_{10}$	Dilithium Hexaborate (c)
$B_6Na_2O_{10}$	Disodium Hexaborate (c)
$B_6O_{10}Pb$	Lead Hexaborate (c)
$B_8K_2O_{13}$	Dipotassium Octaborate (c)
$B_8K_2O_{13}$	Dipotassium Octaborate (ℓ)
$B_8Li_2O_{13}$	Dilithium Octaborate (c)
$B_{10}H_{14}$	Decaborane (c)
$B_{10}H_{14}$	Decaborane (ℓ)
$B_{10}H_{14}$	Decaborane (g)
$B_{10}O_{17}Pb_2$	Dilead Decaborate (c)
Ba	**Barium (ref. st.)
Ba	**Barium (c)
Ba	**Barium (ℓ)
Ba	**Barium (g)
Be	Beryllium (ref. st.)
Be	Beryllium (c)
Be	Beryllium (ℓ)
Be	Beryllium (g)
Be^+	Beryllium Unipositive 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 Unipositive Ion (g)
BeClF	Beryllium Chloride Fluoride (g)
$BeCl_2$	Beryllium Dichloride (c,α)
$BeCl_2$	Beryllium Dichloride (c,β)
$BeCl_2$	Beryllium Dichloride (ℓ)
$BeCl_2$	Beryllium Dichloride (g)
BeF	*Beryllium Monofluoride (g)
BeF_2	Beryllium Difluoride (c)
BeF_2	Beryllium Difluoride (ℓ)
BeF_2	Beryllium Difluoride (g)
BeF_3Li	*Lithium Trifluoroberyllate (c)
BeF_3Li	**Lithium Trifluoroberyllate (ℓ)
BeF_3Li	Lithium Beryllium Fluoride (g)
BeF_4Li_2	*Dilithium Tetrafluoroberyllate (c)
BeF_4Li_2	*Dilithium Tetrafluoroberyllate (ℓ)
BeH	Beryllium Monohydride (g)
BeH^+	Beryllium Monohydride Unipositive Ion (g)
BeHO	Beryllium Monohydroxide (g)
$BeHO^+$	Beryllium Monohydroxide Unipositive Ion (g)
BeH_2	Beryllium Dihydride (g)
BeH_2O_2	Beryllium Hydroxide (c,α)
BeH_2O_2	Beryllium Hydroxide (c, β)
BeH_2O_2	Beryllium Hydroxide (g)
BeI	Beryllium Monoiodide (g)
BeI_2	Beryllium Diiodide (c)

Filing Order	Table Title
BeI_2	Beryllium Diiodide (ℓ)
BeI_2	Beryllium Diiodide (g)
BeN	Beryllium Nitride (g)
BeO	*Beryllium Oxide (c,α)
BeO	*Beryllium Oxide (c,β)
BeO	*Beryllium Oxide (ℓ)
BeO	Beryllium Oxide (g)
BeO_4S	Beryllium Sulfate (c,α)
BeO_4S	Beryllium Sulfate (c,β)
BeO_4S	Beryllium Sulfate (c,γ)
BeO_4W	Beryllium Tungstate (c)
Be_2Cl_4	Beryllium Dichloride, Dimeric (g)
Be_2F_2O	Dilithium Oxide Difluoride (g)
Be_2O	Diberyllium Oxide (g)
Be_2O_2	Beryllium Oxide, Dimeric (g)
Be_2O_4Si	Beryllium Orthosilicate (c)
Be_3N_2	Beryllium Nitride (c,α)
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)
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	Mercurous Bromide (g)
BrI	Iodine Monobromide (g)
BrK	Potassium Bromide (c)
BrK	Potassium Bromide (ℓ)
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)
BrTi	Titanium Monobromide (g)
BrW	Tungsten Monobromide (g)
BrZr	Zirconium Monobromide (g)
Br_2	Bromine (ref. st.)
Br_2	Bromine (ℓ)
Br_2	Bromine, Diatomic (g)

Filing Order	Table Title
Br_2Fe	Iron Dibromide (c)
Br_2Fe	Iron Dibromide (ℓ)
Br_2Fe	Iron Dibromide (g)
Br_2Hg	Mercuric Bromide (c)
Br_2Hg	Mercuric Bromide (ℓ)
Br_2Hg	Mercuric Bromide (g)
Br_2Hg_2	Mercurous Bromide (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_2Na_2	Sodium Bromide, Dimeric (g)
Br_2Pb	Lead Dibromide (c)
Br_2Pb	Lead Dibromide (ℓ)
Br_2Pb	Lead 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)
Br_4Fe_2	Iron 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_5W	Tungsten Pentabromide (c)
Br_5W	Tungsten Pentabromide (ℓ)
Br_5W	Tungsten Pentabromide (g)
Br_6W	Tungsten Hexabromide (c)
Br_6W	Tungsten Hexabromide (g)
C	Carbon (ref. st., Graphite)
C	Carbon, Monatomic (g)
C^-	Carbon Uninegative Ion (g)
CAl	Aluminum Carbide (g)
CB	Boron Carbide (g)
CB_4	Boron Carbide (c)
CB_4	Boron Carbide (ℓ)
CBe_2	Beryllium Carbide (c)
CBe_2	Beryllium Carbide (ℓ)
CBr	Carbon Monobromide (g)
$CBrF_3$	Bromotrifluoromethane (g)
CBrN	Cyanogen Bromide (g)

Filing Order	Table Title
CBr_4	Carbon Tetrabromide (g)
CCl	Carbon Monochloride (g)
CClFO	Carbonyl Chlorofluoride (g)
$CClF_3$	Chlorotrifluoromethane (g)
CClN	Cyanogen Chloride (g)
CClO	Carbonyl Monochloride (g)
CCl_2	Carbon Dichloride (g)
CCl_2F_2	Dichlorodifluoromethane (g)
CCl_2O	Carbonyl Chloride (g)
CCl_3	Trichloromethyl (g)
CCl_3F	Trichlorofluoromethane (g)
CCl_4	Carbon Tetrachloride (g)
CCuN	**Cuprous Cyanide (c)
CF	Carbon Monofluoride (g)
CF^+	**Carbon Monofluoride Unipositive Ion (g)
CFN	Cyanogen Fluoride (g)
CFO	Carbonyl Monofluoride (g)
CF_2	Carbon Difluoride (g)
CF_2^+	**Carbon Difluoride Unipositive Ion (g)
CF_2O	Carbonyl Fluoride (g)
CF_3	Trifluoromethyl (g)
CF_3^+	**Trifluoromethyl Unipositive Ion (g)
CF_3I	Trifluoroiodomethane (g)
CF_4	Carbon Tetrafluoride (g)
CF_4O	Trifluoromethyl Hypofluorite (g)
CH	Methylidyne (g)
CH^+	**Methylidyne Unipositive Ion (g)
CHCl	Monochloromethylene (g)
$CHClF_2$	Chlorodifluoromethane (g)
$CHCl_2F$	Dichlorofluoromethane (g)
$CHCl_3$	Chloroform (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 Unipositive 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	*Methyl Chloride (g)
CH_3Cl_3Si	Trichloromethylsilane (g)
CH_3F	Fluoromethane (g)
CH_3F_3Si	Trifluoromethylsilane (g)
CH_4	Methane (g)
CIN	Cyanogen Iodide (g)

Filing Order	Table Title
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 Unipositive Ion (g)
CN^-	*Cyano Uninegative 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 Uninegative Ion (g)
CP	Carbon Phosphide (g)
CS	Carbon Monosulfide (g)
CS_2	Carbon Disulfide (g)
CSi	Silicon Carbide (c,α)
CSi	Silicon Carbide (c,β)
CSi	Silicon Carbide (ℓ)
CSi	Silicon Carbide (g)
CSi_2	Disilicon Carbide (g)
CTi	Titanium Carbide (c)
CTi	Titanium Carbide (ℓ)
CZr	Zirconium Carbide (c)
CZr	Zirconium Carbide (ℓ)
C_2	Carbon, Diatomic (g)
C_2^-	Dimeric Carbon Uninegative Ion (g)
C_2Be	Beryllium Carbide (g)
C_2Cl_2	Dichloroacetylene (g)
C_2Cl_4	Tetrachloroethylene (g)
C_2Cl_6	Hexachloroethane (g)
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)

Filing Order	Table Title
C_2Mg	Magnesium Carbide (c)
C_2N	CNC Radical
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, Trimeric (g)
C_3Al_4	Aluminum Carbide (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)
Ca	Calcium (ref. st.)
Ca	Calcium (α)
Ca	Calcium (β)
Ca	Calcium (ℓ)
Ca	Calcium (g)
Ca^+	**Calcium Unipositive Ion (g)
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 Unipositive Ion (g)
CaH_2O_2	**Calcium Hydroxide (c)
CaO	**Calcium Oxide (c)
CaO	**Calcium Oxide (ℓ)
CaS	**Calcium Sulfide (c)
Cl	**Chlorine, Monatomic (g)
Cl^+	Chlorine Unipositive Ion (g)
Cl^-	Chlorine Uninegative Ion (g)
ClCs	Cesium Monochloride (c)
ClCs	Cesium Monochloride (ℓ)
ClCs	Cesium Monochloride (g)
ClCu	Copper Monochloride (c)
ClCu	Copper Monochloride (ℓ)
ClCu	Copper Monochloride (g)
ClF	Chlorine Monofluoride (g)
$ClFLi_2$	Lithium Chlorofluoride (g)
ClFMg	Magnesium Chloride Fluoride (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)

Filing Order	Table Title
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	Mercurous Chloride (g)
ClI	Iodine Monochloride (c)
ClI	Iodine Monochloride (ℓ)
ClI	Iodine Monochloride (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 Unipositive 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)
ClSi	Silicon Monochloride (g)
ClTi	Titanium Monochloride (g)
ClW	Tungsten Monochloride (g)
ClZr	Zirconium Monochloride (g)
Cl_2	Chlorine, Diatomic (ref. st., g)
Cl_2Cs_2	Cesium Monochloride, Dimeric (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	Mercuric Chloride (c)
Cl_2Hg	Mercuric Chloride (ℓ)
Cl_2Hg	Mercuric Chloride (g)
Cl_2Hg_2	Mercurous Chloride (c)
Cl_2K_2	Potassium Chloride, Dimeric (g)
Cl_2Li_2	Lithium Chloride, Dimeric (g)

Filing Order	Table Title
Cl_2Mg	Magnesium Dichloride (c)
Cl_2Mg	Magnesium Dichloride (ℓ)
Cl_2Mg	Magnesium Dichloride (g)
Cl_2MoO_2	Molybdenum Dioxydichloride (g)
Cl_2Na_2	Sodium Chloride, Dimeric (g)
Cl_2O	Chlorine Monoxide (g)
Cl_2OTi	Titanium Oxydichloride (g)
Cl_2O_2S	**Sulfuryl Chloride
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)
Cl_2Si	*Silicon 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_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_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 Tatrachloride (c)
Cl_4Ti	Titanium Tetrachloride (ℓ)
Cl_4Ti	Titanium Tetrachloride (g)
Cl_4W	Tungsten Tatrachloride (c)
Cl_4W	Tungsten Tetrachloride (g)
Cl_4Zr	Zirconium Tetrachloride (c)
Cl_4Zr	Zirconium Tetrachloride (g)

Filing Order	Table Title
Cl_5Mo	Molybdenum Pentachloride (c)
Cl_5Mo	Molybdenum Pentachloride (ℓ)
Cl_5Mo	Molybdenum Pentachloride (g)
Cl_5P	Phosphorus 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 (c,α)
Cl_6W	Tungsten Hexachloride (c,β)
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 (g)
Co^+	Cobalt Unipositive 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)
Cs	Cesium (ref. st.)
Cs	Cesium (c)
Cs	Cesium (ℓ)
Cs	Cesium (g)
Cs^+	*Cesium Unipositive 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 Unipositive Ion (g)
CsO	Cesium Monoxide (g)
Cs_2	Cesium, Dimeric (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 (g)
Cu^+	Copper Unipositive 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 Dihydroxide (c)
CuO	Copper Monoxide (c)
CuO	Copper Monoxide (g)
CuO_4S	Copper Sulfate (c)
Cu_2	Copper, Diatomic (g)
Cu_2O	Dicopper Monoxide (c)
Cu_2O	Dicopper Monoxide (ℓ)
Cu_2O_5S	Copper Oxide Sulfate (c)
F	Fluorine, Monatomic (g)
F^-	*Fluorine Uninegative Ion (g)
FFe	Iron Monofluoride (g)
FH	Hydrogen Fluoride (g)
FHO	Hydrogen Oxyfluoride (g)
FHO_3S	**Fluorosulfuric Acid (g)
FH_3Si	Fluorosilane (g)
FHg	Mercurous Fluoride (g)
FI	Iodine Monofluoride (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)
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 Monoxide (g)
FOTi	Titanium Oxyfluoride (g)
FO_2	Monofluorine Dioxide (g)
FP	Phosphorus Monofluoride (g)
FPS	Phosphorus Thiofluoride (g)
FPb	Lead Monofluoride (g)
FSi	Silicon Monofluoride (g)
FTi	Titanium Monofluoride (g)
FW	Tungsten Monofluoride (g)
FZr	Zirconium Monofluoride (g)
F_2	Fluorine, Diatomic (ref. st., g)
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)

Filing Order	Table Title
F_2H_2Si	Difluorosilane (g)
F_2Hg	Mercuric Fluoride (c)
F_2Hg	Mercuric Fluoride (ℓ)
F_2Hg	Mercuric Fluoride (g)
F_2Hg_2	Mercurous Fluoride (c)
F_2K^-	Potassium Difluoride Uninegative Ion (g)
F_2K_2	Potassium Fluoride, Dimeric (g)
F_2Li^-	Lithium Difluoride Uninegative Ion (g)
F_2Li_2	Lithium Fluoride, Dimeric (g)
F_2Mg	Magnesium Fluoride (c)
F_2Mg	Magnesium Fluoride (ℓ)
F_2Mg	Magnesium Fluoride (g)
F_2N	Nitrogen Difluoride (g)
F_2N_2	Difluorodiazine, cis- (g)
F_2N_2	Difluorodiazine, trans- (g)
F_2Na	Sodium Difluoride Uninegative 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 (c)
F_2Pb	Lead Difluoride (ℓ)
F_2Pb	Lead Difluoride (g)
F_2Si	Silicon Difluoride (g)
F_2Ti	Titanium Difluoride (g)
F_2Zr	Zirconium Difluoride (c)
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_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)

Filing Order	Table Title
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_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 Dihydroxide (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)
$Fe_{0.947}O$	Wüstite (c)
FeO	Iron Oxide (c)
FeO	Iron Oxide (ℓ)
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 (g)
H^-	Hydrogen Uninegative 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 Unipositive Ion (g)
HLi	Lithium Hydride (c)
HLi	Lithium Hydride (ℓ)
HLi	Lithium Hydride (g)
HLiO	*Lithium Hydroxide (c)
HLiO	*Lithium Hydroxide (ℓ)

Filing Order	Table Title
HLiO	*Lithium Hydroxide (g)
$HLiO^+$	**Lithium Hydroxide Unipositive Ion (g)
HMg	Magnesium Monohydride (g)
HMgO	Magnesium Monohydroxide (g)
$HMgO^+$	Magnesium Monohydroxide Unipositive 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 (c)
HNaO	*Sodium Hydroxide (ℓ)
HNaO	*Sodium Hydroxide (g)
$HNaO^+$	**Sodium Hydroxide Unipositive Ion (g)
HO	*Hydroxyl (g)
HO^+	*Hydroxyl Unipositive Ion (g)
HO^-	*Hydroxyl Uninegative 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 Unipositive Ion (g)
HZr	Zirconium Hydride (g)
H_2	Hydrogen, Diatomic (ref. st., g)
$H_2K_2O_2$	*Potassium Hydroxide, Dimeric (g)
$H_2Li_2O_2$	*Lithium Hydroxide, Dimeric (g)
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	Diimide (g)
$H_2Na_2O_2$	*Sodium Hydroxide, Dimeric (g)
H_2O	Water (g)
H_2O_2	Hydrogen Peroxide (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	Phosphorus Hydride (g)
H_2S	Hydrogen Sulfide (g)
H_2Ti	Titanium Hydride (c)
H_3N	Ammonia (g)
H_3O^+	Hydronium Unipositive Ion (g)
H_3O_4P	*Orthophosphoric Acid (c)
H_3O_4P	*Orthophosphoric Acid (ℓ)

Filing Order	Table Title
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, Monatomic (g)
HgI	Mercurous Iodide (g)
HgI_2	Mercuric Iodide (c)
HgI_2	Mercuric Iodide (ℓ)
HgI_2	Mercuric Iodide (g)
HgO	Mercuric Oxide (c)
HgO	Mercury Monoxide (g)
Hg_2I_2	Mercurous Iodide (c)
Hg_2I_2	Mercurous Iodide (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)
INO	Nitrosyl Iodide (g)
INa	Sodium Iodide (c)
INa	Sodium Iodide (ℓ)
IPb	Lead Monoiodide (g)
ITi	Titanium Monoiodide (g)
IZr	Zirconium Monoiodide (g)
I_2	Iodine (ref. st.)
I_2	Iodine (ℓ)
I_2	Iodine, Diatomic (g)
I_2K_2	Potassium Iodide, Dimeric (g)
I_2Li_2	Lithium Iodide, Dimeric (g)
I_2Pb	Lead Diiodide (c)
I_2Pb	Lead Diiodide (ℓ)
I_2Pb	Lead 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_4Ti	Titanium Tetraiodide (c)
I_4Ti	Titanium Tetraiodide (ℓ)
I_4Ti	Titanium Tetraiodide (g)
I_4Zr	Zirconium Tetraiodide (c)
I_4Zr	Zirconium Tetraiodide (g)

.ing ler	Table Title
	Potassium (ref. st.)
	Potassium (ℓ)
	Potassium, Monatomic (g)
	Potassium Unipositive Ion (g)
	Potassium Monoxide (g)
-	Potassium Monoxide Uninegative Ion (g)
	*Potassium Superoxide (c)
?	Potassium, Diatomic (g)
)	Potassium Oxide (c)
$)_2$	Potassium Peroxide (c)
$)_3Si$	**Potassium Metasilicate (c)
$)_3Si$	**Potassium Metasilicate (ℓ)
$)_4S$	**Potassium Sulfate (c)
$)_4S$	**Potassium Sulfate (ℓ)
	Lithium (ref. st.)
	Lithium (c)
	Lithium (ℓ)
	Lithium, Monatomic (g)
+	Lithium Unipositive Ion (g)
N	Lithium Nitride (g)
NO	Lithium Nitroxide (g)
NaO	Lithium Sodium Oxide (g)
)	Lithium Monoxide (g)
$)^-$	Lithium Monoxide Uninegative Ion (g)
2	Lithium, Diatomic (g)
$_2O$	Lithium Oxide (c)
$_2O$	Lithium Oxide (ℓ)
$_2O$	Lithium Oxide (g)
$_2O_2$	Lithium Peroxide (c)
$_2O_2$	Lithium Monoxide, Dimeric (g)
$_2O_3Si$	Lithium Metasilicate (c)
$_2O_3Si$	Lithium Metasilicate (ℓ)
$_2O_3Ti$	Lithium Metatitanate (c)
$_2O_3Ti$	Lithium Metatitanate (ℓ)
$_2O_5Si_2$	Lithium Disilicate (c)
$_2O_5Si_2$	Lithium Disilicate (ℓ)
$_3N$	Lithium Nitride (c)
	Magnesium (ref. st.)
	Magnesium (c)
	Magnesium (ℓ)
	Magnesium, Monatomic (g)
+	*Magnesium Unipositive Ion (g)
N	Magnesium Nitride (g)
O	Magnesium Oxide (c)
O	Magnesium Oxide (ℓ)
O	Magnesium Oxide (g)
O_3Si	Magnesium Metasilicate (c)
O_3Si	Magnesium Metasilicate (ℓ)
O_3Ti	Magnesium Metatitanate (c)
O_3Ti	Magnesium Metatitanate (ℓ)

Filing Order	Table Title
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_2O_4Si	Magnesium Orthosilicate (c)
Mg_2O_4Si	Magnesium Orthosilicate (ℓ)
Mg_2O_4Ti	Magnesium Orthotitanate (c)
Mg_2O_4Ti	Magnesium Orthotitanate (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 Unipositive 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 Unipositive Ion (g)
NO_2	Nitrogen Dioxide (g)
NO_2^-	*Nitrogen Dioxide Negative Ion (g)
NO_3	Nitrogen Trioxide (g)
NP	Phosphorous Nitride (g)
NS	Sulfur Nitride (g)
NSi	Silicon Nitride (g)
NSi_2	Disilicon Nitride (g)
NTi	Titanium Nitride (c)
NTi	Titanium Nitride (ℓ)
NZr	Zirconium Nitride (c)
NZr	Zirconium Nitride (ℓ)
NZr	Zirconium Nitride (g)
N_2	Nitrogen (ref. st., g)
N_2O	Dinitrogen Monoxide (g)
N_2O^+	**Dinitrogen Monoxide Unipositive Ion (g)
N_2O_3	Dinitrogen Trioxide (g)
N_2O_4	Nitrogen Tetroxide (c)
N_2O_4	Dinitrogen Tetroxide (ℓ)
N_2O_4	Nitrogen Tetroxide (g)
N_2O_5	Dinitrogen Pentoxide (g)

Filing Order	Table Title
N_3	**Azide (g)
N_4Si_3	Silicon Nitride (c,α)
N_5P_3	Triphosphorus Pentanitride (c)
Na	Sodium (ref. st.)
Na	Sodium (c)
Na	Sodium (ℓ)
Na	Sodium Monatomic (g)
Na^+	Sodium Unipositive Ion (g)
NaO	Sodium Monoxide (g)
NaO^-	Sodium Monoxide Uninegative Ion (g)
NaO_2	Sodium Superoxide (c)
Na_2	Sodium Diatomic (g)
Na_2O	Disodium Monoxide (c)
Na_2O	Disodium Monoxide (ℓ)
Na_2O_2	Disodium Dioxide (c)
Na_2O_3Si	Sodium Metasilicate (c)
Na_2O_3Si	Sodium Metasilicate (ℓ)
Na_2O_4S	Sodium Sulfate (c, V)
Na_2O_4S	Sodium Sulfate (c,III)
Na_2O_4S	Sodium Sulfate (c,I)
Na_2O_4S	Sodium Sulfate (c,δ)
Na_2O_4S	Sodium Sulfate (ℓ)
Na_2O_4W	Sodium Tungstate (c)
$Na_2O_5Si_2$	Sodium Disilicate (c)
$Na_2O_5Si_2$	Sodium isilicate (ℓ)
Na_2S	Sodium Sulfide (c)
Na_2S	Sodium Sulfide (ℓ)
O	Oxygen, Monatomic (g)
O^-	Oxygen Uninegative Ion (g)
OP	*Phosphorus Monoxide (g)
OPb	*Lead Monoxide (c, Red)
OPb	*Lead Monoxide (c, Yellow)
OPb	*Lead Monoxide (ℓ)
OPb	*Lead Monoxide (g)
OS	*Sulfur Monoxide (g)
OS_2	Disulfur Monoxide (g)
OSi	Silicon Monoxide (g)
OTi	Titanium Monoxide (c,α)
OTi	Titanium Monoxide (c,β)
OTi	Titanium Monoxide (ℓ)
OTi	Titanium Monoxide (g)
OW	Tungsten Monoxide (g)
OZr	Zirconium Monoxide (g)
O_2	Oxygen, Diatomic (ref. st., g)
O_2^-	Diatomic Oxygen Uninegative Ion (g)
O_2P	Phosphorus Dioxide (g)
O_2Pb	*Lead Dioxide (c)
O_2S	Sulfur Dioxide (g)
O_2Si	Quartz (c)
O_2Si	Cristobalite (c, low)
O_2Si	Cristobalite (c, high)
O_2Si	Silicon Dioxide (ℓ)
O_2Si	Silicon Dioxide (g)
O_2Ti	Anatase (c)
O_2Ti	Rutile (c)
O_2Ti	Titanium Dioxide (ℓ)
O_2Ti	Titanium Dioxide (g)
O_2W	Tungsten Dioxide (c)
O_2W	Tungsten Dioxide (g)
$O_{2.72}W$	Tungsten Oxide (c)
$O_{2.90}W$	Tungsten Oxide (c)
$O_{2.96}W$	Tungsten Oxide (c)
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_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 Orthosilicate (c)
O_5Ti_3	Trititanium Pentoxide (c,α)
O_5Ti_3	Trititanium Pentoxide (c,β)
O_5Ti_3	Trititanium Pentoxide (ℓ)
O_6P_4	Phosphorus Trioxide, Dimeric (g)
O_6W_2	Tungsten Trioxide, Dimeric (g)
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 (c, Red, V)
P	Phosphorus (c, White)
P	Phosphorus (ℓ)
P	Phosphorus (g)
PS	Phosphorus Sulfide (g)
P_2	Phosphorus, Diatomic (g)
P_4	Phosphorus, Tetratomic (g)
P_4S_3	Phosphorus Sulfide (c)
P_4S_3	Phosphorus Sulfide (ℓ)
P_4S_3	Phosphorus Sulfide (g)
Pb	Lead (ref. st.)
Pb	Lead (c)
Pb	Lead (ℓ)
Pb	Lead (g)
Pb_2	Lead, Diatomic (g)

Filing Order	Table Title
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 Unipositive Ion (g)
Si_2	Silicon, Diatomic (g)
Si_3	Silicon, Triatomic (g)
Sr	**Strontium (ref. st.)
Sr	**Strontium (c)
Sr	**Strontium (ℓ)
Sr	**Strontium (g)

Filing Order	Table Title
Ti	Titanium (ref. st.)
Ti	Titanium (c,α)
Ti	Titanium (c,β)
Ti	Titanium (ℓ)
Ti	Titanium, Monatomic (g)
Ti^+	Titanium Unipositive Ion (g)
W	Tungsten (ref. st.)
W	Tungsten (c)
W	Tungsten (ℓ)
W	Tungsten, Monatomic (g)
W^+	Tungsten Unipositive Ion (g)
Zr	Zirconium (ref. st)
Zr	Zirconium (c,α)
Zr	Zirconium (c,β)
Zr	Zirconium (ℓ)
Zr	Zirconium (g)
Zr^+	*Zirconium Unipositive Ion (g)
e^-	Electron Gas (ref. st.)

* JANAF Thermochemical Tables which are included in this article.

Aluminum Monobromide (AlBr)

(Ideal Gas) GFW = 106.891

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	- 2.287	5.537	5.537	INFINITE
100	7.224	48.628	64.492	- 1.586	5.797	1.743	- 3.809
200	8.092	53.923	58.010	- .817	5.539	- 2.242	2.450
298	8.509	57.243	57.243	.000	3.800	- 5.825	4.270
300	8.514	57.296	57.243	.016	3.788	- 5.885	4.287
400	8.710	59.775	57.580	.878	- .068	- 8.327	4.549
500	8.816	61.731	58.221	1.755	- .264	- 10.370	4.533
600	8.882	63.344	58.945	2.640	- .482	- 12.371	4.506
700	8.927	64.717	59.674	3.530	- .723	- 14.334	4.475
800	8.961	65.911	60.380	4.425	- .994	- 16.260	4.442
900	8.988	66.969	61.055	5.322	- 1.307	- 18.150	4.407
1000	9.010	67.917	61.694	6.222	- 4.190	- 19.819	4.331
1100	9.030	68.776	62.300	7.124	- 4.498	- 21.368	4.245
1200	9.048	69.563	62.873	8.028	- 4.805	- 22.888	4.168
1300	9.065	70.288	63.415	8.934	- 5.110	- 24.382	4.099
1400	9.080	70.960	63.931	9.841	- 5.414	- 25.852	4.036
1500	9.095	71.587	64.420	10.750	- 5.719	- 27.303	3.978
1600	9.109	72.174	64.887	11.660	- 6.022	- 28.731	3.925
1700	9.123	72.727	65.332	12.572	- 6.324	- 30.141	3.875
1800	9.136	73.249	65.757	13.485	- 6.625	- 31.533	3.829
1900	9.149	73.743	66.165	14.399	- 6.926	- 32.909	3.785
2000	9.162	74.213	66.556	15.315	- 7.226	- 34.270	3.745
2100	9.175	74.660	66.931	16.231	- 7.525	- 35.615	3.707
2200	9.188	75.087	67.292	17.150	- 7.824	- 36.946	3.670
2300	9.201	75.496	67.640	18.069	- 8.121	- 38.260	3.636
2400	9.214	75.888	67.976	18.990	- 8.418	- 39.564	3.603
2500	9.227	76.264	68.300	19.912	- 8.715	- 40.858	3.572
2600	9.241	76.627	68.613	20.835	- 9.010	- 42.137	3.542
2700	9.255	76.976	68.916	21.760	- 9.305	- 43.407	3.514
2800	9.270	77.312	69.210	22.686	- 79.029	- 43.834	3.421
2900	9.286	77.638	69.495	23.614	- 79.040	- 42.578	3.209
3000	9.303	77.953	69.772	24.544	- 79.069	- 41.319	3.010
3100	9.321	78.258	70.041	25.475	- 79.098	- 40.060	2.824
3200	9.340	78.555	70.302	26.408	- 79.125	- 38.799	2.650
3300	9.361	78.842	70.557	27.343	- 79.151	- 37.539	2.486
3400	9.385	79.122	70.804	28.280	- 79.176	- 36.280	2.332
3500	9.410	79.395	71.046	29.220	- 79.198	- 35.018	2.187
3600	9.437	79.660	71.282	30.162	- 79.219	- 33.753	2.049
3700	9.467	79.919	71.512	31.107	- 79.238	- 32.492	1.919
3800	9.500	80.172	71.736	32.056	- 79.255	- 31.228	1.796
3900	9.535	80.419	71.956	33.007	- 79.268	- 29.961	1.679
4000	9.573	80.661	72.170	33.963	- 79.280	- 28.700	1.568
4100	9.615	80.898	72.380	34.922	- 79.289	- 27.438	1.463
4200	9.659	81.130	72.586	35.886	- 79.294	- 26.170	1.362
4300	9.706	81.358	72.787	36.854	- 79.296	- 24.905	1.266
4400	9.757	81.582	72.985	37.827	- 79.295	- 23.638	1.174
4500	9.810	81.802	73.178	38.806	- 79.290	- 22.374	1.087
4600	9.867	82.018	73.368	39.789	- 79.281	- 21.108	1.003
4700	9.926	82.231	73.554	40.779	- 79.270	- 19.848	.923
4800	9.989	82.440	73.737	41.775	- 79.254	- 18.585	.846
4900	10.055	82.647	73.917	42.777	- 79.233	- 17.315	.772
5000	10.123	82.851	74.093	43.786	- 79.208	- 16.054	.702
5100	10.195	83.052	74.267	44.802	- 79.180	- 14.791	.634
5200	10.269	83.251	74.438	45.825	- 79.147	- 13.531	.569
5300	10.345	83.447	74.606	46.855	- 79.111	- 12.268	.506
5400	10.423	83.641	74.772	47.894	- 79.069	- 11.007	.445
5500	10.504	83.833	74.935	48.940	- 79.025	- 9.749	.387
5600	10.587	84.023	75.095	49.995	- 78.976	- 8.488	.331
5700	10.671	84.211	75.254	51.058	- 78.923	- 7.231	.277
5800	10.757	84.397	75.410	52.129	- 78.867	- 5.972	.225
5900	10.845	84.582	75.563	53.209	- 78.807	- 4.715	.175
6000	10.933	84.765	75.715	54.298	- 78.744	- 3.462	.126

Dec. 31, 1961; Sept. 30, 1964; June 30, 1972

ALUMINUM MONOBROMIDE (AlBr) (IDEAL GAS) GFW = 106.891 AlBr

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 57.24 ± 0.05 gibbs/mol

ΔHf°_0 = 5.54 ± 3.00 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 3.80 ± 3.00 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
	23647	2
$a\ ^3\Pi$	23779	2
	[23900]	[2]
$A^1\Pi$	35879	2

ω_e = 377.60 cm^{-1} $\omega_e x_e$ = 1.323 cm^{-1} σ = 1

B_e = 0.1587 cm^{-1} α_e = 0.000856 cm^{-1} r_e = 2.29480 Å

Heat of Formation

Gaydon (3), Singh et al (5), Rosen (7), and Barrow (8, 9) reference possible spectroscopic values for the dissociation energy of AlBr(g). The $A^1\Pi$ state yielded three values for the dissociation energy: 106.9 kcal/mol by a short extrapolation, a minimum of 104.4 kcal/mol as indicated by the highest observed vibrational level, and a maximum of 105.7 kcal/mol as determined by predissociation which sets in at v' = 4. Gaydon (3) reports a value of 86.5 kcal/mol based on a ground state linear Birge-Sponer extrapolation (v, 0-11). However, substituting the values tabulated above for ω_e and $x_e\omega_e$ into the equation $D_0 = \omega_e^2/4x_e\omega_e - 0.5\omega_e$, a value of 76.5 kcal/mol is obtained for the dissociation energy. A value of 105 kcal/mol is suggested by Barrow (8) based on wavelengths for maximum photoionization.

Semenkovich (1) measured the vapor pressure of the reaction Al(ℓ) + NaBr(ℓ) → Na(g) + AlBr(g) at 1175 K. By the Third Law method ΔHr°_{298} is equal to 108.60 kcal/mol. Using JANAF auxiliary data (2), ΔHf°_{298}(AlBr, g) is equal to 3.81 kcal/mol and the dissociation energy, D°_0, is 100.08 kcal/mol.

Gross (12) studied the equilibrium involved in the reaction 2Al(ℓ) + $AlBr_3$(g) → 3AlBr(g) in the range 550-1300°C. The reported ΔHr°_{298} is 106.27 kcal/mol. Using JANAF auxiliary data (2), ΔHf°_{298} (AlBr, g) is equal to 4.07 kcal/mol while the dissociation energy, D°_0, is equal to 99.82 kcal/mol.

It should be noted that the highest observed vibrational level in the $A^1\Pi$ state lies approximately 4 kcal/mol above the thermochemical dissociation energy of Semenkovich (1) and Gross (12). This suggests a potential maximum in the $A^1\Pi$ state as mentioned by Barrow (8). A similar maximum is suggested for AlF(g) and AlCl(g) (2, 6, 8). In addition, Wyse and Gordy (4), from nuclear quadrupole coupling, deduce that the ionic character of the AlBr bond is ≥87%. Thus the value of D°_0 = 76.5 kcal/mol as obtained by a linear Birge-Sponer extrapolation is undoubtedly too low (3). This ground state extrapolation value was adjusted to 99.5 kcal/mol and 102.2 kcal/mol using two ionic character correction factors as suggested by Hildenbrand (6, 10). The former value is more suitable for *metal fluorides while the latter is for the more general case. A comparison of* D°_0 *values* (2, 3, 7) for the group IIIA gaseous monohalides suggests a value of 96-103 kcal/mol, which is consistent with the value obtained by Semenkovich (1) and Gross (12).

Due to the high ionic character in the AlBr bond and the possible unreliability of extrapolations of excited states which contain a potential maximum, the spectroscopic data is suspect as to the determination of ΔHf°_{298}. The chosen value for ΔHf°_{298}, 3.80 kcal/mol, is a rounded value from the vapor pressure work of Semenkovich (1).

Heat Capacity and Entropy

The spectroscopic constants for $Al^{79}Br$ and $Al^{81}Br$ were taken from Wyse and Gordy (4) and averaged according to the natural abundance of bromine. The electronic states are from Rosen (7) with the exception of the upper $^3\Pi$ state which is estimated to be approximately in a linear relationship with the two lower $^3\Pi$ states. Lakshminarayana and Haranath (11) also reported values for two of the $a^3\Pi$ states which agree within 15 cm^{-1} with Rosen's values (7).

References

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AlBr

Aluminum Tribromide ($AlBr_3$)

(Crystal) GFW = 266.7085

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	- 5.238	- 117.515	- 117.515	INFINITE
100	16.927	20.655	62.555	- 4.190	- 117.575	- 117.545	256.895
200	21.499	33.990	45.185	- 2.235	- 117.823	- 117.437	128.329
298	24.040	43.075	43.075	.000	- 122.160	- 116.713	85.553
300	24.097	43.224	43.075	.045	- 122.176	- 116.678	85.000
400	28.150	50.618	44.058	2.624	- 132.556	- 112.670	61.560
500	29.630	57.106	46.038	5.534	- 131.601	- 107.808	47.123
600	29.700	62.513	48.346	8.500	- 130.626	- 103.142	37.569
700	29.720	67.092	50.706	11.471	- 129.680	- 98.636	30.796
800	29.740	71.062	53.008	14.444	- 128.768	- 94.264	25.752
900	29.760	74.566	55.212	17.419	- 127.902	- 90.004	21.856
1000	29.780	77.703	57.307	20.396	- 129.608	- 85.653	18.719
1100	29.800	80.542	59.292	23.375	- 128.741	- 81.301	16.153
1200	29.820	83.136	61.173	26.356	- 127.873	- 77.076	14.028
1300	29.840	85.524	62.955	29.335	- 127.006	- 72.823	12.243
1400	29.860	87.736	64.647	32.324	- 126.139	- 68.687	10.723
1500	29.880	89.797	66.256	35.311	- 125.273	- 64.616	9.415

Dec. 31, 1961; June 30, 1964; June 30, 1967; June 30, 1972

ALUMINUM TRIBROMIDE ($AlBr_3$) (CRYSTAL) GFW = 266.7085

ΔHf°_0 = -117.52 ± 0.30 kcal/mol

$S^\circ_{298.15}$ = 43.08 ± 0.25 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -122.16 ± 0.30 kcal/mol

Tm = 370.6 ± 0.2 K

ΔHm° = 2.69 ± 0.20 kcal/mol

Heat of Formation

Gross, Hayman, and Stuart (1) measured calorimetrically the standard heat of formation of $AlBr_3$(c) at 25°C by reacting Al with liquid bromine in a glass combustion vessel. They reported $\Delta Hf^\circ_{298}(AlBr_3, c)$ = -122.16 ± 0.10 kcal/mol.

In an earlier work, Eley and Watts (2), in studying heats of solution of $AlBr_3$ and its complexes with pyridine, trimethylamine, and triethylamine in HCl, reported $\Delta Hf^\circ_{298}(AlBr_3, c)$ = -125.6 kcal/mol. Klemm and Tanke (3) measured the heat of solution of $AlBr_3$(c) at 0°C in aqueous HCl. Using auxiliary data, including estimated heat capacities, Klemm and Tanke (3) reported $\Delta Hf^\circ_{298}(AlBr_3, c)$ = -121 kcal/mol. Gross, Hayman, and Stuart (1) have re-examined the data of Klemm and Tanke (3) and have calculated $\Delta Hf^\circ_{298}(AlBr_3, c)$ = -122.4 kcal/mol. This latter value was based on the heat of solution measurements (3), on the heat of formation of $AlCl_3$(c) [$\Delta Hf^\circ_{298}(AlCl_3, c)$ = -168.65 kcal/mol], and on the heats of formation difference in chloride and bromide ions at the proper concentration.

The value chosen for the heat of formation is the value reported by Gross, Hayman, and Stuart (1), $\Delta Hf^\circ_{298}(AlBr_3, c)$ = -122.16 ± 0.30 kcal/mol where the error limits have been expanded to include data of Klemm and Tanke (3).

Heat Capacity and Entropy

The heat capacity of $AlBr_3$(c) has been measured by Webb, Justice, and Prophet (4) from 11.6 to 308.1 K. The enthalpy has been measured by Fischer (5) from 337 K to 367 K. The heat capacities of $AlBr_3$(c) chosen are from the former work for *T ≤ 308.1 K and derived from the smoothed enthalpies of the latter work for T > 308.1 K*, as discussed in Webb, Justice, and Prophet (4). The entropy of the crystal is based on a value of S°_{12} = 0.961 gibbs/mol, also as discussed in Webb et al. (4).

Melting Data

Fischer (5) determined the melting temperature (Tm) for $AlBr_3$(c). The heat of melting (ΔHm°) is calculated from the enthalpies of $AlBr_3$(c) and $AlBr_3$(ℓ) at the melting temperature. The enthalpy of the crystal at Tm was determined from the curve used for the heat capacity calculations. The enthalpy of the liquid at Tm was determined from a linear least squares fit to the enthalpy data for $AlBr_3$(ℓ) reported by Fischer (5). See Webb et al. (4) for details.

References

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Aluminum Tribromide ($AlBr_3$)

(Liquid) GFW = 266.7085

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	29.869	49.352	49.352	.000	- 119.793	- 116.217	85.190
300	29.869	49.537	49.353	.055	- 119.798	- 116.195	84.648
400	29.869	58.130	50.525	3.042	- 129.770	- 112.889	61.680
500	29.869	64.795	52.737	6.029	- 128.739	- 108.790	47.552
600	29.869	70.241	55.214	9.016	- 127.743	- 104.895	38.208
700	29.869	74.845	57.698	12.003	- 126.781	- 101.164	31.585
800	29.869	78.834	60.096	14.990	- 125.855	- 97.568	26.654
900	29.869	82.352	62.378	17.977	- 124.977	- 94.085	22.847
1000	29.869	85.499	64.535	20.964	- 126.673	- 90.514	19.782
1100	29.869	88.345	66.572	23.950	- 125.798	- 86.942	17.274
1200	29.869	90.944	68.497	26.937	- 124.925	- 83.448	15.198
1300	29.869	93.335	70.317	29.924	- 124.053	- 80.025	13.453
1400	29.869	95.549	72.041	32.911	- 123.184	- 76.671	11.969
1500	29.869	97.610	73.677	35.898	- 122.318	- 73.381	10.697

Dec. 31, 1961; June 30, 1964; June 30, 1967; June 30, 1972

ALUMINUM TRIBROMIDE ($AlBr_3$) (LIQUID) GFW = 266.7085

$S^\circ_{298.15}$ = 49.352 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -119.793 kcal/mol

Tm = 370.6 ± 0.2 K

ΔHm° = 2.69 ± 0.20 kcal/mol

Tb = 527.0 ± 0.5 K

ΔHv° = 5.88 ± 0.20 kcal/mol

Tb = 527.6 ± 0.5 K (to dimer gas)

ΔHv° = 5.69 ± 0.20 kcal/mol (to dimer gas)

Heat of Formation

The heat of formation (ΔHf°_{298}) of $AlBr_3(\ell)$ is calculated from $\Delta Hf^\circ_{298}(AlBr_3, c)$ plus the heat of melting (ΔHm°) and the enthalpy differences ($H_{370.6}-H_{298}$) of the crystal and liquid.

Heat Capacity and Entropy

Fischer (1) has measured the enthalpy of $AlBr_3(\ell)$ from 374 K to 406 K. The heat capacity used is derived from a linear least squares fit to his data. The resulting constant value for the heat capacity is adopted for temperatures above 400 K. The entropy (S°_{298}) of $AlBr_3(\ell)$ was determined in a manner analogous to that for the heat of formation.

Melting Data

See $AlBr_3(c)$ table for details.

Vaporization Data

See $Al_2Br_6(g)$ table for details.

References

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Aluminum Tribromide ($AlBr_3$)

(Ideal Gas) GFW = 266.7085

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	− 4.302	− 92.620	− 92.620	INFINITE
100	13.684	65.994	98.402	− 3.241	− 92.666	− 97.170	212.365
200	16.619	76.497	85.040	− 1.709	− 93.333	− 101.448	110.857
298	18.026	83.429	83.429	.000	− 98.200	− 104.784	76.809
300	18.044	83.541	83.429	.033	− 98.227	− 104.825	76.365
400	18.741	88.838	84.147	1.877	− 109.343	− 104.745	57.230
500	19.114	93.084	85.522	3.771	− 109.404	− 103.590	45.279
600	19.331	96.570	87.080	5.694	− 109.472	− 102.421	37.307
700	19.468	99.561	88.654	7.635	− 109.556	− 101.240	31.609
800	19.559	102.167	90.184	9.586	− 109.665	− 100.045	27.331
900	19.623	104.474	91.646	11.546	− 109.815	− 98.834	24.000
1000	19.669	106.545	93.034	13.510	− 112.533	− 97.420	21.291
1100	19.704	108.421	94.349	15.479	− 112.676	− 95.903	19.054
1200	19.730	110.137	95.594	17.451	− 112.818	− 94.372	17.187
1300	19.751	111.717	96.774	19.425	− 112.960	− 92.827	15.606
1400	19.767	113.181	97.895	21.401	− 113.102	− 91.273	14.248
1500	19.781	114.545	98.960	23.378	− 113.245	− 89.711	13.071
1600	19.792	115.822	99.974	25.357	− 113.389	− 88.136	12.039
1700	19.801	117.022	100.942	27.337	− 113.533	− 86.553	11.127
1800	19.808	118.154	101.867	29.317	− 113.677	− 84.963	10.316
1900	19.815	119.225	102.753	31.298	− 113.823	− 83.361	9.589
2000	19.820	120.242	103.602	33.280	− 113.972	− 81.757	8.934
2100	19.825	121.209	104.418	35.262	− 114.119	− 80.144	8.341
2200	19.829	122.131	105.202	37.245	− 114.270	− 78.523	7.801
2300	19.833	123.013	105.957	39.228	− 114.420	− 76.891	7.306
2400	19.836	123.857	106.686	41.211	− 114.573	− 75.255	6.853
2500	19.839	124.667	107.389	43.195	− 114.726	− 73.616	6.436
2600	19.841	125.445	108.068	45.179	− 114.881	− 71.967	6.049
2700	19.843	126.194	108.726	47.163	− 115.038	− 70.317	5.692
2800	19.845	126.916	109.363	49.148	− 184.607	− 67.826	5.294
2900	19.847	127.612	109.980	51.132	− 184.504	− 63.658	4.797
3000	19.849	128.285	110.579	53.117	− 184.402	− 59.492	4.334
3100	19.850	128.936	111.161	55.102	− 184.303	− 55.328	3.901
3200	19.851	129.566	111.726	57.087	− 184.204	− 51.168	3.495
3300	19.853	130.177	112.276	59.072	− 184.108	− 47.015	3.114
3400	19.854	130.770	112.811	61.058	− 184.012	− 42.865	2.755
3500	19.855	131.345	113.333	63.043	− 183.919	− 38.713	2.417
3600	19.856	131.904	113.841	65.029	− 183.828	− 34.564	2.098
3700	19.857	132.449	114.336	67.014	− 183.737	− 30.421	1.797
3800	19.857	132.978	114.820	69.000	− 183.649	− 26.278	1.511
3900	19.858	133.494	115.292	70.986	− 183.563	− 22.133	1.240
4000	19.859	133.997	115.754	72.972	− 183.479	− 18.002	.984
4100	19.859	134.487	116.205	74.958	− 183.397	− 13.868	.739
4200	19.860	134.966	116.646	76.944	− 183.317	− 9.731	.506
4300	19.860	135.433	117.077	78.930	− 183.240	− 5.598	.285
4400	19.861	135.889	117.500	80.916	− 183.164	− 1.464	.073
4500	19.861	136.336	117.913	82.902	− 183.092	2.662	− .129
4600	19.862	136.772	118.318	84.888	− 183.022	6.791	− .323
4700	19.862	137.200	118.716	86.874	− 182.955	10.915	− .508
4800	19.863	137.618	119.105	88.860	− 182.893	15.034	− .685
4900	19.863	138.027	119.487	90.847	− 182.832	19.165	− .855
5000	19.863	138.429	119.862	92.833	− 182.775	23.285	− 1.018
5100	19.864	138.822	120.230	94.819	− 182.723	27.403	− 1.174
5200	19.864	139.208	120.591	96.806	− 182.674	31.521	− 1.325
5300	19.864	139.586	120.946	98.792	− 182.630	35.643	− 1.470
5400	19.865	139.957	121.295	100.779	− 182.590	39.759	− 1.609
5500	19.865	140.322	121.637	102.765	− 182.556	43.878	− 1.744
5600	19.865	140.680	121.974	104.752	− 182.527	47.993	− 1.873
5700	19.865	141.031	122.305	106.738	− 182.503	52.110	− 1.998
5800	19.866	141.377	122.631	108.725	− 182.485	56.229	− 2.119
5900	19.866	141.716	122.952	110.711	− 182.474	60.344	− 2.235
6000	19.866	142.050	123.267	112.698	− 182.470	64.453	− 2.348

Dec. 31, 1961; June 30, 1964; June 30, 1967; June 30, 1972

ALUMINUM TRIBROMIDE ($AlBr_3$) (IDEAL GAS) GFW = 266.7085

Point Group D_{3h} ΔHf°_0 = −92.6 ± 0.4 kcal/mol

$S^\circ_{298.15}$ = 83.43 ± 0.30 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −98.2 ± 0.4 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
228 (1)
162 (1)
504 (2)
93 (2)

Bond Distance: Al-Br = [2.27 ± 0.10] Å

Bond Angle: Br-Al-Br = 120° σ = 6

Product of the Moments of Inertia: $I_A I_B I_C$ = [2.157 × 10^{-111}] $g^3 cm^6$

Heat of Formation

Fischer, Rahlfs, and Benze (1) have determined the equilibrium constants for the reaction $Al_2Br_6(g) = 2AlBr_3(g)$ from vapor density measurements. The heats of reaction are calculated from these data using both Second Law and Third Law methods. The results of the calculations are as follows, where the ΔHf°_{298} value is based on the Third Law value of ΔHr°_{298} and $\Delta Hf^\circ_{298}(Al_2Br_6, g)$ = −224.0 kcal/mol.

Range T°K	Number of Points	ΔHr°_{298}, kcal/mol Second Law	Third Law	drift eu	$\Delta Hf^\circ_{298}(AlBr_3, g)$ kcal/mol
613-846	4	29.6 ± 1.0	27.70	−2.6±1.3	−98.2
605-854	7	29.3 ± 0.5	27.65	−2.3±0.7	−98.2

The adopted value for the heat of formation is $\Delta Hf^\circ_{298}(AlBr_3, g)$ = −98.2± 2.0 kcal/mol.

Heat Capacity and Entropy

Beattie and Horder (2) studied the gas phase Raman spectra of monomeric $AlBr_3$. The results are consistent with a planar structure of D_{3h} symmetry with ω_1 = 228 cm^{-1} (polarized) and ω_4 = 93 cm^{-1}. The weak antisymmetric stretching mode ω_3 was tentatively assigned as ω_3 = 360 cm^{-1}.

Shirk (3) in examining the infrared spectrum of the monomeric $AlBr_3$, isolated in solid argon, reported ω_2 = 162 cm^{-1} and ω_3 = 504 cm^{-1}. No band was observed in the vicinity of 228 cm^{-1}, which lends further support to a D_{3h} symmetry for planar $AlBr_3(g)$. ω_1 should be only Raman active for D_{3h} symmetry.

The adopted values for ω_1 and ω_4 are taken from Beattie and Horder (2) while ω_2 and ω_3 are from Shirk (3). The Al-Br *bond distance was estimated by Heise and Weiland* (4) and is consistent with the trend of experimentally known bond distances in $AlF_3(g)$, $AlCl_3(g)$, and $AlI_3(g)$ (5).

References

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2. I. R. Beattie and J. R. Horder, J. Chem. Soc. (London) 1969A, 2655 (1969).
3. J. S. Shirk, private communication to M. W. Chase on work by J. S. Shirk and D. Lucas, April 11, 1972.
4. M. Heise and K. Weiland, Helv. Chim. Acta. 34, 2182 (1951).
5. JANAF Thermochemical Tables: $AlF_3(g)$, 6-30-70; $AlCl_3(g)$, 6-30-70; $AlI_3(g)$, 6-30-64.

Aluminum Dichloride ($AlCl_2$)

(Ideal Gas) GFW = 97.8875

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	− 3.047	− 68.759	− 68.759	INFINITE
100	9.190	56.971	79.148	− 2.218	− 68.732	− 69.749	152.436
200	11.395	64.075	69.975	− 1.180	− 68.862	− 70.731	77.292
298	12.509	68.860	68.860	.000	− 69.000	− 71.624	52.502
300	12.523	68.938	68.861	.023	− 69.003	− 71.641	52.190
400	13.061	72.623	69.359	1.305	− 69.150	− 77.498	39.611
500	13.343	75.571	70.317	2.627	− 69.312	− 73.316	32.047
600	13.507	78.019	71.402	3.970	− 69.497	− 74.101	26.991
700	13.610	80.110	72.500	5.326	− 69.704	− 74.852	23.370
800	13.678	81.932	73.568	6.691	− 69.942	− 75.572	20.645
900	13.726	83.546	74.589	8.061	− 70.224	− 76.259	18.518
1000	13.760	84.994	75.558	9.436	− 73.076	− 76.730	16.769
1100	13.786	86.307	76.476	10.813	− 73.355	− 77.082	15.315
1200	13.805	87.507	77.346	12.193	− 73.634	− 77.409	14.098
1300	13.821	88.613	78.171	13.574	− 73.913	− 77.712	13.065
1400	13.833	89.637	78.954	14.957	− 74.193	− 77.993	12.175
1500	13.843	90.592	79.698	16.341	− 74.474	− 78.256	11.402
1600	13.851	91.486	80.407	17.725	− 74.757	− 78.499	10.722
1700	13.859	92.326	81.084	19.111	− 75.039	− 78.722	10.120
1800	13.865	93.118	81.731	20.497	− 75.322	− 78.931	9.584
1900	13.871	93.868	82.350	21.884	− 75.606	− 79.123	9.101
2000	13.877	94.579	82.944	23.271	− 75.893	− 79.302	8.666
2100	13.883	95.257	83.514	24.659	− 76.179	− 79.467	8.270
2200	13.889	95.903	84.063	26.048	− 76.467	− 79.617	7.909
2300	13.896	96.520	84.591	27.437	− 76.755	− 79.750	7.578
2400	13.904	97.112	85.100	28.827	− 77.045	− 79.874	7.274
2500	13.912	97.679	85.592	30.218	− 77.337	− 79.988	6.993
2600	13.922	98.225	86.068	31.610	− 77.629	− 80.087	6.732
2700	13.932	98.751	86.528	33.002	− 77.924	− 80.178	6.490
2800	13.944	99.258	86.973	34.396	− 147.630	− 79.424	6.199
2900	13.956	99.747	87.406	35.791	− 147.665	− 78.990	5.802
3000	13.970	100.221	87.825	37.187	− 147.702	− 74.552	5.431
3100	13.985	100.679	88.232	38.585	− 147.740	− 72.112	5.084
3200	14.001	101.123	88.628	39.984	− 147.780	− 69.672	4.758
3300	14.019	101.554	89.013	41.385	− 147.821	− 67.229	4.452
3400	14.037	101.973	89.388	42.788	− 147.863	− 64.788	4.165
3500	14.056	102.380	89.754	44.193	− 147.906	− 62.346	3.893
3600	14.075	102.777	90.110	45.595	− 147.951	− 59.897	3.636
3700	14.096	103.162	90.458	47.008	− 147.996	− 57.451	3.394
3800	14.117	103.539	90.797	48.418	− 148.043	− 55.006	3.164
3900	14.139	103.906	91.128	49.831	− 148.089	− 52.553	2.945
4000	14.161	104.264	91.452	51.246	− 148.138	− 50.105	2.738
4100	14.183	104.614	91.769	52.663	− 148.186	− 47.657	2.540
4200	14.206	104.956	92.079	54.083	− 148.234	− 45.203	2.352
4300	14.228	105.290	92.382	55.505	− 148.283	− 42.750	2.173
4400	14.251	105.618	92.679	56.929	− 148.332	− 40.289	2.001
4500	14.274	105.938	92.971	58.355	− 148.383	− 37.837	1.838
4600	14.297	106.252	93.256	59.783	− 148.432	− 35.378	1.681
4700	14.319	106.560	93.536	61.214	− 148.483	− 32.924	1.531
4800	14.342	106.862	93.810	62.647	− 148.534	− 30.466	1.387
4900	14.364	107.158	94.080	64.083	− 148.584	− 27.998	1.249
5000	14.385	107.448	94.344	65.520	− 148.636	− 25.541	1.116
5100	14.407	107.733	94.604	66.960	− 148.687	− 23.075	.989
5200	14.427	108.013	94.859	68.401	− 148.741	− 20.613	.866
5300	14.448	108.288	95.110	69.845	− 148.796	− 18.151	.748
5400	14.467	108.558	95.356	71.291	− 148.851	− 15.683	.635
5500	14.487	108.824	95.599	72.738	− 148.910	− 13.219	.525
5600	14.505	109.085	95.837	74.188	− 148.969	− 10.750	.420
5700	14.523	109.342	96.072	75.639	− 149.031	− 8.286	.318
5800	14.541	109.595	96.303	77.093	− 149.095	− 5.811	.219
5900	14.557	109.843	96.530	78.548	− 149.163	− 3.342	.124
6000	14.573	110.088	96.754	80.004	− 149.235	− .868	.032

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

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

Point Group [C_{2v}] ΔHf°_0 = [−68.8 ± 5.0] kcal/mol

$S^\circ_{298.15}$ = [68.86 ± 0.60] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [−69.0 ± 5.0] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[15000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[400] (1)
[215] (1)
[490] (1)

Bond Distance: Al-Cl = [2.10] Å

Bond Angle: Cl-Al-Cl = [120]° σ = 2

Product of Moments of Inertia = [5.8067 x 10^{-114}] g^3cm^6

Heat of Formation

Farber and Harris (1) identified $AlCl_2$ in an effusion-mass spectrometric study of the reaction between $AlCl_3(g)$ and $Al(\ell)$, measurements were performed over the temperature range 1150-1430 K. Intensity data for AlCl(g), $AlCl_2(g)$, and $AlCl_3(g)$ were measured at 3 eV above threshold and led to equilibrium data for the reaction $AlCl(g) + AlCl_3(g) = 2AlCl_2(g)$. From a third law analysis we obtain ΔHr_{298} = 9.9 ± 9.0 kcal/mol with a drift of 34.5 ± 9.6 eu. The second law ΔHr value is −35.7 kcal/mol. The third law value leads to $\Delta Hf^\circ_{298}(AlCl_2, g)$ = −71.1 ± 5.0 kcal/mol when used in conjunction with heats of formation (2) for AlCl(g) and $AlCl_3(g)$.

The only other reported data for $AlCl_2$ involves a transpiration study of the $AlCl_3$/Al reaction in the temperature range 800-1000 K by Chai et al. (3). Measurements were made of the $AlCl_3$ and Al weight losses at various argon flow rates. Four simultaneous equilibria involving the product vapor species AlCl, $AlCl_3$, Al_2Cl_6, $AlCl_2$, and Al_2Cl_4 were assumed to exist. Equilibrium amounts of AlCl(g), $AlCl_3(g)$, and $Al_2Cl_6(g)$ were assumed to be those predicted by a previous effusion study (4). Distribution of the remainder of the Al weight loss between $AlCl_2$ and Al_2Cl_4 was done by adjusting ΔHf of $AlCl_2$ to give linear log K vs. 1/T plots for $2AlCl_3(g) + Al(c, \ell) = 3AlCl_2(g)$ and $4AlCl_3(g) + 2Al(c, \ell) = 3Al_2Cl_4(g)$. This study resulted in $\Delta Hf^\circ_{298}(AlCl_2, g)$ = −66 ± 3 kcal/mol.

The large discrepancy in the second and third law ΔHr values from the equilibrium data of Farber and Harris (1) suggest possible temperature dependent errors in these measurements. Also, we believe the assumed equilibria in the complex $AlCl_3$/Al system by Chai et al. (3) may be significantly in error. We choose to adopt at this time $\Delta Hf^\circ_{298}(AlCl_2, g)$ = −69.0 ± 5.0 kcal/mol, since this value leads to a realistic progression in the stepwise bond dissociation energies for AlCl, $AlCl_2$, and $AlCl_3$. From JANAF heats of formation (2), we obtain D_1(AlCl) = 119.2, D_2(AlCl-Cl) = 85.6, and $D_3(AlCl_2$-Cl) = 99.6 kcal/mol at 298 K. This scheme, $D_1 > D_2 < D_3$, is consistent with that established for the bond dissociation energies of BF_x and AlF_x by Hildenbrand (5) and BCl_x by Srivastava and Farber (6).

Heat Capacity and Entropy

The molecular structure is assumed to be bent by predictions from the correlation diagram of Walsh (7) for AB_2 molecules with seventeen valence electrons. The electronic states, levels, and bond angle are estimated by comparison with those for the isoelectronic molecule NO_2 (8). The Al-Cl bond length is assumed to lie between that for AlCl and $AlCl_3$ (2). The individual moments of inertia are I_A = 42.467 x 10^{-39}, I_B = 38.957 x 10^{-39}, and I_C = 3.5099 x 10^{-39} g cm^2.

The vibrational frequencies are calculated from force constants by the valence force method (8). The force constants are estimated from those for $SiCl_2$, SiF_2, and AlF_2 (2).

References

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2. JANAF Thermochemical Tables: AlCl(g) and $AlCl_3$(g) dated 6-30-70; $SiCl_2$(g) dated 12-31-70; SiF_2(g) dated 12-31-68; AlF_2(g) dated 6-30-72.
3. B. J. Chai, H. C. Ko, M. A. Greenbaum, and M. Farber, J. Phys. Chem. 71, 3331 (1967).
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6. R. D. Srivastava and M. Farber, Trans. Faraday Soc. 67, 2298 (1971).
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$AlCl_2$

Aluminum Dichloride Unipositive Ion ($AlCl_2^+$)

(Ideal Gas) GFW = 97.8869

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	13.460	65.246	65.246	.000	94.200	91.166	− 66.826
300	13.473	65.330	65.247	.025	94.208	91.146	− 66.400
400	13.998	69.285	65.782	1.401	94.652	90.059	− 49.206
500	14.289	72.443	66.809	2.817	95.081	88.862	− 38.841
600	14.462	75.065	67.973	4.255	95.488	87.579	− 31.901
700	14.572	77.303	69.150	5.707	95.873	86.230	− 26.922
800	14.647	79.254	70.294	7.168	96.228	84.827	− 23.174
900	14.699	80.982	71.387	8.636	96.541	83.383	− 20.248
1000	14.736	82.533	72.425	10.108	94.283	82.089	− 17.941
1100	14.765	83.939	73.409	11.583	94.599	80.854	− 16.064
1200	14.787	85.225	74.341	13.060	94.913	79.589	− 14.495
1300	14.804	86.409	75.224	14.540	95.230	78.300	− 13.163
1400	14.817	87.507	76.063	16.021	95.545	76.987	− 12.018
1500	14.828	88.529	76.860	17.503	95.859	75.650	− 11.022
1600	14.837	89.487	77.620	18.987	96.172	74.292	− 10.148
1700	14.845	90.386	78.345	20.471	96.485	72.916	− 9.374
1800	14.851	91.235	79.037	21.955	96.797	71.521	− 8.684
1900	14.856	92.038	79.701	23.441	97.109	70.109	− 8.064
2000	14.861	92.800	80.337	24.927	97.418	68.679	− 7.505
2100	14.865	93.525	80.948	26.413	97.726	67.232	− 6.997
2200	14.868	94.217	81.535	27.900	98.033	65.773	− 6.534
2300	14.871	94.878	82.101	29.387	98.340	64.304	− 6.110
2400	14.874	95.511	82.647	30.874	98.644	62.817	− 5.720
2500	14.876	96.118	83.174	32.361	98.945	61.316	− 5.360
2600	14.878	96.702	83.683	33.849	99.245	59.805	− 5.027
2700	14.880	97.263	84.175	35.337	99.543	58.281	− 4.718
2800	14.882	97.804	84.653	36.825	30.428	57.580	− 4.494
2900	14.883	98.327	85.115	38.314	30.984	58.537	− 4.411
3000	14.885	98.831	85.564	39.802	31.536	59.479	− 4.333
3100	14.886	99.319	86.000	41.290	32.084	60.401	− 4.258
3200	14.887	99.792	86.423	42.779	32.631	61.306	− 4.187
3300	14.888	100.250	86.836	44.268	33.175	62.195	− 4.119
3400	14.889	100.695	87.237	45.757	33.716	63.065	− 4.054
3500	14.890	101.126	87.627	47.246	34.254	63.918	− 3.991
3600	14.890	101.546	88.008	48.735	34.788	64.762	− 3.932
3700	14.891	101.954	88.380	50.224	35.320	65.586	− 3.874
3800	14.892	102.351	88.742	51.713	35.849	66.395	− 3.819
3900	14.892	102.738	89.096	53.202	36.376	67.196	− 3.766
4000	14.893	103.115	89.442	54.691	36.897	67.977	− 3.714
4100	14.894	103.482	89.780	56.181	37.419	68.745	− 3.664
4200	14.894	103.841	90.110	57.670	37.937	69.504	− 3.617
4300	14.894	104.192	90.434	59.159	38.452	70.249	− 3.570
4400	14.895	104.534	90.750	60.649	38.966	70.989	− 3.526
4500	14.895	104.869	91.060	62.138	39.474	71.705	− 3.482
4600	14.896	105.196	91.364	63.628	39.984	72.418	− 3.441
4700	14.896	105.517	91.662	65.118	40.489	73.114	− 3.400
4800	14.896	105.830	91.954	66.607	40.991	73.801	− 3.360
4900	14.897	106.137	92.240	68.097	41.492	74.488	− 3.322
5000	14.897	106.438	92.521	69.586	41.988	75.151	− 3.285
5100	14.897	106.733	92.797	71.076	42.484	75.814	− 3.249
5200	14.897	107.023	93.068	72.566	42.976	76.461	− 3.214
5300	14.898	107.306	93.334	74.056	43.464	77.098	− 3.179
5400	14.898	107.585	93.595	75.545	43.949	77.730	− 3.146
5500	14.898	107.858	93.852	77.035	44.429	78.349	− 3.113
5600	14.898	108.127	94.104	78.525	44.907	78.962	− 3.082
5700	14.898	108.390	94.353	80.015	45.381	79.561	− 3.051
5800	14.899	108.650	94.597	81.505	45.850	80.163	− 3.021
5900	14.899	108.904	94.837	82.995	46.314	80.749	− 2.991
6000	14.899	109.155	95.074	84.484	46.771	81.329	− 2.962

June 30, 1968; June 30, 1972

ALUMINUM DICHLORIDE UNIPOSITIVE ION ($AlCl_2^+$) (IDEAL GAS) GFW = 97.8869

Point Group [$D_{\infty h}$] ΔHf_0° = [92.6 ± 28] kcal/mol

$S^\circ_{298.15}$ = [65.2 ± 2.0] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [94.2 ± 28] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
[350]	(1)
[100]	(2)
[600]	(1)

Bond Distance: Al-Cl = [2.13] Å

Bond Angle: Cl-Al-Cl = [180]° σ = 2

Rotational Constant: B_0 = [0.0524] cm^{-1}

Heat of Formation

Porter and Zeller (1) reported an appearance potential (*AP*) for the positive ion fragment $AlCl_2^+(g)$ from $AlCl_3(g)$ as 13.4 ± 0.5 eV (309 ± 12 kcal/mol). This value has been confirmed by Potter (2) who reported AP = 13.4 ± 0.7 eV. From the reaction $AlCl_3(g) + e^- = AlCl_2^+(g) + Cl(g) + 2e^-$, we obtain $\Delta Hf_0^\circ(AlCl_2^+, g)$ = 141.2 ± 17 kcal/mol by combining the above result with JANAF heats of formation (3) for $AlCl_3(g)$ and Cl(g). The corresponding ionization potential (IP) for $AlCl_2$ is calculated to be 9.1 eV. We consider this value as an upper limit to the true value, since dissociative ionization of $AlCl_3(g)$ may have involved excess kinetic energy within the fragments. However, we note that recently Farber and Harris (4) reported an appearance potential for $AlCl_2^+(g)$ as 12 ± 1 eV; they indicated that $AlCl_2(g)$ was the parent molecule. The study involved a mass spectrometric investigation of the species effusing from a heated alumina Knudsen cell containing $AlCl_3(g)$ and Al(ℓ). On the basis *of absolute magnitude, we believe this result arises from formation of* $AlCl_2^+(g)$ *by dissociative ionization of* $AlCl_3(g)$, *rather* than by direct ionization of $AlCl_2(g)$. Assuming the reaction to be that given above, we obtain $\Delta Hf_0^\circ(AlCl_2^+, g)$ = 108.9 ± 25 kcal/mol, or an IP = 7.7 eV.

A comparison of the ionization potentials for BX_n, CX_n, and MgX_n (X = F or Cl) indicates that the chloride is in general ~0.5 eV per atom less than the fluoride. On this basis we estimate an ionization potential for $AlCl_2(g)$ of 6.5 eV from IP = 8 eV (3) for $AlF_2(g)$. Beckett and Cassidy (5) selected an IP = 8.0 ± 1.0 eV for $AlCl_2(g)$. We choose to adopt IP = 7.0 ± 1.0 eV (161.43 kcal/mol) for $AlCl_2$ as being representative of the most probable range of values, and we calculate $\Delta Hf_0^\circ(AlCl_2^+, g)$ = 92.6 ± 28 kcal/mol from $\Delta Hf_0^\circ(AlCl_2, g)$ = −68.8 ± 5 kcal/mol (3).

Heat Capacity and Entropy

$AlCl_2^+$ is isoelectronic with $MgCl_2$ and CO_2; we therefore assume it to be linear. This assumption is in agreement with predictions from the correlation diagram of Walsh (6) for AB_2 molecules with sixteen valence electrons. By analogy with CO_2 (7) no low lying electronic levels are expected. The Al-Cl bond length is taken equal to that for AlCl(g). The moment of inertia is equal to 53.4151 x 10^{-39} g cm^2.

The asymmetric stretching frequency (ν_3) is calculated from an estimated force constant by the valence force method (7). The stretching force constant is estimated by comparison with that for $MgCl_2$ (3) and CO_2 (7). The symmetric stretching frequency (ν_1) is estimated from that for $MgCl_2$ (3). The doubly degenerate bending frequency (ν_2) is estimated by comparison with similar data for $MgCl_2$ (3) and several transition-metal dichlorides (8). The enthalpy at 0 K is −3.323 kcal/mol.

References

1. R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960).
2. N. D. Potter, Aeronutronic Report No. U-4859, August 31, 1970, under Contract AF49(638)-1577.
3. JANAF Thermochemical Tables: $AlCl_3(g)$ dated 6-30-70; Cl(g) dated 3-31-61; $AlF_2^+(g)$ and $AlCl_2(g)$ dated 6-30-72; $MgCl_2(g)$ dated 12-31-69.
4. M. Farber and S. P. Harris, High Temperature Sci. 3, 231 (1971).
5. C. W. Beckett and E. C. Cassidy, U. S. Natl. Bur. Std. Report 8628, 1965.
6. A. D. Walsh, J. Chem. Soc. 2266 (1953).
7. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
8. W. Weltner, Jr. in "Advances in High Temperature Chemistry," Volume II, Ed. by L. Eyring, Academic Press, New York, 1969.

Aluminum Dichloride Uninegative Ion ($AlCl_2^-$)

(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							
100							
200							
298	12.362	67.413	67.413	.000	- 91.300	- 92.005	67.442
300	12.378	67.489	67.413	.023	- 91.312	- 92.010	67.029
400	12.964	71.140	67.907	1.293	- 91.968	- 92.143	50.345
500	13.276	74.069	68.856	2.607	- 92.635	- 92.110	40.261
600	13.459	76.507	69.934	3.944	- 93.323	- 91.942	33.490
700	13.573	78.591	71.025	5.296	- 94.030	- 91.655	28.616
800	13.650	80.409	72.087	6.658	- 94.768	- 91.267	24.933
900	13.723	82.020	73.103	8.025	- 95.550	- 90.782	22.045
1000	13.741	83.468	74.068	9.398	- 98.901	- 90.026	19.675
1100	13.770	84.777	74.983	10.773	- 99.679	- 89.102	17.703
1200	13.792	85.976	75.850	12.151	- 100.456	- 88.106	16.046
1300	13.809	87.081	76.672	13.532	- 101.232	- 87.045	14.634
1400	13.823	88.105	77.452	14.913	- 102.011	- 85.924	13.413
1500	13.834	89.059	78.195	16.296	- 102.790	- 84.749	12.348
1600	13.843	89.952	78.902	17.680	- 103.569	- 83.520	11.408
1700	13.851	90.791	79.577	19.065	- 104.349	- 82.242	10.573
1800	13.857	91.583	80.222	20.450	- 105.130	- 80.919	9.825
1900	13.863	92.333	80.840	21.836	- 105.912	- 79.552	9.151
2000	13.867	93.044	81.432	23.223	- 106.696	- 78.146	8.539
2100	13.871	93.721	82.002	24.610	- 107.479	- 76.700	7.982
2200	13.875	94.366	82.549	25.997	- 108.266	- 75.216	7.472
2300	13.878	94.983	83.076	27.385	- 109.052	- 73.693	7.002
2400	13.882	95.573	83.585	28.773	- 109.841	- 72.139	6.569
2500	13.885	96.140	84.076	30.161	- 110.633	- 70.554	6.168
2600	13.888	96.685	84.550	31.550	- 111.424	- 68.933	5.794
2700	13.891	97.209	85.010	32.938	- 112.220	- 67.286	5.446
2800	13.895	97.714	85.454	34.328	- 182.427	- 64.776	5.056
2900	13.899	98.202	85.885	35.717	- 182.965	- 60.567	4.564
3000	13.903	98.673	86.304	37.107	- 183.505	- 56.337	4.104
3100	13.908	99.129	86.710	38.498	- 184.046	- 52.088	3.672
3200	13.915	99.571	87.105	39.889	- 184.591	- 47.822	3.266
3300	13.922	99.999	87.490	41.281	- 185.138	- 43.539	2.883
3400	13.930	100.415	87.864	42.674	- 185.687	- 39.241	2.522
3500	13.940	100.819	88.228	44.067	- 186.239	- 34.929	2.181
3600	13.951	101.212	88.583	45.462	- 186.791	- 30.593	1.857
3700	13.963	101.594	88.930	46.857	- 187.347	- 26.247	1.550
3800	13.977	101.967	89.268	48.254	- 187.904	- 21.888	1.259
3900	13.992	102.330	89.598	49.653	- 188.461	- 17.508	.981
4000	14.010	102.684	89.921	51.053	- 189.021	- 13.120	.717
4100	14.029	103.030	90.237	52.455	- 189.581	- 8.719	.465
4200	14.050	103.369	90.545	53.859	- 190.142	- 4.300	.224
4300	14.072	103.700	90.847	55.265	- 190.704	.131	- .007
4400	14.097	104.023	91.143	56.673	- 191.266	4.581	- .228
4500	14.123	104.340	91.433	58.084	- 191.828	9.035	- .439
4600	14.151	104.651	91.717	59.498	- 192.388	13.507	- .642
4700	14.181	104.956	91.995	60.914	- 192.951	17.985	- .836
4800	14.213	105.255	92.268	62.334	- 193.512	22.477	- 1.023
4900	14.247	105.548	92.536	63.757	- 194.072	26.990	- 1.204
5000	14.282	105.836	92.800	65.184	- 194.630	31.504	- 1.377
5100	14.318	106.119	93.058	66.614	- 195.188	36.036	- 1.544
5200	14.357	106.398	93.312	68.047	- 195.747	40.573	- 1.705
5300	14.396	106.672	93.561	69.485	- 196.305	45.120	- 1.861
5400	14.437	106.941	93.807	70.927	- 196.861	49.683	- 2.011
5500	14.480	107.207	94.048	72.372	- 197.418	54.252	- 2.156
5600	14.523	107.468	94.285	73.823	- 197.973	58.833	- 2.296
5700	14.567	107.725	94.519	75.277	- 198.529	63.420	- 2.432
5800	14.613	107.979	94.749	76.736	- 199.085	68.026	- 2.563
5900	14.659	108.229	94.975	78.200	- 199.641	72.633	- 2.691
6000	14.706	108.476	95.198	79.668	- 200.197	77.255	- 2.814

June 30, 1968; June 30, 1972

ALUMINUM DICHLORIDE UNINEGATIVE ION ($AlCl_2^-$) (IDEAL GAS) GFW = 97.8881

Point Group [C_{2v}] $\Delta Hf°_0$ = [-89.5 ± 28] kcal/mol

$S°_{298.15}$ = [67.4 ± 1.0] gibbs/mol $\Delta Hf°_{298.15}$ = [-91.3 ± 28] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[23000]	3
$^1B_1$	[29000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[450] (1)
[225] (1)
[500] (1)

Bond Distance: Al-Cl = [2.13] Å

Bond Angle: Cl-Al-Cl = [100]° σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [7.1325 x 10^{-114}] $g^3 cm^6$

Heat of Formation

There have been no direct determinations of the electron affinity (EA) for $AlCl_2$(g). We have estimated a value from the following considerations. A comparison of the ionization potentials and electron affinities for the isoelectronic molecules NO_2 (1, 2), BF_2 (1), and AlF_2 (1) indicates that in each case the difference between these two quantities (IP-EA) is roughly 7.1 eV. From this relationship, we obtain EA ($AlCl_2$) = 0.9 ± 1.0 eV with an IP ($AlCl_2$) = 8.0 ± 1.0 eV (1). The estimated EA for $AlCl_2$ leads to $\Delta Hf°_0$($AlCl_2^-$, g) = -89.5 ± 28 kcal/mol when combined with $\Delta Hf°_0$($AlCl_2$, g) = -68.8 ± 5.0 kcal/mol (1).

Heat Capacity and Entropy

A bent configuration for $AlCl_2^-$ is adopted based on predictions from the correlation diagram of Walsh (3). The Cl-Al-Cl bond angle is assumed to be 20° less than that for $AlCl_2$ (1). Comparison with bond angles for CF_2 and SiF_2 (1) indicates that the adopted angle for $AlCl_2^-$ is reasonable. The Al-Cl bond length is taken equal to that for AlCl (1). The three principal moments of inertia are: I_A = 37.4206 x 10^{-39}, I_B = 31.3385 x 10^{-39}, and I_C = 6.0821 x 10^{-39} g cm^2.

$AlCl_2^-$ has 18 valence electrons and is isoelectronic with the Group IV A dichlorides. Thus, we assume the ground state configuration ($^1A_1$) and first excited singlet state ($^1B_1$) are similar to those for $SiCl_2$ (1). By analogy with SO_2 (4) and $GeCl_2$ (5) a triplet state is also included. The energy separation of the $^3B_1$ and $^1B_1$ levels is estimated as 6000 cm^{-1}. This compares with the corresponding values for SO_2 (4) and $GeCl_2$ (5) of 3855 and 8581 cm^{-1}, respectively. The vibrational frequencies are estimated by comparison with those for CCl_2, $SiCl_2$, and $AlCl_2$ (1). The enthalpy at 0 K is -3.004 kcal/mol.

References

1. JANAF Thermochemical Tables: NO_2^-(g), BF_2^-(g), AlF_2^+(g), AlF_2^-(g), $AlCl_2^+$(g), and $AlCl_2$(g) dated 6-30-72; BF_2^+(g) and $SiCl_2$(g) dated 12-31-70; CF_2(g) and AlCl(g) dated 6-30-70; SiF_2(g) and CCl_2(g) dated 12-31-68.
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3. A. D. Walsh, J. Chem. Soc., 2266 (1953).
4. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1966.
5. J. W. Hastie, R. H. Hauge, and J. L. Margrave, J. Mol. Spectroscopy, 29, 152 (1969).

Aluminum Diffluoride (AlF_2)

(Ideal Gas) GFW = 64.9783

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	− 2.722	− 174.518	− 174.518	INFINITE
100	8.354	52.581	71.773	− 1.919	− 174.516	− 175.540	383.642
200	9.713	58.778	63.864	− 1.017	− 174.756	− 176.489	192.858
298	10.965	62.900	62.900	.000	− 175.000	− 177.291	129.958
300	10.985	62.968	62.900	.020	− 175.005	− 177.306	129.167
400	11.881	66.260	63.343	1.167	− 175.227	− 178.037	97.275
500	12.460	68.978	64.206	2.386	− 175.446	− 178.715	78.116
600	12.836	71.285	65.158	3.652	− 175.671	− 179.348	65.328
700	13.089	73.284	66.214	4.949	− 175.910	− 179.942	56.180
800	13.264	75.044	67.210	6.267	− 176.175	− 180.501	49.311
900	13.390	76.614	68.169	7.600	− 176.480	− 181.024	43.959
1000	13.483	78.030	69.086	8.944	− 179.354	− 181.328	39.629
1100	13.554	79.318	69.958	10.296	− 179.653	− 181.511	36.063
1200	13.608	80.500	70.788	11.655	− 179.950	− 181.667	33.086
1300	13.651	81.591	71.578	13.018	− 180.248	− 181.797	30.563
1400	13.686	82.604	72.329	14.385	− 180.547	− 181.904	28.397
1500	13.714	83.549	73.046	15.755	− 180.847	− 181.991	26.516
1600	13.737	84.435	73.731	17.127	− 181.149	− 182.058	24.868
1700	13.757	85.269	74.385	18.502	− 181.451	− 182.105	23.411
1800	13.773	86.055	75.012	19.878	− 181.755	− 182.135	22.114
1900	13.787	86.801	75.613	21.256	− 182.060	− 182.148	20.952
2000	13.799	87.508	76.190	22.636	− 182.366	− 182.144	19.904
2100	13.809	88.182	76.745	24.016	− 182.675	− 182.128	18.954
2200	13.818	88.824	77.280	25.398	− 182.985	− 182.095	18.089
2300	13.827	89.439	77.795	26.780	− 183.296	− 182.044	17.298
2400	13.834	90.027	78.293	28.163	− 183.610	− 181.983	16.572
2500	13.841	90.592	78.773	29.547	− 183.926	− 181.911	15.903
2600	13.848	91.135	79.238	30.931	− 184.244	− 181.823	15.284
2700	13.854	91.658	79.689	32.316	− 184.563	− 181.725	14.710
2800	13.860	92.162	80.125	33.702	− 254.293	− 180.784	14.111
2900	13.866	92.648	80.549	35.088	− 254.354	− 178.157	13.426
3000	13.873	93.118	80.960	36.475	− 254.417	− 175.530	12.787
3100	13.879	93.573	81.360	37.863	− 254.480	− 172.899	12.189
3200	13.886	94.014	81.748	39.251	− 254.546	− 170.265	11.629
3300	13.893	94.442	82.126	40.640	− 254.613	− 167.630	11.102
3400	13.901	94.856	82.495	42.030	− 254.682	− 164.995	10.606
3500	13.909	95.260	82.854	43.420	− 254.753	− 162.354	10.138
3600	13.918	95.651	83.204	44.812	− 254.824	− 159.710	9.696
3700	13.928	96.033	83.545	46.204	− 254.898	− 157.070	9.278
3800	13.937	96.405	83.879	47.597	− 254.974	− 154.424	8.881
3900	13.948	96.767	84.205	48.991	− 255.051	− 151.777	8.505
4000	13.959	97.120	84.523	50.387	− 255.129	− 149.129	8.148
4100	13.971	97.465	84.835	51.783	− 255.210	− 146.481	7.808
4200	13.983	97.802	85.139	53.181	− 255.291	− 143.825	7.484
4300	13.996	98.131	85.438	54.580	− 255.374	− 141.169	7.175
4400	14.009	98.453	85.730	55.980	− 255.460	− 138.511	6.880
4500	14.023	98.768	86.016	57.382	− 255.547	− 135.855	6.598
4600	14.038	99.076	86.297	58.785	− 255.635	− 133.192	6.328
4700	14.052	99.378	86.572	60.189	− 255.728	− 130.534	6.070
4800	14.068	99.674	86.842	61.595	− 255.821	− 127.867	5.822
4900	14.083	99.964	87.107	63.003	− 255.916	− 125.195	5.584
5000	14.099	100.249	87.367	64.412	− 256.015	− 122.530	5.356
5100	14.115	100.528	87.622	65.823	− 256.116	− 119.861	5.136
5200	14.132	100.803	87.873	67.235	− 256.221	− 117.186	4.925
5300	14.149	101.072	88.119	68.649	− 256.329	− 114.511	4.727
5400	14.166	101.337	88.362	70.065	− 256.440	− 111.837	4.526
5500	14.183	101.597	88.600	71.482	− 256.556	− 109.159	4.338
5600	14.200	101.852	88.834	72.901	− 256.676	− 106.474	4.155
5700	14.217	102.104	89.065	74.322	− 256.799	− 103.793	3.980
5800	14.235	102.351	89.292	75.745	− 256.927	− 101.106	3.810
5900	14.252	102.595	89.515	77.169	− 257.061	− 98.420	3.646
6000	14.269	102.834	89.735	78.595	− 257.200	− 95.730	3.487

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

ALUMINUM DIFLUORIDE (AlF_2) (IDEAL GAS) GFW = 64.9783 AlF_2

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [62.9 ± 0.5] gibbs/mol

ΔHf°_0 = [−174.5 ± 10] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [−175.0 ± 10] kcal/mol

Electronic Levels and Quantum Weights

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

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
[700] (1)	[330] (1)	[850] (1)

Bond Distance: Al-F = [1.65] Å

Bond Angle: F-Al-F = [120]°

σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [3.3693 x 10^{-115}] g^3cm^6

Heat of Formation

Ehlert and Margrave (1) investigated mass spectrometrically the reaction $2AlF_2(g) = AlF_3(g) + AlF(g)$ and reported ΔHr_{298} = −49.5 ± 4.0 kcal/mol. This result was derived from a third law analysis of equilibrium data determined over the temperature range 1243 to 1301 K. However, no experimental data were published. Combining this result with JANAF (2) heats of formation for $AlF_3(g)$ and AlF(g), we obtain $\Delta Hf^\circ_{298}(AlF_2, g)$ = −151.5 ± 4.0 kcal/mol. In an earlier paper, Ehlert et al. (3) reported that the AlF_3^+ ion was not observed in their mass spectrometric studies of the magnesium fluoride-aluminum system. It is apparent that Ehlert and Margrave (1) have determined equilibrium concentrations for both AlF_2 and AlF_3 from ion intensities for AlF_2^+ at different electron energies. Since at the higher energies where AlF_2^+ is presumably formed from AlF_3 it is quite likely that the ion intensities contained significant contributions from AlF_2, we believe the ΔHf value for AlF_2 obtained from these results may be too positive.

Farber and Harris (4) performed an effusion-mass spectrometric study of the reaction between $AlF_3(g)$ and liquid Al. Ion intensities for AlF(g), $AlF_2(g)$, and Al(g) were measured at ionization energies of 3 eV above appearance potentials in the temperature range 1408 to 1633 K and led to equilibrium data for the reaction $2AlF(g) = AlF_2(g) + Al(g)$. From a third law analysis of these results we obtain ΔHr_{298} = 16.69 ± 0.80 kcal/mol with a drift of −3.83 ± 0.58 eu. The second law value is ΔHr_{298} = 22.48 kcal/mol. The third law value leads to $\Delta Hf^\circ_{298}(AlF_2, g)$ = −188 ± 3 kcal/mol, when combined with JANAF heats of formation (2) for AlF(g) and Al(g). In the same investigation Farber and Harris (4) also performed a separate experiment at 1538 K in which ion intensities for the above species were measured at ionization energies only slightly above appearance potentials (~2 eV). A third law analysis of the equilibrium constant calculated from these relative ion intensities yields ΔHr_{298} = 25.6 kcal/mol, or $\Delta Hf^\circ_{298}(AlF_2, g)$ = −179.4 kcal/mol. Here again the significant influence of the ionization energies on the ΔHf values for AlF_2 obtained from these results suggests possible errors in these Knudsen effusion-mass spectrometric experiments due to ambiguities in the assignment of the molecular species from which the ions originated. Very recently, Uy et al. (11) conducted a mass spectrometric study of the vapor species in equilibrium with the system $AlF_3(g) + Al(\ell) + Al_2O_3(c)$. Presumably, all $AlF_3(g)$ is removed from this system by either the reaction $AlF_3(g) + 2Al(g) = 3AlF(g)$, or $AlF_3(g) + Al_2O_3(c) = 3AlOF(g)$. Equilibrium constants for $2AlF(g) = AlF_2(g) + Al(g)$ were measured directly from the ratios of the ion intensities in the temperature range 1453 to 1675 K. A third law analysis gives ΔHr_{298} = 24.3 ± 0.9 kcal/mol, or $\Delta Hf^\circ_{298}(AlF_2, g)$ = −180.5 ± 3.0 kcal/mol; the drift in the third law is −4.2 ± 1.7 eu. The second law heat of reaction at 298 K is 30.9 kcal/mol.

An upper limit to the ΔHf of AlF_2 can be obtained from established trends in the bond dissociation energies for the Group III A halides. Hildenbrand (5) predicted that for the fluorides the bond dissociation energies would follow the order $D_1(M-F) > D_2(MF-F) < D_3(MF_2-F)$ based on a valence state description of the bonding in these molecules. It is now established that the bond dissociation energies for the boron fluorides, boron and aluminum chlorides (6) are in general agreement with this scheme. Assuming $D_2(AlF-F) = D_3(AlF_2-F)$ = 131.7 kcal/mol, we calculate $\Delta Hf^\circ_{298}(AlF_2, g)$ = −176.2 kcal/mol from heats of formation (2) for AlF(g) and $AlF_3(g)$.

We choose to adopt $\Delta Hf^\circ_{298}(AlF_2, g)$ = −175 ± 10 kcal/mol as being representative of the most probable range of values. The adopted value leads to bond dissociation energies of $D_2(AlF-F)$ = 130.5 and $D_3(AlF_2-F)$ = 132.9 kcal/mol which are consistent with the bond energy scheme predicted by Hildenbrand (5). Also, our value for $D_2(AlF-F)$ is essentially that given by Darwent (7).

Heat Capacity and Entropy

The configuration of AlF_2 is predicted to be bent by Walsh (8), since it has seventeen valence electrons. The electronic states, levels, and bond angle are estimated from those for the isoelectronic molecule NO_2 (9). Molecular orbital calculations by Hastie and Margrave (10) predicted the $^2B_1$ state for AlF_2 to lie at 6453 cm^{-1}. However, this value appears to be unreasonably low in comparison with their data for the other Group III A halides. The Al-F bond length is assumed to lie between that for AlF(g) and $AlF_3(g)$ (2). The individual moments of inertia are I_A = 1.7831 x 10^{-39}, I_B = 12.8833 x 10^{-39}, and I_C = 14.6666 x 10^{-39} g cm^2. The vibrational frequencies are estimated from a valence bond calculation with force constants of k = 3.9 x 10^5 and $k\delta/\ell^2$ = 0.36 x 10^5 dynes/cm. The force constants are estimated from those for $MgF_2(g)$ and $SiF_2(g)$ (2).

References

1. T. C. Ehlert and J. L. Margrave, J. Amer. Chem. Soc. 86, 3901 (1964).
2. JANAF Thermochemical Tables: $AlF_3(g)$ dated 6-30-70; AlF(g) dated 6-30-69; Al(g) dated 12-31-65; $MgF_2(g)$ dated 3-31-66; $SiF_2(g)$ dated 12-31-68.
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Aluminum Difluoride Unipositive Ion (AlF_2^+)

(Ideal Gas) GFW = 64.9777

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	12.317	58.169	58.169	.000	11.200	8.832	−6.474
300	12.337	58.245	58.169	.023	11.207	8.817	−6.423
400	13.169	61.918	58.664	1.301	11.613	7.961	−4.350
500	13.682	64.916	59.624	2.646	12.017	7.000	−3.060
600	14.007	67.442	60.722	4.032	12.409	5.960	−2.171
700	14.221	69.618	61.841	5.444	12.781	4.855	−1.516
800	14.369	71.527	62.935	6.874	13.125	3.698	−1.010
900	14.474	73.226	63.986	8.316	13.426	2.502	−.608
1000	14.552	74.755	64.988	9.768	11.157	1.457	−.318
1100	14.610	76.145	65.940	11.226	11.461	.472	−.094
1200	14.656	77.416	66.844	12.689	11.764	−.541	.099
1300	14.691	78.593	67.703	14.157	12.068	−1.578	.265
1400	14.720	79.683	68.520	15.627	12.369	−2.638	.412
1500	14.743	80.699	69.299	17.100	12.669	−3.721	.542
1600	14.762	81.651	70.041	18.576	12.967	−4.825	.659
1700	14.778	82.547	70.751	20.053	13.264	−5.945	.764
1800	14.791	83.392	71.430	21.531	13.559	−7.084	.860
1900	14.803	84.192	72.081	23.011	13.853	−8.238	.948
2000	14.812	84.951	72.705	24.492	14.145	−9.408	1.028
2100	14.821	85.674	73.306	25.973	14.433	−10.596	1.103
2200	14.828	86.364	73.884	27.456	14.721	−11.794	1.172
2300	14.834	87.023	74.441	28.939	15.008	−13.002	1.236
2400	14.840	87.655	74.978	30.423	15.292	−14.227	1.296
2500	14.845	88.260	75.498	31.907	15.573	−15.465	1.352
2600	14.849	88.843	76.000	33.392	15.852	−16.711	1.405
2700	14.853	89.403	76.486	34.877	16.130	−17.969	1.454
2800	14.857	89.944	76.957	36.362	−53.004	−18.407	1.437
2900	14.860	90.465	77.414	37.848	−52.468	−17.180	1.295
3000	14.863	90.969	77.857	39.334	−51.935	−15.974	1.164
3100	14.865	91.456	78.288	40.821	−51.403	−14.784	1.042
3200	14.868	91.928	78.707	42.307	−50.874	−13.610	.930
3300	14.870	92.386	79.115	43.794	−50.346	−12.454	.825
3400	14.872	92.830	79.512	45.281	−49.821	−11.315	.727
3500	14.874	93.261	79.898	46.769	−49.297	−10.188	.636
3600	14.875	93.680	80.275	48.256	−48.777	−9.075	.551
3700	14.877	94.087	80.643	49.744	−48.258	−7.982	.471
3800	14.878	94.484	81.002	51.231	−47.743	−6.899	.397
3900	14.879	94.871	81.353	52.719	−47.229	−5.832	.327
4000	14.881	95.247	81.695	54.207	−46.719	−4.778	.261
4100	14.882	95.615	82.030	55.695	−46.211	−3.738	.199
4200	14.883	95.973	82.358	57.184	−45.704	−2.706	.141
4300	14.884	96.324	82.679	58.672	−45.201	−1.687	.086
4400	14.885	96.666	82.993	60.160	−44.702	−.678	.034
4500	14.886	97.000	83.300	61.649	−44.206	.313	−.015
4600	14.886	97.327	83.602	63.137	−43.712	1.298	−.062
4700	14.887	97.648	83.897	64.626	−43.223	2.267	−.105
4800	14.888	97.961	84.187	66.115	−42.736	3.232	−.147
4900	14.888	98.268	84.471	67.604	−42.253	4.190	−.187
5000	14.889	98.569	84.750	69.093	−41.776	5.129	−.224
5100	14.890	98.864	85.024	70.581	−41.303	6.061	−.260
5200	14.890	99.153	85.293	72.070	−40.834	6.987	−.294
5300	14.891	99.436	85.557	73.560	−40.369	7.903	−.326
5400	14.891	99.715	85.817	75.049	−39.910	8.807	−.356
5500	14.892	99.988	86.072	76.538	−39.458	9.703	−.386
5600	14.892	100.256	86.323	78.027	−39.011	10.597	−.414
5700	14.892	100.520	86.570	79.516	−38.569	11.477	−.440
5800	14.893	100.779	86.812	81.005	−38.134	12.353	−.465
5900	14.893	101.034	87.051	82.495	−37.705	13.218	−.490
6000	14.893	101.284	87.286	83.984	−37.285	14.077	−.513

June 30, 1968; June 30, 1972

ALUMINUM DIFLUORIDE UNIPOSITIVE ION (AlF_2^+) (IDEAL GAS) GFW = 64.9777

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

ΔHf_0° = [10.0 ± 33] kcal/mol

$S^\circ_{298.15}$ = [58.2 ± 2.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [11.2 ± 33] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[600] (1)
[200] (2)
[800] (1)

Bond Distance: Al-F = [1.65] Å

Bond Angle: F-Al-F = [180]°

σ = 2

Rotational Constant: B_0 = [0.16298] cm^{-1}

Heat of Formation

Ehlert et al. (1) reported the appearance potential (AP) of AlF_2^+ from AlF_3(g) as 15.2 ± 0.3 eV (350.5 ± 7.0 kcal/mol). Subsequent mass spectrometric measurements by Ehlert and Margrave (2) on the same system (MgF_2/Al) have confirmed this value. Assuming the ionization process to be $AlF_3(g) + e^- = AlF_2^+(g) + F(g) + 2e^-$, we calculate $\Delta Hf_0^\circ(AlF_2^+, g)$ = 44 ± 8 kcal/mol by combining the above result with JANAF heats of formation (3) for AlF_3(g) and F(g). The corresponding ionization potential (IP) for AlF_2 is 9.47 eV and would also certainly represent an upper limit to the true value since it is not known whether the AlF_2^+ ion formed by impact had some internal energy.

The AP of AlF_2^+ from AlF_2(g) has been reported as 9 ± 1 eV (2) and 11 ± 1 eV (4). These values lead to ΔHf_0° for AlF_2^+ of 33.1 ± 33 and 79.2 ± 33 kcal/mol, respectively, when combined with $\Delta Hf_0^\circ(AlF_2, g)$ = −174.5 ± 10 kcal/mol (3). Molecular orbital calculations on AlF_2 by Hastie and Margrave (5) have indicated an IP for AlF_2 of 7.8 eV. The bond angle in the difluoride was assumed to be 180° in these calculations.

A comparison of ionizations potentials for BX and BX_2 (5) (X = F,Cl) indicates that the values for the dihalides are some 2-3 eV less than those for the monohalides. Based on an IP = 9.7 eV for AlF (3), we estimate the IP for AlF_2 to be near 7.5 eV which is in reasonable agreement with the calculated value of Hastie and Margrave (3). We choose to adopt IP = 8.0 ± 1 eV for AlF_2(g) which corresponds to $\Delta Hf_0^\circ(AlF_2^+, g)$ = 10.0 ± 33 kcal/mol.

Heat Capacity and Entropy

The molecular structure of AlF_2^+ is assumed to be linear based on predictions from the correlation diagram of Walsh (6). However, we do note that the isoelectronic molecule MgF_2 (3) has been shown to be bent. The Al-F bond length is taken equal to that for AlF (3). By analogy with CO_2 (7) no low lying electronic levels are expected. The moment of inertia is 17.1766 × 10^{-39} g cm^2.

The asymmetric stretching (ν_3) and doubly degenerate bending (ν_2) frequencies for AlF_2^+ are estimated by comparison with similar data for the first-row transition-metal difluorides (8). The symmetric stretching frequency (ν_1) is assumed to lie between that for MgF_2(g) and SiF_2(g) (3). The enthalpy at 0 K is −2.927 kcal/mol.

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2. T. C. Ehlert and J. L. Margrave, J. Amer. Chem. Soc. 86, 3901 (1964).
3. JANAF Thermochemical Tables: AlF_3(g) dated 6-30-70; F(g) dated 9-30-65; AlF_2(g) dated 6-30-72; BF_2^+(g) dated 12-31-70; AlF(g) dated 6-30-69; MgF_2(g) dated 3-31-66; SiF_2(g) 12-31-68; AlF^+(g) dated 6-30-68.
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Aluminum Difluoride Uninegative Ion (AlF_2^-)

(Ideal Gas) GFW = 64.9789

T, °K	Cp°	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	10.811	61.564	61.564	.000	− 222.900	− 223.305	163.687
300	10.831	61.631	61.565	.020	− 222.914	− 223.308	162.680
400	11.745	64.881	62.001	1.152	− 223.648	− 223.327	122.020
500	12.351	67.571	62.854	2.355	− 224.376	− 223.164	97.545
600	12.750	69.861	63.836	3.615	− 225.108	− 222.853	81.174
700	13.021	71.848	64.842	4.904	− 225.851	− 222.417	69.442
800	13.209	73.600	65.829	6.217	− 226.618	− 221.876	60.614
900	13.345	75.164	66.781	7.545	− 227.425	− 221.235	53.723
1000	13.446	76.575	67.691	8.884	− 230.801	− 220.319	48.151
1100	13.522	77.861	68.558	10.233	− 231.600	− 219.233	43.558
1200	13.582	79.040	69.383	11.588	− 232.397	− 218.073	39.717
1300	13.628	80.129	70.168	12.949	− 233.194	− 216.847	36.455
1400	13.666	81.140	70.916	14.314	− 233.992	− 215.559	33.650
1500	13.697	82.084	71.630	15.682	− 234.791	− 214.215	31.211
1600	13.722	82.969	72.311	17.053	− 235.590	− 212.817	29.069
1700	13.743	83.802	72.963	18.426	− 236.391	− 211.368	27.173
1800	13.761	84.588	73.587	19.801	− 237.193	− 209.874	25.482
1900	13.776	85.332	74.186	21.178	− 237.996	− 208.335	23.964
2000	13.789	86.039	74.761	22.556	− 238.801	− 206.752	22.593
2100	13.800	86.712	75.314	23.936	− 239.606	− 205.132	21.348
2200	13.809	87.354	75.847	25.316	− 240.415	− 203.471	20.213
2300	13.818	87.968	76.361	26.698	− 241.223	− 201.771	19.173
2400	13.826	88.556	76.857	28.080	− 242.035	− 200.039	18.216
2500	13.833	89.121	77.336	29.463	− 242.849	− 198.275	17.333
2600	13.839	89.664	77.800	30.846	− 243.664	− 196.474	16.515
2700	13.845	90.186	78.249	32.230	− 244.481	− 194.644	15.755
2800	13.850	90.690	78.684	33.615	− 314.709	− 191.954	14.983
2900	13.856	91.176	79.107	35.000	− 315.268	− 187.559	14.135
3000	13.861	91.646	79.517	36.386	− 315.829	− 183.148	13.342
3100	13.866	92.100	79.915	37.773	− 316.389	− 178.715	12.599
3200	13.872	92.540	80.303	39.160	− 316.953	− 174.264	11.902
3300	13.878	92.967	80.680	40.547	− 317.519	− 169.796	11.245
3400	13.885	93.382	81.048	41.935	− 318.087	− 165.313	10.626
3500	13.892	93.784	81.406	43.324	− 318.656	− 160.810	10.041
3600	13.899	94.176	81.755	44.714	− 319.225	− 156.288	9.488
3700	13.908	94.557	82.096	46.104	− 319.798	− 151.757	8.964
3800	13.918	94.928	82.429	47.495	− 320.373	− 147.207	8.466
3900	13.928	95.290	82.754	48.887	− 320.949	− 142.643	7.993
4000	13.940	95.642	83.072	50.281	− 321.525	− 138.064	7.543
4100	13.952	95.987	83.383	51.675	− 322.105	− 133.473	7.115
4200	13.966	96.323	83.687	53.071	− 322.685	− 128.863	6.705
4300	13.981	96.652	83.985	54.465	− 323.266	− 124.241	6.315
4400	13.997	96.973	84.276	55.868	− 323.850	− 119.604	5.941
4500	14.015	97.288	84.562	57.268	− 324.435	− 114.957	5.583
4600	14.034	97.596	84.842	58.671	− 325.020	− 110.294	5.240
4700	14.054	97.898	85.116	60.075	− 325.610	− 105.625	4.912
4800	14.076	98.195	85.386	61.482	− 326.199	− 100.936	4.596
4900	14.099	98.485	85.650	62.890	− 326.791	− 96.232	4.292
5000	14.124	98.770	85.910	64.301	− 327.384	− 91.523	4.000
5100	14.150	99.050	86.165	65.715	− 327.979	− 86.803	3.720
5200	14.177	99.325	86.415	67.131	− 328.577	− 82.066	3.449
5300	14.205	99.595	86.661	68.550	− 329.177	− 77.319	3.188
5400	14.234	99.861	86.903	69.972	− 329.779	− 72.564	2.937
5500	14.265	100.123	87.141	71.397	− 330.383	− 67.796	2.694
5600	14.297	100.380	87.375	72.825	− 330.991	− 63.013	2.459
5700	14.330	100.633	87.606	74.257	− 331.600	− 58.223	2.232
5800	14.364	100.883	87.833	75.691	− 332.214	− 53.421	2.013
5900	14.399	101.129	88.056	77.130	− 332.830	− 48.611	1.801
6000	14.435	101.371	88.276	78.571	− 333.450	− 43.788	1.595

June 30, 1968; June 30, 1972

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

Point Group [C_{2v}] ΔHf_0° = −220.9 ± 12 kcal/mol

$S^\circ_{298.15}$ = [61.5 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = −222.9 ± 12 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[25000]	3
$^1B_1$	[40000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[796] (1)
[332] (1)
[836] (1)

Bond Distance: Al-F = [1.65] Å

Bond Angle: F-Al-F = [100]° σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = [3.8697 x 10^{-115}] g^3cm^6

Heat of Formation

Farber et al. (1) recently reported equilibrium data for the reaction $AlF_2(g) + F^-(g) = F(g) + AlF_2^-(g)$ in the temperature range 1705 to 1900 K. These results were obtained in a molecular flow effusion-mass spectrometric study of the reduction products formed in the $AlF_3(g)/KF(g)/Al(\ell)$ system. A third law analysis of these equilibrium data yields ΔHr_{298} = 32.0 ± 1.0 kcal/mol with a drift of 1.4 ± 4.7 eu. The second law ΔHr_{298} value is 29.4 kcal/mol. Combining the third law heat of reaction with JANAF heats of formation (2), we calculate $\Delta Hf^\circ_{298}(AlF_2^-, g)$ = −222.9 ± 12 kcal/mol, which is adopted. This value corresponds to an electron affinity (EA) of 2.0 ± 0.5 eV for $AlF_2(g)$.

Heat Capacity and Entropy

The correlation diagram of Walsh (3) predicts a bent configuration for AlF_2^- (18 valence electrons) with a bond angle considerably reduced from that for AlF_2. These predictions are supported by the experimentally determined bond angles for the isoelectronic molecules CF_2 (104.9°) (2), SiF_2 (100.9°) (2), and GeF_2 (94°) (4). Therefore, we assume the bond angle for AlF_2^- is equal to 100°. The Al-F bond length is taken equal to that for AlF_2 (2). The individual moments of inertia are: I_A = 13.027 x 10^{-39}, I_B = 10.080 x 10^{-39}, and I_C = 2.947 x 10^{-39} g cm^2.

Recent ultraviolet absorption studies on SiF_2 (5), GeF_2 (6), SnF_2 and PbF_2 (7) have indicated the ground state for these molecules to be $^1A_1$, and a first excited singlet state ($^1B_1$) has been observed in each case in the region 40000-44000 cm^{-1}. We adopt the ground state of AlF_2^- as $^1A_1$ and assume the $^1B_1$ level to lie at 40000 cm^{-1}. The triplet state ($^3B_1$) is estimated by analogy with the observed triplet levels for SiF_2 (8) and SO_2 (9). The vibrational frequencies are calculated from the stretching and bending force constants of k = 4.28 x 10^5 and $k\delta/\ell^2$ = 0.42 x 10^5 dynes/cm by the valence force method. These force constants are estimated from similar data for CF_2 (2), SiF_2 (2), and GeF_2 (4). The enthalpy at 0 K is −2.702 kcal/mol.

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Lithium Aluminate ($LiAlO_2$)

(Crystal) GFW = 65.9193

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	− 2.723	− 282.549	− 282.549	INFINITE
100	4.293	1.932	23.722	− 2.179	− 282.924	− 278.637	608.960
200	11.461	7.215	14.095	− 1.376	− 283.699	− 274.036	299.452
298	16.208	12.751	12.751	.000	− 284.100	− 269.200	197.329
300	16.283	12.852	12.751	.030	− 284.105	− 269.108	196.045
400	19.490	18.013	13.433	1.832	− 284.234	− 264.082	144.288
500	21.130	22.549	14.813	3.868	− 284.978	− 258.967	113.194
600	22.153	26.497	16.439	6.034	− 284.939	− 253.768	92.435
700	22.885	29.968	18.129	8.288	− 284.848	− 248.579	77.610
800	23.462	33.063	19.806	10.606	− 284.737	− 243.407	66.496
900	23.949	35.855	21.436	12.977	− 284.633	− 238.246	57.854
1000	24.380	38.401	23.007	15.394	− 287.066	− 232.913	50.903
1100	24.774	40.743	24.515	17.851	− 286.895	− 227.507	45.201
1200	25.143	42.915	25.959	20.347	− 286.694	− 222.118	40.453
1300	25.495	44.941	27.342	22.879	− 286.463	− 216.745	36.438
1400	25.834	46.843	28.667	25.446	− 286.204	− 211.391	33.000
1500	26.163	48.637	29.939	28.046	− 285.917	− 206.058	30.023
1600	26.485	50.336	31.162	30.678	− 285.602	− 200.743	27.420
1700	26.802	51.951	32.337	33.343	− 320.305	− 194.122	24.956
1800	27.115	53.492	33.470	36.039	− 319.753	− 186.713	22.670
1900	27.425	54.966	34.563	38.766	− 319.177	− 179.337	20.628
2000	27.733	56.381	35.619	41.524	− 318.576	− 171.995	18.795
2100	28.040	57.742	36.640	44.315	− 317.948	− 164.682	17.139
2200	28.040	59.047	37.629	47.119	− 317.315	− 157.399	15.636
2300	28.040	60.293	38.588	49.923	− 316.685	− 150.143	14.267
2400	28.040	61.487	39.517	52.727	− 316.065	− 142.914	13.014
2500	28.040	62.631	40.419	55.531	− 315.452	− 135.715	11.864
2600	28.040	63.731	41.294	58.335	− 314.845	− 128.537	10.804
2700	28.040	64.789	42.145	61.139	− 314.247	− 121.384	9.825
2800	28.040	65.809	42.972	63.943	− 383.066	− 113.420	8.853
2900	28.040	66.793	43.777	66.747	− 382.223	− 103.805	7.823
3000	28.040	67.743	44.560	69.551	− 381.387	− 94.217	6.864

September 30, 1961; June 30, 1972

LITHIUM ALUMINATE ($LiAlO_2$) (CRYSTAL) GFW = 65.9193

ΔHf°_0 = −282.55 ± 1 kcal/mol

$S^\circ_{298.15}$ = 12.75 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −284.1 ± 1 kcal/mol

Tm = 1883 ± 15 K

ΔHm° = [21 ± 2] kcal/mol

Heat of Formation

The heat of formation of $LiAlO_2$(c) is calculated from two independent experiments. Coughlin (1) measured the heat of solution of $LiAlO_2$(c) in HCl(aq). This value, −46.0 ± 0.05 kcal/mol, was combined with measured heats of solution of Al(c) in HCl(aq) and LiCl(c) in HCl(aq) (2). These heats are combined to give a ΔHr°_{298} = −88.9 ± 0.14 kcal/mol for

$$Al(c) + LiCl(c) + 14.7\ H_2O(\ell) \rightarrow LiAlO_2(c) + 3/2\ H_2(g) + HCl{\cdot}12.7\ H_2O(aq).$$

Combining this result with values for ΔHf°_{298}(LiCl, c) (3), ΔHf°_{298}($HCl{\cdot}12.7\ H_2O$) (4), and ΔHf°_{298}(H_2O, ℓ) (4) we calculate ΔHf°_{298}($LiAlO_2$, c) = −284.3$_3$ ± 0.8 kcal/mol.

Gross et al. (5) measured the heat of solution of $LiAlO_2$(c) in HF(aq) and combined this heat with the heats of solution of Li_2O(c) and $Al_2O_3{\cdot}3\ H_2O$(c) [Gibbsite] to give ΔHr°_{298} = −24.6 ± 1 kcal/mol for the following process

$$Li_2O(c) + Al_2O_3(c, \alpha) \rightarrow 2LiAlO_2(c)$$

Combining this heat with ΔHf°_{298}(Al_2O_3, c) = −400.5 kcal/mol and ΔHf°_{298}(Li_2O, c) = −143.1 kcal/mol (6) we calculate ΔHf°_{298} ($LiAlO_2$, c) = −284.1 ± 1 kcal/mol *in good agreement with the former study. We have adopted a value of* −284.1 ± 1 kcal/mol for $\Delta Hf^\circ_{298.15}$($LiAlO_2$, c).

Heat Capacity and Entropy

Low temperature heat capacities have been measured by King (7) from 51-298 K. Enthalpy measurements (drop calorimetry) have been made by Christensen et al. (8) in the range 398-1795 K. These two sets of data agree well in Cp at 298 K. *No transitions were detected in either study. The entropy is derived from* C_p° and an extrapolation of S_{51} = 0.36 gibbs/mol.

Melting Data

Hummel et al. (9) report a series of 10 melting point measurements on $LiAlO_2$ in which they determined Tm = 1883 ± 15 K. The heat of fusion is estimated by analogy with similar compounds.

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Lithium Aluminate ($LiAlO_2$)

(Liquid) GFW = 65.9193

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	16.208	21.826	21.826	.000	- 266.336	- 254.141	186.291
300	16.283	21.927	21.826	.030	- 266.341	- 254.066	185.087
400	19.490	27.088	22.508	1.832	- 266.470	- 249.948	136.565
500	21.130	31.624	23.888	3.868	- 267.214	- 245.741	107.413
600	22.153	35.572	25.514	6.034	- 267.175	- 241.449	87.948
700	22.885	39.043	27.204	8.288	- 267.084	- 237.168	74.047
800	23.462	42.138	28.881	10.606	- 266.973	- 232.903	63.626
900	23.949	44.930	30.511	12.977	- 266.869	- 228.650	55.524
1000	24.380	47.476	32.082	15.394	- 269.302	- 224.224	49.004
1100	24.774	49.818	33.590	17.851	- 269.131	- 219.725	43.655
1200	25.143	51.990	35.034	20.347	- 268.930	- 215.244	39.201
1300	25.495	54.016	36.417	22.879	- 268.699	- 210.779	35.435
1400	32.000	56.388	37.740	26.079	- 267.807	- 206.356	32.214
1500	32.000	58.596	39.076	29.279	- 266.920	- 201.999	29.431
1600	32.000	60.661	40.361	32.479	- 266.037	- 197.699	27.004
1700	32.000	62.601	41.613	35.679	- 300.205	- 192.127	24.700
1800	32.000	64.430	42.830	38.879	- 299.149	- 185.797	22.539
1900	32.000	66.160	44.013	42.079	- 298.100	- 179.528	20.650
2000	32.000	67.801	45.162	45.279	- 297.057	- 173.317	18.939
2100	32.000	69.363	46.277	48.479	- 296.020	- 167.156	17.396
2200	32.000	70.851	47.361	51.679	- 294.991	- 161.044	15.998
2300	32.000	72.274	48.413	54.879	- 293.965	- 154.977	14.726
2400	32.000	73.636	49.436	58.079	- 292.949	- 148.955	13.564
2500	32.000	74.942	50.430	61.279	- 291.940	- 147.979	12.499
2600	32.000	76.197	51.397	64.479	- 290.937	- 137.040	11.519
2700	32.000	77.405	52.338	67.679	- 289.943	- 131.141	10.615
2800	32.000	78.568	53.254	70.879	- 358.366	- 124.446	9.713
2900	32.000	79.691	54.147	74.079	- 357.127	- 116.114	8.751
3000	32.000	80.776	55.016	77.279	- 355.895	- 107.822	7.855

Sept. 30, 1961; June 30, 1972

LITHIUM ALUMINATE ($LiAlO_2$) (LIQUID) GFW = 65.9193

$S°_{298.15}$ = [21.826 ± 0.5] gibbs/mol

$\Delta Hf°_{298.15}$ = [-266.336 ± 0.3] kcal/mol

Tm = 1883 ± 15 K

$\Delta Hm°$ = [21 ± 2] kcal/mol

Heat of Formation

The $\Delta Hf°_{298}(LiAlO_2, \ell)$ = -266.34 ± 0.2 kcal/mol is calculated by adding the estimated heat of fusion to the heat of formation of the crystal.

Heat Capacity and Entropy

The heat capacity of liquid $LiAlO_2$ is estimated as 32 cal/deg mol above a hypothetical glass transition temperature of 1300 K. Below this temperature the heat capacity is taken the same as the crystal. (See crystal table.) The $S°_{298}$ = 21.8 ± 0.5 gibbs/mol is calculated in a manner analogous to the heat of formation.

Melting Data

See $LiAlO_2$(c) table for details.

Beryllium Aluminate ($BeAl_2O_4$)

(Crystal) GFW = 126.9728

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.128	- 546.322	- 546.322	INFINITE
100	3.911	1.320	21.630	- 3.031	- 547.835	- 539.345	1178.737
200	15.877	7.644	17.874	- 2.046	- 549.264	- 530.275	579.457
298	25.185	15.844	15.844	.000	- 550.000	- 520.787	381.747
300	25.325	16.000	15.844	.047	- 550.008	- 520.606	379.261
400	31.214	24.175	16.919	2.903	- 550.211	- 510.762	279.067
500	34.643	31.533	19.121	6.206	- 550.136	- 500.904	218.945
600	37.030	38.073	21.745	9.797	- 549.915	- 491.078	178.875
700	38.730	43.916	24.502	13.590	- 549.620	- 481.293	150.267
800	39.980	49.173	27.263	17.528	- 549.307	- 471.556	128.823
900	40.910	53.938	29.967	21.574	- 549.030	- 461.853	112.153
1000	41.640	58.286	32.584	25.702	- 553.862	- 451.811	98.743
1100	42.290	62.286	35.105	29.899	- 553.525	- 441.624	87.743
1200	42.900	65.992	37.526	34.158	- 553.169	- 431.468	78.581
1300	43.510	69.450	39.850	38.479	- 552.790	- 421.340	70.834
1400	44.130	72.697	42.082	42.861	- 552.390	- 411.243	64.198
1500	44.780	75.763	44.226	47.306	- 551.965	- 401.178	58.452
1600	45.480	78.675	46.289	51.818	- 554.264	- 391.061	53.416
1700	46.250	81.455	48.276	56.404	- 553.653	- 380.879	48.965
1800	47.100	84.122	50.194	61.071	- 552.978	- 370.732	45.013
1900	48.020	86.693	52.048	65.826	- 552.234	- 360.628	41.482
2000	49.010	89.181	53.843	70.677	- 551.409	- 350.569	38.308
2100	50.070	91.598	55.583	75.630	- 550.497	- 340.548	35.441
2200	51.200	93.953	57.274	80.694	- 549.493	- 330.575	32.840
2300	52.400	96.255	58.919	85.873	- 548.385	- 320.643	30.468
2400	53.670	98.512	60.522	91.176	- 547.172	- 310.764	28.299
2500	55.010	100.730	62.086	96.609	- 545.847	- 300.950	26.309
2600	56.420	102.914	63.614	102.180	- 544.396	- 291.177	24.476
2700	57.900	105.071	65.110	107.896	- 542.816	- 281.470	22.783
2800	59.450	107.205	66.575	113.763	- 750.950	- 269.052	21.000

Mar. 31, 1962; Sept. 30, 1964; June 30, 1972

BERYLLIUM ALUMINATE ($BeAl_2O_4$) (CRYSTAL) GFW = 126.9728

$\Delta Hf°_0$ = -546.3 ± 1.0 kcal/mol

$S°_{298.15}$ = 15.844 ± 0.03 gibbs/mol

$\Delta Hf°_{298.15}$ = -550.0 ± 1.0 kcal/mol

Tm = 2146 ± 10 K

$\Delta Hm°$ = 41.6 ± 1.0 kcal/mol

Heat of Formation

ΔHf° is calculated from ΔHr°(298.15 K) = -4.06 ± 0.3 kcal/mol for BeO(c, α) + Al_2O_3(c, α) → $BeAl_2O_4$(c) using current values of ΔHf° for the reactants (1). ΔHr° is based on the value -4.0 ± 0.3 kcal/mol at 968 K determined by Holm and Kleppa (2) from the difference in heats of solution of the three components in an oxide melt.

For comparison with the above reaction, we derive ΔHr°(298.15 K) = -2.3 kcal/mol from ΔGr°(1800 K) = -3.13 kcal/mol based on equilibrium data. Young (3) used water vapor as a carrier gas to determine the transport of BeO, presumably as $Be(OH)_2$, in equilibrium with BeO(c), $BeAl_2O_4$(c) and $BeAl_6O_{10}$(c). Suitable linear combination of the three equilibria gives the above reaction. We compare at a temperature of 1800 K, near the upper limit of the data, where the experimental method is more sensitive. The resulting difference in ΔHr°(298.15 K) is 1.8 kcal/mol, roughly 1.6 times the uncertainty claimed for ΔGr° (3).

Heat Capacity and Entropy

Cp° and the derived properties below 298 K are taken from calorimetric data (16-380 K) of Furukawa and Saba (4). The entropy is based on $S°_{16}$ = 0.004 gibbs/mol. Cp° above 298 K is based on enthalpy data of Ditmars and Douglas (5, 373-1173 K) and Ishihara and West (6, 1182-2136 K). Cp° up to 900 K is taken from Ditmars and Douglas, but at higher temperatures it is based on graphical smoothing of Cp° curves from the two studies. Near 2000 K there is a sharp rise in Cp° as derived from the enthalpy equation of Ishihara and West. We give little weight to this part of the curve on the assumption that premelting is involved.

Melting Data

See $BeAl_2O_4$(ℓ).

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J. Phys. Chem. Ref. Data, Vol. 3, No. 3, 1974

Al_2BeO_4

Beryllium Aluminate ($BeAl_2O_4$)

(Liquid) GFW = 126.9728

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	25.185	31.301	31.301	.000	- 515.091	- 490.486	359.536
300	25.325	31.457	31.301	.047	- 515.099	- 490.334	357.208
400	31.214	39.632	32.376	2.903	- 515.303	- 482.036	263.372
500	34.643	46.990	34.577	6.206	- 515.227	- 473.724	207.064
600	37.030	53.530	37.202	9.797	- 515.006	- 465.443	169.538
700	38.730	59.373	39.959	13.590	- 514.712	- 457.205	142.746
800	39.980	64.630	42.720	17.528	- 514.399	- 449.013	122.665
900	40.910	69.394	45.423	21.574	- 514.121	- 440.855	107.054
1000	41.640	73.743	48.041	25.702	- 518.953	- 432.359	94.492
1100	42.290	77.743	50.562	29.899	- 518.616	- 423.718	84.185
1200	42.900	81.449	52.983	34.158	- 518.260	- 415.107	75.601
1300	43.510	84.906	55.307	38.479	- 517.881	- 406.525	68.343
1400	44.130	88.154	57.539	42.861	- 517.482	- 397.974	62.127
1500	56.000	92.017	59.710	48.461	- 515.902	- 389.495	56.749
1600	56.000	95.631	61.843	54.061	- 517.113	- 381.039	52.048
1700	56.000	99.026	63.932	59.661	- 515.488	- 372.584	47.899
1800	56.000	102.227	65.971	65.261	- 513.880	- 364.222	44.223
1900	56.000	105.255	67.960	70.861	- 512.291	- 355.952	40.944
2000	56.000	108.127	69.897	76.461	- 510.717	- 347.769	38.002
2100	56.000	110.859	71.783	82.061	- 509.158	- 339.659	35.349
2200	56.000	113.465	73.619	87.661	- 507.618	- 331.625	32.944
2300	56.000	115.954	75.406	93.261	- 506.089	- 323.655	30.754
2400	56.000	118.337	77.145	98.861	- 504.579	- 315.752	28.753
2500	56.000	120.623	78.839	104.461	- 503.087	- 307.925	26.919
2600	56.000	122.820	80.489	110.061	- 501.607	- 300.142	25.229
2700	56.000	124.933	82.096	115.661	- 500.143	- 292.424	23.670
2800	56.000	126.970	83.662	121.261	- 708.544	- 281.988	22.010
2900	56.000	128.935	85.190	126.861	- 706.334	- 266.791	20.106
3000	56.000	130.833	86.680	132.461	- 704.136	- 251.670	18.334
3100	56.000	132.670	88.134	138.061	- 701.947	- 236.626	16.682
3200	56.000	134.447	89.553	143.661	- 699.769	- 221.648	15.138
3300	56.000	136.171	90.940	149.261	- 697.602	- 206.742	13.692
3400	56.000	137.842	92.295	154.861	- 695.450	- 191.904	12.335
3500	56.000	139.466	93.620	160.461	- 693.304	- 177.129	11.060
3600	56.000	141.043	94.915	166.061	- 691.172	- 162.401	9.859
3700	56.000	142.578	96.183	171.661	- 689.052	- 147.747	8.727
3800	56.000	144.071	97.423	177.261	- 686.945	- 133.144	7.658
3900	56.000	145.526	98.638	182.861	- 684.846	- 118.595	6.646
4000	56.000	146.943	99.828	188.461	- 682.765	- 104.110	5.688

June 30, 1972

BERYLLIUM ALUMINATE ($BeAl_2O_4$) (LIQUID) GFW = 126.9728

$S^\circ_{298.15}$ = 31.301 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -515.091 kcal/mol

Tm = 2146 ± 10 K

ΔHm° = 41.6 ± 1.0 kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by adding ΔHm° and the difference in ($H^\circ_{2146}-H^\circ_{298.15}$) between crystal and liquid.

Heat Capacity and Entropy

Ishihara and West (1) reported enthalpy data up to 2348 K and gave a parabolic enthalpy equation for the liquid. This equation yields a temperature derivative of Cp° which is unreasonably large. Cp° at the mean temperature of measurement is about 80 gibbs/mol. We adopt the slightly lower value of 56 gibbs/mol, corresponding to 8 gibbs/g-atom. Below the assumed glass transition at 1400 K, Cp° is taken to be the same as that of the crystal. The entropy is calculated in a way analogous with ΔHf°.

Melting Data

Tm, adjusted to IPTS-68, is from the phase study of Lang et al. (2). ΔHm° is calculated such that the adopted tables reproduce the enthalpy equation (1) near the mean temperature of measurement.

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Al_2BeO_4

Aluminum Tribromide, Dimeric (Al_2Br_6)

(Ideal Gas) GFW = 533.4170

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	− 9.117	− 213.352	− 213.352	INFINITE
100	28.874	92.699	163.743	− 7.104	− 213.555	− 218.634	477.825
200	36.626	115.456	134.338	− 3.776	− 214.624	− 223.348	244.063
298	39.879	130.776	130.776	.000	− 224.000	− 226.411	165.963
300	39.919	131.023	130.776	.074	− 224.047	− 226.425	164.950
400	41.416	142.737	132.363	4.149	− 245.890	− 222.718	121.688
500	42.191	152.071	135.403	8.334	− 245.616	− 216.960	94.833
600	42.636	159.806	138.844	12.577	− 245.355	− 211.254	76.949
700	42.913	166.400	142.321	16.855	− 245.126	− 205.589	64.188
800	43.097	172.143	145.698	21.156	− 244.947	− 199.955	54.625
900	43.224	177.227	148.924	25.473	− 244.848	− 194.337	47.191
1000	43.316	181.786	151.986	29.800	− 249.887	− 188.357	41.165
1100	43.385	185.918	154.886	34.135	− 249.776	− 182.213	36.202
1200	43.437	189.696	157.632	38.476	− 249.662	− 176.076	32.068
1300	43.479	193.174	160.234	42.822	− 249.547	− 169.945	28.570
1400	43.511	196.397	162.703	47.172	− 249.433	− 163.826	25.574
1500	43.538	199.400	165.051	51.524	− 249.323	− 157.720	22.980
1600	43.559	202.211	167.286	55.879	− 249.213	− 151.614	20.710
1700	43.577	204.852	169.419	60.236	− 249.104	− 145.516	18.707
1800	43.592	207.343	171.458	64.595	− 248.994	− 139.427	16.929
1900	43.605	209.701	173.409	68.954	− 248.889	− 133.339	15.338
2000	43.616	211.938	175.280	73.316	− 248.787	− 127.267	13.907
2100	43.625	214.066	177.077	77.678	− 248.685	− 121.194	12.613
2200	43.634	216.096	178.804	82.041	− 248.588	− 115.127	11.437
2300	43.641	218.035	180.468	86.404	− 248.492	− 109.055	10.363
2400	43.647	219.893	182.072	90.769	− 248.399	− 102.992	9.379
2500	43.652	221.675	183.621	95.134	− 248.309	− 96.941	8.475
2600	43.657	223.387	185.118	99.499	− 248.222	− 90.885	7.640
2700	43.662	225.035	186.566	103.865	− 248.137	− 84.842	6.868
2800	43.666	226.623	187.968	108.232	− 386.877	− 77.132	6.020
2900	43.669	228.155	189.328	112.598	− 386.274	− 66.081	4.980
3000	43.672	229.635	190.647	116.965	− 385.673	− 55.050	4.010
3100	43.675	231.067	191.928	121.333	− 385.077	− 44.035	3.104
3200	43.678	232.454	193.173	125.700	− 384.482	− 33.042	2.257
3300	43.680	233.798	194.384	130.068	− 383.892	− 22.074	1.462
3400	43.682	235.102	195.562	134.436	− 383.304	− 11.123	.715
3500	43.684	236.368	196.710	138.805	− 382.719	− .181	.011
3600	43.686	237.599	197.829	143.173	− 382.140	10.742	− .652
3700	43.688	238.796	198.920	147.542	− 381.560	21.644	− 1.278
3800	43.689	239.961	199.985	151.911	− 380.988	32.535	− 1.871
3900	43.691	241.096	201.024	156.280	− 380.417	43.419	− 2.433
4000	43.692	242.202	202.040	160.649	− 379.853	54.266	− 2.965
4100	43.693	243.281	203.033	165.018	− 379.292	65.107	− 3.471
4200	43.695	244.334	204.004	169.388	− 378.733	75.946	− 3.952
4300	43.696	245.362	204.954	173.757	− 378.182	86.768	− 4.410
4400	43.697	246.367	205.883	178.127	− 377.633	97.581	− 4.847
4500	43.697	247.349	206.794	182.497	− 377.091	108.370	− 5.263
4600	43.698	248.309	207.686	186.866	− 376.553	119.156	− 5.661
4700	43.699	249.249	208.560	191.236	− 376.023	129.923	− 6.041
4800	43.700	250.169	209.418	195.606	− 375.501	140.672	− 6.405
4900	43.701	251.070	210.259	199.976	− 374.981	151.436	− 6.754
5000	43.701	251.953	211.084	204.346	− 374.470	162.171	− 7.088
5100	43.702	252.818	211.894	208.716	− 373.969	172.892	− 7.409
5200	43.703	253.667	212.689	213.087	− 373.473	183.608	− 7.717
5300	43.703	254.499	213.470	217.457	− 372.987	194.323	− 8.013
5400	43.704	255.316	214.237	221.827	− 372.511	205.018	− 8.298
5500	43.704	256.118	214.991	226.198	− 372.044	215.712	− 8.572
5600	43.705	256.906	215.733	230.568	− 371.590	226.391	− 8.835
5700	43.705	257.679	216.462	234.939	− 371.144	237.067	− 9.090
5800	43.706	258.439	217.179	239.309	− 370.711	247.741	− 9.335
5900	43.706	259.187	217.885	243.680	− 370.291	258.398	− 9.572
6000	43.706	259.921	218.579	248.050	− 369.885	269.037	− 9.800

Dec. 31, 1961; June 30, 1964; June 30, 1967; June 30, 1972

ALUMINUM TRIBROMIDE, DIMERIC [$(AlBr_3)_2$] (IDEAL GAS) Al_2Br_6 GFW = 533.4170

Point Group D_{2h} ΔHf_0° = −213.4 ± 0.8 kcal/mol

$S^\circ_{298.15}$ = 130.8 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −244.0 ± 0.8 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
409 (1)	59 (1)	[78] (1)	[13] (1)	346 (1)	376 (1)
203 (1)	[20](1)	500 (1)	489 (1)	90 (1)	199 (1)
139 (1)	340(1)	[110] (1)	114 (1)	[47] (1)	112 (1)

Bond Distances: Al-Br = 2.21 ± 0.4 Å $Al\text{-}Br_{bridge}$ = 2.33 ± 0.r Å

Bond Angles: Br-Al-Br = 114°38' $Br_{bridge}\text{-}Al\text{-}Br_{bridge}$ = 86°44' σ = 4

Product of the Moments of Inertia: $I_A I_B I_C = 8.80123 \times 10^{-110}\ g^3 cm^6$

Heat of Formation

The vapor pressures over $AlBr_3(c)$ and $AlBr_3(\ell)$ have been measured by Dunne and Gregory (1) and Fischer, Rahlfs, and Benze (2), respectively. Vapor pressures were corrected for vapor non-ideality by means of the equation $\Delta G^\circ/T = -R\ln p - BP/T$. The Bertholot equation of state and critical constants T_c = 763 K and P_c = 28.5 atm reported by Johnson, Silva, and Cubicciotti (3) were used to calculate B. The corrected vapor pressures were used to calculate ΔHr°_{298} by both Second and Third Law methods. The results of the calculations are as follows with reaction (A) corresponding to $2AlBr_3(c) = Al_2Br_6(g)$ and reaction (B) corresponding to $2AlBr_3(\ell) = Al_2Br_6(g)$:

Reference	Reac.	Method	No. Pts.	Range T°K	ΔHr°_{298}, kcal/mol Second Law	Third Law	drift eu	ΔHf°_{298}*
1	A	Effusion	3	273-310	19.6 ± 0.7	20.26	2.2 ± 2.4	−224.06
2	B	Mass Loss	18**	413-523	15.6 ± 0.1	15.62	0.1 ± 0.1	−223.97
2	B	Transport	4	396-471	16.0 ± 0.1	15.61	−0.9 ± 0.3	−223.98

*Calculation based on Third Law ΔHr°_{298}

**Point at 436.20 K rejected due to statistical test.

The adopted value of ΔHf°_{298} for $Al_2Br_6(g)$ is −224.0 ± 0.8 kcal/mol. Johnson, Silva, and Cubicciotti (3) measured the vapor pressure over $AlBr_3(\ell)$ by an inverted capillary technique from 536 K and 1.18 atm to 761 K and 28.3 atm. They reported a heat of vaporization of 5.79 kcal/mol $AlBr_3$ at Tb = 528 K. This value is in reasonable agreement with ΔHr° = 5.88 kcal/mol which is adopted here.

Heat Capacity and Entropy

The molecular structure, bond distances, and angles were obtained from the electron diffraction work of Palmer and Elliott (4). The bond distances and angles reported by Akishin et al (5) are in good agreement with those given by Palmer and Elliott (4). The principal moments of inertia are $I_A = 2.51547 \times 10^{-37}$, $I_B = 5.36492 \times 10^{-37}$, and $I_C = 6.52171 \times 10^{-37}$ g cm^2. Beattie, Gilson, and Ozin (9) measured the condensed phase IR and Raman bands for aluminum tribromide while Beattie and Horder (8) measured the gas phase Raman spectrum. It has been established that the condensed phases of $AlBr_3$ are dimeric (6, 7), thus spectroscopic studies of the crystal and liquid pertain to the structure of $Al_2Br_6(g)$. However, gas phase values are adopted in preference to condensed phase frequencies whenever possible. Five frequencies (ω_5, ω_7, ω_9, ω_{10}, ω_{15}) were adjusted not only for consistency with the frequencies chosen for $Al_2F_6(g)$ and $Al_2Cl_6(g)$ but also for agreement between Second and Third Law ΔHr°_{298} values in the second data set tabulated above.

References

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Magnesium Aluminate ($MgAl_2O_4$)

(Crystal) GFW = 142.2726

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	.000	.000	INFINITE	- 3.683	- 548.949	- 548.949	INFINITE
100	5.418	4.005	39.315	- 3.531	- 550.551	- 542.115	1184.791
200	18.659	11.907	23.477	- 2.314	- 552.172	- 533.131	582.578
298	27.771	21.198	21.198	.000	- 552.800	- 523.533	383.760
300	27.905	21.370	21.199	.052	- 552.807	- 523.352	381.262
400	33.247	30.189	22.365	3.130	- 552.963	- 513.498	280.562
500	36.088	37.932	24.722	6.605	- 552.854	- 503.640	220.141
600	37.923	44.681	27.498	10.310	- 552.646	- 493.818	179.873
700	39.284	50.632	30.387	14.172	- 552.403	- 484.031	151.121
800	40.392	55.952	33.256	18.157	- 552.173	- 474.282	129.568
900	41.353	60.766	36.049	22.245	- 551.998	- 464.556	112.809
1000	42.222	65.168	38.744	26.424	- 559.058	- 454.297	99.287
1100	43.038	69.231	41.333	30.688	- 558.792	- 443.837	88.182
1200	43.801	73.009	43.817	35.030	- 558.491	- 433.491	78.933
1300	44.539	76.544	46.200	39.447	- 558.157	- 422.988	71.111
1400	45.261	79.871	48.488	43.937	- 588.157	- 412.124	64.335
1500	45.967	83.018	50.686	48.499	- 587.352	- 399.580	58.219
1600	46.658	86.007	52.801	53.130	- 586.490	- 387.090	52.874
1700	47.341	88.856	54.838	57.830	- 585.569	- 374.653	48.165
1800	48.018	91.581	56.805	62.598	- 584.597	- 362.273	43.986
1900	48.690	94.195	58.704	67.433	- 583.561	- 349.951	40.253
2000	49.356	96.710	60.542	72.336	- 582.473	- 337.687	36.901
2100	49.932	99.132	62.322	77.301	- 581.333	- 325.476	33.873
2200	50.475	101.468	64.049	82.322	- 580.151	- 313.319	31.125
2300	50.984	103.723	65.725	87.395	- 578.923	- 301.214	28.622
2400	51.459	105.903	67.356	92.517	- 577.660	- 289.165	26.332
2500	51.900	108.013	68.938	97.686	- 576.363	- 277.180	24.231
2600	52.308	110.056	70.481	102.896	- 575.033	- 265.233	22.295
2700	52.681	112.038	71.983	108.146	- 573.676	- 253.346	20.507
2800	53.021	113.960	73.448	113.431	- 711.114	- 239.847	18.721
2900	53.328	115.826	74.878	118.749	- 709.186	- 223.049	16.809
3000	53.600	117.638	76.273	124.096	- 707.241	- 206.317	15.030

Dec. 31, 1950; Mar. 31, 1963; June 30, 1972

Al_2MgO_4

MAGNESIUM ALUMINATE ($MgAl_2O_4$) (CRYSTAL) GFW = 142.2726

$S^\circ_{298.15}$ = 21.198 ± 1 gibbs/mol

Tm = 2408 ± 20 K

ΔHf°_0 = -548.94 ± 2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -552.8 ± 2 kcal/mol

ΔHm = [47 ± 5] kcal/mol

Heat of Formation

The selected value for $\Delta Hf^\circ_{298}(MgAl_2O_4, c)$ = -552.8 ± 2 kcal/mol is based primarily upon the equilibrium measurements of Grjotheim et al (1), and Rao and Dadape (2) and the heat of solution measurements by Navrotsky and Kleppa (3, 4). A second and third law analysis of all the equilibrium data sets is tabulated below.

Because the synthetic spinels exhibit cation distributions between normal and inverse we take as the standard state an equilibrium $MgAl_2O_4$ spinel with partially inverted cations. The thermodynamic nature of this phenomena has been discussed by Navrotsky and Kleppa (4). *The experiments by Navrotsky and Kleppa involved a high temperature (697°C) solution calorimeter with a molten oxide solvent to compare the heats of solution of MgO(c), Al_2O_3(c, α) and $MgAl_2O_4$(c) at 970°K.* The sum of these heats was ΔHr_{970} = -8.72 ± 0.3 kcal/mol for the reaction,

$$MgO(c) + Al_2O_3(c, \alpha) \rightarrow MgAl_2O_4(c).$$

This value reduces to ΔHr°_{298} = -8.64 ± 0.3 kcal/mol and gives $\Delta Hf^\circ_{298}(MgAl_2O_4, c)$ = -552.8 ± 1 kcal/mol using JANAF auxiliary data (5).

Zaionchkovskii and Rubal'akaya (6) reported heat of combustion experiments for the process

$$Mg(c) + 2Al(c) + O_2(g) \rightarrow MgAl_2O_4(c)$$

and derived $\Delta Hf^\circ_{298}(MgAl_2O_4, c)$ = -567.1 kcal/mol. Their value appears to be widely discordant with the other reported values. It is noteworthy that the heats of formation calculated from references 7, 7 and 8, and 9 are within four kcal/mol of the adopted value despite significant entropy drifts.

Ref.	Reaction	Temp. Range K	Points	ΔHr_{298} kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}* kcal/mol
7	$4MgO(c) + 2Al(\ell) \rightarrow MgAl_2O_4(c) + 3Mg(g)$	1143-1414	9	137.8±1.7	127.6±1.7	-7.8±1.3	-548.8
7,8	*Same Reaction with Activities for Al(ℓ)*	1143-1414	9	141.4±2	126.8±2	-11.2±1.6	-549.8
9	$4MgO(c) + 2Al(Si)(\ell) \rightarrow MgAl_2O_4(c) + 3Mg(g)$	1216-1423	6	134.7±0.1	127.8±0.9	-5.2±0.1	-548.7
8	$MgAl_2O_4(c) \rightarrow Al_2O_3(c,\alpha) + 1/2O_2(g) + Mg(g)$	1866-2155	9	138.3±21	177.8±6.3	19.6±10	-543
10	$MgO(c) + Al_2O_3(c,\alpha) \rightarrow MgAl_2O_4(c)$	803	1		-0.343		-544.5
11	$MgO(c) + Al_2O_3(c,\alpha) \rightarrow MgAl_2O_4(c)$	1273	1		-5.17		-549.4
1	$4MgO(c) + 1/2Al_4C_3(c) \rightarrow MgAl_2O_4(c) + 3/2C(c) + 3Mg(g)$	1324-1452	7	154.1±3	153.4±0.5	-1.0±4.8	-553.0
2	$4MgO(c) + 3AlCl(g) \rightarrow MgAl_2O_4(c) + AlCl_3(g) + 3Mg(g)$	1298-1465	7	26.2±3.4	25.3±0.7	-0.6±2.5	-552.5

*$\Delta Hf^\circ_{298}(MgAl_2O_4, c)$ derived from the third-law values using JANAF auxiliary data (5).

Heat Capacity and Entropy

Low temperature heat capacity experiments on a synthetic sample of $MgAl_2O_4$ were carried out by King (12) over the range 51-298 K. The S°_{298} = 19.26 gibbs/mol was calculated from C°_p an S_{51} extrapolation of 0.32 gibbs/mol. Since heat capacity measurements alone cannot quantitatively detect the entropy of formation of a partially inverted spinel it is necessary to add a configurational entropy term of 1.93 gibbs/mol to give S°_{298} = 21.198 gibbs/mol. This term corrects for approximately 0.15 mole fraction of inverted cations present in synthetic samples of $MgAl_2O_4$. *The method of calculation can be found in reference (4).*

High temperature enthalpy measurements (by drop calorimetry) were carried out from 400-1800 K by Bonnickson (13). The high temperature data are extrapolated to 3000 K.

Melting Data

See $MgAl_2O_4$ (ℓ) table.

References

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5. JANAF Thermochemical Tables: MgO(c) dated 12-31-65; Mg(g) dated 9-30-62; Al(ℓ) dated 6-30-67; Al_2O_3(c,α) dated 6-30-72; Si(ref) dated 3-31-67; Al_4C_3(c) dated 9-30-65; C(ref) dated 3-31-61; AlCl(g) dated 6-30-70; $AlCl_3$(g) dated 6-30-70.
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Magnesium Aluminate ($MgAl_2O_4$)

(Liquid) GFW = 142.2726

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	27.771	38.786	38.786	.000	− 509.641	− 485.618	355.967
300	27.905	38.958	38.787	.052	− 509.648	− 485.469	353.664
400	33.247	47.777	39.953	3.130	− 509.804	− 477.375	260.825
500	36.088	55.520	42.310	6.605	− 509.695	− 469.275	205.120
600	37.923	62.269	45.086	10.310	− 509.487	− 461.212	167.996
700	39.284	68.220	47.975	14.172	− 509.244	− 453.183	141.490
800	40.392	73.540	50.844	18.157	− 509.014	− 445.193	121.621
900	41.353	78.354	53.637	22.245	− 508.839	− 437.226	106.173
1000	42.222	82.756	56.332	26.424	− 515.899	− 428.726	93.698
1100	43.038	86.815	58.921	30.688	− 515.633	− 420.025	83.451
1200	43.801	90.597	61.405	35.030	− 515.332	− 411.347	74.917
1300	44.535	94.132	63.788	39.447	− 514.998	− 402.694	67.699
1400	45.261	97.459	66.076	43.937	− 544.998	− 393.588	61.442
1500	45.967	100.606	68.274	48.499	− 544.193	− 382.803	55.774
1600	46.658	103.595	70.389	53.130	− 543.331	− 372.072	50.823
1700	47.341	106.444	72.426	57.830	− 542.410	− 361.394	46.460
1800	55.000	109.588	74.404	63.330	− 540.701	− 350.793	42.592
1900	55.000	112.561	76.335	68.830	− 539.005	− 340.291	39.142
2000	55.000	115.383	78.218	74.330	− 537.320	− 329.879	36.048
2100	55.000	118.066	80.052	79.830	− 535.665	− 319.549	33.256
2200	55.000	120.625	81.838	85.330	− 533.984	− 309.297	30.726
2300	55.000	123.070	83.578	90.830	− 532.329	− 299.117	28.423
2400	55.000	125.410	85.273	96.330	− 530.688	− 289.011	26.318
2500	55.000	127.655	86.923	101.830	− 529.060	− 278.984	24.389
2600	55.000	129.813	88.532	107.330	− 527.440	− 269.007	22.612
2700	55.000	131.888	90.099	112.830	− 525.833	− 259.101	20.973
2800	55.000	133.889	91.628	118.330	− 663.056	− 247.591	19.325
2900	55.000	135.819	93.119	123.830	− 660.946	− 232.789	17.543
3000	55.000	137.683	94.573	129.330	− 658.848	− 218.058	15.886

June 30, 1972

MAGNESIUM ALUMINATE ($MgAl_2O_4$) (LIQUID) GFW = 142.2726

$S^\circ_{298.15}$ = [38.786] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-509.641] kcal/mol

Tm = 2408 ± 20 K

ΔHm = [47 ± 5] kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298.15}$ ($MgAl_2O_4$, ℓ) = -509.461 kcal/mol is obtained by adding the heat of melting, and the difference between $H_{2408}-H_{298}$ for the crystal and liquid to the heat of formation of the crystal at 298 K.

Heat Capacity and Entropy

A Cp of 55 gibbs/mol is estimated from the heat capacities for MgO(ℓ) and Al_2O_3(ℓ) (1). This Cp is used above a hypothetical glass transition at 1700 K. Below this temperature the Cp is taken as that of the crystal. The S°_{298}($MgAl_2O_4$, ℓ) = 38.786 gibbs/mol is calculated in a manner similar to that of the heat of formation.

Melting Data

Rankin and Merwin (2) studied the binary system alumina + magnesia and detected $MgAl_2O_4$ which melted at 2135 ± 20°C (2408 K). Wilde and Rees (3) confirm this value in a later paper.

References

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2. G. A. Rankin and H. E. Merwin, J. Amer. Chem. Soc. 38, 568 (1916).
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Aluminum Suboxide (Al_2O)

(Ideal Gas) GFW = 69.9624

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	− 2.600	− 32.374	− 32.374	INFINITE
100	8.031	51.091	69.129	− 1.804	− 32.137	− 34.847	76.157
200	9.076	56.924	61.705	− .956	− 32.522	− 37.456	40.930
298	10.377	60.797	60.797	.000	− 33.000	− 39.785	29.163
300	10.399	60.861	60.797	.019	− 33.009	− 39.828	29.014
400	11.402	63.999	61.218	1.112	− 33.470	− 42.029	22.963
500	12.083	66.621	62.044	2.289	− 33.921	− 44.117	19.283
600	12.535	68.867	62.998	3.521	− 34.384	− 46.114	16.797
700	12.852	70.825	63.980	4.792	− 34.872	− 48.030	14.996
800	13.073	72.557	64.964	6.089	− 35.408	− 49.874	13.625
900	13.233	74.106	65.879	7.405	− 36.023	− 51.646	12.541
1000	13.353	75.507	66.773	8.734	− 41.773	− 52.978	11.578
1100	13.444	76.784	67.626	10.074	− 42.171	− 54.071	10.743
1200	13.514	77.957	68.438	11.422	− 42.965	− 55.109	10.037
1300	13.570	79.041	69.213	12.776	− 43.555	− 56.097	9.431
1400	13.615	80.048	69.951	14.136	− 44.146	− 57.038	8.904
1500	13.652	80.989	70.656	15.499	− 44.736	− 57.940	8.442
1600	13.682	81.871	71.330	16.866	− 45.325	− 58.801	8.032
1700	13.708	82.701	71.974	18.236	− 45.915	− 59.625	7.665
1800	13.729	83.495	72.592	19.607	− 46.504	− 60.412	7.335
1900	13.747	84.228	73.185	20.981	− 47.095	− 61.170	7.036
2000	13.763	84.934	73.755	22.357	− 47.688	− 61.897	6.764
2100	13.776	85.606	74.304	23.734	− 48.281	− 62.594	6.514
2200	13.788	86.247	74.832	25.112	− 48.877	− 63.262	6.284
2300	13.798	86.860	75.342	26.491	− 49.472	− 63.898	6.072
2400	13.807	87.447	75.834	27.872	− 50.070	− 64.512	5.875
2500	13.815	88.011	76.310	29.253	− 50.671	− 65.106	5.697
2600	13.822	88.553	76.770	30.635	− 51.273	− 65.670	5.520
2700	13.829	89.075	77.217	32.017	− 51.878	− 66.214	5.360
2800	13.834	89.578	77.649	33.400	− 191.304	− 65.073	5.079
2900	13.839	90.063	78.069	34.784	− 191.389	− 60.565	4.564
3000	13.844	90.533	78.477	36.168	− 191.475	− 56.049	4.083
3100	13.848	90.987	78.873	37.553	− 191.563	− 51.533	3.633
3200	13.852	91.426	79.258	38.938	− 191.653	− 47.014	3.211
3300	13.855	91.853	79.633	40.323	− 191.744	− 42.492	2.814
3400	13.859	92.266	79.999	41.709	− 191.840	− 37.972	2.441
3500	13.861	92.668	80.355	43.095	− 191.935	− 33.447	2.088
3600	13.864	93.059	80.703	44.481	− 192.034	− 28.911	1.755
3700	13.867	93.439	81.042	45.868	− 192.134	− 24.382	1.440
3800	13.869	93.808	81.373	47.254	− 192.238	− 19.847	1.141
3900	13.871	94.169	81.696	48.641	− 192.341	− 15.305	.858
4000	13.873	94.520	82.013	50.029	− 192.450	− 10.769	.588
4100	13.875	94.862	82.322	51.416	− 192.560	− 6.229	.332
4200	13.876	95.197	82.624	52.804	− 192.671	− 1.679	.087
4300	13.878	95.523	82.921	54.191	− 192.787	2.870	− .146
4400	13.879	95.842	83.211	55.579	− 192.905	7.426	− .369
4500	13.881	96.154	83.495	56.967	− 193.027	11.978	− .582
4600	13.882	96.459	83.773	58.355	− 193.151	16.539	− .786
4700	13.883	96.758	84.047	59.743	− 193.282	21.088	− .981
4800	13.884	97.050	84.314	61.132	− 193.415	25.652	− 1.169
4900	13.885	97.337	84.577	62.520	− 193.553	30.225	− 1.348
5000	13.886	97.617	84.835	63.909	− 193.694	34.789	− 1.521
5100	13.887	97.892	85.089	65.298	− 193.841	39.364	− 1.687
5200	13.888	98.162	85.337	66.686	− 193.996	43.932	− 1.846
5300	13.889	98.426	85.582	68.075	− 194.156	48.511	− 2.000
5400	13.890	98.686	85.822	69.464	− 194.322	53.093	− 2.149
5500	13.890	98.941	86.058	70.853	− 194.497	57.671	− 2.292
5600	13.891	99.191	86.291	72.242	− 194.680	62.262	− 2.430
5700	13.892	99.437	86.519	73.631	− 194.869	66.847	− 2.563
5800	13.892	99.679	86.744	75.020	− 195.071	71.445	− 2.692
5900	13.893	99.916	86.965	76.410	− 195.280	76.043	− 2.817
6000	13.894	100.150	87.183	77.795	− 195.500	80.644	− 2.937

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1965; June 30, 1972

ALUMINUM SUBOXIDE (Al_2O) (IDEAL GAS) GFW = 69.9624 Al_2O

Point Group C_{2v} ΔHf°_0 = −32.4 ± 5.0 kcal/mol

$S^\circ_{298.15}$ = 60.80 ± 0.05 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −33.0 ± 5.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
715 (1)	503 (1)	994 (1)

Bond Distance: Al-O = 1.66 Å

Bond Angle: Al-O-Al = 145° ± 5° σ = 2

Product of the Moments of Inertia: $I_A I_B I_C = 263.3850 \times 10^{-117}\ g^3 cm^6$

Heat of Formation

Since the early work of Brewer and Searcy (1), there has been considerable experimental data published on $\Delta Hf^\circ_{298}(Al_2O, g)$. The more recent data is tabulated below, where ΔHf°_{298} refers to the heat of formation of $Al_2O(g)$ based on the Third Law ΔHr_{298}.

reference	reaction	range T°K	No.Pts.	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	drift, eu	ΔHf°_{298}
1.	$4Al(g) + Al_2O_3(c) = 3Al_2O(g)$	1466-1725	12	3.40	-29.58	-20.75	-39.33
3.	$Al_2O(g) = 2Al(g) + O(g)$	2188-2594	17*	282.41	249.04	-14.37	-33.48
3.	$Al_2O(g) = 2Al(g) + O(g)$	2036-2466	13**	270.47	250.67	-8.62	-35.11
4.	$Be(g) + Al_2O_3(s) + 2Al(g) = BeO(s) + 2Al_2O(g)$	1511-1663	11*	-62.21	-42.18	12.72	-31.46
	$Be(g) + Al_2O(g) = BeO(s) + 2Al(g)$	1511-1663	11*	- 5.98	-36.93	-19.45	-30.73
5.	$Al_2O_3(c) + 4Al(\ell) = 3Al_2O(g)$ (effusion)	1585-1623	2	-	224.26	-17.36	-55.98
	$Al_2O_3(c) + 4Al(g) = 3Al_2O(g)$ (effusion)	1585-1623	2	-	4.95	48.28	-27.85
	$Al_2O_3(c) + 4Al(\ell) = 3Al_2O(g)$ (press. compensation)	2009-2129	8	251.73	284.34	16.05	-35.96
	$Al_2O_3(c) + 4Al(g) = 3Al_2O(g)$ (press. compensation)	2009-2129	8	-60.73	-17.87	20.77	-35.46
6.	$4Al(g) + Al_2O_3(c) = 3Al_2O(g)$	1313-1511	15**	+ 0.07	- 1.32	-0.97	-29.91
7.	$4Al(g) + Al_2O_3(c) = 3Al_2O(g)$	1556	1	-	-19.46	-	-35.99
	$4Al(\ell) + Al_2O_3(c) = 3Al_2O(g)$	1556	1	-	290.34	-	-33.96
8.	$Al_2O(g) = 2Al(g) + O(g)$	1943-2093	7	215.35	252.01	18.11	-36.45
9.	$2Al(\ell) + 0.5\ O_2(g) = Al_2O(g)$	1443-1576	8*	-29.64	-42.35	- 8.34	-38.21
	$Al_2O_3(s) + 4Al(\ell) = 3Al_2O(g)$	1443-1576	8	374.70	279.18	-63.04	-37.68
	$Al_2O_3(s) + 4Al(g) = 3Al_2O(g)$	1443-1576	8*	39.02	-12.01	-33.45	-33.50

* one point rejected due to failure of a statistical test. ** two points rejected due to failure of a statistical test.

The early work following Brewer and Searcy (1) is numerous and is discussed and referenced by Farber, et al (8) and Rao and Motzfeldt (7).

The value chosen for the heat of formation, $\Delta Hf^\circ_{298}(Al_2O, g)$ = −33.0 ± 5.0 kcal/mol, is representative of the values tabulated above with somewhat extra weight given to the work by DeMaria, et al. (6).

Heat Capacity and Entropy

Linevsky, White, and Mann (10) investigated the infrared spectrum of Al_2O from 4000-250 cm^{-1} employing the technique of matrix isolation of high temperature vapors. Two frequencies were observed in an argon matrix, ω_1 = 715 cm^{-1} and ω_3 = 994 cm^{-1}. The bending mode was assumed to be below 250 cm^{-1}. Comparison of thermochemical bond dissociation values for AlO and Al_2 with the dissociation energy of Al_2O and isotope studies (10) suggest a symmetrical structure with C_{2v} symmetry and an Al-O-Al bond angle of 145° ± 5°. The Al-O bond length was reported to be 1.66 Å, a value dependent on the principal stretching force constant (10).

Snelson (11) used a similar matrix technique but studied the region 2000-190 cm^{-1}. Excellent agreement was obtained for ω_1 and ω_3 but no bending mode was observed in the region 190-250 cm^{-1}. Force constant calculations by Snelson (11) indicated that ω_2 = 120 cm^{-1}.

Makowiecki, Lynch, and Carlson (12) investigated the aluminum family suboxides by the same technique but extended the infrared region to 40 cm^{-1}. For $Al_2O(g)$, ω_1 = 715.9 cm^{-1} and ω_3 = 991.7 cm^{-1}. No bands were observed in the region 450-40 cm^{-1}. A band, assigned to ω_2, was observed at 503.0 cm^{-1}. This band is consistent with trends in the aluminum family suboxides (12) but lies at a higher frequency than expected. Makowiecki, et al. (12) suggest the possibility of a metal-metal bond to form a cyclic structure A re-examination of Snelson's spectra (11) does show an absorption band in the region 520-530 cm^{-1}, but no mention was made as to the origin of this band. It should be noted that the Al_2O molecule is predicted by Walsh (13) to be linear.

The three principal moments of inertia are calculated to be 0.5106 x 10^{-39}, 22.4584 x 10^{-39}, and 22.9690 x 10^{-39} g cm^2.

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Dialuminum Monoxide Unipositive Ion (Al_2O^+)

(Ideal Gas) GFW = 69.9619

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	10.405	61.625	61.625	.000	146.000	137.481	− 100.776
300	10.427	61.689	61.625	.015	146.000	137.427	− 100.116
400	11.424	64.834	62.047	1.115	146.039	134.566	− 73.524
500	12.098	67.461	62.874	2.293	146.087	131.692	− 57.563
600	12.550	69.709	63.831	3.527	146.122	128.809	− 46.919
700	12.861	71.669	64.814	4.799	146.131	125.922	− 39.315
800	13.080	73.401	65.781	6.096	146.092	123.037	− 33.612
900	13.238	74.951	66.715	7.412	145.974	120.162	− 29.179
1000	13.357	76.352	67.610	8.743	140.722	117.671	− 25.717
1100	13.447	77.630	68.464	10.083	140.622	115.370	− 22.922
1200	13.517	78.803	69.277	11.431	140.524	113.077	− 20.594
1300	13.573	79.887	70.052	12.786	140.431	110.794	− 18.626
1400	13.617	80.895	70.791	14.145	140.338	108.520	− 16.941
1500	13.654	81.836	71.496	15.509	140.245	106.248	− 15.480
1600	13.684	82.718	72.170	16.876	140.152	103.985	− 14.204
1700	13.709	83.548	72.815	18.246	140.059	101.727	− 13.078
1800	13.730	84.332	73.434	19.618	139.968	99.478	− 12.078
1900	13.748	85.075	74.027	20.992	139.873	97.230	− 11.184
2000	13.764	85.781	74.597	22.367	139.778	94.986	− 10.380
2100	13.777	86.453	75.146	23.744	139.680	92.747	− 9.652
2200	13.789	87.094	75.675	25.123	139.582	90.514	− 8.992
2300	13.799	87.707	76.184	26.502	139.484	88.291	− 8.390
2400	13.808	88.295	76.677	27.882	139.382	86.068	− 7.838
2500	13.816	88.858	77.153	29.264	139.279	83.844	− 7.330
2600	13.823	89.400	77.614	30.646	139.173	81.630	− 6.862
2700	13.829	89.922	78.060	32.028	139.065	79.416	− 6.428
2800	13.835	90.425	78.493	33.411	.136	78.871	− 6.156
2900	13.840	90.911	78.912	34.795	.549	81.674	− 6.155
3000	13.844	91.380	79.320	36.175	.959	84.467	− 6.153
3100	13.849	91.834	79.717	37.564	1.368	87.244	− 6.151
3200	13.852	92.274	80.102	38.945	1.775	90.009	− 6.147
3300	13.856	92.700	80.478	40.334	2.180	92.766	− 6.143
3400	13.859	93.114	80.843	41.720	2.581	95.495	− 6.138
3500	13.862	93.516	81.200	43.106	2.983	98.221	− 6.133
3600	13.864	93.906	81.547	44.493	3.381	100.941	− 6.128
3700	13.867	94.286	81.886	45.879	3.777	103.642	− 6.122
3800	13.869	94.656	82.218	47.266	4.170	106.337	− 6.116
3900	13.871	95.016	82.541	48.653	4.564	109.024	− 6.110
4000	13.873	95.367	82.857	50.040	4.952	111.692	− 6.103
4100	13.875	95.710	83.167	51.428	5.339	114.353	− 6.096
4200	13.876	96.044	83.469	52.815	5.725	117.011	− 6.089
4300	13.878	96.371	83.766	54.203	6.105	119.657	− 6.082
4400	13.879	96.690	84.056	55.591	6.485	122.297	− 6.075
4500	13.881	97.002	84.340	56.979	6.858	124.922	− 6.067
4600	13.882	97.307	84.619	58.367	7.232	127.545	− 6.060
4700	13.883	97.606	84.892	59.755	7.598	130.147	− 6.052
4800	13.884	97.898	85.160	61.144	7.962	132.752	− 6.044
4900	13.885	98.184	85.423	62.532	8.323	135.356	− 6.037
5000	13.886	98.465	85.681	63.921	8.676	137.940	− 6.029
5100	13.887	98.740	85.934	65.309	9.025	140.525	− 6.022
5200	13.888	99.009	86.183	66.698	9.368	143.095	− 6.014
5300	13.889	99.274	86.427	68.087	9.704	145.665	− 6.007
5400	13.890	99.534	86.668	69.476	10.036	148.230	− 5.999
5500	13.890	99.788	86.904	70.865	10.356	150.780	− 5.991
5600	13.891	100.039	87.136	72.254	10.670	153.334	− 5.984
5700	13.892	100.285	87.365	73.643	10.979	155.875	− 5.977
5800	13.892	100.526	87.590	75.032	11.274	158.419	− 5.969
5900	13.893	100.764	87.811	76.422	11.562	160.955	− 5.962
6000	13.894	100.997	88.029	77.811	11.837	163.484	− 5.955

June 30, 1968; June 30, 1972

DIALUMINUM MONOXIDE UNIPOSITIVE ION (Al_2O^+) (IDEAL GAS) GFW = 69.9619

Point Group [C_{2v}] ΔHf°_0 = 146 ± 10 kcal/mol

$S^\circ_{298.15}$ = 61.6 ± 0.2 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 146 ± 10 kcal/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[700] (1)
[500] (1)
[1000] (1)

Bond Distance: Al-O = [1.66] Å

Bond Angle: Al-O-Al = [155° ± 5°] σ = 2

Product of the Moments of Inertia: $I_A I_B I_C$ = [1.482 x 10^{-115}] $g^3 cm^6$

Heat of Formation

The ionization potential of $Al_2O(g)$ has been reported to be 7.7 ± 0.2 eV (177.6 kcal/mol) by Porter, Schissel, and Inghram (1), and has been confirmed as 7.7 ± 0.3 eV by DeMaria, Drowart, and Inghram (2). Other values reported are as follows:

reference	value, eV
3	7.7 ± 0.5
4	7.7 ± 0.5
5	8.5 ± 1.0
6	7.9 ± 0.3
9	8.20 ± 0.15

A value of 7.7 ± 0.5 eV is chosen as the ionization potential for $Al_2O(g)$. This same value is also suggested by the NBS (7). Using this value with $\Delta Hf^\circ_{298}(Al_2O, g)$ = −33.0 kcal/mol, we obtain $\Delta Hf^\circ_{298}(Al_2O^+, g)$ = 146 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecule is assumed to be bent by analogy with Al_2O, although both molecules are predicted to be linear according to Walsh (8). The electronic ground state is doublet, since there is an odd number of electrons. The bond length is estimated to be the same as that in Al_2O and the vibrational frequencies are also assumed to be close to those for Al_2O. Since normally the molecule Al_2O ought to be linear, the bending must occur due to the occupancy of an outermost orbital with strong angular variation. Presumably this orbital is occupied by a pair of electrons, one of which will be removed in Al_2O^+, thus causing an opening of the bond angle. On this basis the bond angle is estimated to be greater than that in Al_2O. The individual moments of inertia are: I_A = 23.80 x 10^{-39} g cm^2, I_B = 23.53 x 10^{-39} g cm^2, and I_C = 0.2645 x 10^{-39} g cm^2.

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Aluminum Oxide, Alpha (α-Al_2O_3)

(Crystal) GFW = 101.9612

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	− 2.395	− 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	18.885	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	41.667
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	18.247
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	− 534.033	− 159.051	11.587

rca affirmed

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

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

ΔHf°_0 = −397.6 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 12.175 ± 0.02 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −400.5 ± 0.3 kcal/mol

Tm = 2327 ± 6 K

ΔHm° = 28.0 ± 2 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 $2AlF_3(c) + 3H_2O(g) \rightarrow Al_2O_3(c) + 6HF(g)$.

Heat Capacity and Entropy

Cp° is from Ditmars and Douglas (7) who tabulated functions from 0 to 1200 K. These functions were derived from Cp° data (13-380 K) measured earlier (8) on the Calorimetry Conference Sample and new enthalpies (323-1173 K) measured (7) on NBS Standard Reference Material 720. Entropy and enthalpy were obtained from Cp° based on S°_{13} = 0.0016 gibbs/mol.

Ditmars and Douglas (7) 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 (9). 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 (7) included some twenty of these studies.

Melting Data

See Al_2O_3(ℓ).

References

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Aluminum Oxide, Gamma (γ- Al_2O_3)

(Crystal) GFW = 101.9612

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.885	14.300	14.300	.000	- 395.200	- 373.511	273.791
300	18.991	14.417	14.300	.035	- 395.206	- 373.377	272.005
400	22.965	20.473	15.099	2.150	- 395.356	- 366.069	200.010
500	25.366	25.877	16.725	4.576	- 395.289	- 358.752	156.810
600	26.899	30.647	18.656	7.194	- 395.171	- 351.460	128.019
700	27.946	34.876	20.677	9.939	- 394.913	- 344.198	107.463
800	28.713	38.660	22.693	12.774	- 394.709	- 336.969	92.056
900	29.317	42.078	24.660	15.677	- 394.551	- 329.761	80.077
1000	29.821	45.194	26.560	18.634	- 399.500	- 322.200	70.417
1100	30.260	48.057	28.386	21.638	- 399.273	- 314.483	62.482
1200	30.653	50.707	30.137	24.684	- 399.017	- 306.787	55.873
1300	31.008	53.175	31.815	27.768	- 398.735	- 299.111	50.285
1400	31.329	55.485	33.424	30.885	- 398.432	- 291.458	45.499
1500	31.618	57.656	34.968	34.032	- 398.109	- 283.830	41.354
1600	31.874	59.705	36.451	37.207	- 397.767	- 276.222	37.730
1700	32.100	61.645	37.876	40.406	- 397.409	- 268.636	34.535
1800	32.300	63.485	39.248	43.626	- 397.039	- 261.069	31.698
1900	32.480	65.236	40.570	46.865	- 396.660	- 253.527	29.162
2000	32.650	66.907	41.846	50.122	- 396.272	- 246.007	26.882
2100	32.820	68.504	43.077	53.395	- 395.874	- 238.503	24.821
2200	32.990	70.034	44.268	56.686	- 395.469	- 231.020	22.950
2300	33.160	71.505	45.421	59.993	- 395.052	- 223.550	21.242
2400	33.330	72.920	46.537	63.318	- 394.628	- 216.100	19.679
2500	33.510	74.284	47.620	66.660	- 394.196	- 208.678	18.243
2600	33.690	75.602	48.671	70.020	- 393.752	- 201.262	16.918
2700	33.880	76.877	49.692	73.398	- 393.299	- 193.870	15.693
2800	34.080	78.112	50.685	76.796	- 531.653	- 186.831	14.427
2900	34.300	79.312	51.652	80.215	- 530.650	- 172.463	12.997
3000	34.530	80.479	52.593	83.656	- 529.633	- 160.126	11.665

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Dec. 31, 1965; June 30, 1972

ALUMINUM OXIDE, GAMMA (γ-Al_2O_3) (CRYSTAL) GFW = 101.9612

$S°_{298.15}$ = [14.3 ± 1.5] gibbs/mol

Tm = [2291] K

$\Delta Hf°_0$ = unknown

$\Delta Hf°_{298.15}$ = -395.2 ± 3 kcal/mol

$\Delta Hm°$ = [22.5] kcal/mol

Heat of Formation

$\Delta Hf°$ is calculated from that of Al_2O_3(c, α) and $\Delta Hr°$ = -5.3 kcal/mol for the irreversible process $\gamma \rightarrow \alpha$. Yokokawa and Kleppa (1) determined $\Delta Hr°$ for the two forms from the difference in their heats of solution in an oxide melt at 978 K. Our adopted Cp° implies that $\Delta Hr°$ is independent of temperature. We assign an uncertainty of about 3 kcal/mol to emphasize that samples of γ-phase can show considerable variability, depending on their history, and still retain the often diffuse X-ray pattern of γ-Al_2O_3. Yokokawa and Kleppa studied the variation of heat of solution with temperature of ignition for samples obtained from three different starting materials. Appearance of different crystalline forms was followed by X-ray patterns. The range of ignition temperatures for which γ was the only observed phase varied from 600-800°C to 900-1200°C for different starting materials. Lower ignition temperatures gave values of ΔHr more negative than -5.3 by up to 2.5 kcal/mol. ΔHr = -5.3 was chosen (1) from the highest ignition temperatures prior to the appearance of more stable phases; this should correspond to maximum annealing and minimum imperfections in the crystal.

Other reported values of $\Delta Hr°(\gamma \rightarrow \alpha)$ include -7.7 kcal/mol from HF-solution calorimetry (2) and -11.0 kcal/mol from DTA studies (3) near 1700°C. These reports gave no details on the samples of γ-Al_2O_3 or the actual experimental measurements. Roth (4) measured heats of combustion of mixtures with paraffin oil and derived $\Delta Hr°$ = -7.8 kcal/mol after correction for incomplete dehydration of the sample. Crude values of $\Delta Hr°(\gamma \rightarrow \alpha)$ may be derived by difference from various thermochemical reactions; these include -3 (5), -16 and -23 (6) kcal/mol. The more negative values probably involved gross thermochemical errors or samples other than pure γ-Al_2O_3.

Heat Capacity and Entropy

Cp° is assumed to be identical with that of α-Al_2O_3. S° is selected arbitrarily so that $\Delta Gr°(\gamma \rightarrow \alpha)$ approaches zero near 2500 K. This is consistent with the view that γ-phase is unstable with respect to α-phase at all temperatures below Tm. The conversion $\gamma \rightarrow \alpha$ is activated kinetically at temperatures of 1000 to 1300°C (1).

The adopted S° is 2.12 gibbs/mol larger than that of α-Al_2O_3. $\Delta S°_0(\alpha \rightarrow \gamma)$ = 1.56 gibbs/mol was estimated by Borer and Gunthard (7) for the "defect" spinel structure of γ-Al_2O_3, assuming the Al cations and vacancies to be randomly distributed over all available sites. Alternative interpretations (8) suggest that random distribution may be limited to just the tetrahedral or just the octahedral spinel sites. Ervin (9) attributed the variation in properties of γ-Al_2O_3 to various stages between disorder and order of the Al cations. In contrast, Cowley (10) suggested from electron-diffraction data that all or most of the vacancies could occur along fault planes in the cubic, close-packed lattice of oxygens. These various structural interpretations raise doubt about the validity of the estimated $\Delta S°_0$ (7).

Melting Data

The hypothetical melting point of metastable γ-phase is calculated as the temperature at which $\Delta Gr°(\gamma \rightarrow \ell)$ = 0. $\Delta Hm°$ is the corresponding difference in $\Delta Hf°$.

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Aluminum Oxide (Al_2O_3)

(Liquid) GFW = 101.9612

T, °K	Cp°	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	18.885	21.411	21.411	.000	- 377.898	- 358.329	262.662
300	18.981	21.528	21.412	.035	- 377.904	- 358.209	260.955
400	22.965	27.585	22.210	2.150	- 378.054	- 351.611	192.111
500	25.366	32.988	23.837	4.576	- 377.987	- 345.005	150.802
600	26.899	37.758	25.768	7.194	- 377.819	- 338.424	123.271
700	27.946	41.988	27.788	9.939	- 377.611	- 331.874	103.616
800	28.713	45.772	29.804	12.774	- 377.407	- 325.356	88.883
900	29.317	49.190	31.771	15.677	- 377.249	- 318.859	77.429
1000	29.821	52.305	33.671	18.634	- 382.198	- 312.009	68.190
1100	30.260	55.168	35.497	21.638	- 381.970	- 305.003	60.599
1200	30.653	57.818	37.248	24.684	- 381.714	- 298.018	54.276
1300	31.008	60.286	38.926	27.768	- 381.433	- 291.054	48.931
1400	31.329	62.596	40.535	30.885	- 381.130	- 284.112	44.352
1500	31.618	64.768	42.079	34.032	- 380.806	- 277.195	40.387
1600	31.874	66.816	43.562	37.207	- 380.465	- 270.298	36.921
1700	40.000	69.241	45.002	41.207	- 379.306	- 263.448	33.868
1800	40.000	71.528	46.413	45.207	- 378.156	- 256.663	31.163
1900	40.000	73.690	47.792	49.207	- 377.016	- 249.946	28.750
2000	40.000	75.742	49.139	53.207	- 375.884	- 243.290	26.586
2100	40.000	77.694	50.452	57.207	- 374.760	- 236.688	24.632
2200	40.000	79.555	51.733	61.207	- 373.646	- 230.141	22.862
2300	40.000	81.333	52.982	65.207	- 372.536	- 223.638	21.250
2400	40.000	83.035	54.199	69.207	- 371.437	- 217.186	19.777
2500	40.000	84.668	55.385	73.207	- 370.347	- 210.789	18.427
2600	40.000	86.237	56.542	77.207	- 369.263	- 204.424	17.183
2700	40.000	87.746	57.670	81.207	- 368.188	- 198.107	16.036
2800	40.000	89.201	58.770	85.207	- 505.940	- 190.166	14.843
2900	40.000	90.605	59.844	89.207	- 504.356	- 178.917	13.484
3000	40.000	91.961	60.892	93.207	- 502.780	- 167.719	12.218
3100	40.000	93.272	61.915	97.207	- 501.209	- 156.575	11.039
3200	40.000	94.542	62.915	101.207	- 499.646	- 145.484	9.936
3300	40.000	95.773	63.892	105.207	- 498.089	- 134.441	8.904
3400	40.000	96.967	64.847	109.207	- 496.542	- 123.449	7.935
3500	40.000	98.127	65.782	113.207	- 494.997	- 112.500	7.025
3600	40.000	99.254	66.696	117.207	- 493.460	- 101.586	6.167
3700	40.000	100.350	67.591	121.207	- 491.929	- 90.725	5.359
3800	40.000	101.416	68.467	125.207	- 490.404	- 79.901	4.595
3900	40.000	102.455	69.325	129.207	- 488.882	- 69.117	3.873
4000	40.000	103.468	70.166	133.207	- 487.370	- 58.378	3.190

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

ALUMINUM OXIDE (Al_2O_3) (LIQUID) GFW = 101.9612

$S^\circ_{298.15}$ = 21.411 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -377.898 kcal/mol

Tm = 2327 ± 6 K ΔHm° = 28.0 ± 2 kcal/mol

Heat of Formation

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

Heat Capacity and Entropy

Enthalpy data for the liquid include those of Kantor et al. (1, 2337 to 2480 K), Sheindlin et al. (2, 2350 to 2800 K), and approximate values of West and Ishihara (3, 2345 to 2495 K). The authors derived constant Cp° values of 34.6 (1) and 47.7 (2) gibbs/mol. We adopt a compromise of 40 gibbs/mol, corresponding to 8 gibbs/g-atom. New data (4, 5), still unpublished, may resolve this discrepancy. 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 recently by Schneider (6) as the result of a cooperative measurement of the melting point by nine groups in seven countries. This value is adopted. ΔHm is selected so that there is reasonable agreement with the experimental enthalpies (1, 2) near 2500 K. Reported values of ΔHm include 28.3 ± 0.6 (1) and 25.9 (2) kcal/mol, while the data of West and Ishihara (3) correspond to 30 ± 2 kcal/mol when reduced with our adopted Cp°. A value of 21.4 kcal/mol obtained from cooling curves (7) can be dismissed as too low. New calorimetric studies are in progress (4, 5).

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Aluminum Beryllium Oxide (Al_6BeO_{10})

(Crystal) GFW = 330.8952

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 8.153	−1334.946	−1334.946	INFINITE
100	11.245	3.965	82.515	− 7.855	−1338.764	−1317.460	2879.306
200	41.331	21.018	47.118	− 5.220	−1342.399	−1294.696	1414.779
298	63.381	41.958	41.958	.000	−1344.200	−1270.868	931.571
300	63.706	42.351	41.959	.118	−1344.220	−1270.415	925.496
400	77.502	62.734	44.644	7.236	−1344.690	−1245.710	680.624
500	85.690	80.984	50.125	15.430	−1344.441	−1220.984	533.692
600	90.956	97.103	56.639	24.278	−1343.864	−1196.346	435.769
700	94.666	111.417	63.461	33.569	−1343.145	−1171.813	365.856
800	97.473	124.248	70.272	43.181	−1342.420	−1147.352	313.453
900	99.725	135.863	76.924	53.045	−1341.815	−1123.049	272.713
1000	101.620	146.471	83.356	63.115	−1356.518	−1097.664	239.894
1100	103.250	156.234	89.544	73.360	−1355.686	−1071.824	212.952
1200	104.670	165.280	95.483	83.757	−1354.772	−1046.060	190.514
1300	105.950	173.709	101.180	94.289	−1353.785	−1020.371	171.540
1400	107.150	181.605	106.645	104.944	−1352.740	− 994.760	155.289
1500	108.350	189.038	111.893	115.718	−1351.635	− 969.234	141.217
1600	109.600	196.070	116.936	126.615	−1353.216	− 943.698	128.903
1700	110.950	202.755	121.789	137.642	−1351.846	− 918.144	118.035
1800	112.400	209.137	126.466	148.808	−1350.371	− 892.667	108.385
1900	114.000	215.256	130.979	160.127	−1348.784	− 867.285	99.760
2000	115.750	221.148	135.341	171.613	−1347.060	− 841.997	92.009
2100	117.650	226.840	139.563	183.282	−1345.183	− 816.788	85.004
2200	119.700	232.360	143.657	195.148	−1343.149	− 791.678	78.646
2300	121.900	237.729	147.630	207.227	−1340.921	− 766.646	72.848
2400	124.250	242.966	151.494	219.533	−1338.507	− 741.721	67.543
2500	126.750	248.088	155.256	232.082	−1335.886	− 716.932	62.674
2600	129.400	253.111	158.923	244.888	−1333.032	− 692.217	58.186
2700	132.200	258.046	162.503	257.967	−1329.939	− 667.636	54.041
2800	135.150	262.907	166.002	271.333	−1814.079	− 637.074	49.726
2900	138.250	267.703	169.427	285.002	−1808.632	− 595.134	44.850
3000	141.500	272.445	172.782	298.988	−1802.895	− 553.379	40.314

June 30, 1972

ALUMINUM BERYLLIUM OXIDE (Al_6BeO_{10}) (CRYSTAL) GFW = 330.8952

ΔHf°_0 = −1334.9 ± 1.3 kcal/mol

$S^\circ_{298.15}$ = 41.96 ± 0.06 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −1344.2 ± 1.3 kcal/mol

Tm = 2186 ± 10 K

ΔHm° = [96] kcal/mol

Heat of Formation

ΔHf° is calculated from $\Delta Hr^\circ(298.15\ K)$ = 2.71 ± 0.45 kcal/mol for BeO(c, α) + $3Al_2O_3$(c, α) → Al_6BeO_{10}(c) using current values of ΔHf° for the reactants (1). ΔHr° is based on the value 2.9 ± 0.45 kcal/mol at 968 K determined by Holm and Kleppa (2) from the difference in heats of solution of the three components in an oxide melt.

For comparison with the above reaction, we derive $\Delta Hr^\circ(298.15\ K)$ = 0.8 kcal/mol from $\Delta Gr^\circ(1800\ K)$ = −3.95 kcal/mol based on equilibrium data. Young (3) used water vapor as a carrier gas to determine the transport of BeO, presumably as $Be(OH)_2$, in equilibrium with BeO(c) and Al_6BeO_{10}(c). The difference between the two equilibria gives the above reaction. We compare at 1800 K, near the upper limit of the data, where the experimental method is most sensitive. The resulting difference in $\Delta Hr^\circ(298.15\ K)$ is −2.1 kcal/mol, roughly twice the uncertainty claimed for ΔGr° (3).

Heat Capacity and Entropy

Cp° and the derived properties below 298 K are taken from calorimetric data (15-380 K) of Furukawa and Saba (4). The entropy is based on S°_{15} = 0.011 gibbs/mol. Cp° above 298 K is from the tabulation of Ditmars and Douglas (5) based on enthalpy data (323-1173 K). Cp° is extrapolated above 1200 K by comparison with current tables (1) for $BeAl_2O_4$(c), Al_2O_3(c, α), and BeO(c, α).

Holm and Kleppa (2) combined their ΔHr° for formation from the oxides with the corresponding ΔGr° from Young (3) in order to calculate ΔSr°. Based on the present functions and Young's result at 1800 K, we calculate an entropy which is 1.2 gibbs/mol larger than the adopted calorimetric value. To explain the difference, Holm and Kleppa (2) proposed Be-Al disorder in the crystal, which might provide extra entropy up to 2.76 eu. Crystal structure data were recently published (6), but they do not appear to be sufficient to test the hypothesis of disorder. Although we believe that the discrepancy is within the uncertainty of the equilibrium data, further information is desirable.

Melting Data

See Al_6BeO_{10}(ℓ).

References

1. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Mich.; BeO(c, α) dated June 30, 1971; Al_2O_3(c, α) and $BeAl_2O_4$(c) dated June 30, 1972.
2. J. L. Holm and O. J. Kleppa, Acta Chem. Scand. 20, 2568 (1966).
3. W. A. Young, J. Phys. Chem. 64, 1003 (1960).
4. G. T. Furukawa and W. G. Saba, J. Res. Natl. Bur. Std. 71A, 3 (1967).
5. D. A. Ditmars and T. B. Douglas, J. Res. Natl. Bur. Std. 71A, 97 (1967).
6. L. A. Harris and H. L. Yakel, J. Amer. Ceram. Soc. 53, 359 (1970).

Aluminum Beryllium Oxide (Al_6BeO_{10})

(Liquid) GFW = 330.8952

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	63.381	75.263	75.263	.000	-1266.566	-1203.164	881.943
300	63.706	75.657	75.265	.118	-1266.587	-1202.773	876.219
400	77.502	96.040	77.950	7.236	-1267.056	-1181.398	645.486
500	85.690	114.290	83.430	15.430	-1266.807	-1160.003	507.037
600	90.956	130.408	89.944	24.278	-1266.230	-1138.696	414.769
700	94.666	144.722	96.767	33.569	-1265.511	-1117.493	348.857
800	97.473	157.554	103.577	43.181	-1264.786	-1096.402	299.523
900	99.725	169.169	110.230	53.045	-1264.181	-1075.390	261.140
1000	101.620	179.776	116.662	63.115	-1278.885	-1053.336	230.206
1100	103.250	189.540	122.849	73.360	-1278.052	-1030.826	204.806
1200	104.670	198.586	128.788	83.757	-1277.138	-1008.393	183.653
1300	105.950	207.015	134.485	94.285	-1276.152	- 986.034	165.767
1400	107.150	214.911	139.951	104.944	-1275.106	- 963.754	150.449
1500	136.000	224.294	145.264	118.544	-1271.175	- 941.658	137.199
1600	136.000	233.071	150.481	132.144	-1270.053	- 919.736	125.630
1700	136.000	241.316	155.584	145.744	-1266.110	- 897.961	115.441
1800	136.000	249.089	160.565	159.344	-1262.201	- 876.411	106.411
1900	136.000	256.443	165.419	172.944	-1258.333	- 855.088	98.357
2000	136.000	263.415	170.146	186.544	-1254.495	- 833.974	91.132
2100	136.000	270.054	174.747	200.144	-1250.687	- 813.041	84.614
2200	136.000	276.381	179.224	213.744	-1246.919	- 792.293	78.707
2300	136.000	282.426	183.581	227.344	-1243.170	- 771.698	73.328
2400	136.000	288.214	187.821	240.944	-1239.462	- 751.271	68.413
2500	136.000	293.766	191.948	254.544	-1235.790	- 731.030	63.907
2600	136.000	299.100	195.968	268.144	-1232.142	- 710.899	59.756
2700	136.000	304.233	199.883	281.744	-1228.528	- 690.928	55.927
2800	136.000	309.179	203.699	295.344	-1712.434	- 664.990	51.905
2900	136.000	313.951	207.419	308.944	-1707.056	- 627.676	47.303
3000	136.000	318.562	211.047	322.544	-1701.705	- 590.540	43.021
3100	136.000	323.021	214.588	336.144	-1696.375	- 553.588	39.028
3200	136.000	327.339	218.044	349.744	-1691.071	- 516.809	35.296
3300	136.000	331.524	221.420	363.344	-1685.790	- 480.197	31.802
3400	136.000	335.584	224.718	376.944	-1680.543	- 443.755	28.524
3500	136.000	339.526	227.942	390.544	-1675.307	- 407.464	25.443
3600	136.000	343.357	231.095	404.144	-1670.101	- 371.288	22.540
3700	136.000	347.084	234.180	417.744	-1664.919	- 335.293	19.805
3800	136.000	350.711	237.199	431.344	-1659.763	- 299.422	17.221
3900	136.000	354.243	240.155	444.944	-1654.620	- 263.686	14.777
4000	136.000	357.687	243.050	458.544	-1649.515	- 228.105	12.463

June 30, 1972

ALUMINUM BERYLLIUM OXIDE (Al_6BeO_{10}) (LIQUID) GFW = 330.8952

$S^\circ_{298.15}$ = [75.263] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-1266.566] kcal/mol

Tm = 2186 ± 10 K ΔHm° = [96] kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by adding ΔHm° and the difference in $(H^\circ_{2186}-H^\circ_{298.15})$ between crystal and liquid.

Heat Capacity and Entropy

Cp° is assumed to be 136 gibbs/mol, corresponding to 8 gibbs/g-atom, by analogy with current tables (1) for $BeAl_2O_4(\ell)$ and $Al_2O_3(\ell)$. Below the assumed glass transition at 1400 K, Cp° is taken to be the same as that of the crystal. The entropy is calculated in a way analogous with ΔHf°.

Melting Data

Tm, adjusted to IPTS-68, is from the phase study of Lang et al. (2). ΔHm° is estimated as being slightly smaller than the sum of ΔHm° for the component oxides (1). Data for $BeAl_2O_4$ are consistent with this approach.

References

1. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Mich.; BeO(ℓ) dated June 30, 1971; $Al_2O_3(\ell)$ and $BeAl_2O_4(\ell)$ dated June 30, 1972.

2. S. M. Lang, C. L. Fillmore, and L. H. Maxwell, J. Res. Natl. Bur. Std. 48, 298 (1952).

Boron Unipositive Ion (B^+)

(Ideal Gas) GFW = 10.81045

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	4.968	33.086	33.086	.000	325.607	314.673	= 230.662
300	4.968	33.117	33.086	.009	325.620	314.605	= 229.190
400	4.968	34.546	33.281	.506	326.292	310.830	= 169.829
500	4.968	35.654	33.649	1.003	326.873	306.896	= 134.144
600	4.968	36.560	34.061	1.500	327.392	302.851	= 110.313
700	4.968	37.320	34.474	1.996	327.868	298.722	= 93.265
800	4.968	37.989	34.873	2.493	328.317	294.527	= 80.461
900	4.968	38.575	35.252	2.990	328.745	290.278	= 70.489
1000	4.968	39.098	35.611	3.487	329.154	285.982	= 62.501
1100	4.968	39.571	35.950	3.984	329.544	281.646	= 55.958
1200	4.968	40.004	36.270	4.480	329.917	277.275	= 50.499
1300	4.968	40.401	36.573	4.977	330.277	272.873	= 45.874
1400	4.968	40.770	36.860	5.474	330.624	268.445	= 41.906
1500	4.968	41.112	37.132	5.971	330.957	263.991	= 38.463
1600	4.968	41.433	37.391	6.467	331.276	259.516	= 35.448
1700	4.968	41.734	37.637	6.964	331.585	255.021	= 32.785
1800	4.968	42.018	37.873	7.461	331.884	250.509	= 30.416
1900	4.968	42.287	38.098	7.958	332.175	245.980	= 28.294
2000	4.968	42.541	38.314	8.455	332.460	241.437	= 26.383
2100	4.968	42.784	38.521	8.951	332.737	236.878	= 24.652
2200	4.968	43.015	38.720	9.448	333.011	232.307	= 23.078
2300	4.968	43.236	38.912	9.945	333.280	227.724	= 21.639
2400	4.968	43.447	39.096	10.442	333.544	223.130	= 20.319
2500	4.968	43.650	39.275	10.939	328.417	218.633	= 19.113
2600	4.968	43.845	39.447	11.435	328.679	214.234	= 18.008
2700	4.968	44.032	39.613	11.932	328.943	209.829	= 16.984
2800	4.968	44.213	39.774	12.429	329.207	205.412	= 16.033
2900	4.968	44.387	39.930	12.926	329.471	200.988	= 15.147
3000	4.968	44.556	40.082	13.423	329.735	196.552	= 14.319
3100	4.968	44.719	40.228	13.919	329.997	192.107	= 13.543
3200	4.968	44.876	40.371	14.416	330.261	187.655	= 12.816
3300	4.968	45.029	40.510	14.913	330.525	183.196	= 12.133
3400	4.969	45.178	40.645	15.410	330.789	178.728	= 11.489
3500	4.969	45.322	40.777	15.907	331.053	174.250	= 10.881
3600	4.969	45.462	40.905	16.404	331.316	169.767	= 10.306
3700	4.970	45.598	41.030	16.901	331.580	165.276	= 9.762
3800	4.970	45.730	41.152	17.398	331.844	160.779	= 9.247
3900	4.971	45.859	41.271	17.895	332.108	156.272	= 8.757
4000	4.973	45.985	41.387	18.392	211.192	153.904	= 8.409
4100	4.974	46.108	41.501	18.889	211.687	152.466	= 8.127
4200	4.976	46.228	41.612	19.387	212.184	151.020	= 7.858
4300	4.978	46.345	41.721	19.884	212.679	149.556	= 7.603
4400	4.981	46.460	41.827	20.382	213.174	148.083	= 7.355
4500	4.985	46.572	41.931	20.881	213.669	146.595	= 7.120
4600	4.989	46.681	42.033	21.379	214.164	145.100	= 6.894
4700	4.993	46.789	42.133	21.878	214.659	143.595	= 6.677
4800	4.999	46.894	42.232	22.378	215.154	142.079	= 6.469
4900	5.005	46.997	42.328	22.878	215.645	140.548	= 6.269
5000	5.012	47.098	42.422	23.379	216.142	139.012	= 6.076
5100	5.021	47.197	42.515	23.881	216.636	137.464	= 5.891
5200	5.030	47.295	42.606	24.383	217.130	135.907	= 5.712
5300	5.041	47.391	42.695	24.887	217.625	134.338	= 5.540
5400	5.052	47.485	42.783	25.391	218.118	132.763	= 5.373
5500	5.065	47.578	42.869	25.897	218.612	131.181	= 5.213
5600	5.080	47.669	42.954	26.404	219.106	129.587	= 5.057
5700	5.096	47.759	43.038	26.913	219.600	127.981	= 4.907
5800	5.113	47.848	43.120	27.424	220.095	126.369	= 4.762
5900	5.132	47.936	43.201	27.936	220.590	124.750	= 4.621
6000	5.152	48.022	43.280	28.450	221.084	123.122	= 4.485

Dec. 31, 1967; Dec. 31, 1970

BORON UNIPOSITIVE ION (B^+) (IDEAL GAS) GFW = 10.81045

Ground State Configuration $^1S_0$ ΔHf°_0 = 322.9 ± 4.0 kcal/mol

$S^\circ_{298.15}$ = 33.086 ± 0.005 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 325.6 ± 4.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
37333.5	1
37340.0	3
37356.4	5

Heat of Formation

We calculate the heat of formation at 0°K from the reaction $B(g) - e^-(g) \rightarrow B^+(g)$ using the JANAF auxiliary value for B(g) and an ionization potential of 191.356 kcal/mol from Moore (1).

Heat Capacity and Entropy

The electronic levels and quantum weights are from Moore (2). Levels above 70,000 cm^{-1} are not included since they have no effect on the thermodynamic functions. $H^\circ_0 - H^\circ_{298}$ = −1.481 kcal/mol at 0°K.

References

1. C. E. Moore, NSRDS-NBS 34, 1970.
2. C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, 1949.

Boron Dichloride (BCl_2)

(Ideal Gas) GFW = 81.7170

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 2.811	− 19.324	− 19.324	INFINITE
100	8.708	54.404	74.357	− 1.995	− 19.211	− 20.129	43.951
200	10.106	60.870	66.143	− 1.055	− 19.077	− 21.102	23.059
298	11.323	65.144	65.144	.000	− 19.000	− 22.116	16.212
300	11.342	65.214	65.144	.021	− 18.999	− 22.136	16.126
400	12.170	68.599	65.603	1.200	− 18.972	− 23.187	12.669
500	12.684	71.375	66.486	2.444	− 18.994	− 24.238	10.595
600	13.011	73.718	67.501	3.730	− 19.052	− 25.282	9.209
700	13.227	75.741	68.537	5.043	− 19.133	− 26.314	8.216
800	13.375	77.518	69.551	6.374	− 19.233	− 27.335	7.468
900	13.481	79.099	70.525	7.717	− 19.346	− 28.340	6.882
1000	13.558	80.524	71.455	9.069	− 19.473	− 29.333	6.411
1100	13.617	81.819	72.339	10.428	− 19.615	− 30.313	6.023
1200	13.663	83.006	73.180	11.792	− 19.770	− 31.278	5.697
1300	13.699	84.101	73.978	13.160	− 19.938	− 32.231	5.419
1400	13.729	85.117	74.738	14.531	− 20.118	− 33.169	5.178
1500	13.755	86.066	75.462	15.906	− 20.310	− 34.096	4.968
1600	13.778	86.954	76.153	17.282	− 20.515	− 35.008	4.782
1700	13.800	87.790	76.813	18.661	− 20.730	− 35.906	4.616
1800	13.821	88.579	77.445	20.042	− 20.955	− 36.794	4.467
1900	13.842	89.327	78.051	21.426	− 21.186	− 37.666	4.333
2000	13.864	90.038	78.632	22.811	− 21.425	− 38.527	4.210
2100	13.887	90.715	79.192	24.198	− 21.668	− 39.377	4.098
2200	13.912	91.361	79.730	25.588	− 21.916	− 40.214	3.995
2300	13.937	91.980	80.250	26.981	− 22.167	− 41.040	3.900
2400	13.964	92.574	80.751	28.376	− 22.423	− 41.854	3.811
2500	13.993	93.145	81.235	29.774	− 28.070	− 42.550	3.720
2600	14.023	93.694	81.704	31.175	− 28.324	− 43.124	3.625
2700	14.053	94.224	82.158	32.578	− 28.579	− 43.688	3.536
2800	14.085	94.736	82.598	33.985	− 28.833	− 44.243	3.453
2900	14.117	95.230	83.025	35.395	− 29.086	− 44.787	3.375
3000	14.150	95.710	83.440	36.805	− 29.338	− 45.327	3.302
3100	14.183	96.174	83.843	38.225	− 29.591	− 45.857	3.233
3200	14.217	96.625	84.236	39.645	− 29.843	− 46.377	3.167
3300	14.250	97.063	84.618	41.069	− 30.094	− 46.888	3.105
3400	14.283	97.489	84.990	42.495	− 30.345	− 47.392	3.046
3500	14.316	97.903	85.353	43.925	− 30.596	− 47.894	2.991
3600	14.349	98.307	85.707	45.359	− 30.845	− 48.381	2.937
3700	14.381	98.701	86.053	46.795	− 31.095	− 48.865	2.886
3800	14.412	99.085	86.391	48.235	− 31.343	− 49.342	2.838
3900	14.443	99.459	86.722	49.678	− 31.591	− 49.814	2.791
4000	14.473	99.825	87.045	51.123	− 153.019	− 48.132	2.630
4100	14.503	100.183	87.361	52.572	− 153.034	− 45.512	2.426
4200	14.531	100.533	87.670	54.024	− 153.048	− 42.886	2.232
4300	14.559	100.875	87.973	55.479	− 153.061	− 40.265	2.046
4400	14.586	101.210	88.270	56.936	− 153.075	− 37.638	1.869
4500	14.613	101.538	88.562	58.396	− 153.088	− 35.019	1.701
4600	14.638	101.860	88.847	59.858	− 153.099	− 32.394	1.539
4700	14.663	102.175	89.127	61.323	− 153.110	− 29.767	1.384
4800	14.687	102.484	89.402	62.791	− 153.120	− 27.143	1.236
4900	14.711	102.787	89.672	64.261	− 153.130	− 24.520	1.094
5000	14.733	103.084	89.938	65.733	− 153.138	− 21.895	.957
5100	14.755	103.376	90.198	67.207	− 153.146	− 19.267	.826
5200	14.777	103.663	90.455	68.684	− 153.152	− 16.642	.699
5300	14.798	103.945	90.706	70.163	− 153.158	− 14.021	.578
5400	14.818	104.222	90.954	71.644	− 153.164	− 11.396	.461
5500	14.838	104.494	91.198	73.126	− 153.169	− 8.764	.348
5600	14.857	104.761	91.438	74.611	− 153.173	− 6.146	.240
5700	14.875	105.024	91.674	76.098	− 153.178	− 3.521	.135
5800	14.894	105.283	91.906	77.586	− 153.182	− .892	.034
5900	14.911	105.538	92.135	79.076	− 153.186	1.731	− .064
6000	14.929	105.789	92.361	80.568	− 153.190	4.361	− .159

Dec. 31, 1960; Mar. 31, 1963; Dec. 31, 1964; June 30, 1972

BORON DICHLORIDE (BCl_2) (IDEAL GAS) GFW = 81.7170 BCl_2

Point Group [C_{2v}] ΔHf_0° = −19.3 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = [65.1 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = −19.0 ± 3.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
[11000]	[2]
28003	1
28153	1
29455	1
29542	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[700] (1)
250 (1)
[725] (1)

Bond Distance: B−Cl = [1.73] Å

Bond Angle: Cl−B−Cl = [112]° σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [9.05875 x 10^{-115}] $g^3 cm^6$

Heat of Formation

Srivastava and Farber (1) have investigated the equilibrium vapors over the boron trichloride-boron system by mass spectrometry. Gaseous BCl_3 was allowed to flow into a boron nitride effusion cell which contained metallic boron. A flow variation study indicated that thermal equilibrium had been achieved during their experiments. Ion intensities for the species BCl_3(g), BCl_2(g), and BCl(g) were measured at electron energies slightly above appearance potentials in the temperature range 1513 to 1813 K. JANAF analysis of equilibrium constants for the reaction BCl_3(g) + BCl(g) = 2BCl_2(g) which are obtained from their ion intensity data yields a third law ΔHr_{298} value of 24.56 ± 1.00 kcal/mol with a drift of −2.1 ± 2.0 eu. The second law ΔHr value at 298 K is 28.1 kcal/mol. Using the third law ΔHr value in conjunction with JANAF heats of formation (2) for BCl_3(g) and BCl(g), we calculate ΔHf°_{298}(BCl_2, g) = −19.0 ± 3.0 kcal/mol.

The only other reported data on the heat of formation of BCl_2 comes from explosion studies carried out at elevated temperatures by Rusin and Tatevskii (3). The BCl_2 radical was found to be stable at 2250 K in H_2-Cl_2-BCl_3 mixtures. These workers reported ΔHf(BCl_2, g) = −18.4 ± 1.5 kcal/mol which confirms the results of Srivastava and Farber (1).

We adopt ΔHf°_{298}(BCl_2, g) = −19.0 ± 3.0 kcal/mol. This value also leads to a realistic progression in the stepwise bond dissociation energies for BCl(g), BCl_2(g), and BCl_3(g). Using all JANAF data (2), we calculate D_1(B−Cl) = 127.9, D_2(BCl−Cl) = 81.7, and D_3(BCl_2−Cl) = 106.2 kcal/mol. This bond energy scheme, $D_1 > D_2 < D_3$, is consistent with that predicted for the Group III A fluorides by Hildenbrand (4).

Heat Capacity and Entropy

The point group and the Cl-B-Cl bond angle are assumed to be the same as those for BF_2 (2). The B-Cl bond length is estimated to lie between those for BCl and BCl_3 (2). The individual moments of inertia are: I_A = 25.6682 x 10^{-39}, I_B = 24.2105 x 10^{-39}, and I_C = 1.4577 x 10^{-39} g cm^2.

Dessaux et al. (5, 6) observed a diffuse system of bands in the near ultraviolet which they attributed to the BCl_2 radical. The emission spectrum was obtained as chemiluminescence in the reaction between BCl_3 and atomic hydrogen. They indicated that the frequencies ν_1 = 470, ν_2 = 240, and ν_3 = 990 cm^{-1} were consistent with their spectral data; however, alternate assignments are possible. We prefer the frequencies ν_1 = 700, ν_2 = 250, and ν_3 = 725 cm^{-1}, since these values are more consistent with those for CCl_2, $SiCl_2$, and $AlCl_2$ (2).

By analogy with the isoelectronic molecule NO_2 (7), the ground state for BCl_2 is assumed to be $^2A_1$. Hückel-molecular-orbital calculations by Hastie and Margrave (8) suggest a doublet excited state ($^2B_1$) near 11,000 cm^{-1} which is included. The upper electronic levels are those observed by Dessaux et al. (6).

References

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Boron Dichloride Unipositive Ion (BCl_2^+)

(Ideal Gas) GFW = 81.71645

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	12.661	61.590	61.590	.000	161.100	157.556	− 115.491
300	12.678	61.668	61.590	.023	161.112	157.534	− 114.763
400	13.402	65.423	62.097	1.330	161.764	156.241	− 85.366
500	13.846	68.466	63.076	2.695	162.360	154.791	− 67.659
600	14.128	71.017	64.193	4.094	162.912	153.225	− 55.812
700	14.313	73.209	65.328	5.517	163.437	151.568	− 47.321
800	14.441	75.130	66.436	6.955	163.941	149.837	− 40.933
900	14.532	76.836	67.498	8.404	164.431	148.045	− 35.950
1000	14.599	78.371	68.510	9.861	164.906	146.198	− 31.952
1100	14.650	79.765	69.471	11.323	165.364	144.305	− 28.671
1200	14.689	81.041	70.383	12.790	165.808	142.371	− 25.929
1300	14.720	82.218	71.248	14.261	166.240	140.400	− 23.603
1400	14.745	83.310	72.071	15.734	166.659	138.397	− 21.605
1500	14.765	84.328	72.855	17.210	167.065	136.363	− 19.868
1600	14.781	85.281	73.602	18.687	167.457	134.303	− 18.345
1700	14.795	86.178	74.316	20.166	167.839	132.221	− 16.998
1800	14.807	87.024	74.998	21.646	168.210	130.114	− 15.798
1900	14.818	87.825	75.653	23.127	168.573	127.989	− 14.722
2000	14.827	88.585	76.280	24.609	168.928	125.844	− 13.752
2100	14.836	89.309	76.884	26.093	169.278	123.680	− 12.871
2200	14.844	89.999	77.464	27.577	169.621	121.501	− 12.070
2300	14.853	90.659	78.024	29.062	169.959	119.307	− 11.337
2400	14.861	91.292	78.563	30.547	170.290	117.098	− 10.663
2500	14.870	91.898	79.085	32.034	165.229	114.984	− 10.052
2600	14.879	92.482	79.589	33.521	165.557	112.966	− 9.496
2700	14.889	93.043	80.077	35.010	165.885	110.938	− 8.980
2800	14.899	93.585	80.550	36.499	166.210	108.898	− 8.500
2900	14.911	94.108	81.008	37.989	166.534	106.846	− 8.052
3000	14.923	94.614	81.453	39.481	166.857	104.780	− 7.633
3100	14.936	95.103	81.886	40.974	167.177	102.704	− 7.241
3200	14.950	95.578	82.306	42.468	167.496	100.620	− 6.872
3300	14.965	96.038	82.716	43.964	167.814	98.528	− 6.525
3400	14.981	96.485	83.114	45.461	168.131	96.425	− 6.198
3500	14.997	96.920	83.502	46.960	168.446	94.307	− 5.889
3600	15.015	97.342	83.881	48.461	168.760	92.187	− 5.596
3700	15.033	97.754	84.250	49.963	169.073	90.055	− 5.319
3800	15.052	98.155	84.611	51.467	169.386	87.916	− 5.056
3900	15.072	98.546	84.963	52.974	169.699	85.767	− 4.806
4000	15.092	98.928	85.308	54.482	48.830	85.755	− 4.685
4100	15.113	99.301	85.644	55.992	49.373	86.670	− 4.620
4200	15.134	99.665	85.974	57.504	49.916	87.576	− 4.557
4300	15.156	100.022	86.296	59.019	50.460	88.465	− 4.496
4400	15.178	100.371	86.612	60.536	51.003	89.346	− 4.438
4500	15.200	100.712	86.922	62.054	51.544	90.206	− 4.381
4600	15.222	101.046	87.225	63.575	52.089	91.061	− 4.326
4700	15.245	101.374	87.523	65.099	52.634	91.905	− 4.274
4800	15.267	101.695	87.815	66.624	53.178	92.738	− 4.222
4900	15.290	102.010	88.101	68.152	53.723	93.552	− 4.173
5000	15.313	102.319	88.383	69.682	54.269	94.359	− 4.124
5100	15.335	102.623	88.659	71.215	54.817	95.158	− 4.078
5200	15.358	102.921	88.930	72.749	55.365	95.943	− 4.032
5300	15.380	103.213	89.197	74.286	55.914	96.714	− 3.988
5400	15.402	103.501	89.459	75.825	56.463	97.479	− 3.945
5500	15.424	103.784	89.717	77.367	57.014	98.240	− 3.904
5600	15.446	104.062	89.971	78.910	57.565	98.977	− 3.863
5700	15.467	104.336	90.220	80.456	58.116	99.711	− 3.823
5800	15.488	104.605	90.466	82.004	58.669	100.439	− 3.785
5900	15.509	104.870	90.708	83.554	59.222	101.153	− 3.747
6000	15.530	105.131	90.946	85.106	59.774	101.861	− 3.710

June 30, 1968; Dec. 31, 1970

BORON DICHLORIDE UNIPOSITIVE ION (BCl_2^+) (IDEAL GAS) GFW = 81.71645 BCl_2^+

Point Group [$D_{\infty h}$] ΔHf_0° = 159.05 ± 0.6 kcal/mol

$S^\circ_{298.15}$ = [61.6 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 161.1 ± 0.6 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[16000]	1
$^1A_1$	[35000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[500] (1)
[150] (2)
[800] (1)

Bond Distance: B-Cl = [1.74] Å

Bond Angle: Cl-B-Cl = [180°] σ = 2

Rotational Constant: B_0 = [0.0785] cm^{-1}

Heat of Formation

The appearance potential (AP) of the positive ion fragment $BCl_2^+(g)$ from $BCl_3(g)$ was determined mass spectrometrically by Osberghaus (1), Marriott (2), and Koski (3) as 13.2 ± 0.5, 13.01 ± 0.02, and 11.8 ± 0.2 eV, respectively. From the reaction $BCl_3 + e^- = BCl_2^+ + Cl + 2e^-$, the corresponding values of ΔHf°_{298} for $BCl_2^+(g)$ are derived to be 181.9 ± 11.5, 177.5 ± 0.5, and 149.6 ± 4.6 kcal/mol, using ΔHf_0° = −96.078 and 28.520 kcal/mol for $BCl_3(g)$ and Cl(g). These electron impact values are superseded by the photoionization results of Dibeler and Walker (7) who report the onset of BCl_2^+ from BCl_3 as 12.30 ± 0.02 eV (283.65 ± 0.05 kcal). This yields ΔHf_0° = 159.05 ± 0.6 kcal/mol or $\Delta Hf^\circ_{298.15}$ = 161.1 ± 0.6 kcal/mol, which are adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (4) predictions for 16 valence electron XY_2 molecules. The electronic states, levels and vibrational frequencies are estimated by comparison with those for CO_2 (5). The B-Cl bond distance is estimated using the method of Krasnov (6). The moment of inertia is 3.564 x 10^{-38} g cm^2. The enthalpy at 0°K is −3.07 kcal/mol.

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Boron Dichloride Uninegative Ion (BCl_2^-)

(Ideal Gas) GFW = 81.7176

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.141	63.610	63.610	.000	−35.000	−36.171	26.514
300	11.160	63.679	63.610	.021	−35.008	−36.179	26.356
400	12.907	67.014	64.059	1.182	−35.496	−36.497	19.941
500	12.553	69.756	64.932	2.412	−36.029	−36.686	16.035
600	12.907	72.078	65.935	3.686	−36.596	−36.765	13.392
700	13.144	74.087	66.959	4.990	−37.182	−36.746	11.473
800	13.309	75.854	67.963	6.313	−37.787	−36.644	10.011
900	13.426	77.428	68.929	7.650	−38.403	−36.464	8.855
1000	13.513	78.848	69.851	8.997	−39.032	−36.215	7.915
1100	13.579	80.139	70.728	10.352	−39.675	−35.903	7.133
1200	13.630	81.323	71.562	11.712	−40.330	−35.530	6.471
1300	13.672	82.415	72.356	13.077	−40.998	−35.104	5.901
1400	13.706	83.430	73.111	14.446	−41.677	−34.624	5.405
1500	13.736	84.376	73.831	15.818	−42.369	−34.098	4.968
1600	13.764	85.264	74.518	17.193	−43.071	−33.522	4.579
1700	13.792	86.099	75.175	18.571	−43.784	−32.903	4.230
1800	13.821	86.888	75.804	19.952	−44.506	−32.244	3.915
1900	13.852	87.636	76.407	21.335	−45.235	−31.541	3.628
2000	13.887	88.348	76.986	22.722	−45.969	−30.802	3.366
2100	13.927	89.026	77.544	24.113	−46.704	−30.025	3.125
2200	13.971	89.675	78.081	25.508	−47.444	−29.214	2.902
2300	14.021	90.297	78.598	26.907	−48.186	−28.368	2.696
2400	14.076	90.895	79.098	28.312	−48.929	−27.490	2.503
2500	14.137	91.471	79.582	29.723	−55.060	−26.473	2.314
2600	14.204	92.027	80.050	31.140	−55.794	−25.315	2.128
2700	14.275	92.564	80.503	32.564	−56.525	−24.128	1.953
2800	14.351	93.085	80.943	33.995	−57.252	−22.915	1.789
2900	14.431	93.589	81.371	35.434	−57.973	−21.675	1.633
3000	14.514	94.080	81.786	36.881	−58.689	−20.414	1.487
3100	14.601	94.557	82.191	38.337	−59.398	−19.126	1.348
3200	14.689	95.022	82.584	39.801	−60.103	−17.816	1.217
3300	14.779	95.476	82.968	41.275	−60.801	−16.481	1.092
3400	14.870	95.918	83.343	42.757	−61.493	−15.127	.972
3500	14.961	96.351	83.708	44.249	−62.179	−13.758	.859
3600	15.052	96.773	84.065	45.750	−62.857	−12.361	.750
3700	15.142	97.187	84.414	47.259	−63.531	−10.949	.647
3800	15.230	97.592	84.756	48.778	−64.197	−9.520	.548
3900	15.317	97.989	85.090	50.305	−64.858	−8.073	.452
4000	15.400	98.378	85.417	51.841	−186.691	−4.463	.244
4100	15.481	98.759	85.738	53.385	−187.108	.096	−.005
4200	15.559	99.133	86.053	54.937	−187.519	4.669	−.243
4300	15.633	99.500	86.361	56.497	−187.924	9.248	−.470
4400	15.704	99.860	86.664	58.064	−188.325	13.841	−.688
4500	15.770	100.214	86.961	59.638	−188.720	18.437	−.895
4600	15.833	100.561	87.253	61.218	−189.110	23.046	−1.095
4700	15.891	100.902	87.540	62.804	−189.497	27.664	−1.286
4800	15.945	101.237	87.822	64.396	−189.880	32.288	−1.470
4900	15.995	101.567	88.099	65.993	−190.260	36.919	−1.647
5000	16.040	101.890	88.371	67.595	−190.634	41.560	−1.817
5100	16.082	102.208	88.639	69.201	−191.007	46.210	−1.980
5200	16.119	102.521	88.903	70.811	−191.377	50.865	−2.138
5300	16.152	102.828	89.163	72.425	−191.745	55.522	−2.290
5400	16.181	103.131	89.419	74.041	−192.113	60.192	−2.436
5500	16.206	103.428	89.671	75.661	−192.476	64.874	−2.578
5600	16.227	103.720	89.919	77.282	−192.841	69.549	−2.714
5700	16.245	104.007	90.164	78.906	−193.206	74.237	−2.846
5800	16.259	104.290	90.405	80.531	−193.570	78.935	−2.974
5900	16.270	104.568	90.643	82.158	−193.934	83.634	−3.098
6000	16.278	104.841	90.877	83.785	−194.299	88.346	−3.218

June 30, 1966; Dec. 31, 1968; June 30, 1972

BORON DICHLORIDE UNINEGATIVE ION (BCl_2^-) (IDEAL GAS) GFW = 81.7176

Point Group [C_{2v}] ΔHf°_0 = [−33.8 ± 25] kcal/mol

$S^\circ_{298.15}$ = [63.6 ± 1.0] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [−35.0 ± 25] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[12000]	3
$^1B_1$	[17000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[750] (1)
[250] (1)
[775] (1)

Bond Distance: B-Cl = [1.716] Å

Bond Angle: Cl-B-Cl = [100]° σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [8.5857 x 10^{-115}] g^3cm^6

Heat of Formation

The heat of formation, $\Delta Hf^\circ_0(BCl_2^-, g)$ = −33.8 ± 25 kcal/mol, is obtained from an estimated electron affinity for BCl_2 and $\Delta Hf^\circ_0(BCl_2, g)$ = −19.3 ± 3.0 kcal/mol (1). Comparison of the ionization potentials (IP) and electron affinities (EA) for the isoelectronic molecules NO_2 (1, 2), BF_2 (1), and AlF_2 (1) indicates that in each case the difference between these two quantities (IP−EA) is roughly 7.1 eV. From this relationship, we estimate EA (BCl_2) = 0.63 ± 1.0 eV with IP (BCl_2) = 7.73 eV (1).

Heat Capacity and Entropy

The correlation diagram of Walsh (3) predicts a bent configuration for BCl_2^- (18 valence electrons) with a bond angle considerably reduced from that for BCl_2. Based on the adopted angle for BCl_2 (112°) (1), we estimate the angle in BCl_2^- at 100°. Comparison with angles for CF_2 and SiF_2 (1) indicates that the estimated angle is reasonable. The B-Cl bond length is taken equal to that for BCl (1). The individual moments of inertia are: I_A = 22.2540 x 10^{-39}, I_B = 20.3590 x 10^{-39}, and I_C = 1.8950 x 10^{-39} g cm^2.

The ground state electronic configuration ($^1A_1$) and first excited singlet state ($^1B_1$) for BCl_2^- are estimated by analogy with those for CCl_2 and $SiCl_2$ (1). Also included is a triplet level at 12000 cm^{-1}. The energy separation (5000 cm^{-1}) of the $^3B_1$ and $^1B_1$ levels is estimated by comparison with the corresponding values for SO_2 (4), $SiCl_2$ (1), $GeCl_2$, and $SnCl_2$ (5). The vibrational frequencies are estimated from those for BCl_2, CCl_2, and $SiCl_2$ (1). The enthalpy at 0 K is −2.788 kcal/mol.

References

1. JANAF Thermochemical Tables: BCl_2(g), NO_2^-(g), BF_2^-(g), AlF_2^+(g), and AlF_2^-(g) dated 6-30-72; BF_2^+(g), BCl_2^+(g), and $SiCl_2$(g) dated 12-31-70; CF_2(g) dated 6-30-70; SiF_2(g) and CCl_2(g) dated 12-31-68; BCl(g) dated 12-31-64.
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5. J. W. Hastie, R. H. Hauge, and J. L. Margrave, J. Mol. Spectroscopy, 29, 152 (1969).

Boron Difluoride (BF_2)

(Ideal Gas) GFW = 48.8078

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	− 2.537	− 141.135	− 141.135	INFINITE
100	8.026	49.610	67.024	− 1.741	− 141.040	− 141.924	310.174
200	8.769	55.374	59.902	− .906	− 140.985	− 142.833	156.081
298	9.693	59.046	59.046	.000	− 141.000	− 143.742	105.365
300	9.710	59.106	59.046	.018	− 141.001	− 143.759	104.728
400	10.614	62.026	59.438	1.035	− 141.076	− 144.668	79.043
500	11.351	64.477	60.207	2.135	− 141.196	− 145.553	63.621
600	11.909	66.598	61.099	3.295	− 141.339	− 146.411	53.330
700	12.322	68.467	62.021	4.512	− 141.493	− 147.244	45.972
800	12.628	70.133	62.933	5.760	− 141.656	− 148.056	40.447
900	12.859	71.634	63.818	7.035	− 141.823	− 148.846	36.145
1000	13.035	72.999	64.668	8.330	− 141.998	− 149.616	32.699
1100	13.172	74.248	65.483	9.641	− 142.183	− 150.370	29.876
1200	13.280	75.399	66.262	10.963	− 142.377	− 151.105	27.520
1300	13.366	76.465	67.007	12.296	− 142.581	− 151.824	25.524
1400	13.436	77.458	67.718	13.636	− 142.795	− 152.527	23.810
1500	13.494	78.387	68.399	14.983	− 143.020	− 153.215	22.323
1600	13.542	79.260	69.051	16.335	− 143.256	− 153.886	21.020
1700	13.583	80.082	69.676	17.691	− 143.503	− 154.543	19.868
1800	13.617	80.859	70.275	19.051	− 143.760	− 155.187	18.842
1900	13.647	81.596	70.852	20.414	− 144.024	− 155.814	17.923
2000	13.673	82.297	71.407	21.780	− 144.294	− 156.426	17.093
2100	13.696	82.965	71.942	23.149	− 144.570	− 157.027	16.342
2200	13.717	83.602	72.457	24.520	− 144.852	− 157.613	15.657
2300	13.736	84.213	72.955	25.892	− 145.140	− 158.187	15.031
2400	13.755	84.798	73.436	27.267	− 145.433	− 158.748	14.456
2500	13.772	85.360	73.902	28.643	− 151.119	− 159.188	13.916
2600	13.789	85.900	74.353	30.021	− 151.414	− 159.505	13.408
2700	13.805	86.421	74.791	31.401	− 151.709	− 159.808	12.936
2800	13.822	86.923	75.215	32.782	− 152.005	− 160.105	12.497
2900	13.839	87.408	75.627	34.165	− 152.302	− 160.385	12.087
3000	13.856	87.878	76.028	35.550	− 152.600	− 160.663	11.704
3100	13.874	88.332	76.417	36.936	− 152.898	− 160.928	11.345
3200	13.892	88.773	76.797	38.325	− 153.196	− 161.181	11.008
3300	13.910	89.201	77.166	39.715	− 153.495	− 161.425	10.691
3400	13.930	89.617	77.526	41.107	− 153.794	− 161.660	10.391
3500	13.949	90.021	77.877	42.501	− 154.094	− 161.887	10.109
3600	13.970	90.414	78.220	43.897	− 154.393	− 162.104	9.841
3700	13.991	90.797	78.555	45.295	− 154.693	− 162.315	9.588
3800	14.012	91.170	78.882	46.695	− 154.993	− 162.514	9.347
3900	14.034	91.535	79.202	48.097	− 155.294	− 162.713	9.118
4000	14.056	91.890	79.515	49.502	− 276.772	− 160.753	8.783
4100	14.078	92.237	79.821	50.908	− 276.842	− 157.853	8.414
4200	14.101	92.577	80.120	52.317	− 276.910	− 154.946	8.063
4300	14.124	92.909	80.414	53.729	− 276.977	− 152.041	7.728
4400	14.147	93.234	80.702	55.142	− 277.048	− 149.135	7.408
4500	14.170	93.552	80.984	56.558	− 277.117	− 146.231	7.102
4600	14.193	93.864	81.260	57.976	− 277.186	− 143.321	6.809
4700	14.216	94.169	81.532	59.397	− 277.256	− 140.408	6.529
4800	14.239	94.469	81.798	60.819	− 277.327	− 137.492	6.260
4900	14.262	94.763	82.060	62.244	− 277.399	− 134.582	6.003
5000	14.284	95.051	82.317	63.672	− 277.470	− 131.666	5.755
5100	14.306	95.334	82.569	65.101	− 277.544	− 128.752	5.517
5200	14.328	95.612	82.817	66.533	− 277.617	− 125.830	5.288
5300	14.350	95.885	83.061	67.967	− 277.691	− 122.911	5.068
5400	14.371	96.154	83.301	69.403	− 277.768	− 119.995	4.856
5500	14.391	96.418	83.537	70.841	− 277.844	− 117.066	4.652
5600	14.412	96.677	83.770	72.281	− 277.923	− 114.146	4.455
5700	14.431	96.932	83.998	73.723	− 278.004	− 111.218	4.264
5800	14.450	97.184	84.224	75.167	− 278.085	− 108.292	4.081
5900	14.469	97.431	84.445	76.613	− 278.168	− 105.366	3.903
6000	14.487	97.674	84.664	78.061	− 278.253	− 102.435	3.731

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1964; June 30, 1972

BORON DIFLUORIDE (BF_2) (IDEAL GAS) GFW = 48.8078 BF_2

Point Group C_{2v}

$S^\circ_{298.15}$ = [59.0 ± 0.5] gibbs/mol

ΔHf°_0 = −141.1 ± 3.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −141.0 ± 3.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[16000]	2

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[1080] (1)
[500] (1)
[1213] (1)

Bond Distance: B-F = [1.30] Å

Bond Angle: F-B-F = 112°

σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [4.3690 x 10^{-116}] $g^3 cm^6$

Heat of Formation

Srivastava and Farber (1), using a gas-inlet boron nitride effusion cell, performed a mass spectrometric study of the equilibrium vapor species over the system $BF_3(g) + B(c)$. Ion intensities for $BF_3(g)$, $BF(g)$, and $BF_2(g)$ were measured at ionizing electron energies slightly above appearance potentials (~3 eV) in the temperature range 1477 to 1650 K and were used to obtain equilibrium data for the reaction $BF_3(g) + BF(g) = 2BF_2(g)$. We have analyzed their results and obtain ΔHr_{298} = 17.1 ± 1.0 kcal/mol from the third law method with a drift of −7.4 ± 2.0 eu, the second law ΔHr_{298} value is 28.7 kcal/mol. We adopt the third law heat of reaction and calculate $\Delta Hf^\circ_{298}(BF_2, g)$ = 141.0 ± 3.0 kcal/mol with JANAF heats of formation (2) for $BF_3(g)$ and $BF(g)$.

Although no other experimental determinations of heat of formation of BF_2 have been reported, Margrave (3) combined the appearance potential of BF_2^+ from BF_3 of 16.5 eV with an estimated ionization potential for BF_2 (IP = 9.4 ± 0.1 eV) (4) and calculated $\Delta Hf(BF_2, g) \leq$ −124 ± 9 kcal/mol. Based on the JANAF value for $AP(BF_2^+)$ of 15.81 eV (2), we calculate $\Delta Hf^\circ_0(BF_2, g)$ = −141.3 kcal/mol by the same method. Margrave (3) also derived ΔHf = −135 kcal/mol for BF_2 from average bond energy calculations and selected $\Delta Hf^\circ(BF_2, g)$ = −130 ± 5 kcal/mol as the "best" value. It is now apparent that this value is several kilocalories too positive.

We note that the adopted heat of formation leads to a progression in the stepwise bond dissociation energies for BF(g), $BF_2(g)$, and $BF_3(g)$ which is consistent with the bond energy scheme predicted by Hildenbrand (5) for the Group III A fluorides, namely $D_1 > D_2 < D_3$. Using all JANAF data (2), we calculate bond dissociation energies of $D_1(B-F)$ = 179.4, $D_2(BF-F)$ = 132.2, and $D_3(BF_2-F)$ = 149.3 kcal/mol. The adopted value also corresponds to an ionization potential for BF_2 of 9.4 ± 0.2 eV (2) which appears reasonable in comparison with IP's for other Group III A dihalides (6) and is the value estimated for BF_2 by Steele et al. (4).

Heat Capacity and Entropy

Nelson and Gordy (7) were successful in producing trapped BF_2 radicals by gamma irradiation of solid xenon which contained small concentrations of BF_3. From observations on the electron-spin-resonance spectra of these radicals, a bond angle of 112° for BF_2 was derived by these workers to account for the hybridization of the σ-bonding orbitals of the boron atom. We adopt their result and assume the B-F bond length to be the same as that for BHF_2 (2). The three principal moments of inertia are: I_A = 8.0701 x 10^{-39}, I_B = 7.3317 x 10^{-39}, and I_C = 0.7384 x 10^{-39} g cm^2.

The ground state electronic configuration ($^2A_1$) and doublet excited state ($^2B_1$) are estimated by analogy with those for NO_2 (8). The vibrational frequencies are calculated from the stretching and bending force constants of k = 4.82 x 10^5 and $k\delta/\ell^2$ = 0.84 x 10^5 dynes/cm by the valence force method. These force constants are estimated from those for CF_2 and SiF_2 (2).

References

1. R. D. Srivastava and M. Farber, Trans. Faraday Soc. 67, 2298 (1971).
2. JANAF Thermochemical Tables: $BF_3(g)$ dated 6-30-69; BF(g) dated 12-31-64; $BF_2^+(g)$ dated 12-31-70; $BHF_2(g)$ dated 12-31-65; $CF_2(g)$ dated 6-30-70; $SiF_2(g)$ dated 12-31-68.
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Boron Difluoride Unipositive Ion (BF_2^+)

(Ideal Gas) GFW = 48.80725

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	10.586	53.785	53.785	.000	77.100	74.439	= 54.565
300	10.605	53.851	53.785	.020	77.110	74.422	= 54.216
400	11.513	57.032	54.213	1.128	77.623	73.449	= 40.130
500	12.211	59.679	55.049	2.315	78.087	72.350	= 31.624
600	12.747	61.955	56.014	3.564	78.526	71.162	= 25.921
700	13.156	63.952	57.009	4.860	78.951	69.901	= 21.824
800	13.470	65.730	57.990	6.192	79.369	68.578	= 18.735
900	13.713	67.332	58.940	7.552	79.784	67.204	= 16.319
1000	13.902	68.787	59.853	8.933	80.192	65.785	= 14.377
1100	14.052	70.119	60.727	10.331	80.591	64.324	= 12.780
1200	14.172	71.347	61.561	11.743	80.983	62.829	= 11.443
1300	14.269	72.485	62.358	13.165	81.365	61.300	= 10.305
1400	14.349	73.546	63.120	14.596	81.739	59.744	= 9.326
1500	14.415	74.538	63.849	16.034	82.102	58.159	= 8.474
1600	14.470	75.470	64.546	17.478	82.454	56.551	= 7.724
1700	14.516	76.349	65.215	18.928	82.798	54.922	= 7.061
1800	14.556	77.180	65.857	20.381	83.131	53.271	= 6.468
1900	14.589	77.968	66.473	21.839	83.459	51.604	= 5.936
2000	14.619	78.717	67.067	23.299	83.780	49.921	= 5.455
2100	14.644	79.431	67.639	24.762	84.094	48.218	= 5.018
2200	14.666	80.112	68.190	26.228	84.404	46.503	= 4.620
2300	14.686	80.765	68.723	27.696	84.709	44.774	= 4.254
2400	14.703	81.390	69.238	29.165	85.007	43.031	= 3.919
2500	14.719	81.991	69.736	30.636	79.913	41.385	= 3.618
2600	14.732	82.568	70.219	32.109	80.209	39.837	= 3.349
2700	14.745	83.124	70.686	33.582	80.504	38.281	= 3.099
2800	14.756	83.661	71.140	35.058	80.800	36.710	= 2.865
2900	14.766	84.179	71.581	36.534	81.093	35.134	= 2.648
3000	14.776	84.680	72.009	38.011	81.384	33.540	= 2.443
3100	14.784	85.164	72.426	39.489	81.674	31.939	= 2.252
3200	14.793	85.634	72.831	40.968	81.963	30.332	= 2.072
3300	14.800	86.089	73.226	42.447	82.250	28.715	= 1.902
3400	14.808	86.531	73.611	43.928	82.537	27.089	= 1.741
3500	14.815	86.960	73.986	45.409	82.821	25.454	= 1.589
3600	14.822	87.378	74.353	46.891	83.104	23.812	= 1.446
3700	14.829	87.784	74.710	48.373	83.385	22.161	= 1.309
3800	14.836	88.179	75.059	49.856	83.665	20.505	= 1.179
3900	14.843	88.565	75.401	51.340	83.943	18.838	= 1.055
4000	14.850	88.941	75.735	52.825	= 36.959	19.307	= 1.055
4100	14.857	89.308	76.061	54.310	= 36.453	20.706	= 1.104
4200	14.865	89.666	76.381	55.796	= 35.947	22.099	= 1.150
4300	14.872	90.016	76.694	57.283	= 35.442	23.475	= 1.193
4400	14.880	90.358	77.001	58.771	= 34.941	24.839	= 1.234
4500	14.888	90.692	77.301	60.259	= 34.442	26.188	= 1.272
4600	14.897	91.019	77.596	61.749	= 33.942	27.531	= 1.308
4700	14.905	91.340	77.885	63.239	= 33.446	28.864	= 1.342
4800	14.914	91.654	78.168	64.730	= 32.951	30.188	= 1.374
4900	14.924	91.961	78.447	66.221	= 32.460	31.495	= 1.405
5000	14.933	92.263	78.720	67.714	= 31.970	32.795	= 1.433
5100	14.944	92.559	78.988	69.208	= 31.482	34.083	= 1.461
5200	14.954	92.849	79.252	70.703	= 30.995	35.367	= 1.486
5300	14.965	93.134	79.512	72.199	= 30.510	36.638	= 1.511
5400	14.976	93.414	79.766	73.696	= 30.029	37.896	= 1.534
5500	14.987	93.689	80.017	75.194	= 29.549	39.156	= 1.556
5600	14.999	93.959	80.264	76.693	= 29.072	40.397	= 1.577
5700	15.011	94.224	80.506	78.194	= 28.597	41.635	= 1.596
5800	15.023	94.486	80.745	79.696	= 28.123	42.862	= 1.615
5900	15.035	94.743	80.980	81.198	= 27.653	44.080	= 1.633
6000	15.048	94.995	81.212	82.703	= 27.185	45.294	= 1.650

June 30, 1968; Dec. 31, 1970

BORON DIFLUORIDE UNIPOSITIVE ION (BF_2^+) (IDEAL GAS) GFW = 48.80725 BF_2^+

Point Group [$D_{\infty h}$] ΔHf°_0 = 75.5 ± 0.6 kcal/mol

$S^\circ_{298.15}$ = [53.8 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 77.1 ± 0.6 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[25000]	1

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[900] (1)
[370] (2)
[1550] (1)

Bond Distance: B-F = [1.31] Å

Bond Angle: F-B-F = [180°] σ = 2

Rotational Constant: B_0 = [0.2585] cm^{-1}

Heat of Formation

The electron impact reaction at low pressure in BF_3(g) has been studied with a mass spectrometer by Osberghaus (1), Law (2), and Marriott (3). From the reported appearance potentials 17.0 ± 0.5, 16.2 ± 0.2, and 16.7 ± 0.05 eV and assumed process $BF_3 + e^- = BF_2^+ + F + 2e^-$, we calculate the corresponding values of $\Delta Hf^\circ_{298}(BF_2^+, g)$ as 104.5 ± 11.5, 86.1 ± 4.6, and 85.4 ± 1.2 kcal/mol, using ΔHf°_0 = −270.747 and 18.357 kcal/mol for BF_3(g) and F(g). These electron impact values are superseded by the photoionization results of Dibeler and Liston (7) who report the onset of BF_2^+ from BF_3 as 15.81 eV (364.6 kcal). This yields ΔHf°_0 = 75.5 ± 0.6 kcal/mol or $\Delta Hf^\circ_{298.15}$ = 77.1 ± 0.6 kcal/mol, which are adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (4) prediction for 16 valence electron XY_2 molecules. The electronic states, levels, and vibrational frequencies are estimated by comparison with those for CO_2 (5). The B-F bond distance is calculated by the method recommended by Krasnov (6). The moment of inertia is 1.083 x 10^{-38} g cm^2. The enthalpy at 0°K is −2.54 kcal/mol.

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Boron Difluoride Uninegative Ion (BF_2^-)

(Ideal Gas) GFW = 48.8084

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	9.644	57.511	57.511	.000	−191.700	−192.497	141.104
300	9.661	57.571	57.511	.018	−191.710	−192.502	140.238
400	10.539	60.473	57.901	1.029	−192.288	−192.680	105.275
500	11.272	62.906	58.665	2.121	−192.913	−192.707	84.232
600	11.837	65.014	59.551	3.277	−193.561	−192.605	70.156
700	12.259	66.872	60.467	4.483	−194.218	−192.392	60.068
800	12.574	68.530	61.373	5.726	−194.883	−192.088	52.476
900	12.812	70.026	62.253	6.995	−195.553	−191.698	46.551
1000	12.995	71.385	63.099	8.286	−196.229	−191.234	41.794
1100	13.137	72.631	63.910	9.593	−196.915	−190.702	37.889
1200	13.250	73.779	64.685	10.913	−197.607	−190.104	34.623
1300	13.340	74.843	65.426	12.242	−198.312	−189.451	31.850
1400	13.414	75.835	66.134	13.580	−199.025	−188.743	29.464
1500	13.475	76.762	66.812	14.925	−199.749	−187.984	27.389
1600	13.526	77.634	67.462	16.275	−200.483	−187.174	25.567
1700	13.569	78.455	68.084	17.630	−201.228	−186.320	23.953
1800	13.607	79.232	68.682	18.988	−201.984	−185.423	22.513
1900	13.641	79.968	69.257	20.351	−202.745	−184.482	21.220
2000	13.673	80.669	69.810	21.717	−203.512	−183.500	20.052
2100	13.703	81.337	70.343	23.085	−204.285	−182.481	18.991
2200	13.732	81.975	70.858	24.457	−205.063	−181.424	18.023
2300	13.762	82.586	71.354	25.832	−205.845	−180.332	17.135
2400	13.793	83.172	71.835	27.210	−206.632	−179.206	16.319
2500	13.826	83.736	72.300	28.591	−212.810	−177.938	15.555
2600	13.861	84.279	72.750	29.975	−213.595	−176.528	14.838
2700	13.898	84.803	73.187	31.363	−214.379	−175.085	14.172
2800	13.938	85.309	73.611	32.755	−215.161	−173.618	13.551
2900	13.981	85.799	74.023	34.151	−215.942	−172.116	12.971
3000	14.027	86.273	74.423	35.551	−216.722	−170.597	12.428
3100	14.076	86.734	74.813	36.956	−217.497	−169.046	11.918
3200	14.127	87.182	75.192	38.366	−218.271	−167.470	11.438
3300	14.181	87.617	75.562	39.782	−219.041	−165.870	10.985
3400	14.237	88.042	75.923	41.203	−219.808	−164.247	10.558
3500	14.296	88.455	76.275	42.629	−220.573	−162.602	10.153
3600	14.357	88.859	76.619	44.062	−221.331	−160.932	9.770
3700	14.419	89.253	76.955	45.501	−222.087	−159.245	9.406
3800	14.483	89.638	77.284	46.946	−222.839	−157.534	9.060
3900	14.548	90.015	77.606	48.397	−223.588	−155.811	8.731
4000	14.613	90.384	77.921	49.855	−345.509	−151.916	8.300
4100	14.679	90.746	78.229	51.320	−346.017	−147.072	7.840
4200	14.745	91.101	78.531	52.791	−346.520	−142.209	7.400
4300	14.811	91.448	78.828	54.269	−347.018	−137.339	6.980
4400	14.876	91.790	79.118	55.753	−347.515	−132.458	6.579
4500	14.941	92.125	79.404	57.244	−348.009	−127.567	6.196
4600	15.005	92.454	79.684	58.741	−348.492	−122.662	5.828
4700	15.068	92.777	79.959	60.245	−348.976	−117.747	5.475
4800	15.129	93.095	80.229	61.755	−349.456	−112.819	5.137
4900	15.189	93.408	80.495	63.271	−349.934	−107.888	4.812
5000	15.247	93.715	80.756	64.793	−350.407	−102.941	4.500
5100	15.304	94.017	81.013	66.320	−350.880	−97.991	4.199
5200	15.358	94.315	81.266	67.853	−351.349	−93.023	3.910
5300	15.410	94.608	81.515	69.392	−351.815	−88.053	3.631
5400	15.460	94.897	81.760	70.935	−352.282	−83.076	3.362
5500	15.508	95.181	82.002	72.484	−352.743	−78.080	3.103
5600	15.554	95.461	82.240	74.037	−353.206	−73.086	2.852
5700	15.597	95.736	82.474	75.594	−353.669	−68.077	2.610
5800	15.638	96.008	82.705	77.156	−354.129	−63.064	2.376
5900	15.677	96.276	82.933	78.722	−354.589	−58.044	2.150
6000	15.713	96.539	83.157	80.292	−355.048	−53.011	1.931

June 30, 1968; Dec. 31, 1968; June 30, 1972

BORON DIFLUORIDE UNINEGATIVE ION (BF_2^-) (IDEAL GAS) GFW = 48.8084

Point Group [C_{2v}] ΔHf°_0 = −190.4 ± 8.0 kcal/mol

$S^\circ_{298.15}$ = [57.5 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = −191.7 ± 8.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[15000]	3
$^1B_1$	[35000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1175] (1)
[495] (1)
[1188] (1)

Bond Distance: B-F = [1.265] Å

Bond Angle: F-B-F = [100]° σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [3.7481 x 10^{-116}] $g^3 cm^6$

Heat of Formation

The BF_2^- ion has been detected mass spectrometrically by MacNeil and Thynne (1) and Farber et al. (2). MacNeil and Thynne (1) reported the formation of the negative ion at electron energies of approximately 7.6 eV as a result of electron bombardment of BF_3(g). Assuming the ionization process to be $BF_3(g) + e^- = BF_2^-(g) + F(g)$, we calculate $\Delta Hf^\circ_0(BF_2^-, g)$ = −113.8 kcal/mol from their results with JANAF heats of formation (3) for BF_3(g) and F(g). This value leads to an unrealistic electron affinity (EA) for BF_2 of −1.1 eV. It seems most likely that the BF_2^- ion was formed in the dissociative ionization of BF_3(g) with considerable excess energy.

Farber et al. (2) observed the formation of the BF_2^- ion in a molecular flow effusion-mass spectrometric study of the $BF_3(g) + KF(g) + B(c)$ system. Equilibrium data for the electron transfer reaction $BF_2^-(g) + F(g) = BF_2(g) + F^-(g)$ were reported for the temperature range 1253 to 1640 K. We have analyzed their results with JANAF functions and obtain ΔHr_{298} = −26.3 ± 1.8 kcal/mol by the third law method with a drift of −1.5 ± 3.1 eu, the second law ΔHr_{298} value is −24.2 kcal/mol. We adopt the third law value and calculate $\Delta Hf^\circ_{298}(BF_2^-, g)$ = −191.7 ± 8.0 kcal/mol with JANAF auxiliary data. The adopted heat of formation leads to EA (BF_2) = 2.14 ± 0.5 eV.

Heat Capacity and Entropy

The correlation diagram of Walsh (4) predicts a bent configuration for BF_2^- (18 valence electrons) with a bond angle considerably reduced from that for BF_2(112°) (3). These predictions are supported by the experimentally determined bond angles for the isoelectronic molecules CF_2(104.9°) (3), SiF_2(101°) (3), and GeF_2(94°) (5). Thus, we adopt a bond angle for BF_2^- of 100° and assume the B-F bond length to be the same as that for BF (3). The individual moments of inertia are: I_A = 6.8479 x 10^{-39}, I_B = 5.9240 x 10^{-39}, and I_C = 0.9239 x 10^{-39} g cm^2.

The electronic states, levels, and quantum weights are estimated by analogy with those for CF_2 (3). The vibrational frequencies are calculated from the stretching and bending force constants of k = 5.16 x 10^5 and $k\delta/\ell^2$ = 0.91 x 10^5 dynes/cm by the valence force method. These force constants are estimated by comparison with those for CF_2, SiF_2, and BF_2 (3). The enthalpy at 0 K is −2.536 kcal/mol.

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Potassium Metaborate (KBO_2)

(Crystal) GFW = 81.9118

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	$\Delta Hf°$ (kcal/mol)	$\Delta Gf°$ (kcal/mol)	Log Kp
0	.000	.000	INFINITE	= 2.894	= 236.634	= 236.634	INFINITE
100	6.368	6.005	31.133	= 2.513	= 237.367	= 232.969	509.153
200	12.929	13.354	20.487	= 1.027	= 237.677	= 228.429	249.616
298	16.020	19.116	19.116	.000	= 237.800	= 223.862	164.095
300	16.070	19.215	19.116	.030	= 237.801	= 223.776	163.020
400	18.320	24.158	19.775	1.753	= 238.425	= 218.983	119.647
500	20.070	28.441	21.089	3.676	= 238.389	= 214.125	93.594
600	21.470	32.228	22.636	5.755	= 238.266	= 209.282	76.231
700	22.600	35.625	24.253	7.960	= 238.071	= 204.465	63.837
800	23.540	38.706	25.870	10.268	= 237.818	= 199.683	54.551
900	24.320	41.525	27.455	12.663	= 237.515	= 194.934	47.336
1000	24.970	44.122	28.994	15.128	= 237.183	= 190.219	41.572
1100	25.460	46.526	30.480	17.651	= 255.740	= 184.516	36.660
1200	25.780	48.757	31.911	20.216	= 255.139	= 178.066	32.430
1300	25.950	50.826	33.288	22.802	= 254.541	= 171.669	28.860
1400	26.143	52.758	34.610	25.407	= 253.944	= 165.316	25.807
1500	26.336	54.568	35.881	28.030	= 253.350	= 159.007	23.167
1600	26.529	56.274	37.103	30.674	= 252.753	= 152.735	20.863
1700	26.722	57.888	38.278	33.336	= 252.156	= 146.504	18.834
1800	26.915	59.421	39.411	36.018	= 251.556	= 140.306	17.036
1900	27.107	60.881	40.502	38.719	= 250.953	= 134.143	15.430
2000	27.300	62.276	41.557	41.440	= 250.341	= 128.010	13.988

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POTASSIUM METABORATE (KBO_2) (CRYSTAL) GFW = 81.9118 BKO_2

$\Delta Hf°_0$ = -236.6 ± 2 kcal/mol

$S°_{298.15}$ = 19.116 ± 0.03 gibbs/mol

$\Delta Hf°_{298.15}$ = -237.8 ± 2 kcal/mol

Tm = 1220 ± 3 K

$\Delta Hm°$ = 7.5 ± 1.0 kcal/mol

Heat of Formation

Shartsis and Capps (1) measured the heats of solution in 2N nitric acid of various K_2O-B_2O_3 glass and crystalline mixtures containing 1.1-41.0 mole % of K_2O. When these results are extrapolated to 50 mole %, we obtain $\Delta H°_{soln}(25°C)$ = -11.9 ± 2 kcal/mol for $KBO_2(c) + HNO_3(27.75\ H_2O, aq) + H_2O(\ell) \rightarrow KNO_3(27.75\ H_2O, aq) + H_3BO_3(27.75\ H_2O, aq)$ which leads to $\Delta Hf°_{298}(KBO_2, c)$ = -237.8 ± 2 kcal/mol, using the following auxiliary data: $\Delta Hf°_{298}(HNO_3 \cdot 27.75\ H_2O, aq)$ = -49.433 kcal/mol (2), $\Delta Hf°_{298}(KNO_3 \cdot 27.75\ H_2O, aq)$ = -111.075 kcal/mol (3) and $\Delta Hf°_{298}(H_3BO_3 \cdot 27.75\ H_2O, aq)$ = -256.37 kcal/mol (4). The value, $\Delta Hf°_{298}(KBO_2, c)$ = -237.8 ± 2 kcal/mol, is adopted in the tabulation. Since the heats of formation of $LiBO_2(c)$ and $NaBO_2(c)$ derived from their heat-of-solution data are in good agreement with those values (5) adopted, their heat-of-solution data should be reasonably reliable, although the calorimetric treatment was loose.

Heat Capacity and Entropy

Paukov, Khriplovich and Popov (6) have measured low temperature heat capacities from 12.11 to 312.22 K in an adiabatic calorimeter. The adopted Cp are derived from their experimental heat capacities by a polynomial curve fitting technique. The derived entropy $S°_{298}$ is 19.116 ± 0.03 eu based on $S°_{12.11}$ = 0.0353 eu. Heat capacities above 310 K are estimated by comparison with those of $NaBO_2(c)$ (5) since both $NaBO_2$ and KBO_2 have same type of crystal structure (7).

Thermal analysis data (8) have been interpreted in terms of a crystal transition at 785°C. Details of these studies are not available and it is not clear how reliable this interpretation is. We note, however, that, the reported temperature (785°C) is essentially the same as the eutectic temperature of KBO_2 with $K_2B_4O_7$ (9, 10). We tentatively adopt a single Cp curve without a transition.

Melting Data

Our analysis of several sets of binary phase data (8, 9, 11-14) yields the heat of melting, ΔHm = 7.5 ± 1 kcal/mol. The adopted melting point (947°C) is a weighted average of the observed data (8-15) which vary from 940 to 950°C.

References

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4. This value, -256.37 kcal/mol, is extrapolated from the heats of formation of $H_3BO_3 \cdot 50\ H_2O$ and $H_3BO_3 \cdot 100\ H_2O$ listed in reference 2.
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Potassium Metaborate (KBO_2)

(Liquid) GFW = 81.9118

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	16.020	21.244	21.244	.000	-234.400	-221.096	162.068
300	16.070	21.343	21.244	.030	-234.401	-221.014	161.009
400	18.320	26.286	21.903	1.753	-235.025	-216.434	118.254
500	20.070	30.569	23.217	3.676	-234.989	-211.789	92.573
600	21.470	34.356	24.764	5.755	-234.866	-207.158	75.457
700	22.600	37.753	26.381	7.960	-234.671	-202.555	63.240
800	23.540	40.834	27.998	10.269	-234.417	-197.985	54.087
900	35.000	44.787	29.640	13.632	-233.146	-193.500	46.988
1000	35.000	48.474	31.342	17.132	-231.779	-189.167	41.342
1100	35.000	51.810	33.054	20.632	-249.359	-183.948	36.587
1200	35.000	54.855	34.746	24.132	-247.823	-178.068	32.431
1300	35.000	57.657	36.402	27.632	-246.311	-172.318	28.969
1400	35.000	60.251	38.014	31.132	-244.819	-166.680	26.020
1500	35.000	62.665	39.578	34.632	-243.348	-161.152	23.480
1600	35.000	64.924	41.092	38.132	-241.895	-155.718	21.270
1700	35.000	67.046	42.557	41.632	-240.460	-150.377	19.332
1800	35.000	69.047	43.973	45.132	-239.042	-145.119	17.620
1900	35.000	70.939	45.343	48.632	-237.640	-139.940	16.097
2000	35.000	72.734	46.668	52.132	-236.249	-134.834	14.734

June 30, 1971

POTASSIUM METABORATE (KBO_2) (LIQUID) GFW = 81.9118 BKO_2

$S^\circ_{298.15}$ = 21.244 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -234.400 kcal/mol

Tm = 1220 ± 3 K ΔHm° = 7.5 ± 1.0 kcal/mol

Tb = 1674.6 K ΔHv° = 57.1 kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298}(\ell)$ is calculated from that of the crystal by addition of ΔHm° and the difference between $H_{1220}-H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The constant heat capacity of the liquid is estimated to be 35 gibbs/mol based on that of $LiBO_2(\ell)$ (1) which was derived from high temperature enthalpy measurements. A glass transition is assumed at 812 K below which the heat capacities are assumed to be the same as the crystal.

The entropy, S°_{298} = 21.244 eu, is obtained in a manner analogous to the heat of formation.

Melting Data

See $KBO_2(c)$ table dated June 30, 1971.

Vaporization Data

The boiling point is calculated as the temperature at which $\Delta Gr = 0$ for $KBO_2(\ell) \rightarrow KBO_2(g)$. The heat of vaporization is the difference in ΔHf° at the boiling point between liquid and gas.

Reference

1. JANAF $LiBO_2(\ell)$ table dated June 30, 1971.

Potassium Metaborate (KBO_2)

(Ideal Gas) GFW = 81.9118

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	− 3.371	− 160.411	− 160.411	INFINITE
100	10.424	57.866	82.458	− 2.859	− 160.613	− 161.401	352.742
200	12.507	65.746	72.298	− 1.310	− 160.860	− 162.091	177.125
298	14.106	71.055	71.055	.000	− 161.100	− 162.648	119.224
300	14.133	71.143	71.056	.026	− 161.105	− 162.658	118.496
400	15.294	75.377	71.625	1.501	− 161.977	− 163.023	89.072
500	16.157	78.886	72.736	3.075	− 162.290	− 163.249	71.356
600	16.822	81.893	74.018	4.725	− 162.596	− 163.411	59.522
700	17.384	84.527	75.335	6.435	− 162.896	− 163.522	51.054
800	17.757	86.871	76.633	8.191	− 163.195	− 163.593	44.692
900	18.086	88.943	77.890	9.983	− 163.495	− 163.625	39.733
1000	18.350	90.902	79.097	11.806	− 163.805	− 163.622	35.759
1100	18.563	92.642	80.251	13.652	− 163.039	− 162.564	32.299
1200	18.737	94.284	81.354	15.517	− 163.138	− 160.697	29.247
1300	18.880	95.790	82.407	17.398	− 163.245	− 158.824	26.701
1400	18.999	97.194	83.414	19.292	− 163.359	− 156.940	24.499
1500	19.099	98.508	84.376	21.197	− 163.483	− 155.050	22.591
1600	19.183	99.743	85.299	23.112	− 163.615	− 153.149	20.919
1700	19.254	100.909	86.183	25.033	− 163.759	− 151.242	19.443
1800	19.316	102.011	87.032	26.962	− 163.912	− 149.325	18.130
1900	19.368	103.057	87.848	28.896	− 164.076	− 147.399	16.955
2000	19.414	104.051	88.634	30.836	− 164.245	− 145.464	15.896
2100	19.454	105.000	89.390	32.779	− 164.424	− 143.519	14.936
2200	19.489	105.905	90.121	34.726	− 164.614	− 141.567	14.063
2300	19.520	106.772	90.826	36.677	− 164.811	− 139.608	13.266
2400	19.547	107.604	91.508	38.630	− 165.020	− 137.636	12.533
2500	19.572	108.402	92.168	40.586	− 190.628	− 135.551	11.850
2600	19.593	109.170	92.807	42.544	− 190.850	− 133.341	11.208
2700	19.613	109.910	93.427	44.505	− 191.081	− 131.125	10.614
2800	19.630	110.624	94.028	46.467	− 191.323	− 128.902	10.061
2900	19.646	111.313	94.613	48.431	− 191.574	− 126.663	9.546
3000	19.660	111.979	95.180	50.396	− 191.836	− 124.423	9.064
3100	19.673	112.624	95.733	52.363	− 192.110	− 122.171	8.613
3200	19.685	113.249	96.270	54.330	− 192.398	− 119.910	8.189
3300	19.696	113.855	96.794	56.300	− 192.698	− 117.642	7.791
3400	19.706	114.443	97.305	58.270	− 193.016	− 115.363	7.415
3500	19.715	115.014	97.802	60.241	− 193.349	− 113.077	7.061
3600	19.723	115.570	98.288	62.213	− 193.701	− 110.774	6.725
3700	19.731	116.110	98.763	64.185	− 194.074	− 108.467	6.407
3800	19.738	116.636	99.226	66.159	− 194.468	− 106.146	6.105
3900	19.745	117.149	99.679	68.133	− 194.886	− 103.822	5.818
4000	19.751	117.649	100.122	70.108	− 316.510	− 99.335	5.427
4100	19.757	118.137	100.556	72.083	− 316.754	− 93.909	5.005
4200	19.762	118.613	100.980	74.059	− 317.028	− 88.460	4.603
4300	19.767	119.078	101.395	76.036	− 317.336	− 83.013	4.219
4400	19.772	119.533	101.803	78.013	− 317.685	− 77.563	3.853
4500	19.776	119.977	102.202	79.990	− 318.074	− 72.100	3.502
4600	19.780	120.412	102.593	81.968	− 318.506	− 66.628	3.166
4700	19.784	120.837	102.976	83.946	− 318.987	− 61.146	2.843
4800	19.788	121.254	103.353	85.925	− 319.517	− 55.651	2.534
4900	19.791	121.662	103.722	87.904	− 320.102	− 50.156	2.237
5000	19.794	122.062	104.085	89.883	− 320.742	− 44.641	1.951
5100	19.797	122.454	104.441	91.862	− 321.443	− 39.105	1.676
5200	19.800	122.838	104.792	93.842	− 322.203	− 33.567	1.411
5300	19.802	123.215	105.136	95.822	− 323.025	− 28.007	1.155
5400	19.805	123.586	105.474	97.803	− 323.912	− 22.438	.908
5500	19.807	123.949	105.806	99.783	− 324.863	− 16.840	.669
5600	19.810	124.306	106.134	101.764	− 325.880	− 11.237	.439
5700	19.812	124.657	106.456	103.745	− 326.961	− 5.609	.215
5800	19.814	125.001	106.772	105.726	− 328.106	.041	− .002
5900	19.816	125.340	107.084	107.708	− 329.311	5.710	− .212
6000	19.818	125.673	107.391	109.690	− 330.577	11.406	− .415

June 30, 1971

POTASSIUM METABORATE (KBO_2) (IDEAL GAS) GFW = 81.9118 BKO_2

Point Group C_s ΔHf°_0 = -160.4 ± 6 kcal/mol

$S^\circ_{298.15}$ = 71.1 ± 1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -161.1 ± 6 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1952	577
1081	265
581	88

Bond Distance: K-O = [2.4] Å, O-B = [1.36] Å, B=O = [1.20] Å

Bond Angle: K-O-B = [90°] O-B=O = [180°] σ = 1

Product of the Moments of Inertia: $I_A I_B I_C$ = [5.7898] x 10^{-114} g^3 cm^6

Heat of Formation

Jensen (1) determined equilibrium constants for the reaction: K(g) + HBO_2(g) → KBO_2(g) + H(g) by flame studies. This technique involved several assumptions, the most basic of which was that boron added to $H_2/N_2/O_2$ flames was converted completely to HBO_2. The hydrogen atom concentration was taken from previous studies on such flames. Potassium metaborate was assumed to be formed in the flame. The concentration of K atom was determined by atomic absorption spectrophotometry. JANAF third law analysis of his equilibrium constant equation in the temperature range from 2000 to 2600 K yields ΔHr°(298 K) = 3.66 ± 0.54 kcal/mol and the drift 1.26 eu. (Second law heat of reaction is ΔHr°_{298} = 0.78 kcal/mol.) Using the third law ΔHr°_{298} and JANAF auxiliary data, we obtain ΔHf°_{298}(KBO_2, g) = -181.1 kcal/mol. The uncertainty in this result is about ±6 kcal/mol.

Heat Capacity and Entropy

Seshadri, Nimon and White (2) observed the infrared spectra of KBO_2 in an argon matrix and made a complete assignment of all six fundamentals which are adopted in the tabulation. The uncertainty of the calculated statistical entropy at 298 K is estimated to be ±1 eu which is due to the magnitude of the matrix shifts from the free molecule spectrum, particularly for the lower frequency modes.

The molecular structure, bond distance and bond angle of KBO_2(g) are assumed to be the same as those of $LiBO_2$(g) and $NaBO_2$(g) (3), except the bond distance K-O which is estimated to be intermediate between those of potassium fluoride and chloride. The three individual moments of inertia are: I_A = 27.8884 x 10^{-39}, I_B = 6.1069 x 10^{-39} and I_C = 33.9953 x 10^{-39} g cm^2.

References

1. D. E. Jensen, Trans. Faraday Soc. 65, 2123 (1969).
2. K. S. Seshadri, L. A. Nimon and D. White, J. Mol. Spectry. 30, 128 (1969).
3. JANAF $LiBO_2$(g) and $NaBO_2$(g) tables dated June 30, 1971.

Lithium Metaborate ($LiBO_2$)

(Crystal) GFW = 49.7488

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	- 2.145	- 242.273	- 242.273	INFINITE
100	4.492	2.436	22.236	- 1.980	- 242.927	- 238.887	522.000
200	10.309	7.434	13.559	- 1.225	- 243.388	- 234.565	256.321
298	14.499	12.364	12.364	.000	- 243.600	- 230.184	168.729
300	14.488	12.453	12.364	.027	- 243.602	- 230.101	167.629
400	17.004	16.996	12.967	1.612	- 243.671	- 225.588	123.256
500	18.787	20.989	14.180	3.404	- 244.441	- 220.988	96.594
600	20.329	24.553	15.617	5.361	- 244.427	- 216.297	78.786
700	21.773	27.796	17.128	7.467	- 244.315	- 211.616	66.070
800	23.169	30.795	18.651	9.714	- 244.103	- 206.960	56.539
900	24.540	33.603	20.158	12.100	- 243.788	- 202.335	49.134
1000	25.897	36.259	21.637	14.622	- 243.368	- 197.749	43.218
1100	27.244	38.790	23.082	17.279	- 242.842	- 193.212	38.388
1200	28.586	41.218	24.493	20.071	- 242.205	- 188.728	34.372
1300	29.924	43.559	25.870	22.996	- 241.457	- 184.301	30.984
1400	31.259	45.826	27.215	26.055	- 240.594	- 179.935	28.089
1500	32.593	48.028	28.529	29.248	- 239.616	- 175.638	25.590
1600	33.924	50.174	29.815	32.574	- 238.521	- 171.406	23.413
1700	35.255	52.270	31.075	36.033	- 272.356	- 165.920	21.330
1800	36.585	54.323	32.309	39.625	- 270.845	- 159.701	19.390
1900	37.915	56.337	33.521	43.350	- 269.215	- 153.569	17.665
2000	39.243	58.315	34.712	47.208	- 267.464	- 147.529	16.121

June 30, 1961; Dec. 31, 1964; June 30, 1971

LITHIUM METABORATE ($LiBO_2$) (CRYSTAL) GFW = 49.7488 $BLiO_2$

$\Delta Hf°_0$ = -242.3 ± 0.2 kcal/mol

$S°_{298.15}$ = 12.36 ± 0.05 gibbs/mol

$\Delta Hf°_{298.15}$ = -243.6 ± 0.2 kcal/mol

Tm = 1117 ± 1 K

$\Delta Hm°$ = 8.08 ± 0.12 kcal/mol

Heat of Formation

Sinke (1) measured calorimetrically the heat of solution of $LiBO_2$(c) in 0.5N HNO_3, $\Delta H°_{soln}(25°C)$ = -10.93 ± 0.05 kcal/mol for $LiBO_2$(c) + HNO_3(111 H_2O, aq) + H_2O(ℓ) → H_3BO_3(111 H_2O, aq) + $LiNO_3$(111 H_2O, aq), which leads to the adopted heat of formation, $\Delta Hf°_{298}$($LiBO_2$, c) = -243.6 ± 0.2 kcal/mol, using the following auxiliary data: $\Delta Hf°_{298}$(HNO_3·111 H_2O, aq) = -49.411 kcal/mol (2), $\Delta Hf°_{298}$(H_2O, ℓ) = -68.315 kcal/mol (2), $\Delta Hf°_{298}$(H_3BO_3·111 H_2O, aq) = -256.336 kcal/mol (2) and $\Delta Hf°_{298}$($LiNO_3$·111 H_2O, aq) = -115.944 kcal/mol (3).

Shartsis and Capps (4) measured heats of solution in 2N nitric acid of various Li_2O-B_2O_3 glass and crystalline mixtures containing 2.5-48.4 mole % of Li_2O. When their results are extrapolated to 50 mole %, we obtain $\Delta H°_{soln}(25°C)$ = -10.8 ± 0.5 kcal/mol for $LiBO_2$(c) + HNO_3(27.75 H_2O, aq) + H_2O(ℓ) → $LiNO_3$(27.75 H_2O, aq) + H_3BO_3(27.75 H_2O, aq). The calculated heat of formation based on the following data: $\Delta Hf°_{298}$(HNO_3·27.75 H_2O, aq) = -49.433 kcal/mol (2), $\Delta Hf°_{298}$($LiNO_3$·27.75 H_2O, aq) = -115.854 kcal/mol (5) and $\Delta Hf°_{298}$(H_3BO_3·27.75 H_2O, aq) = -256.37 kcal/mol (6), is $\Delta Hf°_{298}$($LiBO_2$, c) = -243.9 ± 0.5 kcal/mol which is in very good agreement.

Heat Capacity and Entropy

Stull et al. (7) measured low temperature Cp data from 15 to 320 K. We use their smoothed Cp values to derive $S°_{298}$ = 12.36 ± 0.05 eu based on $S°_{15}$ = 0.017 eu. McDonald (8) determined high temperature enthalpy data from 288 to 1116 K by drop calorimetry. The low temperature Cp and high temperature enthalpy data are smoothly joined at 298 K by a polynomial curve fitting technique. The average deviation of the observed enthalpy data from the adopted values is about 0.3% in the temperature range from 428-1062 K, and the maximum is 0.56% at 922 K. The Cp values above Tm are extrapolated from the adopted polynomial function.

Turdakin and Tarasov (9) also measured low temperature heat capacities (55-300 K) in an adiabatic calorimeter. Their values deviate from the adopted Cp by approximately 2%.

Melting curves from binary phase studies (10, 11, 12) have been interpreted in terms of a crystal transition near 800°C, although the most recent paper (13) indicated no transition. Two high-pressure polymorphs have been observed (14) but there is no evidence of their stability at atmospheric pressure. Enthalpy data (8) showed no obvious transition near 800°C; points at 829 and 835°C showed reasonable premelting contributions of about 200 and 300 cal/mol, respectively. Although this evidence does not preclude the existence of a transition, definite evidence would be needed to establish such a transition.

Melting Data

See JANAF $LiBO_2$(ℓ) table dated June 30, 1971.

References

1. G. C. Sinke, private communication, Thermal Research Lab., The Dow Chemical Company, Midland, Mich., April, 1961.
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. This value, $\Delta Hf°_{298}$($LiNO_3$·111 H_2O, aq) = -115.944 kcal/mol, is calculated based on the following auxiliary data:
   a. ϕ_L = 0.171 kcal/mol for $LiNO_3$·(∞ H_2O) → $LiNO_3$·(111 H_2O)
   ϕ_L was obtained from V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
   b. $\Delta Hf°_{298}$($LiNO_3$·∞ H_2O) = -116.115 kcal/mol
   This value is the sum of $\Delta Hf°_{298}$(Li^+·∞ H_2O) = -66.555 kcal/mol and $\Delta Hf°_{298}$(NO_3^-·∞ H_2O) = 49.56 kcal/mol (2). The former is derived from JANAF $\Delta Hf°_{298}$(LiOH·∞ H_2O) = -121.525 kcal/mol and $\Delta Hf°_{298}$(OH^-·∞ H_2O) = -54.97 kcal/mol (2).
4. L. Shartsis and W. Capps, J. Amer. Ceram. Soc. 37, 27 (1954).
5. This value, -115.854 kcal/mol, is calculated from $\Delta Hf°_{298}$($LiNO_3$·∞ H_2O) = -116.115 kcal/mol and ϕ_L = 0.261 kcal/mol for $LiNO_3$·(∞ H_2O) → $LiNO_3$·(27.75 H_2O) reported by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
6. This value, -256.37 kcal/mol, is extrapolated from the heats of formation of H_3BO_3·60 H_2O and H_3BO_3·100 H_2O listed in the U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
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9. V. A. Turdakin and V. V. Tarasov, Russ. J. Phys. Chem. 42, 1483 (1968).
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11. A. G. Bergman, A. I. Kislova and V. I. Posypaiko, Russ. J. Gen. Chem. 25, 1831, 1993 (1955).
12. A. G. Bergman and D. I. Bondareva, Russ. J. Inorg. Chem. 14, 586, 1339 (1969).
13. A. G. Bergman and D. I. Bondareva, Russ. J. Inorg. Chem. 15, 1193, 1339 (1970).
14. C. H. Chang and J. L. Margrave, J. Amer. Chem. Soc. 90, 2020 (1968).

Lithium Metaborate ($LiBO_2$)

(Liquid) GFW = 49.7488

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	14.829	15.667	15.667	.000	-239.067	-226.636	166.128
300	14.888	15.756	15.667	.027	-239.069	-226.559	165.048
400	17.004	20.299	16.269	1.412	-239.138	-222.376	121.501
500	18.787	24.291	17.483	3.408	-239.908	-218.106	95.334
600	20.329	27.855	18.919	5.361	-239.894	-213.745	77.857
700	21.773	31.098	20.431	7.467	-239.782	-209.395	65.376
800	34.491	34.031	21.983	10.358	-238.926	-205.092	56.029
900	34.491	38.993	23.652	13.807	-237.548	-200.946	48.796
1000	34.491	42.627	25.371	17.256	-236.201	-196.950	43.043
1100	34.491	45.915	27.092	20.705	-234.883	-193.090	38.363
1200	34.491	48.916	28.787	24.154	-233.589	-189.348	34.485
1300	34.491	51.677	30.443	27.604	-232.316	-185.713	31.221
1400	34.491	54.233	32.052	31.053	-231.063	-182.175	28.439
1500	34.491	56.612	33.611	34.502	-229.829	-178.728	26.041
1600	34.491	58.838	35.119	37.951	-228.611	-175.359	23.953
1700	34.491	60.929	36.576	41.400	-262.456	-170.740	21.950
1800	34.491	62.901	37.985	44.849	-261.088	-165.383	20.080
1900	34.491	64.766	39.345	48.298	-259.734	-160.103	18.416
2000	34.491	66.535	40.661	51.747	-258.397	-154.895	16.926
2100	34.491	68.218	41.934	55.196	-257.062	-149.753	15.585
2200	34.491	69.822	43.165	58.645	-255.745	-144.673	14.372
2300	34.491	71.355	44.358	62.095	-254.436	-139.655	13.270
2400	34.491	72.823	45.513	65.544	-253.142	-134.691	12.265
2500	34.491	74.231	46.634	68.993	-257.246	-129.672	11.336
2600	34.491	75.584	47.722	72.442	-255.965	-124.597	10.473
2700	34.491	76.886	48.778	75.891	-254.693	-119.568	9.678
2800	34.491	78.140	49.804	79.340	-253.428	-114.587	8.944
2900	34.491	79.350	50.802	82.789	-252.173	-109.647	8.263
3000	34.491	80.520	51.773	86.238	-250.925	-104.754	7.631

June 30, 1961; Dec. 31, 1964; June 30, 1971

LITHIUM METABORATE ($LiBO_2$) (LIQUID) GFW = 49.7488 $BLiO_2$

$S^\circ_{298.15}$ = 15.667 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -239.067 kcal/mol

Tm = 1117 ± 1 K ΔHm° = 8.08 ± 0.12 kcal/mol

Tb = 1992.2 K ΔHv° = 63.5 kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298.15}(\ell)$ is calculated from that of the crystal by addition of ΔHm° and the difference of $H_{1117}-H_{298.15}$ for the crystal and liquid.

Heat Capacity and Entropy

McDonald (1) measured high temperature enthalpy data of the liquid from 1118 to 1707 K by drop calorimetry. The adopted heat capacities are derived from his observed data. The average deviation of the observed enthalpy data from the adopted values is about 0.1%.

A glass transition is assumed at 745 K below which the Cp is assumed to be the same as that of the crystal.

The entropy at 298 K is obtained in a manner similar to the heat of formation.

Melting Data

The adopted heat of melting, ΔHm(1117 K) = 8.08 ± 0.12 kcal/mol, is calculated from the observed enthalpies (1) by use of the adopted Cp functions of both crystal and liquid.

Petit and Jaeger (2) derived ΔHm(1109 K) = 7.4 kcal/mol from phase data for the $LiBO_2$-LiF system. Darmois and Zarzycki (3) determined ΔHm(1113 K) = 8.3 ± 0.6 kcal/mol from cryoscopic studies involving several secondary components.

Vaporization Data

The boiling point is calculated as the temperature at which ΔGr = 0 for $LiBO_2(\ell) \rightarrow LiBO_2(g)$. The heat of vaporization is the difference in ΔHf° at the boiling point between liquid and gas.

Prophet (4) determined the boiling point under argon atmosphere as 2050 ± 100 K which is in good agreement with the value adopted.

References

1. R. A. McDonald, private communication, Thermal Res. Laboratory, The Dow Chemical Company, April, 1961; CPIA Publication No. 44(U), Vol. 1, pp 213-245, 1964.
2. C. Petit and M. Jaeger, Compt. Rend. 244, 1734 (1957).
3. G. Zarzycki, Compt. Rend. 233, 1110 (1951).
4. H. Prophet, private communication, Thermal Res. Laboratory, The Dow Chemical Company, April, 1961.

Lithium Metaborate ($LiBO_2$)

(Ideal Gas) GFW = 49.7488

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	= 3.213	= 154.341	= 154.341	INFINITE
100	9.761	53.175	76.501	= 2.333	= 154.280	= 155.274	339.350
200	11.842	60.542	66.830	= 1.258	= 154.421	= 156.219	170.709
298	13.682	65.634	65.634	.000	= 154.600	= 157.067	115.133
300	13.711	65.719	65.634	.025	= 154.604	= 157.082	114.438
400	15.013	69.852	66.189	1.465	= 154.818	= 157.877	86.260
500	15.955	73.309	67.277	3.016	= 154.829	= 158.536	69.296
600	16.668	76.283	68.535	4.649	= 154.139	= 159.048	57.933
700	17.221	78.896	69.833	6.344	= 154.438	= 159.509	49.801
800	17.657	81.225	71.114	8.089	= 154.728	= 159.930	43.691
900	18.002	83.326	72.356	9.873	= 157.015	= 160.313	38.929
1000	18.279	85.237	73.550	11.687	= 157.303	= 160.662	35.113
1100	18.503	86.990	74.693	13.527	= 157.594	= 160.985	31.985
1200	18.685	88.608	75.786	15.386	= 157.890	= 161.280	29.373
1300	18.835	90.110	76.831	17.263	= 158.190	= 161.551	27.159
1400	18.959	91.510	77.830	19.153	= 158.496	= 161.797	25.258
1500	19.063	92.822	78.786	21.054	= 158.810	= 162.023	23.607
1600	19.151	94.055	79.702	22.965	= 159.130	= 162.225	22.159
1700	19.226	95.219	80.581	24.884	= 194.505	= 161.081	20.708
1800	19.290	96.320	81.425	26.810	= 194.660	= 159.110	19.319
1900	19.345	97.364	82.237	28.741	= 194.824	= 157.129	18.076
2000	19.393	98.358	83.018	30.678	= 194.994	= 155.143	16.953
2100	19.435	99.305	83.771	32.620	= 195.171	= 153.145	15.938
2200	19.471	100.210	84.498	34.565	= 195.358	= 151.139	15.014
2300	19.504	101.076	85.200	36.514	= 195.550	= 149.127	14.170
2400	19.532	101.907	85.879	38.466	= 195.753	= 147.102	13.395
2500	19.558	102.705	86.536	40.420	= 201.352	= 144.963	12.673
2600	19.580	103.472	87.173	42.377	= 201.563	= 142.704	11.995
2700	19.601	104.211	87.791	44.336	= 201.781	= 140.435	11.367
2800	19.619	104.925	88.390	46.297	= 202.004	= 138.160	10.784
2900	19.636	105.613	88.972	48.260	= 202.235	= 135.872	10.240
3000	19.651	106.279	89.538	50.224	= 202.472	= 133.580	9.731
3100	19.664	106.924	90.088	52.190	= 202.717	= 131.280	9.255
3200	19.677	107.548	90.624	54.157	= 202.969	= 128.973	8.808
3300	19.688	108.154	91.146	56.125	= 203.230	= 126.656	8.388
3400	19.698	108.742	91.655	58.095	= 203.499	= 124.330	7.992
3500	19.708	109.313	92.152	60.065	= 203.776	= 122.002	7.618
3600	19.717	109.868	92.636	62.036	= 204.063	= 119.658	7.264
3700	19.725	110.409	93.109	64.008	= 204.359	= 117.311	6.929
3800	19.732	110.935	93.571	65.981	= 204.664	= 114.949	6.611
3900	19.739	111.447	94.023	67.955	= 204.978	= 112.589	6.309
4000	19.746	111.947	94.465	69.929	= 326.483	= 108.072	5.905
4100	19.752	112.435	94.897	71.904	= 326.588	= 102.609	5.470
4200	19.757	112.911	95.321	73.879	= 326.703	= 97.143	5.055
4300	19.762	113.376	95.735	75.855	= 326.829	= 91.674	4.659
4400	19.767	113.830	96.141	77.832	= 326.967	= 86.205	4.282
4500	19.772	114.275	96.539	79.809	= 327.118	= 80.732	3.921
4600	19.776	114.709	96.930	81.786	= 327.281	= 75.252	3.575
4700	19.780	115.135	97.312	83.764	= 327.458	= 69.774	3.244
4800	19.784	115.551	97.688	85.742	= 327.649	= 64.287	2.927
4900	19.787	115.959	98.057	87.721	= 327.855	= 58.806	2.623
5000	19.790	116.359	98.419	89.699	= 328.076	= 53.309	2.330
5100	19.794	116.751	98.774	91.679	= 328.314	= 47.807	2.049
5200	19.796	117.135	99.124	93.658	= 328.569	= 42.309	1.778
5300	19.799	117.512	99.467	95.638	= 328.841	= 36.801	1.518
5400	19.802	117.882	99.805	97.618	= 329.133	= 31.292	1.266
5500	19.804	118.246	100.137	99.598	= 329.444	= 25.765	1.024
5600	19.807	118.603	100.463	101.579	= 329.777	= 20.251	.790
5700	19.809	118.953	100.785	103.560	= 330.132	= 14.718	.564
5800	19.811	119.298	101.101	105.541	= 330.511	= 9.177	.346
5900	19.813	119.636	101.412	107.522	= 330.913	= 3.636	.135
6000	19.815	119.969	101.719	109.503	= 331.342	1.920	.070

June 30, 1962; Dec. 31, 1964; Mar. 31, 1965; June 30, 1971

$BLiO_2$

LITHIUM METABORATE ($LiBO_2$) (IDEAL GAS) GFW = 49.7488

Point Group C_s

$S^\circ_{298.15}$ = 65.6 ± 1 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = −154.3 ± 3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −154.6 ± 3 kcal/mol

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω, cm^{-1}
1976 (1)	569 (1)
1094 (1)	471 (1)
578 (1)	107 (1)

Bond Distances: Li-O = 1.82 Å, O-B = 1.36 Å, B=O = 1.20 Å

Bond Angles: Li-O-B = 90°, O-B=O = 180° σ = 1

Product of the Moments of Inertia: $I_A I_B I_C = 3.91309 \times 10^{-115}$ g^3 cm^6

Heat of Formation

Jensen (1) *determined equilibrium constants for reaction* (A) $Li(g) + HBO_2(g) \rightarrow LiBO_2(g) + H(g)$ *by flame studies.* This technique involves several assumptions, the most basic of which was that boron added to $H_2/N_2/O_2$ flames was converted completely to HBO_2. The hydrogen atom concentration was taken from previous studies on such flames. Lithium metaborate was assumed to be formed in the flame. The concentration of Li atoms was determined by atomic absorption spectrophotometry. JANAF third law analysis of his equilibrium constant equation in the temperature range from 2000 to 2600 K yields ΔHr_{298} = −2.95 ± 1.07 kcal/mol and the drift 2.47 eu. (2nd law heat of reaction is ΔHr_{298} = −8.62 kcal/mol). Using the third law ΔHr_{298} and JANAF auxiliary data, we obtain $\Delta Hf^\circ_{298}(LiBO_2, g)$ = −150.6 kcal/mol. The uncertainty in this result is about ±6 kcal/mol.

Büchler and Berkowitz-Mattuck (2) studied mass spectrometrically the vaporization of lithium metaborate and obtained ΔHv_{1160} = 70 ± 3 kcal/mol for $LiBO_2(\ell) \rightarrow LiBO_2(g)$ and ΔHs_{1060} = 79 ± 3 kcal/mol for $LiBO_2(c) \rightarrow LiBO_2(g)$ by a second law method. JANAF reduction to 298 K gives ΔHv_{298} = 78.1 ± 3 kcal/mol and ΔHs_{298} = 82.4 ± 3 kcal/mol. They also determined the vapor pressure of $LiBO_2$ at 1160 K as 2.0×10^{-6} atm by comparison with the vapor pressure of silver. JANAF third law analysis of this single vapor pressure point gives ΔHv°_{298} = 85.0 kcal/mol which leads to $\Delta Hf^\circ_{298}(LiBO_2, g)$ = −154.0 ± 3 kcal/mol. The latter is in good agreement with the value adopted in the tabulation. The second law heats of vaporization and sublimation are probably in error by about 6 kcal/mol.

Hildenbrand et al. (3) measured the total vapor pressure over liquid $LiBO_2$ in the temperature range from 1120 to 1280 K by a torsion-effusion method. Assuming 100% monomeric vapor species, JANAF third law analysis of their vapor pressure data yields the heat of vaporization ΔHv_{298} = 84.47 kcal/mol and a drift of 0.93 ± 1.0 eu; this corresponds to ΔHs_{298} = 89.0 kcal/mol. (Second law heat of vaporization is ΔHv°_{298} = 83.25 ± 1.20 kcal/mol). Using the third law ΔHv°_{298}, we obtain $\Delta Hf^\circ_{298}(LiBO_2, g)$ = −154.6 kcal/mol. If there are 10% of $LiBO_2$ dimer molecules present in the vapor phase as suggested by Büchler (2), the correction in the 3rd law ΔHv°_{298} is about 0.3 kcal/mol which is much less than the uncertainty assigned to ΔHv°_{298}. The value, $\Delta Hf^\circ_{298}(LiBO_2, g)$ = −154.6 ± 3 kcal/mol, is adopted in the tabulation.

Heat Capacity and Entropy

The adopted vibrational frequencies are obtained from Seshadri, Nimon and White (4) who observed the infrared spectra of $LiBO_2$ in an argon matrix and made a complete assignment of all six fundamentals. The uncertainty of the calculated statistical entropy at 298 K is estimated to be ±1 eu which is due to the magnitude of the matrix shifts from the free molecule spectrum, particularly for the lower frequency modes.

Büchler and Marram (5) observed only two vibrational frequencies 1935 and 600 cm^{-1} in gas-phase infrared spectra. These two frequencies are in reasonable agreement with those reported by Seshadri (4).

By electron diffraction studies, Akishin and Spiridonov (6) determined the molecular structure of gaseous lithium metaborate and found the bond lengths and angles which are adopted in the tabulation. We tentatively select the bond angle Li-O-B as 90° from their reported data, i.e. 90-105°, because Seshadri et al. (4) treated this bond angle as a parameter in the force constant calculations and found that the best fit to the infrared spectrometric data occurs at approximately 90°. A recent electron diffraction study (7) on lithium metaborate confirms the results given by Akishin (6).

The three individual moments of inertia are $I_A = 2.5794 \times 10^{-39}$, $I_B = 11.094 \times 10^{-39}$ and $I_C = 13.6740 \times 10^{-39}$ g cm^2.

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$BLiO_2$

Sodium Metaborate ($NaBO_2$)

(Crystal) GFW = 65.7996

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	= 2.780	= 232.073	= 232.073	INFINITE
100	7.751	4.780	29.399	= 2.462	= 232.774	= 228.535	499.463
200	12.756	11.891	18.928	= 1.407	= 233.082	= 224.154	244.944
298	15.760	17.576	17.576	.000	= 233.200	= 219.745	161.077
300	15.810	17.674	17.576	.029	= 233.201	= 219.661	160.023
400	18.020	22.536	18.224	1.725	= 233.882	= 215.090	117.520
500	19.770	26.751	19.517	3.617	= 233.875	= 210.391	91.962
600	21.170	30.483	21.040	5.666	= 233.777	= 205.701	74.927
700	22.300	33.834	22.632	7.841	= 233.602	= 201.036	62.766
800	23.240	36.875	24.225	10.120	= 233.361	= 196.400	53.658
900	24.020	39.659	25.788	12.484	= 233.067	= 191.797	46.575
1000	24.670	42.224	27.305	14.920	= 232.733	= 187.227	40.918
1100	25.160	44.600	28.771	17.412	= 232.380	= 182.696	36.298
1200	25.480	46.805	30.183	19.946	= 255.253	= 177.737	32.370
1300	25.650	48.851	31.541	22.503	= 254.884	= 171.301	28.798
1400	25.843	50.759	32.846	25.077	= 254.116	= 164.908	25.743
1500	26.036	52.548	34.101	27.671	= 253.553	= 158.556	23.102
1600	26.229	54.235	35.307	30.284	= 252.987	= 152.240	20.795
1700	26.422	55.831	36.468	32.917	= 252.417	= 145.960	18.764
1800	26.615	57.346	37.586	35.569	= 251.846	= 139.716	16.964
1900	26.807	58.790	38.664	38.240	= 251.270	= 133.501	15.356
2000	27.000	60.170	39.705	40.930	= 250.687	= 127.319	13.913

Dec. 31, 1960; Mar. 31, 1965; June 30, 1971

SODIUM METABORATE ($NaBO_2$) (CRYSTAL) GFW = 65.7996 $BNaO_2$

ΔHf°_0 = −232.1 ± 0.6 kcal/mol

$S^\circ_{298.15}$ = 17.576 ± 0.02 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −233.2 ± 0.6 kcal/mol

Tm = 1240 ± 2 K

ΔHm° = 8.0 ± 0.5 kcal/mol

Heat of Formation

Adami and Joe (1) measured heats of solution of B_2O_3(c), NaCl(c) and $NaBO_2$(c) in aqueous HCl solution and derived ΔHr°_{298} = −12.43 ± 0.1 kcal/mol for $NaBO_2$(c) + HCl(12.731 H_2O, aq) → NaCl(c) + 1/2 B_2O_3(c) + 1/2 H_2O(ℓ) which leads to ΔHf°_{298}($NaBO_2$, c) = −233.2 ± 0.6 kcal/mol, using JANAF auxiliary data (2). This value, −233.2 kcal/mol, is adopted in the tabulation.

Grenier and White (3) measured the heat of solution of crystal $Na_2O{\cdot}B_2O_3$ in 2N nitric acid solution at 0°C as −20.43 ± 0.36 kcal/mol. Since the correction term for ΔH°_{soln} from 0° to 25°C is generally small, we may assume the heat of solution is the same at 0°C as at 25°C within the uncertainty of ±1 kcal/mol. Thus we obtain ΔH_{soln} (25°C) = −10.22 ± 1 kcal/mol for $NaBO_2$(c) + HNO_3(27.75 H_2O, aq) + H_2O(ℓ) → $NaNO_3$(27.75 H_2O, aq) + H_3BO_3(27.75 H_2O, aq) from which we derive ΔHf°_{298}($NaBO_2$, c) = −234.7 ± 1.5 kcal/mol, based on JANAF auxiliary data (4).

Shartsis and Capps (5) measured the heats of solution in 2N nitric acid of various Na_2O-B_2O_3 glass and crystalline mixtures containing 1.0-38.7 mole % of Na_2O. When their data are extrapolated to 50 mole %, we obtain ΔH°_{soln}(25°C) = −11.5 ± 1.5 kcal/mol for the same reaction as given before. The derived heat of formation is −233.4 ± 1.5 kcal/mol which is in good agreement with the value adopted.

Heat Capacity and Entropy

Grenier and Westrum (6) measured low temperature heat capacities from 5 to 346 K. The adopted Cp are derived from their experimental heat capacities by a polynomial curve fitting technique. The derived entropy, S°_{298}, is 17.576 ± 0.02 eu based on S° = 0.001 eu at 5.48 K. Pankratz (7) measured high temperature enthalpy data by drop calorimetry in the temperature range 404-1200.3 K. We adopt the smooth Cp derived by Pankratz. The average deviation of the observed enthalpy data from the adopted values is about 0.1%.

Melting Data

Our analysis of several sets of binary phase data (8, 9, 10) yields the heat of melting, ΔHm = 8.0 ± 0.5 kcal/mol. Petit and Jaeger (11) derived ΔHm(1239 K) = 8.0 kcal/mol from their phase data for the $NaBO_2$-NaF system. The adopted melting point (1240 K) is obtained from Pankratz (7). Literature values include 1239 K (8, 9, 10, 11, 12), 1238 K (13) and 1237 K (14).

References

1. L. H. Adami and C. J. Joe, U. S. Bur. Mines RI 7167, Aug. 1968.
2. The following auxiliary data are used in the calculation:
   a. ΔHf°_{298}(B_2O_3, c) = −304.0 ± 0.5 kcal/mol, JANAF B_2O_3(c) table dated June 30, 1971.
   b. ΔHf°_{298}(NaCl, c) = −98.26 ± 0.08 kcal/mol, JANAF NaCl(c) table, dated Sept. 30, 1964.
   c. ΔHf°_{298}(HCl·12.731 H_2O, aq) = −38.82 kcal/mol and ΔHf°_{298}(H_2O, ℓ) = −68.315 kcal/mol, U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. G. Grenier and D. White, J. Chem. Phys. 61, 1681 (1957).
4. The following auxiliary data are used in the calculation:
   a. ΔHf°_{298}(HNO_3·27.75 H_2O, aq) = −49.43 kcal/mol and ΔHf°_{298}(H_3BO_3·27.75 H_2O, aq) = −255.37 kcal/mol are obtained from U. S. Natl. Bur. Std. Tech. Note 270-3, 1968. The latter is extrapolated from the listed ΔHf°_{298} values for H_3BO_3·100 H_2O and H_3BO_3·60 H_2O.
   b. ΔHf°_{298}($NaNO_3$·27.75 H_2O, aq) = −106.30 kcal/mol. This value is calculated from JANAF ΔHf°_{298}($NaNO_3$·∞ H_2O, aq) = −107.03 kcal/mol and the heat of dilution given by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
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Sodium Metaborate ($NaBO_2$)

(Liquid) GFW = 65.7996

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	15.760	19.827	19.827	.000	-229.450	-216.666	158.820
300	15.810	19.925	19.827	.029	-229.451	-216.586	157.783
400	18.020	24.787	20.475	1.725	-230.132	-212.241	115.963
500	19.770	29.002	21.768	3.617	-230.125	-207.766	90.814
600	21.170	32.734	23.291	5.666	-230.027	-203.302	74.053
700	22.300	36.085	24.883	7.841	-229.852	-198.861	62.087
800	23.240	39.126	26.477	10.120	-229.611	-194.451	53.121
900	35.000	42.876	28.079	13.317	-228.484	-190.109	46.165
1000	35.000	46.564	29.747	16.817	-227.086	-185.919	40.632
1100	35.000	49.900	31.430	20.317	-225.725	-181.871	36.134
1200	35.000	52.945	33.097	23.817	-247.632	-177.885	32.324
1300	35.000	55.746	34.733	27.317	-246.120	-171.701	28.666
1400	35.000	58.340	36.328	30.817	-244.628	-166.032	25.919
1500	35.000	60.755	37.877	34.317	-243.157	-160.471	23.381
1600	35.000	63.014	39.378	37.817	-241.704	-155.005	21.173
1700	35.000	65.136	40.832	41.317	-240.287	-149.629	19.236
1800	35.000	67.136	42.236	44.817	-238.848	-144.339	17.525
1900	35.000	69.029	43.599	48.317	-237.443	-139.127	16.003
2000	35.000	70.824	44.915	51.817	-236.050	-133.990	14.642
2100	35.000	72.532	46.190	55.317	-234.667	-128.920	13.417
2200	35.000	74.160	47.425	58.817	-233.297	-123.917	12.310
2300	35.000	75.716	48.621	62.317	-231.936	-118.977	11.305
2400	35.000	77.205	49.781	65.817	-230.587	-114.091	10.389
2500	35.000	78.634	50.907	69.317	-234.635	-109.160	9.543

Dec. 31, 1960; Mar. 31, 1965; June 30, 1971

SODIUM METABORATE ($NaBO_2$) (LIQUID) GFW = 65.7996 $BNaO_2$

$S^\circ_{298.15}$ = 19.827 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -229.450 kcal/mol

Tm = 1240 ± 2 K

ΔHm° = 8.0 ± 0.5 kcal/mol

Tb = 1748.8 K

ΔHv° = 57.3 kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298.15}(\ell)$ is calculated from that of the crystal by addition of ΔHm° and the difference between $H_{1239}-H_{298.15}$ for the crystal and liquid.

Heat Capacity and Entropy

The constant heat capacity of the liquid is estimated to be 35 cal/mol·deg based on that of $LiBO_2(\ell)$, 34.491 cal/mol·deg (1), which was derived from high temperature enthalpy measurements. A glass transition is assumed at 826 K below which the heat capacities are assumed to be the same as the crystal.

The entropy, S°_{298} = 19.827 eu, is obtained in a manner analogous to the heat of formation.

Melting Data

See $NaBO_2(c)$ table dated June 30, 1971.

Vaporization Data

The boiling point is calculated as the temperature at which ΔGr = 0 for $NaBO_2(\ell) \rightarrow NaBO_2(g)$. The heat of vaporization is the difference in ΔHf° at the boiling point between liquid and gas.

Reference

1. JANAF $LiBO_2(\ell)$ table dated June 30, 1971.

Sodium Metaborate ($NaBO_2$)

(Ideal Gas) GFW = 65.7996

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	- 3.275	- 154.367	- 154.367	INFINITE
100	9.945	55.847	79.757	- 2.391	- 154.503	- 155.371	339.563
200	12.171	63.820	69.848	- 1.286	- 154.761	- 156.138	170.620
298	13.918	68.627	68.627	.000	- 155.000	- 156.766	114.912
300	13.945	68.713	68.627	.026	- 155.004	- 156.776	114.211
400	15.176	72.903	69.190	1.485	- 155.922	- 157.277	85.932
500	16.074	76.391	70.291	3.050	- 156.742	- 157.577	68.877
600	16.760	79.385	71.563	4.693	- 156.550	- 157.815	57.484
700	17.295	82.010	72.872	6.397	- 156.846	- 158.003	49.331
800	17.718	84.349	74.163	8.148	- 157.133	- 158.150	43.204
900	18.053	86.455	75.414	9.938	- 157.413	- 158.260	38.431
1000	18.322	88.372	76.615	11.757	- 157.696	- 158.337	34.605
1100	18.540	90.129	77.765	13.600	- 157.992	- 158.390	31.469
1200	18.717	91.750	78.864	15.464	- 181.535	- 157.956	28.767
1300	18.863	93.254	79.913	17.343	- 181.644	- 155.985	26.223
1400	18.988	94.656	80.917	19.235	- 181.760	- 154.007	24.042
1500	19.085	95.970	81.877	21.139	- 181.885	- 152.021	22.149
1600	19.171	97.204	82.797	23.052	- 182.019	- 150.024	20.492
1700	19.244	98.369	83.679	24.973	- 182.161	- 148.020	19.029
1800	19.306	99.471	84.526	26.901	- 182.315	- 146.008	17.728
1900	19.360	100.516	85.340	28.834	- 182.476	- 143.986	16.562
2000	19.406	101.510	86.124	30.772	- 182.645	- 141.957	15.512
2100	19.447	102.458	86.880	32.715	- 182.819	- 139.918	14.561
2200	19.482	103.363	87.608	34.661	- 183.003	- 137.871	13.696
2300	19.514	104.230	88.312	36.611	- 183.192	- 135.817	12.906
2400	19.542	105.061	88.993	38.564	- 183.390	- 133.749	12.180
2500	19.568	105.860	89.652	40.519	- 188.983	- 131.571	11.502
2600	19.588	106.627	90.290	42.477	- 189.188	- 129.269	10.866
2700	19.608	107.367	90.909	44.437	- 189.398	- 126.961	10.277
2800	19.626	108.080	91.509	46.399	- 189.613	- 124.646	9.729
2900	19.642	108.769	92.093	48.362	- 189.833	- 122.316	9.218
3000	19.657	109.436	92.660	50.327	- 190.059	- 119.987	8.741
3100	19.670	110.080	93.212	52.293	- 190.290	- 117.648	8.294
3200	19.682	110.705	93.748	54.261	- 190.527	- 115.301	7.875
3300	19.693	111.311	94.272	56.230	- 190.771	- 112.947	7.480
3400	19.703	111.899	94.781	58.199	- 191.023	- 110.585	7.108
3500	19.712	112.470	95.279	60.170	- 191.281	- 108.216	6.757
3600	19.721	113.026	95.764	62.142	- 191.547	- 105.837	6.425
3700	19.729	113.566	96.238	64.114	- 191.822	- 103.455	6.111
3800	19.736	114.092	96.701	66.088	- 192.104	- 101.057	5.817
3900	19.743	114.605	97.153	68.062	- 192.397	- 98.665	5.529
4000	19.749	115.105	97.596	70.036	- 313.880	- 94.111	5.142
4100	19.755	115.593	98.029	72.011	- 313.964	- 88.614	4.724
4200	19.760	116.069	98.453	73.987	- 314.058	- 83.116	4.325
4300	19.765	116.534	98.868	75.963	- 314.166	- 77.613	3.945
4400	19.770	116.988	99.275	77.940	- 314.290	- 72.115	3.582
4500	19.774	117.433	99.673	79.917	- 314.429	- 66.607	3.235
4600	19.779	117.867	100.064	81.895	- 314.584	- 61.097	2.903
4700	19.782	118.293	100.447	83.873	- 314.759	- 55.585	2.585
4800	19.786	118.709	100.823	85.851	- 314.955	- 50.067	2.280
4900	19.789	119.117	101.193	87.830	- 315.173	- 44.551	1.987
5000	19.793	119.517	101.555	89.809	- 315.415	- 39.025	1.706
5100	19.796	119.909	101.911	91.789	- 315.684	- 33.491	1.435
5200	19.799	120.293	102.261	93.768	- 315.981	- 27.960	1.175
5300	19.801	120.671	102.605	95.748	- 316.308	- 22.415	.924
5400	19.804	121.041	102.943	97.729	- 316.669	- 16.870	.683
5500	19.806	121.404	103.275	99.709	- 317.065	- 11.309	.449
5600	19.809	121.761	103.602	101.690	- 317.500	- 5.754	.225
5700	19.811	122.112	103.924	103.671	- 317.975	- .181	.007
5800	19.813	122.456	104.240	105.652	- 318.493	5.401	.204
5900	19.815	122.795	104.552	107.634	- 319.055	10.991	.407
6000	19.817	123.128	104.859	109.615	- 319.665	16.594	.604

Mar. 31, 1965; June 30, 1971

SODIUM METABORATE ($NaBO_2$) (IDEAL GAS) GFW = 65.7996 $BNaO_2$

Point Group C_s ΔHf°_0 = -154.4 ± 3 kcal/mol

$S^\circ_{298.15}$ = 68.6 ± 1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -155.0 ± 3 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1960	573
1087	363
576	108

Bond Distance: Na-O = 2.14 Å, O-B = 1.36 Å, B=O = 1.20 Å

Bond Angle: Na-O-B = 90° O-B=O = 180° σ = 1

Product of the Moments of Inertia: $I_A I_B I_C = 2.4069 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

Jensen (1) determined equilibrium constants for the reaction: $Na(g) + HBO_2(g) \rightarrow NaBO_2(g) + H(g)$ by flame studies. This technique involved several assumptions, the most basic of which was that boron added to $H_2/N_2/O_2$ flames was converted completely to HBO_2. The hydrogen atom concentration was taken from previous studies on such flames. Sodium metaborate was assumed to be formed in the flame. The concentration of Na atom was determined by atomic absorption spectrophotometry. JANAF third law analysis of his equilibrium constant equation in the temperature range from 2000 to 2600 K yields $\Delta Hr(298\ K)$ = 7.55 ± 1.08 kcal/mol and the drift 2.50 eu. (2nd law heat of reaction is ΔHr°_{298} = 1.81 kcal/mol.) Using the third law ΔHr°_{298} and JANAF auxiliary data, we obtain $\Delta Hf^\circ_{298}(NaBO_2, g)$ = -152.8 kcal/mol. The uncertainty in this result is about ±6 kcal/mol.

Büchler and Berkowitz-Mattuck (2) studied mass spectrometrically the sublimation of sodium metaborate and obtained $\Delta Hs^\circ(1070\ K)$ = 73 ± 3 kcal/mol for $NaBO_2(c) \rightarrow NaBO_2(g)$ by a second law method. JANAF reduction to 298 K gives $\Delta Hs^\circ(298\ K)$ = 76.6 ± 3 kcal/mol which leads to $\Delta Hf^\circ_{298}(NaBO_2, g)$ = -156.6 ± 3 kcal/mol. They also determined the vapor pressure of $NaBO_2$ at 1070 K as 5×10^{-7} atm by comparison with the vapor pressure of silver. JANAF third law analysis of this single vapor pressure point gives $\Delta Hs^\circ(298\ K)$ = 83.37 kcal/mol which leads to $\Delta Hf^\circ_{298}(NaBO_2, g)$ = -149.8 kcal/mol.

Cole and Taylor (3) determined the vapor pressures of $NaBO_2(g)$ by a dynamic method with dry N_2 as carrier gas. Their vapor pressure data were taken over a flow-rate range where the apparent vapor pressure increased with decreasing flow rate, and the data were then extrapolated to zero flow rate. The vapor species of the sample was also assumed to be monomeric $NaBO_2(g)$. JANAF third law analyses of their reported vapor pressure data over the liquid $NaBO_2$ in the temperature range 1150°-1350°C yield ΔHv°_{298} = 75.37 ± 3.32 kcal/mol and the drift -20.6 eu. (Second law heat of vaporization is ΔHv°_{298} = 107 kcal/mol). Using the third law ΔHv°_{298}, we obtain $\Delta Hf^\circ_{298}(NaBO_2, g)$ = -154.1 ± 4 kcal/mol.

A weighted average, $\Delta Hf^\circ_{298}(NaBO_2, g)$ = -155 ± 3 kcal/mol, is adopted in the tabulation.

Heat Capacity and Entropy

The adopted vibrational frequencies are obtained from Seshadri, Nimon and White (4) who observed the infrared spectra of $NaBO_2$ in an argon matrix and made a complete assignment of all six fundamentals. The uncertainty of the calculated statistical entropy at 298 K is estimated to be ±1 eu which is due to the magnitude of the matrix shifts from the free molecule spectrum, particularly for the lower frequency modes.

Büchler and Marram (5) observed only two vibrational frequencies, 1935 and 600 cm^{-1}, in their gas-phase infrared spectra. These two frequencies are in reasonable agreement with those reported by Seshadri (4).

By electron diffraction studies, Akishin and Spiridonov (6) determined the molecular structure of gaseous sodium metaborate and found the bond lengths and angles which are adopted in the tabulation. The bond angle Na-O-B is taken as 90° based on that of $LiBO_2(g)$ (7).

The three principal moments of inertia are $I_A = 5.1900 \times 10^{-39}$, $I_B = 19.0961 \times 10^{-39}$ and $I_C = 24.2860 \times 10^{-39}\ g\ cm^2$.

References

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7. JANAF $LiBO_2(g)$ table dated June 30, 1971.

Boron Monosulfide (BS)

(Ideal Gas) GFW = 42.875

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	- 2.085	57.360	57.360	INFINITE
100	6.956	43.997	57.901	- 1.390	57.885	53.790	- 117.557
200	6.988	48.823	52.293	- .694	58.108	49.585	- 54.184
298	7.182	51.644	51.644	.000	58.100	45.396	- 33.276
300	7.187	51.688	51.644	.013	58.098	45.317	- 33.013
400	7.499	53.798	51.929	.747	57.411	41.097	- 22.455
500	7.799	55.504	52.479	1.513	56.826	37.086	- 16.210
600	8.044	56.949	53.106	2.305	56.286	33.190	- 12.089
700	8.233	58.203	53.747	3.120	55.785	29.405	- 9.181
800	8.379	59.313	54.375	3.950	42.245	24.401	- 6.666
900	8.491	60.306	54.979	4.794	42.085	22.180	- 5.386
1000	8.579	61.206	55.558	5.648	41.913	19.978	- 4.366
1100	8.649	62.027	56.109	6.509	41.727	17.792	- 3.535
1200	8.706	62.782	56.634	7.377	41.532	15.626	- 2.846
1300	8.753	63.481	57.134	8.250	41.326	13.476	- 2.265
1400	8.792	64.131	57.611	9.128	41.110	11.342	- 1.771
1500	8.825	64.739	58.066	10.008	40.881	9.220	- 1.343
1600	8.854	65.309	58.501	10.892	40.644	7.120	- .972
1700	8.880	65.847	58.918	11.779	40.397	5.031	- .647
1800	8.903	66.355	59.317	12.668	40.141	2.957	- .359
1900	8.924	66.837	59.700	13.560	39.880	.900	- .104
2000	8.944	67.295	60.068	14.453	39.613	- 1.145	.125
2100	8.963	67.732	60.423	15.348	39.341	- 3.177	.331
2200	8.982	68.149	60.765	16.246	39.067	- 5.193	.516
2300	9.002	68.549	61.095	17.145	38.788	- 7.200	.684
2400	9.022	68.932	61.413	18.046	38.506	- 9.193	.837
2500	9.043	69.301	61.721	18.949	32.835	- 11.065	.967
2600	9.066	69.656	62.020	19.855	32.557	- 12.817	1.077
2700	9.090	69.999	62.309	20.763	32.281	- 14.556	1.178
2800	9.116	70.330	62.590	21.673	32.006	- 16.288	1.271
2900	9.144	70.650	62.862	22.586	31.734	- 18.005	1.357
3000	9.173	70.961	63.127	23.502	31.464	- 19.716	1.436
3100	9.205	71.262	63.384	24.421	31.198	- 21.419	1.510
3200	9.238	71.555	63.635	25.343	30.933	- 23.112	1.578
3300	9.274	71.840	63.880	26.268	30.672	- 24.796	1.642
3400	9.311	72.117	64.118	27.197	30.414	- 26.471	1.702
3500	9.350	72.388	64.350	28.130	30.159	- 28.145	1.757
3600	9.390	72.651	64.577	29.067	29.909	- 29.805	1.809
3700	9.432	72.909	64.799	30.008	29.661	- 31.460	1.858
3800	9.476	73.161	65.016	30.954	29.419	- 33.108	1.904
3900	9.521	73.408	65.228	31.904	29.180	- 34.753	1.948
4000	9.566	73.650	65.435	32.858	- 92.234	- 34.241	1.871
4100	9.613	73.887	65.638	33.817	- 92.233	- 32.793	1.748
4200	9.660	74.119	65.838	34.781	- 92.227	- 31.339	1.631
4300	9.708	74.347	66.033	35.749	- 92.218	- 29.892	1.519
4400	9.757	74.570	66.224	36.722	- 92.206	- 28.442	1.413
4500	9.805	74.790	66.412	37.700	- 92.189	- 26.993	1.311
4600	9.854	75.006	66.597	38.683	- 92.167	- 25.546	1.214
4700	9.903	75.219	66.778	39.671	- 92.141	- 24.097	1.121
4800	9.952	75.428	66.956	40.664	- 92.112	- 22.649	1.031
4900	10.000	75.633	67.131	41.662	- 92.079	- 21.203	.946
5000	10.048	75.836	67.303	42.664	- 92.043	- 19.757	.864
5100	10.096	76.035	67.472	43.671	- 92.004	- 18.310	.785
5200	10.144	76.232	67.639	44.683	- 91.960	- 16.866	.709
5300	10.190	76.426	67.803	45.700	- 91.912	- 15.425	.636
5400	10.236	76.616	67.964	46.721	- 91.863	- 13.981	.566
5500	10.282	76.805	68.123	47.747	- 91.809	- 12.535	.498
5600	10.326	76.990	68.280	48.778	- 91.753	- 11.098	.433
5700	10.370	77.174	68.434	49.812	- 91.696	- 9.658	.370
5800	10.413	77.354	68.587	50.852	- 91.634	- 8.220	.310
5900	10.455	77.533	68.737	51.895	- 91.570	- 6.784	.251
6000	10.497	77.709	68.885	52.943	- 91.504	- 5.342	.195

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1962; Mar. 31, 1965; June 30, 1972

BORON MONOSULFIDE (BS) (IDEAL GAS) GFW = 42.875

Ground State Configuration $^2\Sigma^+$ ΔHf°_0 = 57.4 ± 4.0 kcal/mol

$S^\circ_{298.15}$ = 51.64 ± 0.10 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 58.1 ± 4.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	{15663, 15998}	2, 2
$B^2\Sigma^+$	35849	2
$C^2\Pi$	{38782, 38897}	2, 2

ω_e = 1188.14 cm^{-1} $\omega_e x_e$ = 6.397 cm^{-1} σ = 1

B_e = 0.80586 cm^{-1} α_e = 0.00617 cm^{-1} r_e = 1.609 Å

Heat of Formation

Gingerich (1), employing mass spectrometric investigations of the Au-Ce-CeS-BN-C system from a tungsten Knudsen effusion cell, reports two values of the BS(g) dissociation energy. The reaction enthalpies were evaluated by the Third-Law method. The two values reported are 140.4 ± 6.0 kcal/mol, based on the dissociation energy of CS(g), and 145.4 ± 6.0 kcal/mol, based on the dissociation energy of CeS(g).

Uy and Drowart (2) also studied the dissociation energy of BS(g) by two different exchange reactions using mass spectrometric Knudsen cell techniques. Molybdenum cells were used. Based on an exchange between B(g) and YS(g), they reported D°_0 = 138.8 ± 3.2 kcal/mol for BS(g). A second determination based on an exchange between BO(g) and YS(g) was reported as D°_0 = 137.0 ± 3.2 kcal/mol.

Gaydon (3) suggests a value of 118 kcal/mol for the dissociation energy based on two linear Birge-Sponer extrapolations from the data of Zeeman (4). This data gave values of 154.5 kcal/mol and 131.4 kcal/mol for extrapolations from the ground state and $A^2\Pi$ state, respectively. McDonald and Innes (5) extended Zeeman's analysis (4), examined perturbative effects, and calculated $\omega_e y_e$ = -0.004 cm^{-1} for the ground state. This perturbative interpretation was supported by Singh, Tewari, and Mohan (7). Accounting for $\omega_e y_e$ value, the Birge-Sponer extrapolation yields a value D°_0 = 142.3 kcal/mol for BS(g). This value was adjusted to 140.0 kcal/mol using an ionic character correction factor as suggested by Hildenbrand and Murad (6).

The value of 140.0 ± 4.0 kcal/mol for the dissociation energy of BS(g) is chosen as the best value. It is an average of the four reported thermochemical values and is the adjusted Birge-Sponer value, the adjustment arising from a correction technique which has been shown to be quite dependable. This value leads to a heat of formation $\Delta Hf^\circ_{298.15}$ = 58.1 ± 4.0 kcal/mol.

Heat Capacity and Entropy

The spectroscopic constants for the $X^2\Sigma^+$ state are from Zeeman (4) and were corrected to account for the natural abundances of the elements. The electronic states X, A, and C are reported by Zeeman (4). The $B^2\Sigma^+$ state is reported by McDonald and Innes (5).

References

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Diboron Tetrafluoromonoxide (B_2F_4O)

(Ideal Gas) GFW = 113.615

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100	12,264	63,967	95,519	- 3,155	- 452,713	- 448,884	981,036
200	15,963	73,586	82,318	- 1,746	- 453,212	- 444,854	486,114
298	19,563	80,643	80,642	- ,000	- 453,650	- 440,663	323,014
300	19,627	80,764	80,643	,036	- 453,658	- 440,583	320,964
400	22,836	86,862	81,453	2,164	- 454,070	- 436,160	238,307
500	25,509	92,255	83,084	4,585	- 454,454	- 431,639	188,669
600	27,689	97,103	85,023	7,248	- 454,783	- 427,043	155,550
700	29,325	101,496	87,068	10,100	- 455,054	- 422,396	131,878
800	30,629	105,501	89,125	13,100	- 455,275	- 417,718	114,115
900	31,647	109,169	91,151	16,216	- 455,450	- 413,012	100,293
1000	32,448	112,547	93,124	19,422	- 455,597	- 408,288	89,231
1100	33,085	115,670	95,034	22,700	- 455,731	- 403,552	80,178
1200	33,597	118,572	96,876	26,035	- 455,852	- 398,801	72,631
1300	34,013	121,278	98,650	29,416	- 455,973	- 394,082	66,244
1400	34,355	123,811	100,358	32,835	- 456,094	- 389,272	60,768
1500	34,638	126,192	102,001	36,285	- 456,224	- 384,496	56,021
1600	34,876	128,435	103,584	39,761	- 456,362	- 379,709	51,866
1700	35,077	130,556	105,109	43,259	- 456,511	- 374,913	48,198
1800	35,248	132,565	106,579	46,776	- 456,673	- 370,113	44,938
1900	35,394	134,475	107,997	50,308	- 456,842	- 365,298	42,019
2000	35,521	136,294	109,367	53,854	- 457,019	- 360,472	39,391
2100	35,631	138,030	110,691	57,412	- 457,203	- 355,643	37,012
2200	35,728	139,690	111,972	60,980	- 457,397	- 350,802	34,849
2300	35,812	141,280	113,211	64,557	- 457,598	- 345,952	32,873
2400	35,887	142,806	114,413	68,142	- 457,810	- 341,092	31,061
2500	35,954	144,272	115,578	71,734	- 468,806	- 336,008	29,374
2600	36,013	145,683	116,709	75,332	- 469,020	- 330,692	27,797
2700	36,066	147,043	117,808	78,936	- 469,235	- 325,363	26,336
2800	36,113	148,356	118,875	82,545	- 469,451	- 320,035	24,980
2900	36,156	149,624	119,914	86,159	- 469,672	- 314,686	23,715
3000	36,195	150,850	120,925	89,777	- 469,896	- 309,348	22,536
3100	36,230	152,038	121,909	93,398	- 470,122	- 303,993	21,431
3200	36,262	153,188	122,869	97,022	- 470,352	- 298,629	20,395
3300	36,292	154,305	123,805	100,650	- 470,585	- 293,257	19,422
3400	36,319	155,389	124,718	104,281	- 470,822	- 287,879	18,505
3500	36,343	156,442	125,609	107,914	- 471,064	- 282,495	17,640
3600	36,366	157,466	126,480	111,549	- 471,308	- 277,100	16,822
3700	36,387	158,463	127,331	115,187	- 471,557	- 271,703	16,049
3800	36,406	159,433	128,163	118,827	- 471,810	- 266,293	15,315
3900	36,424	160,379	128,977	122,468	- 472,068	- 260,893	14,620
4000	36,440	161,301	129,774	126,111	- 714,687	- 251,181	13,724
4100	36,456	162,201	130,554	129,756	- 714,492	- 239,599	12,772
4200	36,470	163,080	131,318	133,402	- 714,298	- 228,010	11,865
4300	36,483	163,938	132,066	137,050	- 714,109	- 216,432	11,000
4400	36,496	164,777	132,800	140,699	- 713,929	- 204,863	10,176
4500	36,507	165,598	133,520	144,349	- 713,751	- 193,302	9,388
4600	36,518	166,400	134,226	148,000	- 713,578	- 181,735	8,634
4700	36,528	167,186	134,919	151,653	- 713,412	- 170,172	7,913
4800	36,538	167,955	135,599	155,306	- 713,251	- 158,609	7,222
4900	36,547	168,708	136,267	158,960	- 713,097	- 147,064	6,559
5000	36,555	169,447	136,923	162,615	- 712,947	- 135,512	5,923
5100	36,563	170,171	137,568	166,271	- 712,806	- 123,970	5,312
5200	36,571	170,881	138,202	169,928	- 712,668	- 112,419	4,725
5300	36,578	171,577	138,825	173,585	- 712,536	- 100,878	4,160
5400	36,585	172,261	139,438	177,243	- 712,415	- 89,349	3,616
5500	36,591	172,932	140,041	180,902	- 712,294	- 77,797	3,091
5600	36,597	173,592	140,634	184,562	- 712,185	- 66,271	2,586
5700	36,603	174,240	141,218	188,222	- 712,083	- 54,734	2,099
5800	36,608	174,876	141,793	191,882	- 711,985	- 43,202	1,628
5900	36,613	175,502	142,359	195,543	- 711,895	- 31,678	1,173
6000	36,618	176,117	142,917	199,205	- 711,813	- 20,144	,738

Dec. 31, 1970; June 30, 1971

DIBORON TETRAFLUOROMONOXIDE (B_2F_4O) (IDEAL GAS) GFW = 113.615 B_2F_4O

Point Group D_{2h} ΔHf°_0 = [-451.9 ± 2] kcal/mol

$S^\circ_{298.15}$ = [80.64 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -453.65 ± 2 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹	ω, cm⁻¹	ω, cm⁻¹
[1400] (1)	[145] (1)	[1370] (1)
[670] (1)	[800] (1)	[145] (1)
[320] (1)	[660] (1)	[1800] (1)
rotation	[660] (1)	[1155] (1)
[1370] (1)	[1600] (1)	[540] (1)

Bond Distance: B-O = [1.4] Å B-F = [1.32] Å

Bond Angle: O-B-O = [180°] F-B-F = [120°] σ = 4

Product of the Moments of Inertia: $I_AI_BI_C$ = [7.69965 x 10^{-113}] g^3 cm^6

Heat of Formation

Bidinosti and Coatsworth (1) have reported ΔHr_{1100} = 18.5 ± 3 kcal for the reaction $4BF_3(g) + B_2O_3(\ell) \rightleftarrows 3B_2OF_4(g)$. This value was obtained from a mass spectrometric study of the variation of the ion intensities with temperature of the BF_3^+ and $B_2OF_4^+$ species. Employing JANAF auxiliary values (2) we obtain $\Delta Hf_{1100}(B_2F_4O, g)$ = -455.75 ± 2 kcal/mol which reduces to $\Delta Hf^\circ_{298.15}$ = -453.65 ± 2 kcal/mol.

Heat Capacity and Entropy

By analogy with $B_2F_4(g)$ (3) free rotation of the BF_2 groups is assumed. Because of the large separation of the two BF_2 groups the molecule is considered to be planar. The B-O distance is assumed to be that in $BF_2O(g)$ (2) and the B-F distance that in $B_2F_4(g)$ (2). The vibrational frequencies are estimated by comparison with those for B_2F_4 (3); the values are given above in the order $3A_g$, A_u, $2B_{1g}$, $2B_{1u}$, B_{2g}, $3B_{2u}$, $3B_{3u}$. The individual moments of inertia are I_A = 1.64897 x 10^{-38} g cm^2, I_B = 6.05835 x 10^{-38} g cm^2 and I_C = 7.70732 x 10^{-38} g cm^2.

References

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Boron Oxide (B_2O_3)

(Crystal) GFW = 69.6202

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	* 2.221	* 302.525	* 302.525	INFINITE
100	4.957	2.625	23.029	* 2.040	* 303.397	* 297.434	650.041
200	10.479	7.856	1.588	1.254	* 301.307	* 288.778	315.561
298	14.959	12.895	12.895	.000	* 304.000	* 285.092	208.978
300	15.040	12.988	12.895	.028	* 304.002	* 284.976	207.604
400	18.630	17.830	13.531	1.719	* 304.021	* 278.627	152.234
500	21.340	22.292	14.844	3.724	* 303.938	* 272.286	119.016
600	23.450	26.377	16.430	5.968	* 303.777	* 265.969	96.879
700	25.150	30.124	18.123	8.401	* 303.543	* 259.684	81.077
800	26.570	33.578	19.842	10.989	* 303.242	* 253.441	69.237
900	27.770	36.778	21.548	13.707	* 302.877	* 247.237	60.037
1000	28.830	39.760	23.222	16.539	* 302.456	* 241.074	52.687
1100	29.760	42.552	24.853	19.469	* 301.992	* 234.960	46.682
1200	30.610	45.179	26.439	22.488	* 301.483	* 228.887	41.686
1300	31.380	47.660	27.977	25.588	* 300.936	* 222.860	37.466
1400	32.100	50.012	29.467	28.763	* 300.352	* 216.875	33.856
1500	32.770	52.250	30.912	32.007	* 299.736	* 210.936	30.733

Dec. 31, 1980; Dec. 31, 1964; June 30, 1971

BORON OXIDE (B_2O_3) (CRYSTAL) GFW = 69.6202 B_2O_3

ΔHf°_0 = -302.5 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 12.90 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -304.0 ± 0.5 kcal/mol

Tm = 723 ± 0.5 K

ΔHm^* = 5.753 ± 0.1 kcal/mol

Heat of Formation

The adopted $\Delta Hf^\circ_{298}(B_2O_3, c)$ = -304.0 ± 0.5 kcal/mol is calculated from JANAF $\Delta Hf^\circ_{298}(BF_3, g)$ = -271.42 ± 0.4 kcal/mol (1) and ΔHc°_{298} = -238.82 ± 0.39 kcal/mol for $B_2O_3(c) + 3\ F_2(g) \rightarrow 2\ BF_3(g) + 1.5\ O_2(g)$. The heat of combustion of $B_2O_3(c)$ in fluorine was determined by Johnson and Hubbard (2). The direct combustion of boron in oxygen has led to ΔHf°_{298}(glass) values which range from -280 to -368 kcal/mol (3, 4, 5, 6, 7, 8, 9) due to incomplete combustions or ill-defined states of combustion products. These values are not reliable.

A reliable heat of formation of boric oxide can be derived from heats of solution of $H_3BO_3(c)$ and $B_2O_3(c)$ which are listed below. Since the heat of dilution of aqueous H_3BO_3 (10) is relatively small, no correction has been applied to the reported heat of solution data. The derived ΔHf values given in the last column are in very good agreement with the values adopted.

Investigator	Heat of Solution (kcal/mol) $\Delta H_{soln}(B_2O_3, c)^{(a)}$	$\Delta H_{soln}(H_3BO_3, c)^{(b)}$	$\Delta Hr^{(c)}$ (kcal/mol)	$\Delta Hf^\circ_{298}(B_2O_3, c)^{(d)}$ (kcal/mol)
Stackelberg (11)	-3.56*	+5.3	-14.16	-303.83
Roth (12)	-3.41*	+5.10	-13.61	-304.38
Katz (13)	-3.49*	+5.3	-14.09	-303.90
Smisko (14)	-3.48	+5.27	-14.02	-303.97
Van Artsdalen (15)	-3.49	+5.17	-13.83	-304.16
Fasolino (16)	-3.45	+5.45	-14.35	-303.64

* The heat of solution of B_2O_3(amorph.) was combined with ΔHr(25°C) = 4.44 kcal/mol (2) to obtain the $\Delta H^\circ_{soln}(B_2O_3, c)$.

(a) $B_2O_3(c) + 3\ H_2O(\ell) \rightarrow 2\ H_3BO_3(aq)$ (b) $H_3BO_3(c) \rightarrow H_3BO_3(aq)$ (c) $B_2O_3(c) + 3\ H_2O(\ell) \rightarrow 2\ H_3BO_3(c)$

(d) The auxiliary data $\Delta Hf^\circ_{298}(H_3BO_3, c)$ = -261.47 ± 0.2 kcal/mol (1) and $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 kcal/mol (10) are used in the calculation.

Other solution calorimetric measurements (17, 18, 19) which involve the hydrolysis of $B_2H_6(g)$ and $BCl_3(\ell)$ lead to heats of formation of boric oxide (c) with a relatively large uncertainty since the techniques were indirect and many questionable auxiliary data were employed in the derivation.

Heat Capacity and Entropy

The adopted heat capacities are derived from Cp data of Kerr, Hersh and Johnston (20) and Shmidt (21) in the temperature regions 18-296.6 K and 303-703 K, respectively. These two sets of Cp data were measured adiabatically and are smoothly joined at 298 K by a polynomial curve fitting technique. The derived entropy, $S^\circ_{298.15}$ = 12.90 ± 0.1 eu, is based on $S^\circ_{18.08}$ = 0.025 eu.

Kelley (22) also measured low temperature Cp from 53 to 295 K which are in very good agreement with the values adopted. Southard (23) determined high temperature enthalpy data from 350 to 721.5 K by drop calorimetry. The deviations of the observed enthalpy data from the adopted values are about 5% at 360 K, 1% at 570 K and 0.5% at 720 K.

Melting Data

The melting point, 723 ± 0.5 K, was determined by Shmidt (21), in excellent agreement with the value 723 ± 2 K reported by Kracek et al. (24). The adopted heat of fusion, ΔHm = 5.75 ± 0.1 kcal/mol, is derived from ΔHr(298 K) = 4.44 kcal/mol (2) for B_2O_3(crystal) → B_2O_3(amorph) and the adopted relative enthalpies of the two forms at 723 K. This value is in reasonable agreement with ΔHm(723 K) = 5.87 ± 0.1 kcal/mol determined calorimetrically by Shmidt (21).

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Boron Oxide (B_2O_3)

(Liquid) GFW = 69.6202

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	= 2.404	= 298.268	= 298.268	INFINITE
100	6.163	7.810	29.241	= 2.143	= 299.060	= 293.615	641.695
200	10.974	13.588	19.997	= 1.282	= 299.402	= 288.019	314.733
298	15.010	18.749	18.749	.000	= 299.560	= 282.398	207.003
300	15.080	18.842	18.749	.028	= 299.562	= 282.292	205.649
400	18.500	23.662	19.383	1.711	= 299.589	= 276.527	151.087
500	21.320	28.109	20.889	3.710	= 299.513	= 270.769	118.353
600	31.750	33.066	22.316	6.450	= 298.855	= 265.060	96.548
700	31.020	37.898	24.207	9.583	= 297.921	= 259.503	81.021
800	31.000	42.037	26.183	12.684	= 297.107	= 254.074	69.410
900	31.000	45.689	28.151	15.784	= 296.360	= 248.740	60.402
1000	31.000	48.955	30.071	18.884	= 295.671	= 243.484	53.213
1100	31.000	51.910	31.924	21.984	= 295.037	= 238.298	47.345
1200	31.000	54.607	33.704	25.084	= 294.447	= 233.165	42.465
1300	31.000	57.088	35.408	28.184	= 293.901	= 228.081	38.344
1400	31.000	59.388	37.040	31.284	= 293.391	= 223.037	34.818
1500	31.000	61.524	38.602	34.384	= 292.919	= 218.031	31.767
1600	31.000	63.525	40.098	37.484	= 292.481	= 213.050	29.101
1700	31.000	65.404	41.532	40.584	= 292.074	= 208.099	26.753
1800	31.000	67.176	42.908	43.684	= 291.697	= 203.171	24.668
1900	31.000	68.852	44.229	46.784	= 291.346	= 198.263	22.805
2000	31.000	70.443	45.501	49.884	= 291.014	= 193.373	21.131
2100	31.000	71.955	46.725	52.984	= 290.701	= 188.496	19.617
2200	31.000	73.397	47.904	56.084	= 290.409	= 183.637	18.243
2300	31.000	74.775	49.043	59.184	= 290.133	= 178.792	16.989
2400	31.000	76.094	50.143	62.284	= 289.876	= 173.953	15.841
2500	31.000	77.360	51.206	65.384	= 300.410	= 168.913	14.766
2600	31.000	78.576	52.236	68.484	= 300.168	= 163.657	13.757
2700	31.000	79.746	53.233	71.584	= 299.935	= 158.409	12.822
2800	31.000	80.873	54.200	74.684	= 299.710	= 153.173	11.956
2900	31.000	81.961	55.139	77.784	= 299.492	= 147.938	11.149
3000	31.000	83.012	56.051	80.884	= 299.281	= 142.716	10.397

Dec. 31, 1960; Dec. 31, 1964; June 30, 1971

BORON OXIDE (B_2O_3) (LIQUID) GFW = 69.6202 B_2O_3

$S^\circ_{298.15}$ = 18.75 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −299.56 ± 0.6 kcal/mol

Tm = 723 ± 0.5 K

ΔHm° = 5.753 ± 0.1 kcal/mol

Tb = 2338.2 K

ΔHv° = 86.4 kcal/mol

Heat of Formation

The adopted value, $\Delta Hf^\circ_{298}(\ell)$ = −299.56 kcal/mol, is calculated from $\Delta Hr^\circ(25^\circ C)$ = 4.44 ± 0.06 kcal/mol (1) for $B_2O_3(c) \rightarrow B_2O_3(glass)$, using JANAF $\Delta Hf^\circ_{298}(B_2O_3, c)$ = −304.0 ± 0.5 kcal/mol. The value of ΔHr° was determined as the difference of heats of solution of crystalline and glassy B_2O_3 by Johnson and Hubbard (1).

Heat Capacity and Entropy

Heat capacities of B_2O_3(glass) have been measured adiabatically in the temperature regions 59.6-295 K by Turdakin and Tarasov (2), and 306.7-910.8 K by Shmidt (3), respectively. Thomas and Parks (4) also measured isothermally the heat capacities from 308 to 594 K in a radiation calorimeter. Both Shmidt (3) and Thomas and Parks (4) observed a rapid rise in heat capacity in the region 500-580 K. This rise indicates a glass transition in liquid B_2O_3.

Southard (5) and Krasovitskaya et al. (6) determined enthalpy changes by drop calorimetry in the temperature regions 381.7-1776.8 K and 1015-2154 K, respectively.

We have adopted the Cp data of Turdakin (60-295 K) and Shmidt (307-600 K) which are smoothly joined at 298 K by a polynomial curve fitting technique. The drop calorimetric data of Southard in this region 381 to 600 K are less reliable since the final state of the sample was dependent upon previous thermal history through the glass transition region. Above the melting point, we have chosen a constant Cp, 31.0 cal/mol deg, which is a compromise between the adiabatic Cp and drop calorimetric data. The uncertainty of this choice, ±0.6 cal/mol deg, is within the experimental errors of both techniques.

Melting Data

See JANAF B_2O_3(c) table dated June 30, 1971.

Vaporization Data

The boiling point is calculated as the temperature at which ΔGr = 0 for $B_2O_3(\ell) \rightarrow B_2O_3(g)$. The heat of vaporization is the difference in ΔHf° at the boiling point between liquid and gas.

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Boron Oxide (B_2O_3)

(Ideal Gas) GFW = 69.6202

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	= 3.427	= 199.530	= 199.530	INFINITE
100	9.570	54.224	80.030	= 2.581	= 199.737	= 198.934	434.770
200	13.224	61.962	69.176	= 1.443	= 199.803	= 198.095	216.468
298	15.979	67.795	67.795	.000	= 199.800	= 197.261	144.596
300	16.020	67.894	67.795	.030	= 199.800	= 197.246	143.693
400	17.860	72.771	68.488	1.729	= 199.811	= 196.393	107.304
500	19.207	76.907	69.736	3.585	= 199.877	= 195.532	85.467
600	20.272	80.507	71.238	5.561	= 199.984	= 194.653	70.902
700	21.137	83.699	72.794	7.633	= 200.111	= 193.754	60.493
800	21.845	86.569	74.340	9.783	= 200.248	= 192.839	52.681
900	22.426	89.177	75.846	11.998	= 200.386	= 191.905	46.601
1000	22.902	91.565	77.300	14.265	= 200.529	= 190.952	41.733
1100	23.294	93.767	78.698	16.576	= 200.685	= 189.989	37.747
1200	23.618	95.808	80.040	18.922	= 200.849	= 189.008	34.423
1300	23.888	97.709	81.327	21.297	= 201.027	= 188.015	31.608
1400	24.115	99.488	82.561	23.698	= 201.217	= 187.006	29.193
1500	24.306	101.159	83.746	26.119	= 201.424	= 185.987	27.098
1600	24.468	102.733	84.884	28.558	= 201.647	= 184.948	25.263
1700	24.607	104.220	85.978	31.012	= 201.886	= 183.897	23.642
1800	24.726	105.630	87.031	33.479	= 202.142	= 182.833	22.199
1900	24.829	106.970	88.045	35.956	= 202.413	= 181.753	20.906
2000	24.919	108.246	89.024	38.444	= 202.694	= 180.659	19.741
2100	24.998	109.464	89.968	40.940	= 202.985	= 179.548	18.686
2200	25.067	110.628	90.881	43.443	= 203.290	= 178.425	17.725
2300	25.128	111.744	91.764	45.953	= 203.604	= 177.290	16.846
2400	25.182	112.814	92.619	48.469	= 203.931	= 176.135	16.039
2500	25.230	113.843	93.448	50.989	= 215.045	= 174.755	15.277
2600	25.273	114.834	94.251	53.514	= 215.378	= 173.137	14.553
2700	25.312	115.788	95.031	56.044	= 215.715	= 171.503	13.882
2800	25.347	116.709	95.789	58.577	= 216.057	= 169.862	13.258
2900	25.379	117.599	96.526	61.113	= 216.402	= 168.200	12.676
3000	25.407	118.460	97.243	63.652	= 216.753	= 166.535	12.132
3100	25.434	119.294	97.941	66.194	= 217.106	= 164.856	11.622
3200	25.457	120.102	98.621	68.739	= 217.464	= 163.166	11.144
3300	25.479	120.885	99.284	71.286	= 217.827	= 161.462	10.693
3400	25.499	121.646	99.930	73.835	= 218.194	= 159.747	10.268
3500	25.517	122.386	100.561	76.386	= 218.564	= 158.029	9.868
3600	25.534	123.105	101.178	78.938	= 218.939	= 156.289	9.488
3700	25.550	123.805	101.780	81.492	= 219.318	= 154.544	9.129
3800	25.564	124.486	102.368	84.048	= 219.699	= 152.784	8.787
3900	25.577	125.150	102.944	86.605	= 220.084	= 151.027	8.463
4000	25.590	125.798	103.507	89.163	= 462.832	= 144.960	7.920
4100	25.601	126.430	104.059	91.723	= 462.763	= 137.014	7.304
4200	25.612	127.047	104.599	94.284	= 462.694	= 129.063	6.716
4300	25.622	127.650	105.128	96.845	= 462.630	= 121.120	6.156
4400	25.631	128.239	105.646	99.408	= 462.572	= 113.181	5.622
4500	25.640	128.815	106.155	101.972	= 462.516	= 105.244	5.111
4600	25.648	129.379	106.654	104.536	= 462.462	= 97.299	4.623
4700	25.656	129.931	107.143	107.101	= 462.414	= 89.361	4.155
4800	25.663	130.471	107.623	109.667	= 462.368	= 81.420	3.707
4900	25.670	131.000	108.095	112.234	= 462.327	= 73.497	3.278
5000	25.676	131.519	108.558	114.801	= 462.288	= 65.559	2.866
5100	25.682	132.027	109.014	117.369	= 462.256	= 57.620	2.469
5200	25.688	132.526	109.461	119.937	= 462.225	= 49.692	2.089
5300	25.693	133.015	109.901	122.506	= 462.196	= 41.756	1.722
5400	25.698	133.496	110.333	125.076	= 462.174	= 33.830	1.369
5500	25.703	133.967	110.759	127.646	= 462.151	= 25.884	1.029
5600	25.708	134.430	111.177	130.217	= 462.137	= 17.966	.701
5700	25.712	134.885	111.589	132.788	= 462.126	= 10.032	.385
5800	25.716	135.333	111.995	135.359	= 462.118	= 2.097	.079
5900	25.720	135.772	112.394	137.931	= 462.113	5.833	= .216
6000	25.724	136.205	112.787	140.503	= 462.114	13.771	= .502

Mar. 31, 1961; Dec. 31, 1964; June 30, 1971

BORON OXIDE (B_2O_3) (IDEAL GAS) GFW = 69.6202 B_2O_3

Point Group C_{2v}

ΔHf°_0 = -199.5 ± 1 kcal/mol

$S^\circ_{298.15}$ = 67.8 ± 1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -199.8 ± 1 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies (ω, cm^{-1}, all singly degenerate)

2073 730 521 [172] [460] 2073 1240 457 480

Bond Distance: O-B = 1.36 ± 0.02 Å B=O = 1.20 ± 0.03 Å

Bond Angle: O-B-O = 180° B-O-B = [120°] σ = 2

Product of the Moments of Inertia: $I_A I_B I_C = 3.15302 \times 10^{-114}$ g^3 cm^6

Heat of Formation

The vapor pressure of $B_2O_3(\ell)$ was measured by many investigators using various methods. Second and third law analyses of these data (1-11) are given below. We have adopted the 3rd law heat of vaporization, ΔHv°_{298} = 99.75 kcal/mol, to derive $\Delta Hf^\circ_{298}(B_2O_3, g)$ = -199.8 ± 1 kcal/mol, using $\Delta Hf^\circ_{298}(B_2O_3, \ell)$ = -299.56 kcal/mol. The adopted ΔHv°_{298} is calculated from Hildenbrand's data (1) and this value also serves as an average of all derived heats of vaporization except that of Cole (11). The uncertainty is assigned to be at least ±1 kcal/mol since the bending frequency was estimated to be either 172 or 260 cm^{-1} (12) which could lead to a difference ±1 kcal/mol in the ΔHv calculation through the free energy functions of $B_2O_3(g)$.

Investigator	Temp (K)	Method	No. of Points	ΔHv_{298} (kcal/mol) 2nd law	3rd law	Drift (eu)[a]	$\Delta Hf^\circ_{298}(g)$[b] (kcal/mol)
Hildenbrand (1)	1436-1584	Torsion-effusion	24	100.97± 1.34	99.75±0.35	-0.8 ± 0.7	-199.81
Greene (2)	1946-2419	Transpiration and direct boiling point	16	92.55± 2.52	102.80±1.8	4.5 ± 1.2	-196.76
Büchler (3)	1300	Mass spectrometric	--	100.5 ± 3	---	---	-199.06
Blackburn (4)	1325-1547	Knudsen-effusion	9	93.08± 1.37	99.08±0.74	4.2 ± 1.0	-200.48
Sommer (5)	1228-1641	Mass spectrometric	16	92.32± 0.94	99.17±1.40	4.6 ± 0.6	-200.39
Nesmeyanov (6)	1229-1515	Knudsen-effusion	12	82.65± 2.85	98.52±1.70	11.1 ± 2.0	-201.04
Scheer (7)	1414-1621	Torsion-effusion	19	95.55± 0.91	101.50±0.56	3.80± 0.62	-198.06
Searcy (8)	1501-1566	Effusion	6	101.67±12.46	98.31±0.79	-2.2 ± 8.1	-201.25
Soulen (9)	1567-1808	Carrier gas	6	66.17± 7.8	98.00±5.06	18.8 ± 4.9	-201.56
Speiser (10)	1331-1642	Knudsen-effusion	22[c]	89.64± 1.62	99.06±1.44	6.4 ± 1.1	-200.50
Cole (11)	1473-1673	Carrier gas	6	73.27± 2.28	87.36±1.48	9.0 ± 1.4	-212.20

a: Drift is defined as the difference between ΔSr°(JANAF functions) and ΔSr°(2nd law). b: The 3rd law ΔHv_{298} is used to derive $\Delta Hf^\circ_{298}(g)$, except the ref. 3. c: Four points were rejected due to failure of a statistical test.

Heat Capacity and Entropy

The V shaped molecular structure for B_2O_3 was proposed by many investigators on the basis of infrared spectrometry (12, 13) and electron diffraction (14). This structure has been reconfirmed by recent electric deflection (15) and electron diffraction (16) studies which definitely rule out any non-polar structure such as the bipyramidal model as suggested by Hanst et al. (17). Thus the assignment of vibrational frequencies, based on the V shaped structure, should be valid. The adopted vibrational frequencies (including two estimated values) were obtained from Sommer et al. (12) in their infrared spectrometric studies. Their values have been adjusted to the average isotopic species. Other spectrometric data (13, 18) are in reasonable agreement with those adopted in the tabulation.

Akishin and Spiridonov (14) determined the bond distances and the bond angle (B-O-B = 95°) by electron diffraction. We have adopted their bond distances in the tabulation, but tentatively select an apex angle B-O-B = 120° based on force-constant calculations of Weltner and Warn (13) and Sommer et al. (12). The three principal moments of inertia are $I_A = 2.9760 \times 10^{-39}$, $I_B = 31.0956 \times 10^{-39}$ and $I_C = 34.0716 \times 10^{-39}$ g cm^2.

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BARIUM (Ba) (REFERENCE STATE) GFW = 137.34 Ba

Barium (Ba)

(Reference State) GFW = 137.34

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	* 1.652	.000	.000	.000
100	5.808	8.146	20.607	* 1.246	.000	.000	.000
200	6.302	12.343	15.533	* .638	.000	.000	.000
298	6.715	14.932	14.932	.000	.000	.000	.000
300	6.726	14.974	14.932	.012	.000	.000	.000
400	7.942	17.040	15.206	.734	.000	.000	.000
500	10.455	19.066	15.774	1.646	.000	.000	.000
600	8.112	21.083	16.499	2.751	.000	.000	.000
700	10.175	22.485	17.253	3.663	.000	.000	.000
800	9.337	23.868	17.997	4.697	.000	.000	.000
900	9.337	24.966	18.711	5.630	.000	.000	.000
1000	9.337	25.951	19.387	6.564	.000	.000	.000
1100	10.040	28.836	20.203	9.498	.000	.000	.000
1200	9.770	29.699	20.959	10.488	.000	.000	.000
1300	9.560	30.473	21.682	11.454	.000	.000	.000
1400	9.400	31.175	22.317	12.402	.000	.000	.000
1500	9.290	31.820	22.929	13.336	.000	.000	.000
1600	9.230	32.417	23.503	14.262	.000	.000	.000
1700	9.220	32.976	24.044	15.184	.000	.000	.000
1800	9.259	33.504	24.555	16.107	.000	.000	.000
1900	9.349	34.007	25.040	17.037	.000	.000	.000
2000	9.490	34.490	25.500	17.979	.000	.000	.000
2100	9.684	34.957	25.939	18.937	.000	.000	.000
2200	7.844	51.131	26.917	53.270	.000	.000	.000
2300	8.392	51.491	27.978	54.081	.000	.000	.000
2400	8.957	51.861	28.965	54.949	.000	.000	.000
2500	9.526	52.238	29.889	55.873	.000	.000	.000
2600	10.086	52.622	30.755	56.854	.000	.000	.000
2700	10.625	53.013	31.573	57.889	.000	.000	.000
2800	11.131	53.409	32.345	58.978	.000	.000	.000
2900	11.597	53.808	33.079	60.114	.000	.000	.000
3000	12.017	54.208	33.776	61.295	.000	.000	.000
3100	12.385	54.608	34.442	62.516	.000	.000	.000
3200	12.701	55.007	35.078	63.771	.000	.000	.000
3300	12.963	55.402	35.688	65.054	.000	.000	.000
3400	13.174	55.792	36.274	66.362	.000	.000	.000
3500	13.336	56.176	36.837	67.688	.000	.000	.000
3600	13.454	56.554	37.379	69.027	.000	.000	.000
3700	13.532	56.923	37.902	70.377	.000	.000	.000
3800	13.573	57.285	38.408	71.733	.000	.000	.000
3900	13.585	57.638	38.896	73.091	.000	.000	.000
4000	13.570	57.981	39.369	74.449	.000	.000	.000
4100	13.534	58.316	39.827	75.804	.000	.000	.000
4200	13.481	58.642	40.271	77.155	.000	.000	.000
4300	13.415	58.958	40.702	78.500	.000	.000	.000
4400	13.338	59.266	41.121	79.837	.000	.000	.000
4500	13.255	59.564	41.527	81.167	.000	.000	.000
4600	13.166	59.855	41.923	82.488	.000	.000	.000
4700	13.076	60.137	42.307	83.800	.000	.000	.000
4800	12.984	60.411	42.681	85.103	.000	.000	.000
4900	12.892	60.678	43.046	86.397	.000	.000	.000
5000	12.802	60.938	43.401	87.682	.000	.000	.000
5100	12.714	61.190	43.748	88.958	.000	.000	.000
5200	12.629	61.436	44.085	90.225	.000	.000	.000
5300	12.547	61.676	44.415	91.484	.000	.000	.000
5400	12.469	61.910	44.737	92.734	.000	.000	.000
5500	12.394	62.138	45.051	93.977	.000	.000	.000
5600	12.322	62.361	45.358	95.213	.000	.000	.000
5700	12.254	62.578	45.658	96.442	.000	.000	.000
5800	12.188	62.791	45.952	97.664	.000	.000	.000
5900	12.126	62.999	46.239	98.880	.000	.000	.000
6000	12.067	63.202	46.520	100.089	.000	.000	.000

Dec. 31, 1970

0	to	582.53°K	Crystal alpha
582.53	to	768.13°K	Crystal beta
768.13	to	1000°K	Crystal gamma
1000	to	2122.16°K	Liquid
2122.16	to	6000°K	Ideal Monatomic Gas

Barium, Alpha-Beta-Gamma (Ba)

(Crystal) GFW = 137.34

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	1.652	.000	.000	INFINITE
100	5.806	8.146	20.607	1.246	.000	.000	.000
200	6.302	12.343	15.533	.638	.000	.000	.000
298	6.715	14.932	14.932	.000	.000	.000	.000
300	6.726	14.974	14.932	.012	.000	.000	.000
400	7.942	17.040	15.206	.734	.000	.000	.000
500	10.455	19.066	15.774	1.646	.000	.000	.000
600	8.112	21.083	16.499	2.751	.000	.000	.000
700	10.125	22.485	17.253	3.663	.000	.000	.000
800	9.337	23.868	17.997	4.697	.000	.000	.000
900	9.337	24.968	18.711	5.630	.000	.000	.000
1000	9.337	25.951	19.387	6.564	.000	.000	.000
1100	9.337	26.841	20.025	7.498	2.000	.196	.039
1200	9.337	27.654	20.627	8.431	2.057	.398	.073
1300	9.337	28.401	21.197	9.365	2.089	.605	.102
1400	9.337	29.093	21.737	10.299	2.103	.812	.127
1500	9.337	29.737	22.249	11.233	2.103	1.020	.149

Dec. 31, 1970

BARIUM, ALPHA-BETA-GAMMA (Ba) (CRYSTAL) GFW = 137.34 Ba

$S^\circ_{298.15}$ = 14.932 ± [0.2] gibbs/mol

Tt = [582.53]°K (α→β)

Tt = [768.13]°K (β→γ)

Tm = 1000 ± 3°K

ΔHf°_0 = 0 kcal/mol

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

ΔHt° = [0.0] kcal/mol

ΔHt° = [0.0] kcal/mol

ΔHm° = 1.915 ± 0.15 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 42.8 ± 1.2 kcal/mol

Heat of Formation: Zero by definition.

Heat Capacity and Entropy

The adopted values below 298°K are based on Cp°(18-370°K) of Furukawa and Ishihara (1) and Cp°(1.5-20°K) of Roberts (2). S°_{298} is calculated from Cp° based on an extrapolation of about 0.001 gibbs/mol below 1.5°K. We estimate that S°_{298} is uncertain by about 0.2 gibbs/mol, due mainly to possible effects of impurities. Furukawa and Ishihara (1) reported impurities (in mole %) of about 3% BaO, 1% Sr and 0.2% Ca. Further details on adjustment of the data for impurities are given in the original paper (1).

Relative enthalpies were measured by Jauch (3), Shpil'rain (4) and Ditmars and Douglas (5). Earlier reviewers dismissed the abnormally high Cp° values of Jauch as due to a very impure sample. The new data confirm this decision, but at least one new study (5) may also involve bias due to impurities. Separate portions from a common sample consisting of three Ba rods were used in the heat capacity study (1), the enthalpy study (5) and the analytical studies (1, 5). The calorimetric data suggest variability in the impurity contents of the separate portions. The second new enthalpy study (4) used Ba which was not analyzed for O or N which are the most likely contaminants. Since the premelting effect in the enthalpy at 979°K appears to be 1/4 as large in (4) as in (5), the sample of (4) may have been more pure; however, such a conclusion would be quite speculative. Liquid enthalpies are in reasonable agreement, but the crystal enthalpies of (4) are 4 to 20% lower than those of (5). Another major difference is that (4) suggests a single "transition" near 650°K, while (5) suggests two "transitions" near 580 and 770°K (see further discussion in Transition Data). Further confusion arises because the enthalpies reported (4) for CsF(c, ℓ) are unreasonably large.

We tentatively adopt the smoothed Cp° of Ditmars and Douglas (5), pending resolution of the transition discrepancy. The following alternative functions reproduce the enthalpies of Shpil'rain (4) and provide estimates of the possible bias in the adopted functions. Ba(α): Cp°(gibbs/mol) = 5.023 ± 0.005657 T (298-650°K), ΔHt = 0.345 kcal/mol at 650°K; Ba(γ): Cp°(gibbs/mol) = 9.4 (650-999.6°K), ΔHm° = 2.048 kcal/mol at 999.6°K; Ba(ℓ): Cp°(gibbs/mol) = 10.0 (999.6-1300°K). There is reasonable agreement between the alternative and adopted Cp° for Ba(ℓ) and Ba(γ), suggesting that the γ-phases are identical in the two studies. Cp°(α) from the equation is a reasonable extension of the data below 298°K (1); i.e., Cp° does not show the abnormally steep rise just above 300°K which appears in the enthalpy data (5) and, to a lesser degree, in the Cp° data (1). The alternative functions suggest that the adopted γ-phase entropy may be biased by about +0.6 gibbs/mol (about +6% in $S^\circ_T - S^\circ_{298}$) due to impurities. Ditmars and Douglas stressed the possibility of such systematic errors (5) and estimated errors of up to 5% in Cp° and H°. Our alternative functions suggest that the maximum error in Cp°(α) may be much larger than 5%.

Transition Data

Recent data for Sr and Ca indicate that the pure metals exist in the fcc and bcc polymorphs but that impurities probably stabilize the hcp form. Although enthalpy data (4, 5) suggest a similar controversy for Ba, the pure metal is usually reported to have the bcc form at all temperatures at atmospheric pressure (6-9). Several high-pressure polymorphs are known (10-12). Earlier literature (13) contains much evidence for a "transition" near 648°K at one atmosphere; this is consistent with new enthalpy data (4) and could correspond to the "transition" found by Bridgman (13) near 17 kbar at room temperature. Bridgman's "transition" is in dispute; it seems to involve a very small volume contraction (12, 14) and no obvious change in X-ray pattern (15). We speculate that these two "transitions" are identical; however, evidence for their being a property of pure Ba is inconclusive. The main support comes from the relatively small premelting effect in enthalpy (4). The enthalpy data (4) are insufficient to distinguish whether the "transition" is first or second order.

We tentatively adopt the two "transitions" with zero enthalpies selected by Ditmars and Douglas (5). These values are placed in brackets to emphasize that there is no confirmatory evidence whatsoever. The authors suggest that these "transitions" may have resulted wholly from impurities. We speculate further that Tt = 582°K could be due to impurity lowering of Tt = 650°K, while Tt = 768°K could result from crossing of a solid-solubility limit below the eutectic temperature of the Ba-BaO system. This case would favor the alternative functions given above. It is also possible that the Sr and Ca impurities could nucleate other polymorphs.

The adopted functions include ΔHt° = 0.97 cal/mol at 57°K from a small λ-anomaly observed in Cp° between 50 and 60°K (1).

Melting Data and Sublimation Data: See Ba(ℓ) and Ba(g) for details.

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Ba

Barium (Ba)

(Liquid) GFW = 137.34

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	6.715	15.853	15.853	.000	1.192	.917	.672
300	6.726	15.894	15.853	.012	1.192	.916	.667
400	7.942	17.961	16.127	.734	1.191	.823	.450
500	10.455	19.987	16.694	1.646	1.192	.731	.320
600	12.109	22.126	17.421	2.823	1.263	.638	.232
700	11.594	23.953	18.226	4.007	1.536	.508	.159
800	11.129	25.470	19.041	5.143	1.637	.355	.097
900	10.715	26.757	19.829	6.235	1.796	.186	.045
1000	10.350	27.866	20.579	7.284	1.915	.000	.000
1100	10.040	28.838	21.286	8.307	.000	.000	.000
1200	9.770	29.699	21.952	9.297	.000	.000	.000
1300	9.540	30.473	22.578	10.263	.000	.000	.000
1400	9.400	31.175	23.168	11.210	.000	.000	.000
1500	9.290	31.820	23.723	12.144	.000	.000	.000
1600	9.230	32.417	24.248	13.070	.000	.000	.000
1700	9.220	32.976	24.745	13.992	.000	.000	.000
1800	9.259	33.504	25.217	14.916	.000	.000	.000
1900	9.349	34.007	25.667	15.846	.000	.000	.000
2000	9.490	34.490	26.095	16.787	.000	.000	.000
2100	9.684	34.957	26.507	17.745	.000	.000	.000
2200	9.926	35.413	26.901	18.726	−33.353	1.276	.122
2300	10.222	35.861	27.281	19.733	−33.157	2.794	.265
2400	10.566	36.303	27.648	20.772	−32.986	4.353	.396
2500	10.960	36.742	28.003	21.848	−32.834	5.906	.516
2600	11.402	37.180	28.347	22.965	−32.697	7.452	.626
2700	11.896	37.620	28.683	24.130	−32.566	8.995	.728
2800	12.440	38.062	29.010	25.346	−32.440	10.531	.822
2900	13.034	38.509	29.330	26.619	−32.303	12.064	.909
3000	13.680	38.961	29.643	27.955	−32.149	13.591	.990
3100	14.376	39.421	29.951	29.357	−31.967	15.113	1.065
3200	15.124	39.889	30.254	30.832	−31.746	16.628	1.136
3300	15.922	40.367	30.553	32.383	−31.479	18.136	1.201
3400	16.770	40.854	30.849	34.018	−31.153	19.634	1.262
3500	17.670	41.353	31.142	35.739	−30.757	21.122	1.319

Dec. 31, 1970

BARIUM (Ba) (LIQUID) GFW = 137.34 Ba

$S^\circ_{298.15}$ = [15.853] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [1.192] kcal/mol

Tm = 1000 ± 3°K

ΔHm° = 1.915 ± 0.15 kcal/mol

Tb = [2122.16]°K

ΔHv° = [33.523] kcal/mol

Heat of Formation

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

Heat Capacity and Entropy

Cp° is based on the parabolic equation derived by Douglas and Krause (1) from enthalpy data of Ditmars and Douglas (2). The enthalpy data (1003 to 1173°K) may be biased due to impurities in the sample (2); however, enthalpy data (1035 to 1253°K) of Shpil'rain (3) are in reasonable agreement. This suggests that the large discrepancies for Ba(c) are partially compensated by different values of ΔHm°. Detailed discussions of the discrepancies and possible alternative functions are given on the crystal table. The alternative functions, derived from the possibly purer sample of Shpil'rain (3), suggest that the adopted liquid entropies may be biased by about +0.4 gibbs/mol.

Douglas and Krause emphasized the uncertain nature (1) of the parabolic extrapolation of Cp° from 1200 to 2000°K. The extrapolation is reasonable provided that the temperature coefficient of Cp° is not grossly biased due to effects of impurities on the observed enthalpies. Such bias seems unlikely because of the agreement in enthalpy between samples of different purity (2, 3) and because the impurites (2) are present in amounts much below their solubility limits (2, 4, 5) in Ba(ℓ). We note also that S°_{2000} is not significantly changed when the parabolic fit is replaced by a two-constant fit in which Cp° approaches a constant (8.48 gibbs/mol) at high temperature.

The parabolic Cp° is extrapolated to 580°K, the assumed glass transition temperature. Cp° below 580°K is taken to be the same as the crystal. S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data

Ditmars and Douglas (2) considered early melting point data and arbitrarily selected 991°K. Recent data yield higher values of 998 ± 1 (6, 7) and 1002 ± 1°K (8-10). These values represent more carefully purified samples. We adopt 1000 ± 3°K and adjust ΔHm° slightly so that the result is consistent with the smoothed enthalpy (2) of the liquid. Alternative functions based on enthalpies of Shpil'rain (3) suggest that the adopted ΔHm° may be too small by about 0.15 kcal/mol (see the crystal table).

Vaporization Data

Tb is calculated as the temperature at which $\Delta Gr^\circ = 0$ for Ba(ℓ) → Ba(g). ΔHv° is the difference between ΔHf°(g) and ΔHf°(ℓ) at Tb. Bohdansky and Schins (11) reported Tb = 2063°K based on extrapolation of their vapor pressure data from 2024°K. Our calculated Tb is some 60° higher due to the entropy difference between the adopted functions and vapor pressure data (11) and to adoption of the mean third-law ΔHs° rather than the apparent value at 2024°K. See Ba(g) for further details.

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Barium (Ba)

(Ideal Gas) GFW = 137.34

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	− 1.481	42.971	42.971	INFINITE
100	4.968	35.236	45.080	− .984	43.062	40.353	− 88.191
200	4.968	38.679	41.117	− .488	42.950	37.683	− 41.178
298	4.968	40.663	40.663	.000	42.800	35.128	− 25.750
300	4.968	40.694	40.663	.009	42.797	35.081	− 25.557
400	4.968	42.123	40.858	.506	42.572	32.539	− 17.778
500	4.968	43.231	41.226	1.003	42.157	30.074	− 13.145
600	4.968	44.137	41.638	1.500	41.549	27.718	− 10.096
700	4.968	44.903	42.051	1.996	41.133	25.441	− 7.943
800	4.968	45.566	42.450	2.493	40.596	23.237	− 6.348
900	4.970	46.152	42.829	2.990	40.160	21.094	− 5.122
1000	4.976	46.675	43.188	3.487	39.723	18.999	− 4.152
1100	4.991	47.150	43.527	3.986	37.288	17.144	− 3.406
1200	5.022	47.588	43.847	4.486	36.798	15.334	− 2.793
1300	5.079	47.990	44.151	4.991	36.337	13.565	− 2.280
1400	5.171	48.369	44.439	5.503	35.901	11.829	− 1.847
1500	5.307	48.731	44.713	6.027	35.491	10.124	− 1.475
1600	5.496	49.079	44.975	6.566	35.104	8.446	− 1.154
1700	5.743	49.419	45.226	7.128	34.744	6.791	− .873
1800	6.052	49.756	45.469	7.717	34.410	5.156	− .626
1900	6.422	50.093	45.704	8.340	34.103	3.540	− .407
2000	6.848	50.433	45.931	9.003	33.824	1.938	− .212
2100	7.326	50.778	46.154	9.712	33.575	.350	− .036
2200	7.844	51.131	46.372	10.470	.000	.000	.000
2300	8.392	51.491	46.586	11.281	.000	.000	.000
2400	8.957	51.861	46.799	12.149	.000	.000	.000
2500	9.526	52.238	47.009	13.073	.000	.000	.000
2600	10.086	52.622	47.217	14.054	.000	.000	.000
2700	10.625	53.013	47.424	15.089	.000	.000	.000
2800	11.131	53.409	47.631	16.178	.000	.000	.000
2900	11.597	53.808	47.837	17.314	.000	.000	.000
3000	12.017	54.208	48.043	18.495	.000	.000	.000
3100	12.385	54.608	48.248	19.716	.000	.000	.000
3200	12.701	55.007	48.453	20.971	.000	.000	.000
3300	12.963	55.402	48.658	22.254	.000	.000	.000
3400	13.174	55.792	48.862	23.562	.000	.000	.000
3500	13.336	56.176	49.065	24.888	.000	.000	.000
3600	13.454	56.554	49.268	26.227	.000	.000	.000
3700	13.532	56.923	49.470	27.577	.000	.000	.000
3800	13.573	57.285	49.671	28.933	.000	.000	.000
3900	13.585	57.638	49.871	30.291	.000	.000	.000
4000	13.576	57.981	50.069	31.649	.000	.000	.000
4100	13.534	58.316	50.266	33.004	.000	.000	.000
4200	13.481	58.642	50.462	34.355	.000	.000	.000
4300	13.415	58.958	50.656	35.700	.000	.000	.000
4400	13.338	59.266	50.848	37.037	.000	.000	.000
4500	13.255	59.564	51.038	38.367	.000	.000	.000
4600	13.166	59.855	51.227	39.688	.000	.000	.000
4700	13.076	60.137	51.413	41.000	.000	.000	.000
4800	12.984	60.411	51.598	42.303	.000	.000	.000
4900	12.892	60.678	51.781	43.597	.000	.000	.000
5000	12.802	60.936	51.961	44.882	.000	.000	.000
5100	12.714	61.190	52.140	46.158	.000	.000	.000
5200	12.629	61.436	52.316	47.425	.000	.000	.000
5300	12.547	61.676	52.490	48.684	.000	.000	.000
5400	12.469	61.910	52.663	49.934	.000	.000	.000
5500	12.394	62.138	52.833	51.177	.000	.000	.000
5600	12.322	62.361	53.001	52.413	.000	.000	.000
5700	12.254	62.578	53.167	53.642	.000	.000	.000
5800	12.186	62.791	53.331	54.864	.000	.000	.000
5900	12.120	62.999	53.493	56.080	.000	.000	.000
6000	12.067	63.202	53.654	57.289	.000	.000	.000

Dec. 31, 1970

BARIUM (Ba) (IDEAL GAS) GFW = 137.34 Ba

Ground State Configuration ^1S

$S^\circ_{298.15}$ = 40.663 gibbs/mol

ΔHf°_0 = 43.0 ± 1.2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 42.8 ± 1.2 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.0	1	22947	7	25704	3	33188	15	39765	[21]	[42000]	33
3034.0	3	23757	9	25957	5	33837	8	39905	[9]	[36440]	1
9215.5	5	23068	10	26160	3	35142	10	40736	3	[40000]	63
9596.6	7	23209	1	26816	7	34649	28	40893	15	[20000]	21
11395.4	5	23480	3	28230	1	35658	20	41097	9	[24000]	9
12266.0	1	23919	5	28554	3	35893	3	42012	3	[25000]	1
12636.6	3	24192	3	30237	5	36400	55	42436	9	[19000]	20
13514.7	5	24532	5	30771	15	36974	56	43264	3	[39000]	20
18060	3	24980	7	30803	9	37425	58	35500	9	[42000]	120
22065	5	25642	1	32547	3	38031	37	37700	9		

Heat of Formation

ΔHf° is ΔHs°, 42.8 ± 1.2 kcal/mol, selected from third-law analyses of pressure data tabulated below. The adopted value is from the recent boiling-point study of Bohdansky and Schins (1). Except for the very scattered effusion data of Zavitsanos (4), the other studies differ by unusually large amounts: −2 (2), −6 (3) and +3 kcal/mol (5). Data of Ruff and Hartmann (3) are readily dismissed due to the large entropy discrepancy; their data for other metals have similar discrepancies. Data of Rudberg and Lempert (5) for Ca and Ba show almost identical biases, presumably due to poor effusion geometry or to impurities. A similar bias seems to exist in the effusion-resonance-fluorescence data of Hinnov and Ohlendorf (6); our analysis is not tabulated below since the graphical data include large discrepancies in temperature. Hartmann and Schneider's Ba data (2) deviate considerably more from the selected value than do their data for Li, Mg, Ca and Sr. The differences probably arise from impurity effects. Since Ba is the least volatile of the reactive metals studied (1, 2), purification by distillation presents special problems. Even Bohdansky and Schins (1) noted that their Ba data may be biased by impurities.

Analyses of the pressure data assume that the monatomic gas is the only significant species in the vapor and that gas imperfection is negligible. Evidence supporting the unimportance of the dimer was reviewed by Douglas and Krause (7). Estimated bond energies for the dimers of Mg, Ca, Sr and Ba are less than 8.6 kcal/mol (8-10).

Source	Method	Range[a] T, °K	$\Delta Hf^\circ_{298.}$ kcal/mol 2nd Law	3rd Law	Entropy Test[b] δS, gibbs/mol
(1) Bohdansky (1967)	Boiling Point	1498-2027	46.7±0.3	42.78±0.94	2.2±0.1
(2) Hartmann (1929)	Boiling Point	1334-1421	41.4±3.3	40.75±0.33	0.4±2.4
(3) Ruff (1924)	Boiling Point	1204-1404	92.6±3.0	37.0 ±6.1	43 ±2.3
(4) Zavitsanos (1968)	Effusion	1120-1710	65 ±10	43.8 ±1.6	18 ±8.8
(4) Zavitsanos (1968)	Torsion Effusion	1103-1216	36 ±10	43.5 ±1.9	−6.3±8.4
(5) Rudberg (1935)	Effusion	798-1024	43.2±1.2	45.91±0.77	−3.0±1.3

[a] Temperature adjusted to IPTS-68 assuming published values to be IPTS-48.

[b] δS = ΔSr°_{298}(2nd law) − ΔSr°(3rd law).

Heat Capacity and Entropy

Observed energy levels and quantum weights are from Moore (11) as modified by Garton et al. (12, 13). Additional levels above the cutoffs have been reported (14, 15). We adopt an energy-level cutoff which is about kTmax (Tmax = 6000°K) below each series limit. For Ba I this corresponds to omitting levels above 9s, 8p, 7d and 5f. Energies of unobserved but predicted terms (11) are estimated by comparison of Ca I, Sr I, Ba I and their isoelectronic ions. The most important are terms of the $5d^2$ configuration (20000-25000 cm^{-1}) and those of the 5d6s' configuration (estimated at 19000 ± 10000 cm^{-1}). Levels above 30000 cm^{-1} are averaged. The adopted functions are essentially identical with earlier tables up to 2000°K; however, the entropies at 6000°K differ as follows: Hilsenrath et al. (16), 62.26; JANAF, 63.20; Gurvich et al. (17), 63.65 gibbs/mol. These differences arise from different methods of cutoff and different degrees of accounting for the unobserved terms.

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Ba

Beryllium Monofluoride (BeF)

(Ideal Gas) GFW = 28.0106

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	− 2.082	− 41.159	− 41.159	INFINITE
100	6.957	41.517	55.390	− 1.388	− 40.822	− 42.926	93.814
200	6.980	46.338	49.795	− .691	− 40.614	− 45.125	49.310
298	7.140	49.149	49.149	.000	− 40.600	− 47.352	34.710
300	7.144	49.193	49.149	.013	− 40.601	− 47.394	34.526
400	7.431	51.286	49.432	.721	− 40.697	− 49.645	27.125
500	7.726	52.977	49.977	1.500	− 40.846	− 51.866	22.671
600	7.978	54.408	50.600	2.285	− 41.018	− 54.054	19.689
700	8.178	55.654	51.234	3.093	− 41.208	− 56.212	17.550
800	8.335	56.756	51.857	3.919	− 41.410	− 58.342	15.938
900	8.458	57.745	52.457	4.759	− 41.625	− 60.445	14.678
1000	8.555	58.642	53.032	5.610	− 41.857	− 62.525	13.665
1100	8.634	59.461	53.579	6.470	− 42.107	− 64.579	12.831
1200	8.698	60.215	54.101	7.336	− 42.378	− 66.610	12.131
1300	8.752	60.913	54.599	8.209	− 42.669	− 68.618	11.536
1400	8.797	61.564	55.073	9.086	− 42.981	− 70.603	11.022
1500	8.836	62.172	55.527	9.968	− 43.315	− 72.564	10.573
1600	8.869	62.743	55.960	10.853	− 46.426	− 74.424	10.166
1700	8.899	63.282	56.375	11.742	− 46.689	− 76.166	9.792
1800	8.925	63.791	56.773	12.633	− 46.957	− 77.893	9.458
1900	8.949	64.274	57.155	13.527	− 47.228	− 79.604	9.157
2000	8.970	64.734	57.523	14.423	− 47.504	− 81.301	8.884
2100	8.990	65.172	57.877	15.321	− 47.784	− 82.984	8.636
2200	9.008	65.591	58.218	16.221	− 48.068	− 84.654	8.410
2300	9.025	65.992	58.547	17.122	− 48.357	− 86.309	8.201
2400	9.041	66.376	58.865	18.025	− 48.651	− 87.952	8.009
2500	9.056	66.745	59.173	18.930	− 48.951	− 89.585	7.832
2600	9.070	67.101	59.471	19.837	− 49.254	− 91.203	7.666
2700	9.084	67.444	59.760	20.745	− 49.560	− 92.810	7.512
2800	9.097	67.774	60.041	21.654	− 120.902	− 93.300	7.282
2900	9.110	68.094	60.313	22.564	− 120.967	− 92.310	6.957
3000	9.122	68.403	60.577	23.475	− 121.034	− 91.323	6.653
3100	9.134	68.702	60.835	24.388	− 121.101	− 90.338	6.369
3200	9.145	68.992	61.085	25.302	− 121.169	− 89.337	6.101
3300	9.156	69.274	61.329	26.217	− 121.241	− 88.342	5.851
3400	9.167	69.547	61.567	27.133	− 121.315	− 87.344	5.614
3500	9.178	69.813	61.796	28.051	− 121.392	− 86.344	5.392
3600	9.189	70.072	62.025	28.969	− 121.472	− 85.339	5.181
3700	9.199	70.324	62.246	29.888	− 121.557	− 84.337	4.982
3800	9.210	70.569	62.461	30.809	− 121.646	− 83.329	4.793
3900	9.220	70.808	62.672	31.730	− 121.740	− 82.319	4.613
4000	9.231	71.042	62.879	32.653	− 121.839	− 81.308	4.442
4100	9.242	71.270	63.081	33.577	− 121.945	− 80.296	4.280
4200	9.252	71.493	63.278	34.501	− 122.057	− 79.278	4.125
4300	9.263	71.711	63.472	35.427	− 122.175	− 78.254	3.977
4400	9.274	71.924	63.662	36.354	− 122.303	− 77.233	3.836
4500	9.285	72.132	63.847	37.282	− 122.437	− 76.208	3.701
4600	9.297	72.337	64.030	38.211	− 122.580	− 75.180	3.572
4700	9.308	72.537	64.209	39.141	− 122.732	− 74.149	3.448
4800	9.320	72.733	64.384	40.073	− 122.893	− 73.111	3.329
4900	9.333	72.925	64.557	41.005	− 123.064	− 72.072	3.215
5000	9.345	73.114	64.726	41.939	− 123.244	− 71.027	3.105
5100	9.359	73.299	64.892	42.875	− 123.434	− 69.983	2.999
5200	9.372	73.481	65.056	43.811	− 123.635	− 68.935	2.897
5300	9.386	73.659	65.216	44.749	− 123.847	− 67.879	2.799
5400	9.400	73.835	65.374	45.688	− 124.069	− 66.824	2.705
5500	9.415	74.008	65.530	46.629	− 124.302	− 65.761	2.613
5600	9.431	74.177	65.683	47.571	− 124.547	− 64.693	2.525
5700	9.446	74.345	65.833	48.515	− 124.801	− 63.620	2.439
5800	9.463	74.509	65.981	49.461	− 125.067	− 62.542	2.357
5900	9.480	74.671	66.127	50.408	− 125.344	− 61.467	2.277
6000	9.497	74.830	66.271	51.357	− 125.632	− 60.384	2.199

Dec. 31, 1960; Sep. 30, 1961; Mar. 31, 1963; Dec. 31, 1971

BERYLLIUM MONOFLUORIDE (BeF) (IDEAL GAS) GFW = 28.0106 BeF

Ground State Configuration $^2\Sigma^+$ ΔHf°_0 = -41.2 ± 2 kcal/mol

$S^\circ_{298.15}$ = 49.149 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -40.6 ± 2 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.0	2	50419	2
33180	4	63916	[4]
49573	2	66373	[4]

ω_e = 1265.9 cm^{-1} $\omega_e x_e$ = 9.35 cm^{-1} σ = 1

B_e = 1.489 cm^{-1} α_e = 0.0176 cm^{-1} r_e = 1.361 Å

Heat of Formation

ΔHf° is based on third-law analysis of Kp data for three gas-phase reactions observed mass spectrometrically by Hildenbrand et al. (1, 2). Our analysis is summarized below. Also included are data for heterogeneous reaction of Be(c, ℓ) with BeF_2(g), observed with a molecular-flow-effusion method by Greenbaum et al. (3). The mutual consistency of the gas-phase results prompts us to adopt a weighted average of -40.6 ± 2 kcal/mol rather than the mean value of -53.1 kcal/mol derived from the heterogeneous reaction.

Analogous studies of BeCl(g) gave a similar discrepancy which was reaffirmed by new transport studies of Gross and Lewin (4). These authors suggested that transport via $(BeCl)_2$ provides a possible, but inconclusive, explanation of the discrepancy. This explanation may also apply to BeF, but new data would be needed to establish this.

The adopted ΔHf° yields D°_0 = 5.98 ± 0.1 eV which is consistent with spectroscopic results within their probable uncertainties (5). Spectroscopic values (1, 5) include 5.3 or 6.0 ± 0.5 eV (from $A^2\Pi$) and 5.3 eV (from $X^2\Sigma$). Rationales have been given (5-8) for the lowness of the value derived from the ground state. Recent calculations (13) showed that the ground-state potential energy curve is consistent with D°_0 = 5.85 eV. The flow-effusion data (3) yield 6.52 eV.

Source	Method	Reaction[a]	Range T, K	$\Delta Hr^\circ_{298.15}$, kcal/mol 2nd Law	3rd Law	δS[b] gibbs/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol
Hildenbrand (1)	Mass Spec.	A	1458-1609	25.9±9	28.28±2	-1.6±5.7	-41.86±1.3
		A	1321-1518	31.2±2	29.09±2	1.5±1.5	-41.46±1.3
		A	1423-1443	-4.1	30.4 ±3	24.	-40.8 ±1.7
		B	1321-1503	-6.7±3	-7.86±2	-0.8±2.1	-37.46±3.0
		B	1423-1443	-38.	-6.7 ±3	20.	-38.3 ±3.8
		C	1423-1443	12.7	24.2 ±3	8.	-38.9 ±3.4
Greenbaum (3)	Flow Eff.	D	1420-1525	97. ±10	84.7 ±3	8.2±7.3	-52.8 ±1.6
		E	1570-1675	83. ±6	80.7 ±3	-1.2±3.7	-53.4 ±1.6

[a] A = Be(g) + BeF_2(g) → 2BeF(g); B = Be(g) + CaF(g) → BeF(g) + Ca(g);
C = Be(g) + AlF(g) → BeF(g) + Al(g); D = BeF_2(g) + Be(c) → 2BeF(g);
E = BeF_2(g) + Be(ℓ) → 2BeF(g).

[b] δS = ΔSr(2nd Law) − ΔSr(3rd Law).

Heat Capacity and Entropy

Rotational constants are from a new analysis of the A-X system by Walker and Barrow (9). Vibrational constants are those derived by Novikov and Gurvich (10) from data of Tatevskii et al. (11). Excited states are from Novikov and Gurvich (10). We assume that the two highest states are $^2\Pi$ as postulated by Walker and Barrow (9) from comparison with quantum calculations (12).

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BeF

Lithium Trifluoroberyllate ($LiBeF_3$)

(Crystal) GFW = 72.9464

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	21.945	21.330	21.330	.000	−394.800	−376.740	276.158
300	22.000	21.466	21.330	.041	−394.798	−376.628	274.373
400	25.000	28.206	22.229	2.391	−394.663	−370.587	202.479
500	28.000	34.107	24.075	5.041	−395.146	−364.521	159.332
600	31.000	39.477	26.159	7.991	−394.699	−358.433	130.559
700	34.000	44.441	28.473	11.241	−393.997	−352.441	110.037
800	37.000	49.217	30.728	14.791	−393.033	−346.569	94.678
900	40.000	53.748	33.036	18.641	−391.805	−340.831	82.765
1000	43.000	58.118	35.327	22.791	−390.313	−335.245	73.268
1100	46.000	62.357	37.592	27.241	−388.553	−329.821	65.529
1200	49.000	66.498	39.829	31.991	−386.525	−324.569	59.112

June 30, 1966; Dec. 31, 1971

LITHIUM TRIFLUOROBERYLLATE ($LiBeF_3$) (CRYSTAL) GFW = 72.9464

ΔHf°_0 = unknown

$S^\circ_{298.15}$ = 21.33 ± 1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −394.8 ± 1.5 kcal/mol

Tm = [650 K]

ΔHm° = [6.5] kcal/mol

Heat of Formation

Interpolation of the calorimetric enthalpies of mixing of Holm and Kleppa (1) yields ΔHr° = −0.56 ± 0.1 kcal/mol for $LiF(\ell) + BeF_2(\ell) \rightarrow LiBeF_3(\ell)$ at 1135 K. Reduction with the estimated JANAF functions yields ΔHr° = −3.07 ± 1.0 kcal/mol at 298.15 K for $LiF(c) + BeF_2(\ell) \rightarrow LiBeF_3(c)$, where $BeF_2(\ell)$ is the supercooled liquid. $\Delta Hr^\circ_{298.15}$ for the latter reaction may also be calculated as −2.77 ± 0.2 kcal/mol from the difference of two calorimetric reactions measured by Gross (2). These results at 298.15 K were ΔHr° = −2.28 ± 0.12 kcal/mol for $LiF(c) + LiBeF_3(c) \rightarrow Li_2BeF_4(c)$ and ΔHr° = −5.06 ± 0.06 kcal/mol for $2LiF(c) + BeF_2(\ell) \rightarrow Li_2BeF_4(c)$. We adopt the high-temperature results of Holm and Kleppa since the entropy must be calculated by combination of ΔHr° with ΔGr° obtained at high temperature.

Heat Capacity and Entropy

Cp° is estimated from Cp° of $Li_2BeF_4(c)$ minus Cp° of $LiF(c)$. Existing information leads to three values for S° at 298.15 K; namely, 21.41 gibbs/mol from ΔGr° and ΔHr° for mixing of molten LiF and BeF_2, 21.33 gibbs/mol from ΔGr° = 0 at 552 K for disproportionation of $LiBeF_3(c)$ to $Li_2BeF_4(c)$ and $BeF_2(c)$, and 21.28 gibbs/mol estimated from S° of $LiF(c)$ and $BeF_2(c)$. We adopt the intermediate value but emphasize that $S^\circ_{298.15}$ is much more uncertain than indicated by the consistency of the three values. There is less uncertainty in S°_{900} since it does not involve large contributions from the estimated values of Cp° and ΔHm°.

Hitch and Baes (3) reported emf data and activity coefficients which yield ΔGr° = −5.91 kcal/mol at 900 K for $LiF(\ell) + BeF_2(\ell) \rightarrow LiBeF_3(\ell)$. Combining ΔGr° with ΔHr° = −1.05 kcal/mol derived with JANAF functions from data of Holm and Kleppa (1), we obtain ΔSr° = 5.4 and $S^\circ(LiBeF_3, \ell)$ = 64.46 gibbs/mol, both at 900 K. The corresponding values from the adopted tables are ΔGr° = −5.84 kcal/mol and $S^\circ(LiBeF_3, \ell)$ = 64.38 gibbs/mol.

Disproportionation Data

No transitions are known between room temperature and Tm, but $LiBeF_3(c)$ does disproportionate into $Li_2BeF_4(c)$ and BeF_2 (high quartz). Disproportionation occurs at 553 K according to the latest phase diagrams (4, 5) or at 573 K according to Roy et al. (6). The adopted tables yield ΔGr° = 0 at 552 K, but this temperature is very sensitive to the value selected for S°, which in turn depends on the estimates of Cp° and ΔHm°.

Melting Data

See $LiBeF_3(\ell)$.

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Lithium Trifluoroberyllate ($LiBeF_3$)

(Liquid) GFW = 72.9464

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	21.945	26.692	26.692	.000	- 390.613	- 374.151	274.260
300	22.000	26.828	26.693	.041	- 390.611	- 374.049	272.495
400	25.000	33.568	27.591	2.391	- 390.476	- 368.545	201.383
500	38.000	42.088	29.666	6.191	- 389.808	- 363.154	158.734
600	38.000	48.976	32.325	9.991	- 388.511	- 357.945	130.381
700	38.000	54.833	35.133	13.791	- 387.260	- 352.950	110.196
800	38.000	59.908	37.919	17.591	- 386.046	- 348.134	95.106
900	38.000	64.383	40.616	21.391	- 384.868	- 343.465	83.405
1000	38.000	68.387	43.196	25.191	- 383.725	- 338.927	74.072
1100	38.000	72.009	45.654	28.991	- 382.615	- 334.501	66.459
1200	38.000	75.315	47.990	32.791	- 381.538	- 330.175	60.133
1300	38.000	78.357	50.210	36.591	- 380.490	- 325.936	54.795
1400	38.000	81.173	52.323	40.391	- 379.472	- 321.779	50.232
1500	38.000	83.795	54.334	44.191	- 378.481	- 317.692	46.288
1600	38.000	86.247	56.253	47.991	- 380.274	- 313.593	42.835
1700	38.000	88.551	58.086	51.791	- 414.271	- 308.129	39.613
1800	38.000	90.723	59.839	55.591	- 413.049	- 301.921	36.658
1900	38.000	92.778	61.519	59.391	- 411.835	- 295.779	34.022
2000	38.000	94.727	63.131	63.191	- 410.631	- 289.702	31.657

Dec. 31, 1971

LITHIUM TRIFLUOROBERYLLATE ($LiBeF_3$) (LIQUID) GFW = 72.9464

$S°_{298.15}$ = [26.692] gibbs/mol $\Delta Hf°_{298.15}$ = [-390.612] kcal/mol

Tm = [650 K] $\Delta Hm°$ = [6.5] kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by addition of ΔHm° and the difference between ($H°_{650} - H°_{298.15}$) for crystal and liquid. Note that the result is based on direct measurements of the enthalpy of mixing of molten LiF and BeF_2 at 1135 K (1).

Heat Capacity and Entropy

Cp° is estimated on the basis of 7.6 gibbs/(g atom) by comparison with the liquid phases of LiF, BeF_2 and Li_2BeF_4. A glass transition is assumed at 400 K and below this temperature Cp° is obtained from that of the crystal. The entropy is derived in a manner analogous to that of ΔHf°. Note that the resulting value of $S°_{900}$ differs by only 0.08 gibbs/mol from that based on measurements of $\Delta Hr°_{1135}$ (1) and $\Delta Gr°_{900}$ (2) for mixing of molten LiF and BeF_2.

Melting Data

The composition corresponding to $LiBeF_3$ melts incongruently (3), starting with the eutectic composition of 53 mole percent BeF_2 at 636.6 ± 0.5 K and finishing at a liquidus temperature near 653 K. Just below the melting region, the solid consists of an equimolar mixture of Li_2BeF_4(c) and BeF_2 (high quartz). We arbitrarily adopt 650 K as the hypothetical, congruent melting point of metastable $LiBeF_3$. We estimate ΔHm° on the basis of ΔSm° = 7.0 gibbs/(g atom) by comparison with Li_2BeF_4.

Vaporization Data

Mass-spectrometric data (4, 5) for the LiF-BeF_2 system suggest that the vapor consists mainly of BeF_2(g), some $LiBeF_3$(g), and traces of other molecules.

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2. B. F. Hitch and C. F. Baes, Inorg. Chem. 8, 201 (1969); U. S. Atomic Energy Comm., ORNL-4257, 46 pp., 1968.
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Dilithium Tetrafluoroberyllate (Li_2BeF_4)

(Crystal) GFW = 98.8838

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	32.330	31.210	31.210	.000	- 543.400	- 518.990	380.430
300	32.390	31.410	31.211	.060	- 543.397	- 518.839	377.974
400	35.960	41.217	32.524	3.477	- 543.201	- 510.678	279.022
500	39.520	49.624	35.121	7.251	- 544.381	- 502.431	219.812
600	43.080	57.144	38.175	11.381	- 543.883	- 494.081	179.969
700	46.650	64.053	41.384	15.868	- 543.070	- 485.842	151.686
800	50.215	70.515	44.626	20.711	- 541.938	- 477.762	130.513
900	53.777	76.635	47.845	25.911	- 540.489	- 469.800	114.083
1000	57.340	82.485	51.019	31.467	- 538.723	- 462.038	100.978
1100	60.903	88.118	54.137	37.379	- 536.635	- 454.467	90.294
1200	64.467	93.570	57.197	43.647	- 534.224	- 447.102	81.428
1300	68.031	98.871	60.200	50.272	- 531.491	- 439.949	73.962
1400	71.595	104.043	63.147	57.253	- 528.430	- 433.020	67.597
1500	75.160	109.106	66.043	64.591	- 525.040	- 426.321	62.115

June 30, 1966; Dec. 31, 1971

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4) (CRYSTAL) GFW = 98.8838

$\Delta Hf°_0$ = unknown

$S°_{298.15}$ = 31.21 ± 0.5 gibbs/mol

$\Delta Hf°_{298.15}$ = -543.4 ± 1.2 kcal/mol

Tm = 732.2 ± 0.2 K

ΔHm° = 10.515 ± 0.5 kcal/mol

Heat of Formation

Interpolation of the calorimetric enthalpy of mixing data of Holm and Kleppa (1) yields ΔHr° = -3.2 ± 0.1 kcal/mol for $2LiF(\ell) + BeF_2(\ell) \rightarrow Li_2BeF_4(\ell)$ at 1135 K. Reduction with JANAF functions yields ΔHr° = -4.24 ± 0.2 kcal/mol at 298.15 for $2LiF(c) + BeF_2(\ell) \rightarrow Li_2BeF_4(c)$, where $BeF_2(\ell)$ is the supercooled liquid. Gross (2) studied the latter reaction calorimetrically and obtained ΔHr° = -5.05 ± 0.06 kcal/mol at 298.15 K. The difference of 0.8 kcal/mol between the two results is greater than the combined uncertainties but probably is not unreasonable in this case. We adopt the high-temperature results of Holm and Kleppa since the entropy must be calculated by combination of ΔHr° with ΔGr° obtained at high temperatures.

Heat Capacity and Entropy

Cp° is taken from the enthalpy study (323-873 K) of Douglas and Payne (3). Their sample was only 98.6% pure and extensive premelting corrections were necessary above 650 K. Thus, Cp° may be more uncertain than usual in this region. The premelting corrections could also be affected by new phase data which show that pure Li_2BeF_4 melts congruently at a temperature 12° lower than assumed in the premelting analysis. The magnitude of the adopted Cp° is confirmed by data of Levina et al. (4) for samples prepared by fusion.

Hitch and Baes (5) reported emf data and activity coefficients which yield ΔGr° = -9.33 kcal/mol at 900 K for $2LiF(\ell) + BeF_2(\ell) \rightarrow Li_2BeF_4(\ell)$. Combining ΔGr° with ΔHr° = -4.19 kcal/mol derived from data of Holm and Kleppa (1), we obtain ΔSr° = 5.71 gibbs/mol at 900 K and S° = 31.21 ± 0.5 gibbs/mol for $Li_2BeF_4(c)$ at 298.15 K. This experimental entropy may be compared with 29.8 ± 2 gibbs/mol estimated by assuming ΔSr° = 0 for formation from LiF(c) and $BeF_2(c)$.

Transition Data

Li_2BeF_4 has a hexagonal unit cell (space group $R\bar{3}$) isotypic with phenacite (6). This structure shows no phase transitions between room temperature and Tm (3, 4, 7), but exposure to traces of moisture at elevated temperatures causes decomposition to LiF and BeO (7, 8). Metastable forms have been reported (4) but not confirmed or identified.

Melting Data

New electrochemical measurements (9) of the liquidus in the LiF-BeF_2 system show that Li_2BeF_4 melts congruently at 459.1 ± 0.2°C with the eutectic point at 458.9 ± 0.2°C and 32.8 mole percent BeF_2. The close proximity of the eutectic explains previous conflicting reports of incongruent (8) and congruent (4, 8) melting. We adopt Tm = 732.2 ± 0.2 K and derive ΔHm° = 10.515 kcal/mol from the difference in smoothed enthalpies for liquid and crystal (3). The uncertainty estimated for ΔHm° emphasizes the nature of the premelting corrections.

References

1. J. L. Holm and O. J. Kleppa, Inorg. Chem. 8, 207 (1969).
2. P. Gross, Fulmer Res. Inst. Rept., R.163/23/May 1966 and R.163/22/Jan. 1966, Contract AF 61(052)-863; R.163/18/Dec. 1964, Contract AF 61(052)-447.
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Dilithium Tetrafluoroberyllate (Li_2BeF_4)

(Liquid) GFW = 98.8838

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	32.330	40.964	40.964	.000	- 535.628	- 514.126	376.865
300	32.390	41.165	40.965	.060	- 535.625	- 513.994	374.444
400	35.960	50.972	42.278	3.477	- 535.429	- 506.808	276.907
500	39.520	59.379	44.875	7.252	- 536.609	- 499.536	218.347
600	55.470	69.492	48.161	12.799	- 534.694	- 492.301	179.320
700	55.470	78.043	51.835	18.346	- 532.821	- 485.385	151.544
800	55.470	85.450	55.584	23.893	- 530.985	- 478.736	130.785
900	55.470	91.983	59.272	29.440	- 529.189	- 472.312	114.693
1000	55.470	97.827	62.841	34.987	- 527.432	- 466.088	101.863
1100	55.470	103.114	66.266	40.534	- 525.709	- 460.037	91.401
1200	55.470	107.941	69.540	46.081	- 524.021	- 454.142	82.711
1300	55.470	112.381	72.667	51.628	- 522.364	- 448.386	75.380
1400	55.470	116.492	75.653	57.175	- 520.737	- 442.756	69.117
1500	55.470	120.319	78.504	62.722	- 519.138	- 437.241	63.706
1600	55.470	123.899	81.231	68.269	- 520.322	- 431.754	58.975
1700	55.470	127.261	83.840	73.816	- 588.758	- 423.613	54.459
1800	55.470	130.432	86.342	79.363	- 586.747	- 413.957	50.261
1900	55.470	133.431	88.742	84.910	- 584.745	- 404.410	46.518
2000	55.470	136.276	91.048	90.457	- 582.756	- 394.970	43.160
2100	55.470	138.983	93.267	96.004	- 580.780	- 385.634	40.133
2200	55.470	141.563	95.404	101.551	- 578.817	- 376.386	37.390
2300	55.470	144.029	97.465	107.098	- 576.863	- 367.226	34.894
2400	55.470	146.390	99.454	112.645	- 574.926	- 358.154	32.614
2500	55.470	148.654	101.377	118.192	- 573.003	- 349.163	30.524

June 30, 1966; Dec. 31, 1971

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4) (LIQUID) GFW = 98.8838

$S^\circ_{298.15}$ = 40.964 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -535.628 kcal/mol

Tm = 732.2 ± 0.2 K ΔHm° = 10.515 ± 0.5 kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by addition of ΔHm° and the difference between ($H^\circ_{732.2} - H^\circ_{298.15}$) for crystal and liquid. Note that the result is based on direct measurement of the enthalpy of mixing of molten LiF and BeF_2 at 1135 K (1).

Heat Capacity and Entropy

The constant Cp° is derived from enthalpy data (743-873 K) of Douglas and Payne (2). A glass transition is assumed at 500 K and below this temperature Cp° is obtained from that of the crystal. The entropy is derived in a manner analogous to that of ΔHf°. Note that the result is based on measurements of ΔHr°_{1135} (1) and ΔGr°_{900} (3) for mixing of molten LiF and BeF_2.

Melting Data

See Li_2BeF_4(c).

Vaporization Data

Mass spectra of vapor effusing from twin-crucible Knudsen cells (4) suggest that the vapor consists of BeF_2, $LiBeF_3$ and traces of other molecules.

References

1. J. L. Holm and O. J. Kleppa, Inorg. Chem. 8, 207 (1969).
2. T. B. Douglas and W. H. Payne, J. Res. Natl. Bur. Std. 73A, 479 (1969).
3. B. F. Hitch and C. F. Baes, Inorg. Chem. 8, 201 (1969); U. S. Atomic Energy Comm., ORNL-4257, 46 pp., 1968.
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Beryllium Oxide, Alpha (α-BeO)

(Crystal) GFW = 25.0116

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	-.689	-144.583	-144.583	INFINITE
100	.630	.197	4.935	-.674	-144.925	-142.862	312.225
200	3.384	1.407	3.737	-.466	-145.204	-140.661	153.707
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	8.070	5.381	3.558	.729	-145.479	-135.989	74.301
500	9.301	7.324	4.119	1.602	-145.475	-133.615	58.403
600	10.124	9.097	4.804	2.576	-145.421	-131.247	47.807
700	10.709	10.704	5.534	3.619	-145.339	-128.891	40.242
800	11.150	12.164	6.272	4.713	-145.239	-126.549	34.572
900	11.498	13.498	7.002	5.846	-145.130	-124.218	30.164
1000	11.786	14.724	7.714	7.010	-145.019	-121.900	26.641
1100	12.032	15.859	8.403	8.201	-144.912	-119.594	23.761
1200	12.248	16.916	9.069	9.416	-144.810	-117.297	21.363
1300	12.443	17.904	9.711	10.650	-144.716	-115.008	19.335
1400	12.622	18.833	10.330	11.904	-144.631	-112.726	17.597
1500	12.788	19.709	10.926	13.174	-144.556	-110.450	16.093
1600	12.945	20.539	11.501	14.461	-147.247	-108.100	14.766
1700	13.095	21.329	12.056	15.763	-147.079	-105.658	13.583
1800	13.239	22.081	12.593	17.080	-144.904	-103.227	12.533
1900	13.376	22.801	13.111	18.411	-144.724	-100.805	11.595
2000	13.513	23.491	13.613	19.755	-144.537	-98.394	10.752
2100	13.645	24.153	14.099	21.113	-146.345	-95.991	9.990
2200	13.775	24.791	14.571	22.484	-146.148	-93.598	9.298
2300	13.902	25.406	15.029	23.868	-145.945	-91.213	8.667
2400	14.026	26.000	15.473	25.264	-145.738	-88.837	8.090
2500	14.151	26.575	15.906	26.673	-145.527	-86.473	7.559
2600	14.274	27.133	16.327	28.095	-145.309	-84.113	7.070
2700	14.395	27.674	16.737	29.528	-145.087	-81.763	6.618
2800	14.516	28.200	17.137	30.974	-215.890	-78.315	6.113
2900	14.635	28.711	17.528	32.431	-215.406	-73.408	5.532
3000	14.754	29.209	17.909	33.901	-214.915	-68.520	4.992
3100	14.872	29.695	18.281	35.382	-214.415	-63.651	4.487
3200	14.990	30.169	18.645	36.875	-213.907	-58.793	4.015
3300	15.107	30.632	19.002	38.380	-213.392	-53.954	3.573
3400	15.223	31.085	19.350	39.897	-212.871	-49.131	3.158
3500	15.339	31.528	19.692	41.425	-212.342	-44.325	2.768

Dec. 31, 1960; Sept. 30, 1963; June 30, 1971

BERYLLIUM OXIDE, ALPHA (α-BeO) (CRYSTAL) GFW = 25.0116 BeO

$S^\circ_{298.15}$ = 3.291 ± 0.05 gibbs/mol

Tt = 2373 ± 40 K (α→β)

Tm = 2720 ± 30 K (β→ℓ)

Tm = [2681] K (α→ℓ)

ΔHf°_0 = -144.6 ± 0.8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -145.4 ± 0.8 kcal/mol

ΔHt° = 1.57 ± 0.4 kcal/mol

ΔHm° = [14.13 ± 3] kcal/mol

ΔHm° = [15.68 ± 3] kcal/mol

Heat of Formation

Parker (1) thoroughly reviewed the data as of 1969 and selected -145.4 ± 0.8 kcal/mol. This selection has been revised (2) to -145.7 ± 0.5 kcal/mol due to preliminary results of HF-solution calorimetry on BeF_2 (amorphous) performed by Kilday et al. Values of ΔHf° from Parker's revised analysis (2) 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 value (4) in place of NBS value (3) causes a change of +0.9 kcal/mol in the results based on BeF_2(am).

Direct Determinations of ΔHf°		Indirect Determinations of ΔHf°	
kcal/mol	Source	kcal/mol	Source
-136.2	Mielenz & von Wartenberg (1921)	-144.9	Neumann et al. (1934, 1932), ΔHc & ΔHf of Be_3N_2
-134.4	Moose & Parr (1924)	-141.1	Smirnov & Chukreev (1958), Emf data
-145.3	Neumann et al. (1934)	-145.9 ± 2.0	Kilday et al. (1969), Thomson et al. (1962)[a]
-147.3	Roth et al. (1938)	-144.2 ± 1.5	Kilday et al. (1969), Armstrong & Coyle (1965)[b]
-143.1	Cosgrove & Snyder (1953)	-145.7	Kolesov et al. (1959), Bear & Turnbull (1965)[b]
		-146.2, -145.8, -145.9, -145.7	Kilday et al. (1969), Bear & Turnbull (1965)[b]
		-144.9 (-145.8)[d], -144.5 (-145.4)[d]	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 16 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 curve fit of enthalpy data of Victor and Douglas (8, 323 to 1173 K) and Conway and Hein (9, 2161 to 2365 K) constrained to join smoothly with the Cp° data (5). Maximum deviations from the adopted enthalpies are 0.8% (9), 0.13% (8) above 373 K and 0.9% (8) at 323 K. Deviations of other enthalpy data include ±2.3% (10, 1142 to 2697 K), -18 ± 8% (11, 2273 to 2523 K), -2.0 ± 0.8% (12, 400 to 1100 K), and +0.4 to -0.7% (13, 363 to 1127 K). Cp° data from the cooling-rate method (14) deviate by less than 2% (1300 to 1600 K) but are up to 7% lower near 2000 K.

Transition Data

See BeO(β, c).

Melting Data

See BeO(ℓ).

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Beryllium Oxide, Beta (β-BeO)

(Crystal) GFW = 25.0116

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	6.109	3.953	3.953	.000	− 143.830	− 137.023	100.441
300	6.153	3.991	3.953	.011	− 143.832	− 136.981	99.791
400	8.070	6.043	4.219	.729	− 143.909	− 134.683	73.587
500	9.301	7.985	4.781	1.602	− 143.905	− 132.376	57.861
600	10.124	9.758	5.465	2.576	− 143.851	− 130.074	47.379
700	10.709	11.365	6.195	3.619	− 143.769	− 127.784	39.896
800	11.150	12.825	6.934	4.713	− 143.669	− 125.508	34.287
900	11.498	14.159	7.664	5.846	− 143.560	− 123.244	29.928
1000	11.786	15.386	8.376	7.010	− 143.449	− 120.992	26.443
1100	12.032	16.521	9.065	8.201	− 143.342	− 118.751	23.594
1200	12.248	17.577	9.731	9.416	− 143.240	− 116.521	21.221
1300	12.443	18.565	10.373	10.650	− 143.146	− 114.298	19.215
1400	12.622	19.494	10.992	11.904	− 143.061	− 112.083	17.497
1500	12.788	20.371	11.588	13.174	− 142.986	− 109.873	16.008
1600	12.945	21.201	12.163	14.461	− 145.677	− 107.589	14.696
1700	13.095	21.990	12.718	15.763	− 145.509	− 105.213	13.526
1800	13.239	22.743	13.254	17.080	− 145.334	− 102.848	12.487
1900	13.378	23.463	13.773	18.411	− 145.154	− 100.492	11.559
2000	13.513	24.152	14.275	19.755	− 144.967	− 98.148	10.725
2100	13.645	24.815	14.761	21.113	− 144.775	− 95.811	9.971
2200	13.775	25.452	15.232	22.484	− 144.578	− 93.484	9.287
2300	13.902	26.068	15.690	23.868	− 144.375	− 91.165	8.663
2400	14.028	26.662	16.135	25.264	− 144.168	− 88.854	8.091
2500	14.151	27.237	16.568	26.673	− 143.957	− 86.557	7.567
2600	14.274	27.794	16.989	28.095	− 143.739	− 84.263	7.083
2700	14.395	28.335	17.399	29.528	− 143.517	− 81.980	6.636
2800	14.516	28.861	17.799	30.974	− 214.320	− 78.597	6.135
2900	14.635	29.373	18.189	32.431	− 213.836	− 73.756	5.558
3000	14.754	29.871	18.570	33.901	− 213.345	− 68.935	5.022
3100	14.872	30.357	18.943	35.382	− 212.845	− 64.132	4.521
3200	14.990	30.831	19.307	36.875	− 212.337	− 59.340	4.053
3300	15.107	31.294	19.663	38.380	− 211.822	− 54.568	3.614
3400	15.223	31.746	20.012	39.897	− 211.301	− 49.811	3.202
3500	15.339	32.189	20.354	41.425	− 210.772	− 45.071	2.814

June 30, 1971

BERYLLIUM OXIDE, BETA (β-BeO) (CRYSTAL) GFW = 25.0116 BeO

$S^\circ_{298.15}$ = [3.953] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [−143.83] kcal/mol

Tt = 2373 ± 40 K (α→β)

ΔHt° = 1.57 ± 0.4 kcal/mol

Tm = 2720 ± 30 K (β→ℓ)

ΔHm° = [14.13 ± 3] 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 −0.6 to +1.0%. Other enthalpy data (2, 3) 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 (4-6), optical properties (5, 7), thermal expansion (1, 8), thermal analysis (9-11), enthalpy (1), and decrepitation of single crystals (5, 8, 12) indicate the existence of a reversible transition near 2100°C. β-BeO is tetragonal (4), while α-BeO is hexagonal close packed (13, 14). The transition on cooling usually occurs about 60° below that on heating (6, 9, 11). The observed temperatures depend on the sample (6), probably due to effects of impurities and differences in size and sintering of the particles. Reported values of Tt on heating include 2100 ± 10°C (1), 2095°C (9), 2050-2100°C (6), 2100-2250°C (6), 2144 ± 40°C (11), and 2050 ± 25°C (5). Reported values of ΔHt° include 1.35 ± 0.1 (1), 1.25 ± 0.25 (11), and 0.95 ± 0.3 kcal/mol (10), the latter two derived from thermal analysis. We adopt Tt = 2100 ± 40°C and derive ΔHt° = 1.57 ± 0.4 kcal/mol from the enthalpy data for β-BeO (1) and the JANAF Cp° for α-BeO.

Melting Data

See BeO(ℓ).

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Beryllium Oxide (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	8.745	8.745	.000	-130.594	-125.217	91.786
300	6.153	8.783	8.745	.011	-130.596	-125.183	91.196
400	8.070	10.835	9.012	.729	-130.673	-123.364	67.403
500	9.301	12.778	9.573	1.602	-130.670	-121.536	53.123
600	10.124	14.551	10.258	2.574	-130.615	-119.714	43.606
700	10.709	16.158	10.988	3.619	-130.533	-117.903	36.811
800	11.150	17.618	11.727	4.713	-130.433	-116.106	31.719
900	11.498	18.952	12.456	5.844	-130.325	-114.321	27.761
1000	11.786	20.178	13.168	7.010	-130.214	-112.549	24.597
1100	12.032	21.313	13.857	8.201	-130.106	-110.787	22.011
1200	12.248	22.370	14.523	9.416	-130.005	-109.036	19.858
1300	12.443	23.358	15.165	10.650	-129.911	-107.292	18.037
1400	12.622	24.287	15.784	11.904	-129.825	-105.556	16.478
1500	12.788	25.163	16.380	13.174	-129.750	-103.826	15.127
1600	12.945	25.994	16.955	14.461	-132.441	-102.021	13.935
1700	13.095	26.783	17.510	15.763	-132.273	-100.125	12.872
1800	13.239	27.535	18.047	17.080	-132.099	-98.239	11.928
1900	13.378	28.255	18.565	18.411	-131.918	-96.362	11.084
2000	15.000	29.024	19.069	19.911	-131.576	-94.501	10.327
2100	15.000	29.756	19.561	21.411	-131.242	-92.655	9.643
2200	15.000	30.454	20.040	22.911	-130.916	-90.825	9.023
2300	15.000	31.121	20.507	24.411	-130.597	-89.009	8.458
2400	15.000	31.759	20.963	25.911	-130.286	-87.206	7.941
2500	15.000	32.372	21.407	27.411	-129.984	-85.420	7.467
2600	15.000	32.960	21.840	28.911	-129.688	-83.641	7.031
2700	15.000	33.526	22.263	30.411	-129.399	-81.876	6.627
2800	15.000	34.071	22.675	31.911	-200.147	-79.013	6.167
2900	15.000	34.598	23.077	33.411	-199.621	-74.694	5.629
3000	15.000	35.108	23.469	34.911	-199.100	-70.396	5.128
3100	15.000	35.598	23.853	36.411	-198.581	-66.117	4.661
3200	15.000	36.074	24.227	37.911	-198.066	-61.850	4.224
3300	15.000	36.536	24.593	39.411	-197.556	-57.601	3.815
3400	15.000	36.984	24.951	40.911	-197.052	-53.369	3.430
3500	15.000	37.419	25.301	42.411	-196.551	-49.152	3.069
3600	15.000	37.841	25.644	43.911	-196.056	-44.944	2.728
3700	15.000	38.252	25.979	45.411	-195.567	-40.755	2.407
3800	15.000	38.652	26.307	46.911	-195.084	-36.577	2.104
3900	15.000	39.042	26.629	48.411	-194.607	-32.411	1.816
4000	15.000	39.422	26.944	49.911	-194.138	-28.260	1.544
4100	15.000	39.792	27.253	51.411	-193.677	-24.121	1.286
4200	15.000	40.153	27.556	52.911	-193.222	-19.991	1.040
4300	15.000	40.506	27.853	54.411	-192.776	-15.867	.806
4400	15.000	40.851	28.144	55.911	-192.340	-11.760	.584
4500	15.000	41.188	28.430	57.411	-191.912	-7.661	.372
4600	15.000	41.518	28.711	58.911	-191.495	-3.571	.170
4700	15.000	41.841	28.987	60.411	-191.087	.509	.024
4800	15.000	42.156	29.258	61.911	-190.689	4.583	.209
4900	15.000	42.466	29.525	63.411	-190.302	8.645	.386
5000	15.000	42.769	29.787	64.911	-189.925	12.704	.555

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1971

BERYLLIUM OXIDE (BeO) (LIQUID) GFW = 25.0116 BeO

$S^\circ_{298.15}$ = [8.745] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-130.594] kcal/mol

Tm = 2720 ± 30 K (β→ℓ)

ΔHm° = [14.13 ± 3] kcal/mol

Tm = [2681] K (α→ℓ)

ΔHm° = [15.68 ± 3] kcal/mol

Heat of Formation

ΔHf° is obtained from that of β-BeO by adding ΔHm° and the difference of (H°_{2720}−H°_{298}) for β and liquid phases.

Heat Capacity and Entropy

Cp° is assumed to be 15 gibbs/mol since enthalpy data for the liquid (1, 2) are inadequate for deriving Cp°. The adopted value assumes that the change in Cp° on melting of BeO is similar to that of LiF. Cp° below the assumed glass transition at 1900 K is taken to be the same as that of the crystal. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

Four new melting-point determinations have become available since the review of Schneider (3). Schneider listed six values -- 2410, 2452, 2508, 2557, 2570 and 2573°C -- which extend over a rather wide range. Recent determinations include 2430 ± 10°C (4), 2444 ± 30°C (5), 2547 ± 9°C (1), 2450 ± 30 and 2470 ± 20°C (6); these may be compared with 2452°C from the most recent (7) of the earlier studies reviewed by Schneider. The highest melting-point values are supported only by Kandyba et al. (1), whose result is very poorly documented. The weight of evidence supports a lower value, so we adopt 2447 ± 30°C or 2720 ± 30 K.

The enthalpy data (1, 2) and crystal-liquid phase data for binary systems (5, 8-12) both appear to be *inadequate for* calculation of an accurate ΔHm°. This is not surprising since the molten oxide presents many experimental difficulties including volatilization, corrosion of containers, gross nonideality of melts and problems in the determination of both temperature and melting.

Our approximate ΔHm° is derived from the enthalpy data but the interpretation is complicated by uncertainties in temperature, in the degree of melting, and in the phases existing below the melting point and after the drop. The enthalpy data (1, 2) showed no obvious transition to β-BeO and the phase resulting from molten BeO was not identified. Both studies reported three points in the liquid region, but those of Kandyba et al. (1) were described as "partially melted" (two points were 6 kcal/mol lower than the third). The temperature scales of both enthalpy studies correspond to Tm = 2820 K rather than the adopted value of 2720 K. Enthalpy data for the crystal extend no higher than 2697 K and the data from one study (2) are 2 to 5 kcal/mol lower than those of the other study (1) in this region. On the positive side are the following. Assuming that the liquid drops to α-BeO, we calculate apparent values of ΔHm°(α-BeO) of 15.4 (1), 14.6, 15.8, and 16.9 kcal/mol (2) based on JANAF enthalpies of the crystal. The agreement is encouraging. Since the resulting ΔSm° is comparable to that of LiF, we can probably eliminate glass formation *as a possibility. This is consistent with the observation* (13) that the quenched sample was "a fine microcrystalline fused powder in contrast to the solid rod used initially."

We select a median value of 15.7 kcal/mol and subtract ΔHt° in order to obtain ΔHm°(β→ℓ) = 14.13 kcal/mol. This value is arbitrarily assigned to Tm rather than to 2820 K. The uncertainty in ΔHm° is estimated as 3 kcal/mol due to contributions from the temperature scale and lack of identification of the solid phase. Finally, we calculate Tm(α→ℓ) as the temperature at which ΔGr° = 0 for BeO(α)-BeO(ℓ). ΔHm°(α→ℓ) is the corresponding difference in ΔHf° at Tm(α→ℓ). MgO could provide a comparison for confirmation of ΔSm°, but unfortunately Tm and ΔHm° appear to be even more uncertain for MgO than for BeO.

Vaporization Data

The vapor over BeO is composed mainly of trimer, tetramer and individual atoms, along with minor amounts of several other molecules. See BeO(g) for details.

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BeO

CCuN

Cuprous Cyanide (CuCN)

(Crystal) GFW = 89.5578

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	2.881	22.302	22.302	INFINITE
100	8.422	8.812	32.945	2.413	22.250	23.538	51.442
200	12.544	16.087	22.786	1.340	22.417	24.775	27.073
298	14.585	21.511	21.511	.000	22.700	25.874	18.966
300	14.665	21.607	21.511	.027	22.706	25.893	18.863
400	15.950	26.035	22.108	1.571	23.058	26.903	14.699
500	16.790	29.687	23.269	3.209	23.410	27.824	12.162
600	17.480	32.811	24.605	4.923	23.757	28.674	10.445
700	18.090	35.551	25.977	6.703	24.102	29.667	9.200
800	18.650	38.006	27.330	8.540	24.452	30.209	8.253
900	19.180	40.233	28.642	10.432	24.811	30.907	7.505
1000	19.680	42.280	29.905	12.375	25.183	31.564	6.898

Dec. 31, 1971

CUPROUS CYANIDE (CuCN) (CRYSTAL) GFW = 89.5578

ΔHf°_0 = 22.3 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 21.51 ± 0.06 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 22.7 ± 0.5 kcal/mol

Tm = 746 K

ΔHm° = 3 ± 1 kcal/mol

Heat of Formation

Taylor, Brown and Taylor (1) determined by solution calorimetry the heat of reaction, ΔHr°_{298} = -13,437 ± 100 cal/mol for $NaCN(c) + 0.5Cu_2O(c) + 0.5H_2O(\ell) \rightarrow CuCN(c) + NaOH(128.5\ H_2O)$ which leads to $\Delta Hf^\circ_{298}(CuCN, c)$ = 22.70 ± 0.5 kcal/mol using auxiliary data: $\Delta Hf^\circ_{298}(NaCN, c)$ = -21.68 ± 0.3 kcal/mol (2), $\Delta Hf^\circ_{298}(Cu_2O, c)$ = -40.7 ± 0.5 kcal/mol (3), $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 kcal/mol (4) and $\Delta Hf^\circ_{298}(NaOH \cdot 128.5\ H_2O, aq)$ = -112.321 kcal/mol (5).

Heat Capacity and Entropy

The heat capacity of CuCN(c) has been measured adiabatically over the temperature range from 8 to 402 K by Taylor, Brown and Taylor (1). The smooth Cp values are adopted in the tabulation. The value of S°_{298} is calculated from the Cp data and is based on an extrapolation of S°_8 = 0.104 eu. They also found an anomaly in the heat capacity at 300 K which is considered as a second order phase transition. Heat capacities above 402 K are estimated by extrapolation of the measured Cp data.

Melting Data

The melting point 746 K was determined by Truthe (6). The heat of melting is calculated from the phase diagram studies of KCN - CuCN and NaCN - CuCN reported by Truthe (6).

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Carbon Monofluoride Unipositive Ion (CF^+)

(Ideal Gas) GFW = 31.009

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	7.084	48.134	48.134	.000	274.717	266.506	= 195.354
300	7.088	48.178	48.134	.013	274.728	266.454	= 194.112
400	7.333	50.249	48.415	.733	275.314	263.607	= 144.028
500	7.611	51.915	48.954	1.481	275.836	260.618	= 113.916
600	7.863	53.326	49.568	2.255	276.313	257.529	= 93.805
700	8.072	54.554	50.194	3.052	276.756	254.363	= 79.416
800	8.240	55.683	50.808	3.868	277.177	251.135	= 68.607
900	8.374	56.622	51.401	4.699	277.580	247.855	= 60.187
1000	8.482	57.510	51.968	5.542	277.971	244.531	= 53.482
1100	8.569	58.323	52.509	6.394	278.352	241.169	= 47.916
1200	8.641	59.071	53.025	7.255	278.724	237.772	= 43.304
1300	8.701	59.765	53.517	8.122	279.088	234.345	= 39.397
1400	8.752	60.412	53.987	8.995	279.448	230.891	= 36.044
1500	8.795	61.017	54.436	9.872	279.803	227.410	= 33.134
1600	8.832	61.586	54.865	10.754	280.153	223.904	= 30.584
1700	8.865	62.123	55.276	11.639	280.502	220.378	= 28.332
1800	8.895	62.630	55.671	12.527	280.847	216.831	= 26.327
1900	8.921	63.112	56.050	13.417	281.190	213.266	= 24.531
2000	8.944	63.570	56.415	14.311	281.532	209.683	= 22.913
2100	8.966	64.007	56.766	15.206	281.872	206.082	= 21.447
2200	8.986	64.425	57.105	16.104	282.209	202.463	= 20.113
2300	9.004	64.824	57.432	17.003	282.546	198.833	= 18.893
2400	9.022	65.208	57.748	17.905	282.880	195.186	= 17.774
2500	9.038	65.577	58.054	18.808	283.214	191.524	= 16.743
2600	9.053	65.931	58.350	19.712	283.544	187.850	= 15.790
2700	9.067	66.273	58.637	20.618	283.874	184.162	= 14.907
2800	9.081	66.603	58.916	21.526	284.204	180.464	= 14.086
2900	9.094	66.922	59.186	22.435	284.531	176.755	= 13.321
3000	9.107	67.231	59.449	23.345	284.857	173.031	= 12.605
3100	9.120	67.530	59.705	24.256	285.181	169.299	= 11.936
3200	9.132	67.819	59.954	25.169	285.504	165.556	= 11.307
3300	9.143	68.101	60.197	26.082	285.825	161.800	= 10.716
3400	9.155	68.374	60.433	26.997	286.146	158.039	= 10.159
3500	9.166	68.639	60.664	27.913	286.464	154.266	= 9.633
3600	9.177	68.898	60.889	28.830	286.780	150.484	= 9.136
3700	9.189	69.149	61.109	29.749	287.096	146.694	= 8.665
3800	9.200	69.394	61.324	30.668	287.410	142.898	= 8.219
3900	9.211	69.633	61.534	31.589	287.722	139.090	= 7.794
4000	9.223	69.867	61.739	32.510	288.033	135.275	= 7.391
4100	9.234	70.095	61.940	33.433	288.342	131.450	= 7.007
4200	9.246	70.317	62.137	34.357	288.650	127.623	= 6.641
4300	9.259	70.535	62.330	35.282	288.956	123.785	= 6.291
4400	9.271	70.748	62.519	36.209	289.260	119.939	= 5.957
4500	9.284	70.957	62.704	37.137	289.563	116.084	= 5.638
4600	9.298	71.161	62.886	38.066	289.864	112.228	= 5.332
4700	9.313	71.361	63.064	38.996	290.165	108.364	= 5.039
4800	9.328	71.557	63.239	39.928	290.463	104.495	= 4.758
4900	9.343	71.750	63.410	40.862	290.761	100.618	= 4.488
5000	9.360	71.939	63.579	41.797	291.056	96.733	= 4.228
5100	9.378	72.124	63.745	42.734	291.350	92.837	= 3.978
5200	9.396	72.306	63.908	43.673	291.644	88.946	= 3.738
5300	9.416	72.486	64.068	44.613	291.936	85.048	= 3.507
5400	9.436	72.662	64.225	45.556	292.227	81.140	= 3.284
5500	9.458	72.835	64.380	46.501	292.516	77.229	= 3.069
5600	9.481	73.006	64.533	47.448	292.806	73.312	= 2.861
5700	9.505	73.174	64.683	48.397	293.093	69.387	= 2.660
5800	9.531	73.339	64.831	49.349	293.381	65.460	= 2.467
5900	9.557	73.502	64.976	50.303	293.668	61.531	= 2.279
6000	9.585	73.663	65.120	51.260	293.954	57.589	= 2.098

Dec. 31, 1970

CARBON MONOFLUORIDE UNIPOSITIVE ION (CF^+) (IDEAL GAS) GFW = 31.009 CF^+

Ground State Configuration $^1\Sigma$ ΔHf°_0 = 272.464 ± 1.2 kcal/mol

$S^\circ_{298.15}$ = [48.13 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 274.72 ± 1.2 kcal/mol

Electronic Levels and Quantum Weights

State	t_i, cm^{-1}	g_i
$X^1\Sigma$	0	1
$a^3\Pi$	[35000]	6

ω_e = [1380] cm^{-1} $\omega_e x_e$ = [11.6] cm^{-1} σ = 1

B_e = [1.4361] cm^{-1} α_e = [0.0193] cm^{-1} r_e = [1.263] Å

Heat of Formation

There have been no direct determinations of the ionization potential but Johns and Barrow (1) have calculated a value by assuming the $B^2\Sigma^+$ state of CF to be the first of a Rydberg series. They report an ionization potential of 8.91 eV (205.464 kcal) which yields $\Delta Hf^\circ_0(CF^+, g)$ = 265.6 ± 10 kcal/mol. An identical value has been calculated by Carroll and Grennan (7) who assumed the $A^2\Sigma^+$ state of CF to be the start of a Rydberg series and estimated the termination by comparison with the same series in N_2, CO and NO.

Dibeler and Liston (2) have measured the photoionization onset of the process

$$FCN + h\nu \rightarrow CF^+ + N + e^- \qquad \Delta H^\circ_0 = 377.03 \text{ kcal}$$

Using JANAF auxiliary data (3) we obtain $\Delta Hf^\circ_0(CF^+, g)$ = 273.0 ± 4 kcal/mol.

Walter et al. (4) have observed the photoionization onset of the process

$$C_2F_4 + h\nu \rightarrow CF^+ + CF_3 + e^- \qquad \Delta H^\circ_0 = 317.306 \pm 0.23 \text{ kcal}$$

The JANAF values (3) for C_2F_4 and CF_3 are consistent since they are both derived from the same simultaneous solution, they yield $\Delta Hf^\circ_0(CF^+, g)$ = 272.464 ± 1.2 kcal/mol, which is adopted. This corresponds to an ionization potential of 212.328 kcal (9.21 eV).

Heat Capacity and Entropy

Spectra reported in the literature, Verma (5), were later shown to belong to BF by Verma (6). We estimated the molecular constants by comparison with CF(g) and BF(g) (3). The $^3\Pi$ electronic level was estimated by comparison with AlCl(g) (3). The enthalpy between 0° and 298.15°K is 2.072 kcal/mol.

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J. Phys. Chem. Ref. Data, Vol. 3, No. 2, 1974

Carbon Difluoride Unipositive Ion (CF_2^+)

(Ideal Gas) GFW = 50.0074

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	9.262	58.952	58.952	.000	225.094	220.880	- 161.909
300	9.279	59.010	58.952	.017	225.102	220.853	- 160.891
400	10.183	61.805	59.327	.991	225.557	219.368	- 119.857
500	10.956	64.163	60.065	2.049	225.986	217.771	- 95.187
600	11.563	66.217	60.922	3.177	226.401	216.089	- 78.710
700	12.024	68.035	61.811	4.357	226.801	214.338	- 66.919
800	12.375	69.665	62.693	5.578	227.194	212.531	- 58.061
900	12.642	71.139	63.551	6.829	227.579	210.674	- 51.159
1000	12.849	72.482	64.378	8.104	227.960	208.775	- 45.628
1100	13.011	73.714	65.171	9.397	228.335	206.838	- 41.095
1200	13.140	74.852	65.931	10.705	228.706	204.868	- 37.311
1300	13.244	75.908	66.658	12.025	229.071	202.866	- 34.105
1400	13.329	76.893	67.355	13.354	229.434	200.838	- 31.352
1500	13.399	77.815	68.022	14.690	229.792	198.784	- 28.963
1600	13.458	78.682	68.661	16.033	230.146	196.702	- 26.868
1700	13.507	79.499	69.275	17.381	230.499	194.602	- 25.018
1800	13.550	80.272	69.865	18.734	230.848	192.479	- 23.370
1900	13.586	81.006	70.432	20.091	231.196	190.340	- 21.894
2000	13.619	81.704	70.978	21.451	231.541	188.182	- 20.564
2100	13.648	82.369	71.505	22.815	231.884	186.004	- 19.358
2200	13.674	83.005	72.013	24.181	232.223	183.809	- 18.260
2300	13.699	83.613	72.504	25.549	232.561	181.604	- 17.256
2400	13.722	84.196	72.979	26.921	232.897	179.381	- 16.335
2500	13.744	84.757	73.439	28.294	233.230	177.143	- 15.486
2600	13.766	85.297	73.885	29.669	233.559	174.893	- 14.701
2700	13.786	85.816	74.317	31.047	233.889	172.630	- 13.973
2800	13.809	86.318	74.737	32.427	234.218	170.356	- 13.297
2900	13.831	86.803	75.145	33.809	234.543	168.071	- 12.666
3000	13.853	87.272	75.541	35.193	234.866	165.771	- 12.076
3100	13.875	87.727	75.927	36.580	235.189	163.463	- 11.524
3200	13.898	88.168	76.303	37.968	235.509	161.145	- 11.006
3300	13.921	88.596	76.669	39.359	235.826	158.813	- 10.518
3400	13.945	89.012	77.026	40.752	236.146	156.477	- 10.058
3500	13.969	89.416	77.374	42.148	236.462	154.129	- 9.624
3600	13.993	89.810	77.714	43.546	236.777	151.773	- 9.214
3700	14.018	90.194	78.046	44.947	237.091	149.407	- 8.825
3800	14.043	90.568	78.371	46.350	237.404	147.036	- 8.457
3900	14.069	90.933	78.688	47.755	237.714	144.652	- 8.106
4000	14.094	91.290	78.999	49.164	238.025	142.263	- 7.773
4100	14.120	91.638	79.303	50.574	238.333	139.862	- 7.455
4200	14.145	91.979	79.601	51.987	238.640	137.460	- 7.153
4300	14.171	92.312	79.892	53.403	238.947	135.048	- 6.864
4400	14.196	92.638	80.178	54.822	239.252	132.627	- 6.588
4500	14.221	92.957	80.459	56.242	239.554	130.196	- 6.323
4600	14.246	93.270	80.734	57.666	239.857	127.764	- 6.070
4700	14.271	93.577	81.004	59.092	240.158	125.325	- 5.828
4800	14.295	93.877	81.269	60.520	240.457	122.882	- 5.595
4900	14.319	94.172	81.529	61.951	240.755	120.430	- 5.371
5000	14.342	94.462	81.785	63.384	241.050	117.970	- 5.156
5100	14.365	94.746	82.037	64.819	241.343	115.497	- 4.949
5200	14.388	95.025	82.284	66.257	241.636	113.033	- 4.751
5300	14.409	95.300	82.527	67.697	241.927	110.560	- 4.559
5400	14.431	95.569	82.766	69.139	242.215	108.075	- 4.374
5500	14.451	95.834	83.001	70.583	242.500	105.590	- 4.196
5600	14.471	96.095	83.232	72.029	242.784	103.099	- 4.024
5700	14.490	96.351	83.460	73.477	243.065	100.599	- 3.857
5800	14.509	96.603	83.685	74.927	243.345	98.097	- 3.696
5900	14.527	96.851	83.906	76.379	243.622	95.592	- 3.541
6000	14.544	97.096	84.124	77.832	243.895	93.074	- 3.390

Dec. 31, 1970

CARBON DIFLUORIDE UNIPOSITIVE ION (CF_2^+) (IDEAL GAS) GFW = 50.0074 CF_2^+

Point Group C_{2v} ΔHf°_0 = 223.5 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = [58.95 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 225.094 ± 3.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[15000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1100] (1)
[650] (1)
[1400] (1)

Bond Distance: C-F = [1.32] Å

Bond Angle: F-C-F = [116 ± 10°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.0688 x 10^{-116}] g^3 cm^6

Heat of Formation

The ionization potential has been reported as 11.7 eV (1), 11.8 eV (2, 3) and 11.85 eV (4) from electron impact measurements. Since there may be excess energy involved we prefer the lowest value, 11.7 ± 0.2 eV. This leads to $\Delta Hf^\circ_0(CF_2^+, g)$ = 226.2 ± 6 kcal/mol using the JANAF $\Delta Hf^\circ_0(CF_2, g)$ = -43.61 ± 1.5 kcal/mol (5).

A more precise value is available from the photoionization measurements of Walter et al. (6), who measured the photoionization threshold for the process

$$C_2F_4 + h\nu \rightarrow CF_2^+ + CF_2 + e^- \qquad \Delta H^\circ_0 = 337.4 \pm 0.9 \text{ kcal/mol}$$

Employing JANAF auxiliary heats (5) we obtain $\Delta Hf^\circ_0(CF_2^+, g)$ = 223.5 ± 3.0 kcal/mol, which is adopted.

Heat Capacity and Entropy

The configuration of CF_2^+ is predicted to be bent by Walsh (7), since it has 17 electrons, thus, its ground state is $^2A_1$, a low lying electronic state is predicted by analogy with NO_2 (8). We estimate the angle to be 116 ± 10°, which is larger than CF_2 at 105°, this is expected from the Walsh correlations (7), but smaller than isoelectronic CO_2^- at 127° and NO_2 at 134°. The vibrational frequencies were estimated by comparison with those for CF_2, CO_2^- and COF (7) as 1100 ± 150 cm^{-1}, 650 ± 50 cm^{-1} and 1400 ± 200 cm^{-1}.

The enthalpy between 0° and 298.15°K is 2.475 kcal/mol. The individual moments of interia were I_A = 7.414 x 10^{-40} g cm^2, I_B = 7.906 x 10^{-39} g cm^2 and I_C = 8.647 x 10^{-39} g cm^2.

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Trifluoromethyl Unipositive Ion (CF_3^+)

(ideal Gas) GFW = 69.0058

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.865	60.807	60.807	.000	100.623	103.078	= 75.558
300	11.900	60.881	60.808	.022	100.629	103.092	= 75.103
400	13.621	64.549	61.296	1.301	101.004	103.860	= 56.746
500	14.976	67.740	62.273	2.734	101.404	104.526	= 45.688
600	16.002	70.566	63.424	4.285	101.827	105.112	= 38.287
700	16.772	73.094	64.628	5.926	102.262	105.625	= 32.978
800	17.352	75.373	65.831	7.633	102.708	106.075	= 28.978
900	17.793	77.443	67.008	9.392	103.163	106.468	= 25.854
1000	18.133	79.336	68.147	11.189	103.623	106.810	= 23.343
1100	18.399	81.077	69.245	13.016	104.086	107.106	= 21.280
1200	18.611	82.688	70.299	14.867	104.553	107.362	= 19.553
1300	18.781	84.184	71.310	16.737	105.015	107.576	= 18.085
1400	18.920	85.581	72.280	18.622	105.481	107.757	= 16.822
1500	19.035	86.891	73.211	20.520	105.945	107.905	= 15.722
1600	19.130	88.122	74.105	22.428	106.408	108.017	= 14.754
1700	19.210	89.285	74.964	24.345	106.871	108.105	= 13.898
1800	19.278	90.385	75.790	26.270	107.330	108.161	= 13.133
1900	19.337	91.429	76.586	28.201	107.790	108.198	= 12.446
2000	19.387	92.422	77.353	30.137	108.247	108.209	= 11.825
2100	19.430	93.369	78.094	32.078	108.703	108.194	= 11.260
2200	19.468	94.274	78.809	34.023	109.155	108.157	= 10.744
2300	19.502	95.140	79.500	35.971	109.605	108.104	= 10.272
2400	19.531	95.970	80.169	37.923	110.051	108.029	= 9.837
2500	19.557	96.768	80.817	39.877	110.495	107.934	= 9.436
2600	19.580	97.536	81.445	41.834	110.936	107.823	= 9.063
2700	19.601	98.275	82.055	43.793	111.374	107.697	= 8.717
2800	19.620	98.988	82.647	45.754	111.811	107.552	= 8.395
2900	19.636	99.677	83.223	47.717	112.241	107.395	= 8.094
3000	19.652	100.343	83.782	49.682	112.668	107.214	= 7.811
3100	19.665	100.987	84.327	51.647	113.093	107.027	= 7.545
3200	19.678	101.612	84.857	53.615	113.514	106.828	= 7.296
3300	19.689	102.218	85.374	55.583	113.931	106.609	= 7.060
3400	19.700	102.806	85.878	57.552	114.344	106.384	= 6.838
3500	19.709	103.377	86.370	59.523	114.752	106.145	= 6.628
3600	19.718	103.932	86.850	61.494	115.159	105.894	= 6.429
3700	19.726	104.473	87.319	63.466	115.560	105.628	= 6.239
3800	19.734	104.999	87.778	65.439	115.958	105.360	= 6.060
3900	19.740	105.511	88.226	67.413	116.351	105.072	= 5.888
4000	19.747	106.011	88.664	69.387	116.740	104.779	= 5.725
4100	19.753	106.499	89.093	71.362	117.124	104.470	= 5.569
4200	19.758	106.975	89.514	73.338	117.505	104.163	= 5.420
4300	19.764	107.440	89.925	75.314	117.882	103.842	= 5.278
4400	19.768	107.894	90.328	77.291	118.252	103.511	= 5.141
4500	19.773	108.339	90.724	79.268	118.619	103.165	= 5.010
4600	19.777	108.773	91.111	81.245	118.982	102.821	= 4.885
4700	19.781	109.199	91.492	83.223	119.340	102.466	= 4.765
4800	19.785	109.615	91.865	85.202	119.694	102.106	= 4.649
4900	19.788	110.023	92.231	87.180	120.042	101.737	= 4.538
5000	19.792	110.423	92.591	89.159	120.385	101.360	= 4.430
5100	19.795	110.815	92.945	91.138	120.723	100.964	= 4.327
5200	19.798	111.199	93.292	93.118	121.058	100.584	= 4.227
5300	19.800	111.577	93.633	95.098	121.388	100.188	= 4.131
5400	19.803	111.947	93.969	97.078	121.712	99.779	= 4.038
5500	19.805	112.310	94.299	99.059	122.031	99.374	= 3.949
5600	19.808	112.667	94.624	101.039	122.344	98.957	= 3.862
5700	19.810	113.018	94.944	103.020	122.653	98.539	= 3.778
5800	19.812	113.362	95.258	105.001	122.958	98.110	= 3.697
5900	19.814	113.701	95.568	106.982	123.256	97.679	= 3.618
6000	19.816	114.034	95.873	108.964	123.550	97.242	= 3.542

Dec. 31, 1971

TRIFLUOROMETHYL UNIPOSITIVE ION (CF_3^+) (IDEAL GAS) GFW = 69.0058

Point Group D_{3h} ΔHf°_0 = 99.8 ± 2.8 kcal/mol

$S^\circ_{298.15}$ = 60.81 ± 0.4 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 100.6 ± 2.8 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[888] (1)
830 (1)
[1404] (2)
[480] (2)

Bond Distance: C-F = [1.33] Å

Bond Angle: F-C-F = [120°] σ = 6

Product of the Moments of Inertia: $I_A I_B I_C$ = [1.1728 x 10^{-114}] $g^3 cm^6$

Heat of Formation

The ionization potential of CF_3 has been carefully measured by Lifshitz and Chupka (1). They used a photoionization technique on CF_3 radicals prepared by heating CF_3CH_2ONO. Because of the low ionization cross-section near the threshold it is very difficult to determine the value exactly. The authors conclude that it is improbable that the ionization potential differs from 9.25 eV by as much as 0.2 eV. They choose to accept a value of 9.25 ± 0.04 eV (213.3 ± 0.9 kcal) based on their interpretation of the regular structure near the threshold. In a later paper Walter, Lifshitz, Chupka and Berkowitz (9) use photodissociative ionization of CF_3I, CF_3Br and CF_3Cl to obtain an indirect ionization potential for CF_3 of 9.11 eV. We adopt a median value of 9.17 ± 0.08 eV (211.5 ± 1.8 kcal), which with $\Delta Hf^\circ_0(CF_3, g)$ = -111.7 ± 1.0 kcal/mol (2) gives $\Delta Hf^\circ_0(CF_3^+, g)$ = 99.8 ± 2.8 kcal/mol.

The above value supercedes all earlier values for the ionization potential of CF_3 which generally were obtained by electron impact methods, which do not have the energy resolution available in the photoionization technique. For further details of the older values see references 3, 4, 5, 6 and 7.

Heat Capacity and Entropy

The correlation rules proposed by Walsh (8) for AB_3 molecules indicate that molecules with less than 25 valence electrons are planar in their ground states. Since BF_3 is isoelectronic with CF_3^+ we estimate the vibrational frequencies by transferring the valence force field constants from BF_3 to CF_3^+. This gives 888, 674, 1404 and 480 cm^{-1}, however, Lifshitz and Chupka (1) conclude that the 674 cm^{-1} frequency is in fact at 830 cm^{-1}. This value is obtained from the spacings in the fine structure of the photoionization curve near threshold. They believe that the out-of-plane motion is most likely to be excited by the transition from pyramidal CF_3 to planar CF_3^+, thus, they ascribe the 830 cm^{-1} spacing to this motion. We adopt this one frequency in place of the calculated value. The bond lengths are assumed equal to those in CF_3. The individual moments of inertia are $I_A = I_B$ = 8.37 x 10^{-39} g cm^2, and I_C = 16.74 x 10^{-39} g cm^2.

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CH^+

Methylidyne Unipositive Ion (CH^+)

(Ideal Gas) GFW = 13.01857

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	6.988	41.004	41.003	.000	388.800	380.145	- 278.654
300	6.988	41.047	41.004	.013	388.811	380.091	- 276.896
400	6.982	43.053	41.277	.710	389.413	377.092	- 206.033
500	7.023	44.614	41.794	1.410	389.941	373.949	- 163.453
600	7.104	45.901	42.374	2.116	390.416	370.705	- 135.029
700	7.219	47.005	42.959	2.832	390.852	367.385	- 114.703
800	7.356	47.977	43.526	3.561	391.266	364.004	- 99.441
900	7.502	48.852	44.070	4.304	391.663	360.572	- 87.559
1000	7.648	49.650	44.589	5.061	392.052	357.096	- 78.043
1100	7.788	50.386	45.083	5.833	392.435	353.582	- 70.250
1200	7.919	51.069	45.554	6.618	392.813	350.034	- 63.750
1300	8.039	51.708	46.003	7.416	393.187	346.453	- 58.244
1400	8.148	52.308	46.432	8.226	393.561	342.846	- 53.521
1500	8.247	52.873	46.843	9.046	393.931	339.211	- 49.423
1600	8.337	53.408	47.236	9.875	394.297	335.548	- 45.834
1700	8.419	53.916	47.615	10.713	394.664	331.866	- 42.664
1800	8.493	54.400	47.978	11.558	395.029	328.161	- 39.844
1900	8.560	54.861	48.328	12.411	395.394	324.437	- 37.319
2000	8.622	55.301	48.666	13.270	395.758	320.693	- 35.044
2100	8.678	55.723	48.992	14.135	396.120	316.932	- 32.983
2200	8.730	56.128	49.307	15.006	396.480	313.150	- 31.109
2300	8.778	56.517	49.612	15.881	396.841	309.357	- 29.396
2400	8.823	56.892	49.908	16.761	397.200	305.546	- 27.824
2500	8.865	57.253	50.195	17.646	397.558	301.718	- 26.376
2600	8.904	57.601	50.473	18.534	397.913	297.877	- 25.039
2700	8.941	57.938	50.743	19.427	398.269	294.022	- 23.799
2800	8.976	58.264	51.006	20.322	398.624	290.155	- 22.648
2900	9.009	58.580	51.262	21.222	398.978	286.276	- 21.574
3000	9.041	58.886	51.511	22.124	399.330	282.383	- 20.572
3100	9.073	59.183	51.753	23.030	399.682	278.479	- 19.633
3200	9.103	59.471	51.990	23.939	400.033	274.564	- 18.752
3300	9.133	59.752	52.221	24.850	400.382	270.636	- 17.923
3400	9.162	60.025	52.447	25.765	400.731	266.700	- 17.143
3500	9.191	60.291	52.667	26.683	401.078	262.752	- 16.407
3600	9.220	60.550	52.882	27.603	401.424	258.794	- 15.711
3700	9.249	60.803	53.093	28.527	401.769	254.828	- 15.052
3800	9.278	61.050	53.299	29.453	402.115	250.855	- 14.427
3900	9.307	61.291	53.501	30.382	402.458	246.871	- 13.834
4000	9.337	61.527	53.699	31.315	402.800	242.876	- 13.270
4100	9.367	61.758	53.893	32.250	403.142	238.872	- 12.733
4200	9.398	61.984	54.082	33.188	403.483	234.864	- 12.221
4300	9.429	62.206	54.269	34.129	403.823	230.844	- 11.733
4400	9.461	62.423	54.452	35.074	404.163	226.816	- 11.266
4500	9.494	62.636	54.631	36.022	404.501	222.778	- 10.820
4600	9.527	62.845	54.808	36.973	404.839	218.740	- 10.392
4700	9.561	63.050	54.981	37.927	405.178	214.691	- 9.983
4800	9.596	63.252	55.151	38.885	405.515	210.636	- 9.591
4900	9.631	63.450	55.318	39.846	405.853	206.573	- 9.214
5000	9.667	63.645	55.483	40.811	406.189	202.501	- 8.851
5100	9.703	63.837	55.645	41.780	406.525	198.420	- 8.503
5200	9.741	64.026	55.804	42.752	406.862	194.337	- 8.168
5300	9.778	64.212	55.961	43.728	407.199	190.251	- 7.845
5400	9.817	64.395	56.116	44.708	407.536	186.154	- 7.534
5500	9.856	64.575	56.268	45.691	407.871	182.051	- 7.234
5600	9.895	64.753	56.418	46.679	408.208	177.940	- 6.944
5700	9.935	64.929	56.565	47.670	408.545	173.823	- 6.665
5800	9.976	65.102	56.711	48.668	408.881	169.702	- 6.395
5900	10.016	65.273	56.855	49.665	409.218	165.581	- 6.133
6000	10.057	65.441	56.996	50.669	409.555	161.442	- 5.881

Dec. 31, 1971

METHYLIDYNE UNIPOSITIVE ION (CH^+) (IDEAL GAS) GFW = 13.01857

Ground State Quantum Weight = 1

ΔHf°_0 = 386.5 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 41.00 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 388.8 ± 0.5 kcal/mol

Electronic Levels and Degeneracies

ϵ_i, cm^{-1}	g_i
0	1
23596.94	2

ω_e = 2885.7 cm^{-1} $\omega_e x_e$ = [73] cm^{-1} σ = 1

B_e = 14.1776 cm^{-1} α_e = 0.4917 cm^{-1} r_e = 1.3909 Å

Heat of Formation

Douglas and Herzberg (1) first observed the spectrum of CH^+ and concluded that $D_0(CH^+)$ = 3.61 ± 0.22 eV from a short extrapolation of the A state vibrational separations, this leads to an ionization potential of 11.13 ± 0.22 eV. Later Douglas and Morton (2) showed that the basis for this extrapolation was incorrect and the value was thus invalidated. Herzberg and Johns (3) then reported a value for the ionization potential of CH of 10.64 eV (245.36 kcal) which was obtained from the limit of the Rydberg states of CH (see also Herzberg (4)). This value in conjunction with the JANAF value for $\Delta Hf^\circ_0(CH, g)$ = 141.178 kcal/mol leads to $\Delta Hf^\circ_0(CH^+, g)$ = 386.5 ± 0.5 kcal/mol and is adopted.

Heat Capacity and Entropy

The molecular constants are those reported by Douglas and Morton (2). The value for ω_e is derived from the observed $\Delta G_{1/2}$ by adding $2\omega_e x_e$. The $\omega_e x_e$ value is that calculated by Moore et al. (5) from ab initio variational calculations of the $^1\Sigma$ and $^3\Pi$ states.

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Hydrogen Isocyanate (HNCO)

(Ideal Gas) GFW = 43.0252

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.620	-23.582	-23.582	INFINITE
100	7.999	47.135	65.378	-1.824	-23.874	-23.369	51.072
200	9.146	52.952	57.845	-.979	-24.104	-22.777	24.890
298	10.765	56.911	56.911	.000	-24.300	-22.082	16.187
300	10.793	56.978	56.911	.020	-24.304	-22.069	16.077
400	12.174	60.274	57.352	1.169	-24.452	-21.300	11.638
500	13.147	63.094	58.225	2.435	-24.571	-20.498	8.960
600	13.960	65.565	59.247	3.791	-24.676	-19.673	7.166
700	14.634	67.769	60.310	5.222	-24.775	-18.831	5.879
800	15.207	69.762	61.368	6.715	-24.864	-17.976	4.911
900	15.703	71.582	62.404	8.261	-24.946	-17.111	4.155
1000	16.136	73.260	63.406	9.853	-25.021	-16.236	3.548
1100	16.516	74.816	64.374	11.486	-25.087	-15.355	3.051
1200	16.849	76.268	65.305	13.155	-25.146	-14.466	2.635
1300	17.142	77.628	66.201	14.855	-25.201	-13.575	2.282
1400	17.406	78.908	67.064	16.582	-25.249	-12.677	1.979
1500	17.627	80.116	67.894	18.334	-25.295	-11.777	1.716
1600	17.827	81.261	68.694	20.107	-25.337	-10.877	1.486
1700	18.005	82.347	69.465	21.898	-25.376	-9.971	1.282
1800	18.162	83.380	70.210	23.707	-25.414	-9.064	1.101
1900	18.302	84.366	70.929	25.530	-25.449	-8.153	.938
2000	18.426	85.308	71.625	27.367	-25.484	-7.243	.791
2100	18.537	86.210	72.298	29.215	-25.519	-6.329	.659
2200	18.637	87.075	72.950	31.074	-25.556	-5.416	.538
2300	18.726	87.905	73.582	32.942	-25.592	-4.498	.427
2400	18.807	88.704	74.196	34.819	-25.630	-3.579	.326
2500	18.879	89.473	74.792	36.703	-25.670	-2.663	.233
2600	18.945	90.215	75.371	38.594	-25.713	-1.740	.146
2700	19.005	90.931	75.934	40.492	-25.757	-.818	.066
2800	19.059	91.623	76.482	42.395	-25.803	.106	-.008
2900	19.109	92.293	77.016	44.304	-25.853	1.035	-.078
3000	19.154	92.941	77.536	46.217	-25.906	1.962	-.143
3100	19.196	93.570	78.043	48.134	-25.960	2.892	-.204
3200	19.234	94.180	78.538	50.056	-26.016	3.823	-.261
3300	19.269	94.773	79.021	51.981	-26.080	4.755	-.315
3400	19.301	95.348	79.493	53.910	-26.145	5.692	-.366
3500	19.331	95.908	79.954	55.841	-26.214	6.626	-.414
3600	19.359	96.453	80.404	57.776	-26.286	7.566	-.459
3700	19.384	96.984	80.845	59.713	-26.362	8.509	-.503
3800	19.408	97.501	81.277	61.653	-26.441	9.455	-.544
3900	19.430	98.006	81.699	63.595	-26.524	10.401	-.583
4000	19.451	98.498	82.113	65.539	-26.611	11.348	-.620
4100	19.470	98.978	82.519	67.485	-26.702	12.296	-.655
4200	19.488	99.448	82.916	69.433	-26.797	13.251	-.690
4300	19.505	99.907	83.306	71.382	-26.896	14.206	-.722
4400	19.521	100.355	83.688	73.334	-26.998	15.160	-.753
4500	19.535	100.794	84.064	75.286	-27.106	16.117	-.783
4600	19.549	101.224	84.432	77.241	-27.216	17.084	-.812
4700	19.562	101.644	84.794	79.196	-27.330	18.048	-.839
4800	19.575	102.056	85.149	81.153	-27.449	19.017	-.866
4900	19.586	102.460	85.498	83.111	-27.571	19.982	-.891
5000	19.597	102.856	85.842	85.070	-27.698	20.954	-.916
5100	19.607	103.244	86.179	87.030	-27.830	21.925	-.940
5200	19.617	103.625	86.511	88.992	-27.963	22.902	-.963
5300	19.626	103.998	86.837	90.954	-28.102	23.887	-.985
5400	19.635	104.365	87.158	92.917	-28.244	24.866	-1.006
5500	19.643	104.726	87.475	94.881	-28.391	25.854	-1.027
5600	19.651	105.080	87.786	96.846	-28.542	26.838	-1.047
5700	19.659	105.428	88.092	98.811	-28.697	27.827	-1.067
5800	19.666	105.770	88.394	100.777	-28.856	28.822	-1.086
5900	19.672	106.106	88.691	102.744	-29.019	29.820	-1.105
6000	19.679	106.436	88.984	104.712	-29.186	30.814	-1.122

Dec. 31, 1960; Dec. 31, 1970

HYDROGEN ISOCYANATE (HNCO) (IDEAL GAS) GFW = 43.0252 CHNO

Point Group C_s ΔHf°_0 = -23.6 ± 2 kcal/mol

$S^\circ_{298.15}$ = 56.9 ± 0.1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -24.3 ± 2 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
3531 (1)	659.8 (1)
2274 (1)	577.5 (1)
1327 (1)	777.1 (1)

Bond Distance: H-N = 0.987 Å N-C = 1.207 Å C-O = 1.171 Å

Bond Angle: H-N-C = 128.1° N-C-O = 180° σ = 1

Product of the Moments of Inertia: $I_A I_B I_C = 5.3178 \times 10^{-117}\ g^3\ cm^6$

Heat of Formation

Okabe (1) has measured the onset of photodissociation for the process HNCO(g) → NH(c'Π) + CO(g) as 8.79 ± 0.03 eV (202.7 ± 0.7 kcal). Okabe and Lenzi (2) have also reported the onset of photodissociation for the process NH_3(g) → NH(c'Π) + H_2(g) as 9.35 ± 0.06 eV (215.6 ± 1.4 kcal). Elimination of the NH(c'Π) gives

$$NH_3(g) + CO(g) \rightarrow HNCO\ (g) + H_2(g) \qquad \Delta H^\circ_0 = 12.9 \pm 2 \text{ kcal}$$

which with JANAF auxiliary data (3) yields ΔHf°_0(HNCO, g) = -23.6 ± 2 kcal/mol, or ΔHf°_{298}(HNCO, g) = -24.3 ± 2 kcal/mol.

The heat of formation of ionized cyanic acid in aqueous solution is -34.9 kcal/mol (4). Since the ions from cyanic acid and isocyanic acid are identical in solution we can use this value for aqueous isocyanic acid. Assuming the heat of solution is -3 ± 3 kcal/mol, a value covering the range of heats of solution of most organic liquids (4), we obtain ΔHf°_{298}(HNCO, ℓ) = -32 ± 3 kcal/mol. Using ΔHv° = 7.2 kcal/mol (5) we obtain ΔHf°_{298}(HNCO, g) = -25 ± 3 kcal/mol. If we assume that ΔHf°_{298}(HNCO, g) - ΔHf°_{298}(HCNO, ionized aq) = ΔHf°_{298}(HNCS, g) - ΔHf°_{298}(HCNS, ionized aq) then we obtain ΔHf°_{298}(HNCO, g) = -23 kcal/mol employing values from (4). We adopt the value ΔHf°_{298}(HNCO, g) = -24.3 ± 2 kcal/mol.

Heat Capacity and Entropy

The vibrational frequency determinations have been summarized by Herzberg and Reid (6). Ashby and Werner (7) have remeasured the three lower fundamentals under much higher resolution. They reverse the assignments of ν_5 and ν_6 of Herzberg and Reid. Dixon and Kirby (8) have discussed the corrections due to Coriolis interaction made by Ashby and Werner and conclude they are in the wrong direction. On this basis they reverse the ν_4 and ν_6 assignments of Herzberg and Reid.

The bond distances and angles are from the microwave measurements of Jones et al. (9) which give rotational constants in good agreement with the later microwave work of Kewley (10).

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Formyl (HCO)

(Ideal Gas) GFW = 29.01852

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	- 2.387	10.314	10.314	INFINITE
100	7.969	44.912	60.836	- 1.593	10.368	9.87	- 20.079
200	7.994	50.429	54.411	- .798	10.437	7.969	- 8.708
298	8.269	53.665	53.665	.000	10.400	6.762	- 4.957
300	8.276	53.717	53.666	.015	10.398	6.740	- 4.910
400	8.731	56.157	53.995	.865	10.299	5.534	- 3.024
500	9.257	58.161	54.633	1.764	10.164	4.358	- 1.905
600	9.791	59.896	55.369	2.716	10.011	3.210	- 1.169
700	10.293	61.444	56.128	3.721	9.851	2.090	- .653
800	10.746	62.848	56.882	4.773	9.692	.992	- .271
900	11.143	64.138	57.617	5.868	9.537	- .087	.021
1000	11.485	65.330	58.330	7.000	9.391	- 1.148	.251
1100	11.774	66.439	59.017	8.164	9.249	- 2.196	.436
1200	12.029	67.475	59.679	9.354	9.112	- 3.229	.588
1300	12.243	68.446	60.317	10.568	8.977	- 4.253	.715
1400	12.426	69.360	60.930	11.802	8.845	- 5.264	.822
1500	12.584	70.223	61.521	13.053	8.714	- 6.267	.913
1600	12.720	71.040	62.091	14.318	8.581	- 7.263	.992
1700	12.840	71.814	62.640	15.596	8.451	- 8.249	1.060
1800	12.945	72.551	63.171	16.885	8.318	- 9.228	1.120
1900	13.037	73.254	63.683	18.185	8.185	- 10.198	1.173
2000	13.120	73.925	64.178	19.493	8.051	- 11.163	1.220
2100	13.194	74.567	64.658	20.808	7.915	- 12.118	1.261
2200	13.262	75.182	65.122	22.131	7.775	- 13.071	1.299
2300	13.323	75.773	65.573	23.460	7.634	- 14.014	1.332
2400	13.379	76.341	66.010	24.796	7.490	- 14.951	1.361
2500	13.430	76.888	66.434	26.136	7.343	- 15.886	1.389
2600	13.476	77.416	66.846	27.482	7.194	- 16.811	1.413
2700	13.523	77.926	67.247	28.832	7.041	- 17.733	1.435
2800	13.564	78.418	67.637	30.186	6.886	- 18.647	1.455
2900	13.603	78.895	68.017	31.544	6.728	- 19.554	1.474
3000	13.640	79.357	68.388	32.907	6.567	- 20.459	1.490
3100	13.674	79.804	68.749	34.272	6.404	- 21.356	1.506
3200	13.707	80.239	69.101	35.641	6.237	- 22.249	1.520
3300	13.738	80.661	69.445	37.014	6.067	- 23.139	1.532
3400	13.767	81.072	69.781	38.389	5.894	- 24.020	1.544
3500	13.795	81.471	70.109	39.767	5.718	- 24.900	1.555
3600	13.822	81.860	70.430	41.148	5.539	- 25.771	1.565
3700	13.846	82.239	70.744	42.531	5.356	- 26.637	1.573
3800	13.872	82.609	71.052	43.917	5.171	- 27.497	1.581
3900	13.895	82.970	71.353	45.306	4.983	- 28.355	1.589
4000	13.917	83.322	71.648	46.696	4.791	- 29.207	1.596
4100	13.939	83.666	71.937	48.089	4.597	- 30.057	1.602
4200	13.959	84.002	72.220	49.484	4.399	- 30.897	1.608
4300	13.979	84.330	72.498	50.881	4.197	- 31.736	1.613
4400	13.998	84.652	72.770	52.280	3.993	- 32.571	1.618
4500	14.017	84.967	73.038	53.681	3.785	- 33.402	1.622
4600	14.034	85.275	73.300	55.083	3.575	- 34.222	1.626
4700	14.051	85.577	73.558	56.487	3.361	- 35.041	1.629
4800	14.068	85.873	73.812	57.893	3.144	- 35.854	1.632
4900	14.084	86.163	74.061	59.301	2.925	- 36.667	1.635
5000	14.100	86.448	74.306	60.710	2.702	- 37.473	1.638
5100	14.115	86.727	74.547	62.121	2.475	- 38.276	1.640
5200	14.130	87.002	74.784	63.533	2.246	- 39.078	1.642
5300	14.145	87.271	75.017	64.947	2.014	- 39.861	1.644
5400	14.159	87.536	75.246	66.362	1.779	- 40.651	1.645
5500	14.173	87.795	75.472	67.779	1.540	- 41.433	1.646
5600	14.187	88.051	75.694	69.197	1.299	- 42.215	1.648
5700	14.201	88.302	75.913	70.616	1.054	- 42.993	1.648
5800	14.215	88.549	76.129	72.037	.807	- 43.762	1.649
5900	14.228	88.792	76.342	73.459	.556	- 44.525	1.649
6000	14.242	89.032	76.551	74.883	.303	- 45.291	1.650

Mar. 31, 1961; Dec. 31, 1970

FORMYL (HCO) (IDEAL GAS) GFW = 29.01852 CHO

Point Group C_s ΔHf°_0 = 10.3 ± 2 kcal/mol

$S^\circ_{298.15}$ = 53.66 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 10.4 ± 2 kcal/mol

Ground State Quantum Weight = 2

Electronic Levels and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}	B_0, cm^{-1}	$I_A I_B I_C$ g^3 cm^6
X^2A'	0	2	2488 (1)	1083 (1)	1820 (1)	--	0.4654 x 10^{-117}
$\tilde{A}^2\Sigma^-$	9294	2	3316.2(1)	802.3(2)	1813.4(1)	1.3377	---
$\tilde{B}^2A'$	38691	2	[2488] (1)	[1083] (1)	[1820] (1)	--	1.0085 x 10^{-117}
$\tilde{C}^2A''$	41270	2	[2488] (1)	[1083] (1)	[1820] (1)	--	[0.4654] x 10^{-117}

Bond Distance (X^2A'): C-H = 1.16 Å C-O = 1.17 Å

Bond Angle (X^2A'): H-C-O = 123.8° σ = 1

Heat of Formation

The adopted ΔHf°_{298}(HCO, g) = 10.4 ± 2 kcal/mol is calculated from D(OHC-CHO, g) = 71.5 ± 2 kcal/mol and ΔHf°_{298}(glyoxal, g) = -50.66 ± 0.2 kcal/mol. The C-C bond dissociation energy in glyoxal was determined from chemiluminescent recombination of formyl radicals by Hartley (1). The heat of formation of glyoxal was determined from flame combustion calorimetry by Fletcher and Pilcher (2).

The other route to derive the heat of formation of formyl radical was from D(H-CHO) which has been studied by many investigators listed below. There are several conflicting values between 77 to 91 kcal for D(H-CHO). Based on the adopted ΔHf°_{298}(HCO, g) = 10.4 ± 2 kcal/mol, we have derived D(H-CHO) = 89.3 ± 2 kcal/mol which is in essential agreement with the high values of D(H-CHO). The low values were probably not reliable as pointed out by Calvert (3), Walsh and Benson (5), Haney and Franklin (9).

Investigator	Method	D(H-CHO) kcal/mol
Calvert (3)	Kinetic	91
Klein and Schoen (4)	Kinetic	77
Walsh and Benson (5)	Kinetic	87 ± 1
Brand and Reed (6)	Spectroscopic	<82.3
Reed and Brand (7)	Electron Impact	75 ± 2.3
Shannon and Harrison (8)	Electron Impact	79 ± 3
Haney and Franklin (9)	Electron Impact	87 ± 3

Heat Capacity and Entropy

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states. The observed molecular constants and electronic levels were taken from Herzberg and Ramsay (10, 11, 12) and Dixon (13).- The vibrational frequency (ω_1 = 2488 cm^{-1}) was observed using the matrix isolation infrared technique by Milligan and Jacox (14). Using the same technique, Ewing, Thompson and Pimentel (15) found ω_2 = 1091 cm^{-1} and ω_3 = 1860 cm^{-1} which are in good agreement with the values adopted (10). These small differences are probably due to matrix shifts. The bond lengths and angle were calculated from the normal coordinate analyses by Shirk and Pimentel (16). These values are a better fit than those calculated by Johns, Priddle and Ramsay (12) who assumed a normal CH bond length of 1.08 Å.

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Formyl Unipositive Ion (HCO^+)

(Ideal Gas) GFW = 29.01797

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	6.595	48.591	48.591	.000	199.100	195.488	≈ 143.297
300	6.612	48.644	48.591	.016	199.108	195.465	≈ 142.396
400	9.399	51.236	48.939	.919	199.559	194.183	≈ 106.097
500	9.995	53.399	49.621	1.889	199.993	192.789	≈ 84.268
600	10.690	55.267	50.409	2.914	200.409	191.308	≈ 69.684
700	10.929	56.917	51.223	3.986	200.812	189.760	≈ 59.246
800	11.326	58.403	52.029	5.099	201.211	188.153	≈ 51.401
900	11.686	59.758	52.814	6.250	201.609	186.497	≈ 45.288
1000	12.010	61.006	53.572	7.435	202.012	184.796	≈ 40.387
1100	12.300	62.165	54.301	8.650	202.419	183.055	≈ 36.370
1200	12.556	63.246	55.002	9.894	202.832	181.276	≈ 33.015
1300	12.786	64.261	55.675	11.161	203.246	179.463	≈ 30.170
1400	12.987	65.216	56.323	12.450	203.667	177.619	≈ 27.798
1500	13.165	66.118	56.946	13.758	204.090	175.744	≈ 25.606
1600	13.322	66.973	57.546	15.082	204.513	173.838	≈ 23.745
1700	13.461	67.785	58.125	16.421	204.940	171.909	≈ 22.100
1800	13.584	68.558	58.683	17.774	205.368	169.953	≈ 20.635
1900	13.693	69.295	59.223	19.138	205.796	167.975	≈ 19.322
2000	13.790	70.000	59.744	20.512	206.225	165.973	≈ 18.137
2100	13.877	70.675	60.246	21.896	206.653	163.951	≈ 17.063
2200	13.954	71.322	60.737	23.287	207.079	161.905	≈ 16.084
2300	14.024	71.944	61.211	24.686	207.505	159.844	≈ 15.189
2400	14.087	72.542	61.671	26.092	207.928	157.764	≈ 14.366
2500	14.143	73.119	62.117	27.503	208.349	155.663	≈ 13.606
2600	14.194	73.674	62.551	28.920	208.767	153.548	≈ 12.907
2700	14.240	74.211	62.973	30.342	209.183	151.415	≈ 12.256
2800	14.282	74.730	63.384	31.768	209.598	149.269	≈ 11.651
2900	14.320	75.231	63.784	33.198	210.006	147.109	≈ 11.086
3000	14.355	75.717	64.173	34.632	210.415	144.932	≈ 10.558
3100	14.387	76.189	64.553	36.069	210.820	142.742	≈ 10.063
3200	14.417	76.646	64.924	37.509	211.221	140.540	≈ 9.598
3300	14.444	77.090	65.286	38.952	211.619	138.323	≈ 9.161
3400	14.468	77.522	65.640	40.398	212.013	136.097	≈ 8.744
3500	14.491	77.941	65.985	41.846	212.404	133.857	≈ 8.358
3600	14.513	78.350	66.323	43.296	212.790	131.607	≈ 7.990
3700	14.532	78.748	66.653	44.748	213.173	129.348	≈ 7.640
3800	14.550	79.135	66.977	46.203	213.554	127.080	≈ 7.309
3900	14.567	79.514	67.293	47.659	213.930	124.799	≈ 6.994
4000	14.583	79.883	67.604	49.116	214.301	122.508	≈ 6.694
4100	14.598	80.243	67.908	50.575	214.670	120.207	≈ 6.408
4200	14.612	80.595	68.205	52.036	215.034	117.902	≈ 6.135
4300	14.624	80.939	68.496	53.497	215.394	115.584	≈ 5.875
4400	14.637	81.275	68.784	54.960	215.751	113.257	≈ 5.626
4500	14.648	81.604	69.065	56.425	216.103	110.920	≈ 5.387
4600	14.658	81.926	69.342	57.890	216.453	108.584	≈ 5.159
4700	14.668	82.242	69.613	59.356	216.798	106.236	≈ 4.940
4800	14.678	82.551	69.879	60.824	217.139	103.881	≈ 4.730
4900	14.687	82.853	70.141	62.292	217.477	101.516	≈ 4.528
5000	14.695	83.150	70.398	63.761	217.810	99.144	≈ 4.334
5100	14.703	83.441	70.651	65.231	218.139	96.766	≈ 4.147
5200	14.710	83.727	70.900	66.701	218.466	94.382	≈ 3.967
5300	14.717	84.007	71.144	68.173	218.789	91.999	≈ 3.794
5400	14.724	84.282	71.385	69.645	219.107	89.601	≈ 3.626
5500	14.730	84.552	71.622	71.118	219.421	87.201	≈ 3.465
5600	14.736	84.818	71.855	72.591	219.732	84.792	≈ 3.309
5700	14.742	85.079	72.085	74.065	220.039	82.376	≈ 3.158
5800	14.747	85.335	72.311	75.539	220.342	79.960	≈ 3.013
5900	14.752	85.587	72.534	77.014	220.641	77.541	≈ 2.872
6000	14.757	85.835	72.754	78.490	220.936	75.108	≈ 2.736

June 30, 1966; Dec. 31, 1970

FORMYL UNIPOSITIVE ION (HCO^+) (IDEAL GAS) GFW = 29.01797 CHO^+

Point Group [$C_{\infty v}$] ΔHf°_0 = 197.7 ± 2 kcal/mol

$S^\circ_{298.15}$ = [48.6 ± 1] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 199.1 ± 2 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[3223] (1)
[707] (2)
[2088] (1)

Bond Distance: C-H = [1.07] Å C-O = [1.17] Å

Bond Angle: H-C-O = [180°] σ = 1

Rotational Constant: B_0 = [1.367] cm^{-1}

Heat of Formation

Using the photoionization technique, Matthews and Warneck (1) measured the appearance potentials of HCO^+(g) from formaldehyde, formic acid and acetaldehyde as 11.95, 12.79 and 11.79 eV, respectively, whose average yields $\Delta Hf^\circ_0(HCO^+, g)$ = 197.7 ± 1.5 kcal/mol, based on the following ΔHf°_0 data (in units of kcal/mol): 51.63 for H(g), 9.35 for OH(g), 35.62 for CH_3(g), -26.78 for H_2CO(g) (2), -88.74 for HCOOH(g) (3) and -37.14 for CH_3CHO (4). The appearance potentials obtained from photoionization are several tenths to 1 eV lower than the recent electron impact data (5, 6, 7, 8, 9). The appearance potentials determined by the electron impact method tend to be high because the fundamental nature of the process does not lead to a sharp onset in contrast to the step-function behavior of photoionization onset.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear based on two reasons: (1) the molecule HCO^+(g) is isoelectronic with HCN(g) which is linear; (2) A. D. Walsh (10) predicted that "HAB' molecules with 10 or less valence electrons will be linear in their ground state. HCO^+(g) has 10 valence electrons.

The bond distances HC and CO were estimated to be the same as those in HCN and HCO molecules, respectively. The principal moment of inertia is 2.0476×10^{-39} g cm^2. The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants which were obtained from HCN (g). The enthalpy at 0°K is -2.211 kcal/mol.

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Methyl Chloride (CH_3Cl)

(Ideal Gas) GFW = 50.488

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	− 2.489	− 18.104	− 18.104	INFINITE
100	7.955	46.810	63.754	− 1.694	− 18.810	− 17.554	38.365
200	8.401	52.408	56.830	− .884	− 19.345	− 16.111	17.606
298	9.735	55.988	55.988	.000	− 20.000	− 14.387	10.546
300	9.765	56.048	55.988	.018	− 20.013	− 14.352	10.455
400	11.509	59.095	56.392	1.081	− 20.652	− 12.367	6.757
500	13.180	61.846	57.212	2.317	− 21.210	− 10.229	4.471
600	14.647	64.382	58.198	3.710	− 21.679	− 7.988	2.910
700	15.919	66.737	59.252	5.240	− 22.067	− 5.673	1.771
800	17.026	68.937	60.326	6.888	− 22.379	− 3.310	.904
900	17.995	70.999	61.399	8.641	− 22.627	− .911	.221
1000	18.844	72.940	62.457	10.483	− 22.814	1.511	− .330
1100	19.587	74.772	63.494	12.406	− 22.952	3.951	− .785
1200	20.236	76.505	64.507	14.398	− 23.047	6.402	− 1.166
1300	20.804	78.147	65.493	16.450	− 23.111	8.858	− 1.489
1400	21.300	79.708	66.453	18.556	− 23.144	11.320	− 1.767
1500	21.734	81.192	67.387	20.708	− 23.158	13.784	− 2.008
1600	22.115	82.607	68.294	22.901	− 23.156	16.243	− 2.219
1700	22.449	83.958	69.176	25.130	− 23.136	18.708	− 2.405
1800	22.744	85.250	70.034	27.390	− 23.106	21.166	− 2.570
1900	23.005	86.487	70.867	29.677	− 23.066	23.627	− 2.718
2000	23.236	87.673	71.678	31.989	− 23.019	26.083	− 2.850
2100	23.441	88.812	72.467	34.324	− 22.965	28.537	− 2.970
2200	23.624	89.906	73.235	36.677	− 22.910	30.986	− 3.078
2300	23.788	90.960	73.983	39.048	− 22.849	33.438	− 3.177
2400	23.935	91.976	74.712	41.434	− 22.788	35.885	− 3.268
2500	24.068	92.956	75.422	43.834	− 22.729	38.324	− 3.350
2600	24.187	93.902	76.114	46.247	− 22.667	40.768	− 3.427
2700	24.296	94.817	76.790	48.671	− 22.608	43.204	− 3.497
2800	24.394	95.702	77.450	51.106	− 22.549	45.640	− 3.562
2900	24.483	96.560	78.094	53.550	− 22.493	48.078	− 3.623
3000	24.565	97.391	78.724	56.002	− 22.439	50.507	− 3.679
3100	24.639	98.198	79.339	58.463	− 22.386	52.938	− 3.732
3200	24.708	98.981	79.941	60.930	− 22.339	55.367	− 3.781
3300	24.770	99.743	80.529	63.404	− 22.296	57.795	− 3.828
3400	24.828	100.483	81.105	65.884	− 22.255	60.221	− 3.871
3500	24.881	101.203	81.669	68.369	− 22.222	62.645	− 3.912
3600	24.931	101.905	82.222	70.860	− 22.191	65.070	− 3.950
3700	24.976	102.589	82.763	73.355	− 22.168	67.495	− 3.987
3800	25.018	103.255	83.293	75.855	− 22.147	69.920	− 4.021
3900	25.058	103.906	83.814	78.359	− 22.135	72.344	− 4.054
4000	25.094	104.541	84.324	80.867	− 22.127	74.766	− 4.085
4100	25.128	105.161	84.825	83.378	− 22.125	77.185	− 4.114
4200	25.160	105.767	85.316	85.892	− 22.130	79.611	− 4.143
4300	25.190	106.359	85.798	88.410	− 22.140	82.030	− 4.169
4400	25.218	106.938	86.272	90.930	− 22.156	84.453	− 4.195
4500	25.244	107.505	86.738	93.453	− 22.179	86.870	− 4.219
4600	25.268	108.060	87.195	95.979	− 22.207	89.300	− 4.243
4700	25.291	108.604	87.645	98.507	− 22.241	91.726	− 4.265
4800	25.313	109.137	88.087	101.037	− 22.282	94.151	− 4.287
4900	25.333	109.659	88.522	103.569	− 22.327	96.579	− 4.308
5000	25.352	110.171	88.950	106.103	− 22.379	99.001	− 4.327
5100	25.370	110.673	89.371	108.640	− 22.438	101.430	− 4.347
5200	25.388	111.166	89.786	111.178	− 22.501	103.859	− 4.365
5300	25.404	111.650	90.194	113.717	− 22.571	106.295	− 4.383
5400	25.419	112.125	90.595	116.258	− 22.647	108.723	− 4.400
5500	25.434	112.591	90.991	118.801	− 22.730	111.158	− 4.417
5600	25.448	113.050	91.381	121.345	− 22.818	113.589	− 4.433
5700	25.461	113.500	91.765	123.890	− 22.912	116.024	− 4.449
5800	25.473	113.943	92.144	126.437	− 23.013	118.463	− 4.464
5900	25.485	114.379	92.517	128.985	− 23.120	120.908	− 4.479
6000	25.496	114.807	92.885	131.534	− 23.231	123.342	− 4.493

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

METHYL CHLORIDE (CH_3Cl) (IDEAL GAS) GFW = 50.488

Point Group C_{3v} ΔHf°_0 = −18.1 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 55.99 ± 0.10 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −20.0 ± 0.5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2968 (1)	3054 (2)
1355 (1)	1455 (2)
732 (1)	1017 (2)

Bond Distance: C-H = 1.0959 Å C-Cl = 1.7812 Å

Bond Angle: H-C-H = 108° H-C-Cl = 110°55′ σ = 3

Product of the Moments of Inertia: $I_A I_B I_C = 21.477 \times 10^{-117}$ $g^3 cm^6$

Heat of Formation

The heat of formation has been determined by hydrogenation of methyl chloride to give methane and hydrogen chloride by Lacher, Kianpour, Oetting, and Park (1), and by Lacher, Emery, Bohmfalk, and Park (2). They reported an average heat of hydrogenation at 248°C to be −19,665 ± 45 cal/mol. Using this value, together with JANAF data (5) for $H_2(g)$, $CH_4(g)$, and $HCl(g)$, the heat of formation of methyl chloride is calculated to be ΔHf°_{298} = −20.69 kcal/mol. Fowell, Lacher, and Park (3), using a similar hydrogenation technique almost ten years later, report a value $\Delta Hf^\circ_{298}(CH_3Cl, g)$ = −20.471 kcal/mol.

Fletcher and Pilcher (4) derived the heat of formation by measuring the heat of combustion of methyl chloride by flame calorimetry. They reported a value $\Delta Hf^\circ_{298}(CH_3Cl, g)$ = −19.59 ± 0.16 kcal/mol where the error, according to the authors, is twice the standard deviation of the mean including the uncertainty in calibration, measurement, determination of ignition energy, and values of auxiliary data used.

In support of their results Fletcher and Pilcher (4) have compared the heats of formation of $C_2H_5Cl(g)$ and i-$C_3H_7Cl(g)$ as determined by equilibrium studies (Second and Third Law) with their work via flame calorimetry. The agreement is excellent (<0.2 kcal/mol difference) but in both cases results for hydrogenation studies are at least 1 kcal/mole less negative. In the case of $CH_3Cl(g)$ no equilibrium results are currently available and the results of ΔHf°_{298} from hydrogenation studies are approximately 1 kcal/mol more negative than the results from flame calorimetry.

The value chosen as the heat of formation is $\Delta Hf^\circ_{298}(CH_3Cl, g)$ = −20.0 ± 0.5 kcal/mol. This value is close to the median value and is arbitrarily chosen as it is uncertain whether the flame calorimetry or hydrogenation studies are the more accurate. Slightly more weight was given to the flame calorimetry work due to favorable comparisons with equilibrium studies in related compounds. An error of ± 0.5 kcal/mol is chosen so as to encompass the current ΔHf°_{298} experimental values even though the actual experimental error is considerably less.

Heat Capacity and Entropy

The vibrational frequencies are essentially typical values which were taken from the experimental work of Plyler and Benedict (6), Reichman and Overend (7), Morino and Nakamura (8), Jones, Popplewell, and Thompson (9), Fletcher (10), and King, Mills, and Crawford (11). The value of ω_1 as given by Plyler and Benedict (6) appears too low and was not included. Costain (12) has calculated the bond distances and angles based on an isotopic substitution method. From this latter data, the moments of inertia were calculated to be

$$I_A = I_B = 6.3885 \times 10^{-39} \text{ g cm}^2 \text{ and } I_C = 0.5262 \times 10^{-39} \text{ g cm}^2.$$

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Cyano Unipositive Ion (CN^+)

(Ideal Gas) GFW = 26.01730

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	7.034	50.986	50.986	.000	430.870	421.410	- 308.901
300	7.037	51.029	50.986	.013	430.882	421.351	- 306.954
400	7.240	53.079	51.264	.726	431.497	418.080	- 228.428
500	7.514	54.723	51.796	1.463	432.061	414.659	- 181.247
600	7.788	56.118	52.403	2.229	432.589	411.129	- 149.754
700	8.027	57.337	53.023	3.020	433.087	407.512	- 127.231
800	8.225	58.422	53.631	3.833	433.567	403.826	- 110.320
900	8.385	59.400	54.219	4.664	434.028	400.080	- 97.153
1000	8.518	60.291	54.782	5.509	434.477	396.283	- 86.608
1100	8.624	61.108	55.320	6.366	434.914	392.443	- 77.971
1200	8.718	61.862	55.835	7.233	435.341	388.563	- 70.767
1300	8.797	62.563	56.325	8.109	435.759	384.647	- 64.665
1400	8.870	63.218	56.795	8.992	436.173	380.701	- 59.430
1500	8.937	63.832	57.244	9.883	436.582	376.725	- 54.889
1600	9.001	64.411	57.674	10.779	436.987	372.719	- 50.911
1700	9.061	64.958	58.086	11.683	437.392	368.690	- 47.398
1800	9.119	65.478	58.482	12.592	437.794	364.638	- 44.273
1900	9.175	65.972	58.864	13.506	438.197	360.564	- 41.474
2000	9.229	66.444	59.231	14.427	438.601	356.468	- 38.953
2100	9.281	66.896	59.585	15.352	439.004	352.351	- 36.670
2200	9.331	67.329	59.926	16.283	439.406	348.213	- 34.592
2300	9.379	67.745	60.258	17.218	439.814	344.061	- 32.693
2400	9.425	68.145	60.579	18.158	440.220	339.889	- 30.951
2500	9.469	68.530	60.889	19.103	440.629	335.700	- 29.347
2600	9.510	68.903	61.190	20.052	441.036	331.494	- 27.865
2700	9.550	69.262	61.483	21.005	441.447	327.272	- 26.491
2800	9.587	69.610	61.767	21.962	441.859	323.037	- 25.214
2900	9.622	69.947	62.043	22.923	442.272	318.787	- 24.024
3000	9.656	70.274	62.312	23.886	442.685	314.522	- 22.913
3100	9.687	70.591	62.574	24.854	443.099	310.242	- 21.872
3200	9.716	70.899	62.829	25.824	443.514	305.950	- 20.895
3300	9.743	71.199	63.078	26.797	443.929	301.643	- 19.977
3400	9.769	71.490	63.322	27.772	444.346	297.328	- 19.112
3500	9.793	71.773	63.559	28.750	444.762	292.994	- 18.295
3600	9.815	72.050	63.791	29.731	445.177	288.652	- 17.524
3700	9.835	72.319	64.018	30.713	445.594	284.299	- 16.793
3800	9.854	72.581	64.240	31.698	446.010	279.937	- 16.100
3900	9.872	72.838	64.457	32.684	446.427	275.562	- 15.442
4000	9.888	73.088	64.670	33.672	446.842	271.174	- 14.816
4100	9.903	73.332	64.878	34.662	447.257	266.776	- 14.220
4200	9.917	73.571	65.082	35.653	447.671	262.372	- 13.653
4300	9.930	73.804	65.282	36.645	448.084	257.955	- 13.111
4400	9.942	74.033	65.479	37.639	448.497	253.527	- 12.593
4500	9.953	74.256	65.671	38.633	448.907	249.089	- 12.097
4600	9.963	74.475	65.860	39.629	449.317	244.647	- 11.623
4700	9.972	74.690	66.046	40.626	449.727	240.193	- 11.169
4800	9.980	74.900	66.228	41.624	450.134	235.733	- 10.733
4900	9.988	75.106	66.407	42.622	450.540	231.259	- 10.315
5000	9.995	75.307	66.583	43.621	450.944	226.782	- 9.913
5100	10.001	75.505	66.756	44.621	451.346	222.288	- 9.526
5200	10.007	75.700	66.926	45.622	451.747	217.796	- 9.154
5300	10.012	75.890	67.094	46.622	452.145	213.294	- 8.795
5400	10.017	76.078	67.258	47.624	452.543	208.785	- 8.450
5500	10.022	76.261	67.420	48.626	452.936	204.268	- 8.117
5600	10.025	76.442	67.580	49.628	453.330	199.742	- 7.795
5700	10.029	76.619	67.737	50.631	453.720	195.208	- 7.485
5800	10.032	76.794	67.891	51.634	454.108	190.670	- 7.185
5900	10.035	76.965	68.044	52.637	454.494	186.128	- 6.895
6000	10.037	77.134	68.194	53.641	454.877	181.571	- 6.614

June 30, 1969; Dec. 31, 1970

CYANO UNIPOSITIVE ION (CN^+) (IDEAL GAS) GFW = 26.01730 CN^+

Ground State Configuration [$^3\Pi$] ΔHf°_0 = 428.6 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = [50.99 ± 1.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 430.87 ± 3.0 kcal/mol

Electronic Levels and Degeneracies

ϵ_i, cm^{-1}	g_i
0	[6]
[1500]	[1]
[6000]	[2]
[8000]	[3]
[15000]	[2]

ω_e = [1580] cm^{-1} $\omega_e x_e$ = [12.5] cm^{-1} σ = 1

B_e = [1.565] cm^{-1} α_e = [0.017] cm^{-1} r_e = [1.29] Å

Heat of Formation

Dibeler and Liston (1) have measured the photoionization thresholds for the processes:

$ClCN + h\nu \rightarrow Cl^+ + CN + e^-$ ΔHr°_0 = 399.44 ± 0.5 kcal

$ClCN + h\nu \rightarrow Cl + CN^+ + e^-$ ΔHr°_0 = 426.65 ± 0.5 kcal

By subtraction we obtain

$Cl + CN^+ \rightarrow Cl^+ + CN$ ΔHr°_0 = -27.21 ± 0.7 kcal

Using JANAF values for Cl, Cl^+ and CN we obtain $\Delta Hf^\circ_0(CN^+)$ = 430.6 ± 3.0 kcal/mol and the ionization potential of CN(g) is 327.42 ± 0.7 kcal/mol.

Berkowitz et al. (2) have measured the photoionization thresholds for the processes:

$HCN + h\nu \rightarrow H^+ + CN + e^-$ ΔHr°_0 = 438.18 ± 0.3 kcal

$HCN + h\nu \rightarrow H + CN^+$ ΔHr°_0 = 448.09 ± 0.3 kcal

By subtraction we obtain

$H + CN^+ \rightarrow H^+ + CN$ ΔHr°_0 = -9.91 ± 0.4 kcal

Using JANAF values for H, H^+ and CN we obtain $\Delta Hf^\circ_0(CN^+)$ = 426.7 ± 3.0 kcal/mol, and the ionization potential of CN(g) is 323.51 ± 0.4 kcal/mol.

We adopt a median value for $\Delta Hf^\circ_0(CN^+)$ = 428.6 ± 3.0 kcal/mol and 325.4 ± 2 kcal/mol for the ionization potential of CN.

Heat Capacity and Entropy

The molecule has eight valence electrons and thus we expect that its molecular constants should fall between those for C_2 and BN. The ground electronic state is either $^1\Sigma$ or $^3\Pi$ and the two levels are likely to be very close. As a consequence the thermodynamic functions are dominated by the $^3\Pi$ contribution and so we choose this to be the ground state. The other levels are estimated based on the values of Fougere and Nesbet (3) for C_2 and of Verhaegen et al. (4) for BN. The vibrational constants and bond length are estimated between those for the $^3\Pi$ states of BN and C_2. The rotational constants B_e is obtained from the estimated bond length and α_e is calculated from the other constants assuming a Morse potential function. The enthalpy at 0°K is -2.076 kcal/mol.

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Cyano Uninegative Ion (CN^-)

(Ideal Gas) GFW = 26.01840

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	6.963	46.813	46.813	.000	14.500	9.259	6.787
300	6.963	46.856	46.813	.013	14.493	9.226	6.721
400	7.002	48.863	47.086	.711	14.100	7.528	4.113
500	7.097	50.435	47.604	1.415	13.637	5.937	2.595
600	7.240	51.741	48.188	2.132	13.122	4.444	1.619
700	7.406	52.869	48.776	2.864	12.569	3.047	.950
800	7.575	53.869	49.353	3.613	11.991	1.720	.470
900	7.735	54.770	49.905	4.379	11.393	.470	.114
1000	7.880	55.593	50.434	5.159	10.784	.711	.155
1100	8.006	56.350	50.937	5.954	10.164	1.831	.364
1200	8.120	57.052	51.418	6.760	9.538	2.892	.527
1300	8.216	57.706	51.877	7.578	8.904	3.903	.656
1400	8.303	58.318	52.315	8.404	8.267	4.866	.759
1500	8.377	58.893	52.735	9.238	7.625	5.779	.842
1600	8.442	59.436	53.137	10.079	6.982	6.652	.909
1700	8.496	59.950	53.523	10.926	6.337	7.485	.962
1800	8.546	60.437	53.893	11.778	5.689	8.280	1.005
1900	8.592	60.900	54.250	12.635	5.040	9.037	1.039
2000	8.631	61.342	54.594	13.496	4.390	9.761	1.067
2100	8.666	61.764	54.925	14.361	3.741	10.452	1.088
2200	8.696	62.168	55.245	15.230	3.089	11.114	1.104
2300	8.726	62.555	55.555	16.101	2.436	11.744	1.116
2400	8.752	62.927	55.854	16.975	1.783	12.347	1.124
2500	8.775	63.285	56.144	17.851	1.129	12.923	1.130
2600	8.796	63.629	56.426	18.730	.474	13.471	1.132
2700	8.816	63.962	56.699	19.610	-.182	13.996	1.133
2800	8.834	64.283	56.964	20.493	-.838	14.495	1.131
2900	8.850	64.593	57.222	21.377	-1.496	14.971	1.128
3000	8.866	64.893	57.472	22.263	-2.155	15.425	1.124
3100	8.880	65.184	57.716	23.150	-2.812	15.855	1.118
3200	8.894	65.466	57.954	24.039	-3.473	16.266	1.111
3300	8.906	65.740	58.186	24.929	-4.135	16.657	1.103
3400	8.918	66.006	58.412	25.820	-4.797	17.025	1.094
3500	8.929	66.265	58.633	26.712	-5.460	17.378	1.085
3600	8.940	66.517	58.848	27.606	-6.124	17.708	1.075
3700	8.950	66.762	59.059	28.500	-6.789	18.020	1.064
3800	8.960	67.001	59.265	29.396	-7.456	18.313	1.053
3900	8.969	67.233	59.466	30.292	-8.123	18.589	1.042
4000	8.978	67.461	59.663	31.190	-8.791	18.849	1.030
4100	8.986	67.682	59.856	32.088	-9.461	19.095	1.018
4200	8.994	67.899	60.045	32.987	-10.133	19.319	1.005
4300	9.002	68.111	60.230	33.887	-10.806	19.531	.993
4400	9.009	68.318	60.412	34.787	-11.481	19.727	.980
4500	9.017	68.520	60.589	35.688	-12.156	19.908	.967
4600	9.024	68.719	60.764	36.590	-12.834	20.078	.954
4700	9.030	68.913	60.935	37.493	-13.512	20.221	.940
4800	9.037	69.103	61.104	38.397	-14.193	20.354	.927
4900	9.043	69.289	61.269	39.301	-14.875	20.479	.913
5000	9.050	69.472	61.431	40.205	-15.558	20.583	.900
5100	9.056	69.651	61.590	41.110	-16.245	20.683	.886
5200	9.062	69.827	61.747	42.016	-16.932	20.760	.873
5300	9.067	70.000	61.901	42.923	-17.622	20.827	.859
5400	9.073	70.169	62.053	43.830	-18.313	20.880	.845
5500	9.079	70.336	62.202	44.737	-19.006	20.919	.831
5600	9.084	70.500	62.349	45.646	-19.701	20.949	.818
5700	9.090	70.660	62.493	46.554	-20.399	20.967	.804
5800	9.095	70.819	62.635	47.463	-21.099	20.971	.790
5900	9.100	70.974	62.775	48.373	-21.800	20.960	.776
6000	9.105	71.127	62.913	49.283	-22.503	20.944	.763

June 30, 1969; Dec. 31, 1970

CYANO UNINEGATIVE ION (CN^-) (IDEAL GAS) GFW = 26.01840 CN^-

Ground State Configuration $[^1\Sigma^+]$ ΔHf°_0 = 15.2 ± 3 kcal/mol

$S^\circ_{298.15}$ = 46.81 ± 0.5 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 14.50 ± 3 kcal/mol

Electronic Levels and Degeneracies

ϵ_i, cm^{-1}	g_i
0	[1]
[67000]	[2]

ω_e = [2250] cm^{-1} $\omega_e x_e$ = [13.6] cm^{-1} σ = 1

B_e = [2.116] cm^{-1} α_e = [0.0177] cm^{-1} r_e = [1.11] Å

Heat of Formation

Berkowitz et al. (1) have recently obtained 88 ± 0.5 kcal for the electron affinity of CN from the photoionization thresholds of the reactions $HCN \rightarrow N^+ + CN^- + e^-$ and $HCN \rightarrow H^+ + CN + e^-$.

Other values have been reported by Page (2), who reinterpreted his earlier data (3), to yield 73 ± 1 kcal/mol; Bakulina and Ionov (4) in conjunction with the data of Branscomb and Smith (5) reported 78 ± 5 kcal/mol and Inoue (6) who obtained 83 ± 7 kcal/mol.

We adopt the value given by Berkowitz et al. (1) as being the most well defined in terms of both the precision of measurements and the reactions being studied. This leads to $\Delta Hf^\circ_0(CN^-, g)$ = 15.2 ± 3 kcal/mol or $\Delta Hf^\circ_{298}(CN^-, g)$ = 14.5 ± 3 kcal/mol.

Heat Capacity and Entropy

The electronic structure and molecular constants are estimated by analogy with the isoelectronic species CO and N_2. The uncertainties in the constants are generally small since N_2 and CO are quite similar, thus the entropy has an uncertainty of only 0.5 eu. The enthalpy at 0°K is -2.072 kcal/mol.

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NCO Radical (NCO)

(Ideal Gas) GFW = 42.0173

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	− 2.437	37.989	37.989	INFINITE
100	7.666	46.387	63.238	− 1.685	38.033	37.393	− 81.723
200	8.487	51.874	56.318	− .888	38.056	36.745	− 40.153
298	9.573	55.476	55.476	.000	38.100	36.093	− 26.457
300	9.591	55.536	55.477	.018	38.101	36.081	− 26.285
400	10.484	58.421	55.864	1.023	38.156	35.399	− 19.341
500	11.225	60.843	56.624	2.110	38.207	34.704	− 15.169
600	11.841	62.946	57.506	3.264	38.249	33.999	− 12.384
700	12.345	64.810	58.419	4.474	38.281	33.289	− 10.393
800	12.753	66.486	59.324	5.730	38.308	32.573	− 8.899
900	13.083	68.008	60.206	7.022	38.327	31.855	− 7.735
1000	13.350	69.401	61.057	8.344	38.342	31.135	− 6.805
1100	13.566	70.684	61.874	9.690	38.352	30.413	− 6.042
1200	13.743	71.872	62.659	11.056	38.357	29.692	− 5.408
1300	13.889	72.978	63.410	12.438	38.356	28.969	− 4.870
1400	14.011	74.012	64.131	13.833	38.353	28.248	− 4.410
1500	14.113	74.982	64.822	15.239	38.345	27.527	− 4.011
1600	14.199	75.896	65.486	16.655	38.334	26.805	− 3.661
1700	14.272	76.759	66.124	18.079	38.321	26.085	− 3.353
1800	14.334	77.576	66.738	19.509	38.304	25.366	− 3.080
1900	14.386	78.353	67.329	20.945	38.284	24.649	− 2.835
2000	14.435	79.092	67.899	22.386	38.261	23.931	− 2.615
2100	14.476	79.797	68.449	23.832	38.236	23.216	− 2.416
2200	14.512	80.472	68.980	25.281	38.205	22.500	− 2.235
2300	14.544	81.117	69.494	26.734	38.174	21.788	− 2.070
2400	14.572	81.737	69.991	28.190	38.138	21.077	− 1.919
2500	14.597	82.332	70.473	29.649	38.099	20.365	− 1.780
2600	14.619	82.905	70.940	31.109	38.056	19.657	− 1.652
2700	14.639	83.457	71.394	32.572	38.011	18.949	− 1.534
2800	14.656	83.990	71.834	34.037	37.963	18.245	− 1.424
2900	14.674	84.505	72.262	35.504	37.910	17.543	− 1.322
3000	14.690	85.002	72.676	36.972	37.854	16.841	− 1.227
3100	14.704	85.484	73.084	38.442	37.797	16.142	− 1.138
3200	14.717	85.951	73.479	39.913	37.735	15.444	− 1.055
3300	14.729	86.404	73.864	41.385	37.669	14.746	− .977
3400	14.741	86.844	74.239	42.858	37.601	14.055	− .903
3500	14.752	87.272	74.605	44.333	37.530	13.359	− .834
3600	14.762	87.688	74.963	45.809	37.455	12.671	− .769
3700	14.772	88.092	75.312	47.285	37.378	11.985	− .708
3800	14.782	88.486	75.654	48.763	37.298	11.302	− .650
3900	14.792	88.870	75.988	50.242	37.216	10.619	− .595
4000	14.802	89.245	76.314	51.722	37.131	9.937	− .543
4100	14.811	89.611	76.634	53.202	37.042	9.257	− .493
4200	14.821	89.968	76.946	54.684	36.951	8.582	− .447
4300	14.831	90.316	77.254	56.166	36.858	7.909	− .402
4400	14.840	90.657	77.555	57.650	36.762	7.234	− .359
4500	14.850	90.991	77.850	59.134	36.663	6.563	− .319
4600	14.860	91.318	78.139	60.620	36.563	5.899	− .280
4700	14.871	91.637	78.423	62.107	36.461	5.233	− .243
4800	14.881	91.950	78.702	63.594	36.355	4.572	− .208
4900	14.892	92.257	78.975	65.083	36.248	3.906	− .174
5000	14.903	92.558	79.244	66.572	36.138	3.249	− .142
5100	14.914	92.854	79.508	68.063	36.028	2.587	− .111
5200	14.926	93.143	79.767	69.555	35.913	1.935	− .081
5300	14.938	93.428	80.022	71.049	35.798	1.285	− .053
5400	14.950	93.707	80.273	72.543	35.680	.634	− .026
5500	14.963	93.982	80.520	74.039	35.561	− .011	.000
5600	14.976	94.251	80.763	75.536	35.440	− .659	.026
5700	14.989	94.516	81.002	77.034	35.316	− 1.306	.050
5800	15.002	94.777	81.237	78.533	35.191	− 1.944	.073
5900	15.016	95.034	81.469	80.034	35.065	− 2.582	.096
6000	15.030	95.286	81.697	81.537	34.937	− 3.222	.117

Dec. 31, 1970

NCO RADICAL (NCO) (IDEAL GAS) GFW = 42.0173 CNO

Point Group $C_{\infty v}$ ΔHf°_0 = 38 ± 2.5 kcal/mol

$S^\circ_{298.15}$ = 55.48 ± 0.2 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 38.1 ± 2.5 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{3/2}$	0	2
$X^2\Pi_{1/2}$	95.6	2
$A^2\Sigma^+$	22802	2
$B^2\Pi$	31811	4

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1922 (1)
536 (2)
1275 (1)

Bond Distance: N-C = [1.23] Å C-O = [1.18] Å

Bond Angle: 180° σ = 1

Rotational Constant: B_0 = 0.3894 cm^{-1}

Heat of Formation

Okabe (1) has measured the onset of photodissociation for the process HNCO(g) → H(g) + NCO($A^2\Sigma$) as 7.73 ± 0.01 eV (178.25 ± 0.25 kcal). This result in combination with JANAF auxiliary data (2) results in ΔHf°_0(NCO, g) = 38 ± 2.5 kcal/mol.

Dixon (3) has discussed the diffuseness in the $^2\Pi$-$^2\Pi$ bands of NCO above 33700 cm^{-1} and concludes this is due to either predissociation or unresolved groups of lines due to a perturbing state. Assuming the dissociation is to N(^{2}D) + CO($^1\Sigma$) yields D(N-CO) ≤ 91 kcal, or ΔHf°_0(NCO) ≥ 44 kcal/mol; assuming the products CN($^2\Sigma$) + O(^{3}P) then D(NC-O) ≤ 97 kcal, or ΔHf°_0(NCO) ≥ 85 kcal/mol. Milligan and Jacox (4) confirm the diffuseness and observe increased amounts of CO. Thus, they prefer the first dissociation mechanism which favors ΔHf°_0(NCO) ≥ 44 kcal/mol. An upper limit to the heat of formation can be obtained from HNCO(g) (2) by assuming a maximum D(H-NCO) ≤ 122 kcal, equal to D(H-CN), which yields ΔHf°_0(NCO) ≤ 45 kcal/mol. Another estimate may be obtained by making the reasonable assumption that the sum of the atomization energies of NCN + NNO equal those of NNN + NCO, where the central atoms are simply interchanged. Using respective atomization values (2) of 282, 254 and 242 kcal yields 304 kcal for NCO, or ΔHf°_0(NCO) = 38 kcal/mol. It appears that the diffuseness in the spectrum is not due to predissociation, since all the estimates and measurements fall below the values calculated on that basis. We adopt ΔHf°_0(NCO, g) = 38 ± 2.5 kcal/mol.

Heat Capacity and Entropy

The electronic levels, structure, and ν_2 are from Dixon (3). The ν_1 and ν_3 vibrational frequencies are from the matrix isolation data of Milligan and Jacox (4). The individual bond lengths are those selected by Milligan and Jacox (4) to fit the overall length determined by Dixon (3).

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CNO

NCN Radical (CN_2)

(Ideal Gas) GFW = 40.0246

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	− 2.448	112.876	112.876	INFINITE
100	7.291	44.643	62.160	− 1.748	112.869	112.239	− 245.298
200	8.923	50.243	54.923	− .936	112.907	111.601	− 121.957
298	10.084	54.035	54.035	.000	113.000	110.941	− 81.322
300	10.103	54.098	54.035	.019	113.002	110.928	− 80.811
400	11.035	57.136	54.443	1.077	113.117	110.220	− 60.221
500	11.805	59.684	55.243	2.220	113.236	109.481	− 47.854
600	12.416	61.892	56.171	3.433	113.361	108.719	− 39.601
700	12.887	63.843	57.131	4.699	113.474	107.936	− 33.699
800	13.253	65.589	58.081	6.007	113.580	107.138	− 29.269
900	13.534	67.167	59.004	7.347	113.674	106.326	− 25.819
1000	13.753	68.605	59.893	8.711	113.756	105.505	− 23.058
1100	13.927	69.924	60.746	10.096	113.832	104.675	− 20.797
1200	14.065	71.142	61.562	11.496	113.895	103.841	− 18.912
1300	14.177	72.272	62.343	12.908	113.947	103.000	− 17.316
1400	14.269	73.327	63.090	14.330	113.992	102.158	− 15.948
1500	14.344	74.314	63.806	15.761	114.030	101.311	− 14.761
1600	14.408	75.241	64.492	17.199	114.062	100.461	− 13.722
1700	14.461	76.117	65.150	18.642	114.088	99.610	− 12.806
1800	14.506	76.944	65.783	20.091	114.109	98.758	− 11.991
1900	14.545	77.730	66.391	21.543	114.126	97.907	− 11.262
2000	14.578	78.477	66.977	23.000	114.140	97.052	− 10.605
2100	14.607	79.189	67.542	24.459	114.150	96.198	− 10.011
2200	14.633	79.869	68.087	25.921	114.155	95.341	− 9.471
2300	14.655	80.520	68.613	27.385	114.158	94.487	− 8.978
2400	14.675	81.144	69.122	28.852	114.159	93.632	− 8.526
2500	14.692	81.743	69.615	30.320	114.156	92.775	− 8.110
2600	14.708	82.320	70.093	31.790	114.150	91.921	− 7.727
2700	14.722	82.875	70.556	33.262	114.143	91.065	− 7.371
2800	14.734	83.411	71.006	34.735	114.134	90.211	− 7.041
2900	14.746	83.928	71.442	36.209	114.122	89.358	− 6.734
3000	14.756	84.428	71.867	37.684	114.107	88.504	− 6.448
3100	14.765	84.912	72.280	39.160	114.091	87.650	− 6.179
3200	14.774	85.381	72.682	40.637	114.072	86.798	− 5.928
3300	14.782	85.836	73.074	42.115	114.050	85.944	− 5.692
3400	14.790	86.277	73.456	43.593	114.027	85.096	− 5.470
3500	14.797	86.706	73.828	45.072	114.001	84.241	− 5.260
3600	14.803	87.123	74.192	46.552	113.973	83.391	− 5.063
3700	14.810	87.529	74.547	48.033	113.944	82.543	− 4.876
3800	14.816	87.924	74.894	49.514	113.912	81.697	− 4.699
3900	14.822	88.309	75.233	50.996	113.879	80.852	− 4.531
4000	14.828	88.684	75.564	52.479	113.844	80.004	− 4.371
4100	14.835	89.050	75.889	53.962	113.806	79.156	− 4.219
4200	14.841	89.408	76.206	55.446	113.766	78.314	− 4.075
4300	14.847	89.757	76.517	56.930	113.724	77.471	− 3.937
4400	14.854	90.099	76.822	58.415	113.680	76.626	− 3.806
4500	14.861	90.432	77.121	59.901	113.634	75.783	− 3.681
4600	14.868	90.759	77.414	61.388	113.587	74.946	− 3.561
4700	14.876	91.079	77.701	62.875	113.538	74.105	− 3.446
4800	14.884	91.392	77.983	64.363	113.485	73.269	− 3.336
4900	14.892	91.699	78.260	65.851	113.431	72.427	− 3.230
5000	14.901	92.000	78.532	67.341	113.376	71.595	− 3.129
5100	14.910	92.295	78.799	68.832	113.318	70.752	− 3.032
5200	14.920	92.585	79.061	70.323	113.259	69.923	− 2.939
5300	14.931	92.869	79.319	71.816	113.198	69.090	− 2.849
5400	14.942	93.148	79.573	73.309	113.135	68.259	− 2.763
5500	14.954	93.423	79.822	74.804	113.069	67.432	− 2.679
5600	14.966	93.692	80.067	76.300	113.003	66.600	− 2.599
5700	14.979	93.957	80.309	77.798	112.935	65.771	− 2.522
5800	14.993	94.218	80.546	79.296	112.864	64.945	− 2.447
5900	15.007	94.474	80.780	80.796	112.792	64.121	− 2.375
6000	15.022	94.727	81.010	82.298	112.719	63.293	− 2.305

June 30, 1966; Dec. 31, 1970

NCN RADICAL (CN_2) (IDEAL GAS) GFW = 40.0246 CN_2

Point Group $D_{\infty h}$ ΔHf°_0 = 112.9 ± 5 kcal/mol

$S^\circ_{298.15}$ = 54.04 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 113 ± 5 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^3\Sigma_g^-$	0	3
$A^3\Pi_u$	30384	6
$a^1\Delta$	[38000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1197 (1)
423 (2)
1475 (1)

Bond Distance: C-N = 1.232 Å

Bond Angle: N-C-N = 180° σ = 2

Rotational Constant: B_0 = 0.3968 cm^{-1}

Heat of Formation

Okabe and Mele (1) have measured the photodissociation onset of the process

$$CN{\cdot}N_3(g) \rightarrow NCN(g) + N_2(A^3\Sigma) \qquad \Delta H^\circ_0 = 149.3 \pm 2.5 \text{ kcal}$$

Using $\Delta Hf^\circ_{298}N_2(A^3\Sigma)$ = 143.5 kcal/mol (2) and $\Delta Hf^\circ_{298}(CN{\cdot}N_3, g)$ = 107 ± 3 kcal/mol (3) we obtain $\Delta Hf^\circ_{298}(NCN, g)$ = 113 ± 5 kcal/mol.

Heat Capacity and Entropy

The X and A electronic levels, ground state structure, and rotational constants are from Herzberg and Travis (4), the $a^1\Delta$ level is estimated from the work of Schoen (5). The vibrational frequencies have been observed in the matrix-isolated species by Milligan and Jacox (6, 7). Wasserman et al. (8) have confirmed the ground state is linear and triplet by electron paramagnetic resonance.

References

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8. E. Wasserman, L. Barash and W. A. Yager, J. Amer. Chem. Soc. 87, 2075 (1965).

Calcium Unipositive Ion (Ca^+)

(Ideal Gas) GFW = 40.0745

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	4.968	38.369	38.369	.000	185.302	175.336	~ 128.525
300	4.968	38.400	38.369	.009	185.304	175.274	~ 127.687
400	4.968	39.829	38.564	.506	185.665	171.675	~ 93.908
500	4.968	40.937	38.932	1.003	186.013	168.388	~ 73.602
600	4.968	41.843	39.344	1.500	186.356	164.831	~ 60.040
700	4.968	42.609	39.757	1.994	186.695	161.216	~ 50.334
800	4.968	43.272	40.156	2.493	186.696	157.583	~ 43.050
900	4.966	43.857	40.535	2.990	186.838	153.935	~ 37.380
1000	4.968	44.381	40.894	3.487	186.927	150.273	~ 32.842
1100	4.968	44.854	41.233	3.984	186.963	146.606	~ 29.128
1200	4.968	45.287	41.553	4.480	185.161	143.089	~ 26.060
1300	4.969	45.684	41.856	4.977	185.437	139.572	~ 23.464
1400	4.969	46.052	42.142	5.474	185.711	136.034	~ 21.236
1500	4.971	46.395	42.415	5.971	185.985	132.476	~ 19.302
1600	4.975	46.716	42.674	6.468	186.258	128.899	~ 17.607
1700	4.980	47.018	42.920	6.966	186.533	125.306	~ 16.109
1800	4.989	47.303	43.156	7.465	189.915	122.377	~ 14.859
1900	5.002	47.573	43.381	7.964	150.412	120.834	~ 13.899
2000	5.019	47.830	43.597	8.465	150.910	119.264	~ 13.033
2100	5.042	48.075	43.805	8.968	151.407	117.669	~ 12.246
2200	5.071	48.311	44.004	9.474	151.906	116.051	~ 11.529
2300	5.107	48.537	44.197	9.982	152.403	114.410	~ 10.871
2400	5.151	48.755	44.382	10.495	152.900	112.748	~ 10.267
2500	5.202	48.966	44.561	11.013	153.397	111.065	~ 9.709
2600	5.260	49.171	44.735	11.536	153.890	109.361	~ 9.193
2700	5.326	49.371	44.903	12.065	154.381	107.639	~ 8.713
2800	5.400	49.566	45.066	12.601	154.869	105.900	~ 8.266
2900	5.481	49.757	45.224	13.145	155.353	104.142	~ 7.848
3000	5.568	49.944	45.378	13.698	155.831	102.369	~ 7.458
3100	5.661	50.128	45.529	14.259	156.300	100.578	~ 7.091
3200	5.759	50.310	45.675	14.830	156.762	98.774	~ 6.746
3300	5.863	50.488	45.818	15.411	157.213	96.954	~ 6.421
3400	5.970	50.665	45.958	16.003	157.654	95.122	~ 6.114
3500	6.080	50.840	46.095	16.605	158.081	93.277	~ 5.824
3600	6.192	51.012	46.229	17.219	158.493	91.419	~ 5.550
3700	6.306	51.184	46.361	17.844	158.890	89.550	~ 5.290
3800	6.421	51.353	46.490	18.480	159.269	87.671	~ 5.042
3900	6.535	51.522	46.617	19.128	159.629	85.782	~ 4.807
4000	6.649	51.689	46.742	19.787	159.969	83.883	~ 4.583
4100	6.762	51.854	46.864	20.458	160.290	81.978	~ 4.370
4200	6.873	52.018	46.985	21.139	160.588	80.065	~ 4.166
4300	6.981	52.181	47.104	21.832	160.864	78.143	~ 3.972
4400	7.087	52.343	47.221	22.536	161.119	74.218	~ 3.786
4500	7.188	52.504	47.337	23.249	161.347	74.284	~ 3.608
4600	7.286	52.663	47.451	23.973	161.555	72.347	~ 3.437
4700	7.380	52.820	47.564	24.706	161.739	70.407	~ 3.274
4800	7.470	52.977	47.675	25.449	161.900	68.462	~ 3.117
4900	7.554	53.132	47.785	26.200	162.038	66.514	~ 2.967
5000	7.634	53.285	47.893	26.960	162.154	64.562	~ 2.822
5100	7.709	53.437	48.000	27.727	162.246	62.610	~ 2.683
5200	7.779	53.587	48.106	28.501	162.321	60.655	~ 2.549
5300	7.843	53.736	48.211	29.282	162.374	58.700	~ 2.421
5400	7.903	53.883	48.315	30.070	162.409	56.743	~ 2.297
5500	7.957	54.029	48.417	30.863	162.424	54.785	~ 2.177
5600	8.006	54.173	48.519	31.661	162.423	52.829	~ 2.062
5700	8.051	54.315	48.619	32.464	162.407	50.873	~ 1.951
5800	8.090	54.455	48.719	33.271	162.375	48.916	~ 1.843
5900	8.125	54.594	48.817	34.082	162.330	46.961	~ 1.740
6000	8.155	54.730	48.914	34.896	162.271	45.005	~ 1.639

Dec. 31, 1970

CALCIUM UNIPOSITIVE ION (Ca^+) (IDEAL GAS) GFW = 40.0745 Ca^+

Ground State Configuration $^2S_{1/2}$ ΔHf°_0 = 183.7 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 38.369 ± 0.005 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 185.3 ± 0.3 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
13650.2	4
13710.9	6
25191.5	2
25414.4	4
52167.0	2
56839.3	4
56858.5	6
60535.0	2
60613.2	4
68057.0	14

Heat of Formation

Moore (1) gives the first ionization limit of calcium as 49305.72 cm^{-1} (140.971 kcal). Using this value in conjunction with the JANAF $\Delta Hf^\circ_0(Ca, g)$ = 42.74 ± 0.3 kcal/mol yields $\Delta Hf^\circ_0(Ca^+, g)$ = 183.711 ± 0.3 kcal/mol or $\Delta Hf^\circ_{298}(Ca^+, g)$ = 185.302 kcal/mol.

Heat Capacity and Entropy

Moore (2) gives the ground state configuration and electronic levels. Levels above 70,000 cm^{-1} are not used since they do not affect the thermodynamic functions.

The enthalpy H_0-H_{298} = −1.481 kcal/mol.

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Calcium Hydroxide ($Ca(OH)_2$)

(Crystal) GFW = 74.0948

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	- 3.384	- 233.594	- 233.594	INFINITE
100	7.777	6.117	35.160	- 3.104	- 235.001	- 228.454	499.285
200	16.390	12.472	21.717	- 1.849	- 235.587	- 221.630	242.186
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	26.473	20.787	2.274	- 235.486	- 207.619	113.438
500	24.800	31.864	22.479	4.693	- 235.143	- 200.689	87.721
600	25.800	36.474	24.436	7.223	- 234.719	- 193.837	70.605
700	26.800	40.526	26.451	9.853	- 234.222	- 187.061	58.403
800	27.800	44.176	28.442	12.583	- 233.989	- 180.333	49.265
900	28.800	47.502	30.377	15.413	- 233.537	- 173.652	42.169
1000	29.800	50.589	32.246	18.343	- 233.057	- 167.024	36.503
1100	30.800	53.476	34.046	21.373	- 232.550	- 160.485	31.878
1200	31.800	56.198	35.780	24.503	- 233.794	- 153.761	28.004
1300	32.800	58.783	37.451	27.733	- 232.865	- 147.129	24.735
1400	33.800	61.251	39.063	31.063	- 231.893	- 140.569	21.944

Dec. 31, 1971

CALCIUM HYDROXIDE ($Ca(OH)_2$) (CRYSTAL) GFW = 74.0948

$S^\circ_{298.15}$ = 19.93 ± 0.1 gibbs/mol

Td = 794.7 K

ΔHf°_0 = −233.59 ± 0.3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −235.68 ± 0.3 kcal/mol

ΔHd = 23.7 kcal/mol

Heat of Formation

Taylor and Wells (1) measured heats of solution of $Ca(OH)_2(c)$ and $CaO(c)$ in dilute HCl and obtained $\Delta Hr^\circ(298\ K)$ = −15.58 ± 0.1 kcal/mol for $CaO(c) + H_2O(\ell) \rightarrow Ca(OH)_2(c)$ which leads to $\Delta Hf^\circ_{298}(Ca(OH)_2, c)$ = −235.68 ± 0.3 kcal/mol using $\Delta Hf^\circ_{298}(CaO, c)$ = −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 $\Delta Hr^\circ(298\ K)$ = −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 vapor pressure data (9, 10, 11) for $Ca(OH)_2(c) \rightarrow CaO(c) + H_2O(g)$ are listed below. The data of Halstead (9) and Tamaru (10) are in good agreement, but the pressures reported by Johnson (11) are too low due to failure to reach equilibrium. The heat of formation derived from third law ΔHr of Halstead or Tamaru 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.

$$Ca(OH)_2(c) \rightarrow CaO(c) + H_2O(g)$$

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 (9)	Static	635-776.5	14	25.54	25.76±0.15	0.2±0.4	-235.35
Tamaru (10)	Static	694-776.5	8	26.51	25.91±0.07	-0.8±0.3	-235.50
Johnson (11)	Static	663-804	7	26.95	26.77±0.24	-0.5±1.0	-236.36

*3rd law ΔHr is used in the calculation.

Heat Capacity and Entropy

Hatton et al. (12) measured low temperature heat capacities from 19 to 330 K in an adiabatic calorimeter. Their smoothed Cp values have been adopted in the tabulation. Kobayashi (13) measured high temperature heat capacities from 310 to 670 K in a heat-conduction calorimeter. Both low temperature and high temperature heat capacities are smoothly joined at 298 K. Heat capacities above 670 are estimated based on the extrapolation of the measured Cp curve. The entropy, S°_{298} = 19.93 ± 0.1 eu is derived from the adopted low temperature Cp values, based on S° = 0.070 eu at 20 K.

Decomposition

Td is the temperature at which the vapor pressure of $H_2O(g)$ reaches one atmosphere. The heat of decomposition at Td for $Ca(OH)_2(c) \rightarrow CaO(c) + H_2O(g)$ is calculated as 23.7 kcal/mol.

Under the pressure of 1000 bars, Wyllie and Tuttle (14) found $Ca(OH)_2$ melts congruently at 1108 K.

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Calcium Oxide (CaO)

(Crystal) GFW = 56.0794

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	= 1.613	= 150.995	= 150.995	INFINITE
100	3.517	1.487	16.531	= 1.504	= 151.467	= 149.165	325.998
200	8.049	5.507	9.997	= .898	= 151.750	= 146.726	160.334
298	10.067	9.133	9.133	.000	= 151.790	= 144.247	105.735
300	10.096	9.195	9.133	.019	= 151.790	= 144.200	105.049
400	11.144	12.261	9.544	1.047	= 151.714	= 141.680	77.410
500	11.707	14.814	10.350	2.232	= 151.581	= 139.184	60.837
600	12.065	16.982	11.279	3.421	= 151.420	= 136.720	49.800
700	12.322	18.862	12.231	4.641	= 151.222	= 134.284	41.925
800	12.524	20.521	13.166	5.884	= 151.391	= 131.845	36.018
900	12.694	22.006	14.067	7.145	= 151.389	= 129.402	31.423
1000	12.843	23.351	14.929	8.422	= 151.431	= 126.957	27.746
1100	12.978	24.581	15.751	9.713	= 151.517	= 124.507	24.737
1200	13.105	25.716	16.535	11.017	= 153.429	= 121.694	22.200
1300	13.224	26.770	17.282	12.334	= 153.261	= 119.273	20.051
1400	13.339	27.754	17.996	13.662	= 153.085	= 116.665	18.212
1500	13.450	28.678	18.677	15.001	= 152.901	= 114.070	16.620
1600	13.558	29.550	19.330	16.352	= 152.709	= 111.487	15.228
1700	13.665	30.375	19.955	17.713	= 152.509	= 108.917	14.002
1800	13.769	31.159	20.556	19.085	= 189.195	= 105.678	12.831
1900	13.873	31.906	21.134	20.467	= 188.760	= 101.050	11.623
2000	13.975	32.620	21.691	21.859	= 188.317	= 96.446	10.539
2100	14.076	33.305	22.228	23.262	= 187.869	= 91.863	9.560
2200	14.177	33.962	22.746	24.674	= 187.417	= 87.301	8.673
2300	14.277	34.594	23.248	26.097	= 186.960	= 82.761	7.864
2400	14.376	35.204	23.733	27.530	= 186.501	= 78.240	7.125
2500	14.475	35.793	24.204	28.972	= 186.041	= 73.739	6.446
2600	14.574	36.362	24.661	30.425	= 185.580	= 69.256	5.821
2700	14.672	36.914	25.104	31.887	= 185.122	= 64.791	5.244
2800	14.770	37.450	25.536	33.359	= 184.666	= 60.342	4.710
2900	14.868	37.970	25.955	34.841	= 184.215	= 55.909	4.213
3000	14.966	38.475	26.364	36.333	= 183.772	= 51.493	3.751
3100	15.063	38.968	26.763	37.834	= 183.337	= 47.090	3.320
3200	15.161	39.447	27.152	39.345	= 182.913	= 42.702	2.916
3300	15.258	39.915	27.532	40.866	= 182.502	= 38.328	2.538
3400	15.355	40.372	27.903	42.397	= 182.105	= 33.965	2.183
3500	15.452	40.819	28.265	43.937	= 181.724	= 29.614	1.849

June 30, 1971

ΔHf°_0 = −150.99 ± 0.21 kcal/mol

$S^\circ_{298.15}$ = 9.133 ± 0.03 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −151.79 ± 0.21 kcal/mol

Tm = 3223 ± 15 K

ΔHm° = [19 ± 2] kcal/mol

Heat of Formation

Huber and Holley (1) determined the heat of combustion of calcium metal in a bomb calorimeter and derived the heat of formation of calcium oxide (c) as −151.79 ± 0.21 kcal/mol which is adopted in the tabulation. The adopted value is in good agreement with the value, −151.9 kcal/mol (2) derived from solution calorimetry.

Heat Capacity and Entropy

Gmelin (3) measured low temperature Cp data from 4 to 300 K in an adiabatic calorimeter. We use his smoothed Cp values to derive S°_{298} = 9.133 ± 0.03 eu based on S° = 0.0001 eu at 4 K. Lander (4) determined high temperature enthalpy data from 563.6 to 1176.4 K by drop calorimetry. The low temperature Cp and high temperature enthalpy data are smoothly joined at 298 K by a polynomial curve fitting method. The deviations of the observed enthalpies from the adopted values are about 0.2-1%, except the enthalpy value at 753 K (2.0%). Heat capacities above 1200 K are extrapolated from the adopted Cp functions. The extrapolated Cp at the melting point (2887 K), 14.8 gibbs/mol, is in reasonable agreement with the value 2 x 7.25 gibbs/mol suggested by Kubaschewski (5).

Combination of the earlier low temperature Cp measurements of Nernst and Schwers (28-80 K) (6) and Parks and Kelley (87-293 K) (7) yields S°_{298} = 9.5 ± 0.2 eu, based on S°_{28} = 0.04 eu (8). These Cp measurements are less accurate than those of Gmelin (3), and are not adopted in the tabulation.

Fischer and Ertmer (9) determined high temperature enthalpy data by drop calorimetry in the temperature range from 0° to 1716°C. *The accuracy was claimed to be approximately ±4%. We have not adopted their enthalpy data in the tabulation since the* heat capacities which we derive from their data are always less than those of MgO (10) when the temperature is above 1000 K. The deviations between their enthalpy data and the adopted values are approximately 1.8% at 693 K, 3.3% at 1283 K and 5.3% at 1989 K.

Melting Data

Schneider (11) reviewed literature data (12, 13, 14, 15) for the melting point of CaO and selected the value 2887 K based on Kanolt's observations (12) with proper corrections for the temperature scale change. However, Foex (16) determined recently the melting point as 3223 K in a solar furnace using a calibrated pyrometer. His method was relatively free of contamination between sample holder and sample at high temperatures. Foex also found the measurement of Kanolt would be falsified by the presence of tungsten supports in contact with calcium oxide. The latter will react with metallic tungsten to form $WO_3 \cdot 3CaO$ at high temperature. This may be the reason leading to a lower melting point in Kanolt's measurement. The value, 3223 K is tentatively adopted in the tabulation.

The heat of melting is assumed to be 19 ± 2 kcal/mol which is calculated from the estimated ΔSm° = 6 eu at the melting point. The latter is estimated to be the same as that of MgO (10).

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Calcium Oxide (CaO)

(Liquid) GFW = 56.0794

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	10.067	14.806	14.806	.000	= 133.257	= 127.405	93.390
300	10.094	14.868	14.806	.019	= 133.257	= 127.369	92.788
400	11.144	17.934	15.217	1.087	= 133.181	= 125.416	68.524
500	11.707	20.487	16.023	2.232	= 133.048	= 123.488	53.977
600	12.065	22.655	16.952	3.421	= 132.887	= 121.591	44.289
700	12.322	24.535	17.904	4.641	= 132.709	= 119.722	37.379
800	12.524	26.194	18.839	5.884	= 132.856	= 117.851	32.195
900	12.694	27.679	19.740	7.145	= 132.856	= 115.975	28.163
1000	12.843	29.024	20.602	8.422	= 132.898	= 114.097	24.936
1100	12.978	30.254	21.424	9.713	= 132.984	= 112.214	22.295
1200	13.105	31.389	22.208	11.017	= 134.896	= 110.168	20.064
1300	13.224	32.443	22.955	12.334	= 134.728	= 108.115	18.176
1400	13.339	33.427	23.669	13.662	= 134.552	= 106.078	16.559
1500	13.450	34.351	24.350	15.001	= 134.368	= 104.046	15.160
1600	13.558	35.223	25.003	16.352	= 134.176	= 102.031	13.937
1700	13.665	36.048	25.628	17.713	= 133.976	= 100.028	12.859
1800	13.769	36.832	26.229	19.085	= 170.662	= 97.356	11.821
1900	13.873	37.579	26.807	20.467	= 170.227	= 93.295	10.731
2000	14.500	38.315	27.364	21.902	= 169.742	= 89.259	9.754
2100	14.860	39.032	27.903	23.370	= 169.228	= 85.247	8.872
2200	15.140	39.730	28.424	24.871	= 168.687	= 81.261	8.073
2300	15.340	40.407	28.931	26.396	= 168.128	= 77.300	7.345
2400	15.460	41.063	29.423	27.936	= 167.562	= 73.362	6.681
2500	15.500	41.695	29.901	29.485	= 166.995	= 69.450	6.071
2600	15.189	42.297	30.366	31.019	= 166.453	= 65.558	5.511
2700	14.934	42.865	30.819	32.525	= 165.951	= 61.688	4.993
2800	14.734	43.404	31.259	34.008	= 165.485	= 57.834	4.514
2900	14.589	43.919	31.687	35.473	= 165.050	= 53.997	4.069
3000	14.500	44.412	32.103	36.927	= 164.645	= 50.174	3.655
3100	14.500	44.887	32.507	38.377	= 164.261	= 46.365	3.269
3200	14.500	45.348	32.901	39.827	= 163.898	= 42.568	2.907
3300	14.500	45.794	33.285	41.277	= 163.558	= 38.783	2.568
3400	14.500	46.227	33.660	42.727	= 163.242	= 35.006	2.250
3500	14.500	46.647	34.025	44.177	= 162.951	= 31.239	1.951
3600	14.500	47.055	34.381	45.627	= 162.688	= 27.479	1.668
3700	14.500	47.453	34.729	47.077	= 162.458	= 23.726	1.401
3800	14.500	47.839	35.069	48.527	= 162.250	= 19.979	1.149
3900	14.500	48.216	35.401	49.977	= 162.079	= 16.239	.910
4000	14.500	48.583	35.726	51.427	= 161.940	= 12.502	.683
4100	14.500	48.941	36.044	52.877	= 161.835	= 8.766	.467
4200	14.500	49.291	36.355	54.327	= 161.763	= 5.034	.262
4300	14.500	49.632	36.660	55.777	= 161.727	= 1.302	.066
4400	14.500	49.965	36.959	57.227	= 161.725	2.428	= .121
4500	14.500	50.291	37.252	58.677	= 161.756	6.159	= .299

June 30, 1971

CALCIUM OXIDE (CaO) (LIQUID) GFW = 56.0794 CaO

$S^\circ_{298.15}$ = [14.806] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [−133.257] kcal/mol

Tm = 3223 ± 15 K ΔHm° = [19 ± 2] kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(\ell)$ is calculated from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm and the difference between $H^\circ_{3223}-H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1924 K. Heat capacities of the liquid below 1924 K are assumed to be the same as those of the crystal. Above 1924 K the heat capacity is assumed to be constant at 7.25 cal/deg·(g·atom).

The entropy at 298 K is calculated in a manner analogous to that of the heat of formation.

Melting Data

See CaO(c) table for details.

Decomposition

CaO(ℓ) does not vaporize simply to CaO(g), and extensive dissociation of CaO(g) to Ca(g) was found mass-spectrometrically (1).

Reference

1. J. Pelchowith, Philip Res. Report 9, 42 (1954).

Calcium Sulfide (CaS)

(Crystal) GFW = 72.144

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	= 2.151	= 113.227	= 113.227	INFINITE
100	6.201	3.460	22.614	= 1.915	= 113.389	= 113.058	247.087
200	10.087	9.228	14.534	= 1.061	= 113.470	= 112.688	123.139
298	11.339	13.528	13.528	.000	= 113.500	= 112.297	82.316
300	11.353	13.598	13.528	.021	= 113.501	= 112.290	81.803
400	11.800	16.981	13.981	1.184	= 114.074	= 111.860	61.117
500	12.000	19.595	14.847	2.374	= 114.468	= 111.259	48.631
600	12.200	21.801	15.828	3.584	= 114.766	= 110.588	40.281
700	12.400	23.697	16.819	4.814	= 114.989	= 109.849	34.296
800	12.600	25.365	17.785	6.064	= 128.557	= 110.341	30.144
900	12.800	26.861	18.712	7.334	= 128.577	= 108.063	26.241
1000	13.000	28.220	19.596	8.624	= 128.633	= 105.781	23.118
1100	13.200	29.468	20.437	9.934	= 128.724	= 103.493	20.562
1200	13.400	30.626	21.239	11.264	= 130.630	= 101.041	18.402
1300	13.600	31.706	22.003	12.614	= 130.445	= 98.582	16.573
1400	13.800	32.721	22.733	13.984	= 130.242	= 96.139	15.008
1500	14.000	33.680	23.431	15.374	= 130.020	= 93.712	13.654
1600	14.200	34.590	24.100	16.784	= 129.778	= 91.298	12.471
1700	14.400	35.457	24.743	18.214	= 129.517	= 88.901	11.429
1800	14.600	36.286	25.361	19.664	= 166.131	= 85.839	10.422
1900	14.800	37.080	25.957	21.134	= 165.610	= 81.392	9.362
2000	15.000	37.845	26.533	22.624	= 165.071	= 76.974	8.411
2100	15.200	38.581	27.089	24.134	= 164.515	= 72.584	7.554
2200	15.400	39.293	27.628	25.664	= 163.941	= 68.218	6.777
2300	15.600	39.982	28.150	27.214	= 163.352	= 63.881	6.070
2400	15.800	40.650	28.657	28.784	= 162.748	= 59.568	5.424
2500	16.000	41.299	29.150	30.374	= 162.129	= 55.281	4.833
2600	16.200	41.931	29.629	31.984	= 161.499	= 51.020	4.289
2700	16.400	42.546	30.096	33.614	= 160.858	= 46.784	3.787
2800	16.600	43.146	30.551	35.264	= 160.208	= 42.572	3.323
2900	16.800	43.732	30.996	36.934	= 159.550	= 38.381	2.892
3000	17.000	44.305	31.430	38.624	= 158.888	= 34.213	2.492

Dec. 31, 1971

ΔHf°_0 = −113.2 ± 0.5 kcal/mol

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

$\Delta Hf^\circ_{298.15}$ = −113.5 ± 0.5 kcal/mol

Tm = [2673] K

Heat of Formation

Wartenberg (1) measured the heat of solution of CaS in hydrochloric acid solution as ΔHr = −20.6 ± 0.4 kcal/mol for CaS(c) + 2HCl(30 H_2O, aq) → $CaCl_2$(30 H_2O, aq) + H_2S(g). We derive ΔHf°_{298}(CaS, c) = −114.0 ± 0.6 kcal/mol based on the following auxiliary data: ΔHf°_{298}(HCl · 30 H_2O, aq) = −39.357 kcal/mol (2), ΔHf°_{298}(H_2S, g) = −4.88 kcal/mol (3) and ΔHf°_{298}($CaCl_2$ · 30 H_2O, aq) = −208.47 kcal/mol (4).

JANAF analyses of equilibrium studies of Rosenqvist (9) and Uno (10) are listed below.

Investigator	Reaction	Temp (K)	No. of Points	ΔHr°(298 K)(kcal/mol) 2nd Law	3rd Law	Drift (eu)	ΔHf°_{298}(CaS, c) * (kcal/mol)
Rosenqvist (9)	A	1031-1698	12	15.19±0.3	14.03	−1.0±0.2	−112.90
Uno (10)	A	1173-1373	Equation	14.28	14.04	−0.2	−112.91
Uno (10)	B	1173-1373	Equation	23.01	23.06	0.03	−113.31

A: CaS(c) + H_2O(g) → CaO(c) + H_2S(g)

B: CaO(c) + 0.5 S_2(g) → CaS(c) + 0.5 O_2(g)

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

The calculated 3rd law ΔHr°(298 K) may have an uncertainty of 0.5 kcal/mol since the JANAF free energy functions are partially based on the estimated Cp data (above 300 K). Thus the heat of formation of CaS(c) derived from equilibrium studies is in reasonably good agreement with that derived from heat of solution studies (1) within combined experimental errors.

A weighted average, ΔHf°_{298}(CaS, c) = −113.5 ± 0.5 kcal/mol is adopted in the tabulation.

Heat Capacity and Entropy

Anderson (7) measured low temperature heat capacities from 58.1 to 294.9 K in an isothermal calorimeter. We have smoothed his Cp data by a polynomial curve fitting technique and obtain S°_{298} = 13.5 ± 0.3 eu based on S°_{60} = 1.192 eu. The value of S°_{60} is calculated from the combination of Debye and Einstein functions (Θ_D = 284 and Θ_E = 369). Heat capacities above 300 K are estimated graphically.

Melting Data

Literature melting data for CaS(c) are not available. The melting point is very roughly estimated to be about 2400°C (8).

References

1. H. V. Wartenberg, Z. Anorg. Chem. 252, 136 (1943).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. JANAF H_2S(g) table dated Dec. 31, 1965.
4. The value, ΔHf°_{298}($CaCl_2$ · 30 H_2O, aq) = −208.47 kcal/mol, is derived from ΔH°_{dil} = −1175 cal/mol for $CaCl_2$(30 H_2O, aq) → $CaCl_2$(∞ H_2O, aq), using ΔHf°_{298}($CaCl_2$ · ∞ H_2O, aq) = −209.644 kcal/mol. The heat of dilution, ΔH°_{dil} = −1175 cal/mol, is obtained from Φ_L data listed by Lewis and Randall (5). The heat of formation, ΔHf°_{298}($CaCl_2$ · ∞ H_2O, aq) = −209.644 kcal/mol, is calculated from ΔHf°_{298}(Ca^{++} · ∞ H_2O, aq) = −129.74 kcal/mol (6) and ΔHf°_{298}(Cl^- · ∞ H_2O, aq) = −39.952 kcal/mol (2).
5. G. N. Lewis and M. Randall, "Thermodynamics" revised by K. S. Pitzer and L. Brewer, 2nd Ed., McGraw-Hill Book Company, p. 653, 1961.
6. V. B. Parker, National Bureau of Standards, private communication, 1969.
7. C. T. Anderson, J. Amer. Chem. Soc., 53, 476 (1931).
8. G. J. Janz, "Molten Salts Handbook,: 1967 Academic Press, New York.
9. T. Rosenqvist, J. Metals 3, 538 (1951).
10. Tatsuji Uno, Tetsu-to-Hagane 37, 14 (1951) (CA 46, 2382 (1952)).

Chlorine, Monatomic (Cl)

(Ideal Gas) GFW = 35.453

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 1.499	28.587	28.587	INFINITE
100	4.968	33.954	43.975	− 1.002	28.736	27.598	− 60.315
200	5.038	37.410	39.926	− .503	28.872	26.405	− 28.855
298	5.219	39.454	39.454	.000	28.989	25.170	− 18.450
300	5.223	39.487	39.454	.010	28.991	25.146	− 18.319
400	5.370	41.011	39.661	.540	29.106	23.847	− 13.029
500	5.436	42.218	40.056	1.081	29.221	22.519	− 9.843
600	5.445	43.210	40.502	1.625	29.331	21.168	− 7.710
700	5.424	44.048	40.950	2.169	29.435	19.799	− 6.182
800	5.389	44.771	41.384	2.710	29.533	18.415	− 5.031
900	5.351	45.403	41.796	3.247	29.625	17.021	− 4.133
1000	5.314	45.965	42.185	3.780	29.711	15.615	− 3.413
1100	5.279	46.470	42.552	4.309	29.792	14.201	− 2.822
1200	5.248	46.928	42.898	4.836	29.869	12.781	− 2.328
1300	5.221	47.347	43.224	5.355	29.941	11.354	− 1.909
1400	5.196	47.733	43.533	5.880	30.010	9.921	− 1.549
1500	5.175	48.090	43.825	6.399	30.076	8.484	− 1.236
1600	5.156	48.424	44.102	6.915	30.138	7.042	− .962
1700	5.140	48.736	44.365	7.430	30.198	5.598	− .720
1800	5.125	49.029	44.616	7.943	30.256	4.148	− .504
1900	5.112	49.306	44.856	8.455	30.312	2.697	− .310
2000	5.101	49.568	45.085	8.965	30.365	1.242	− .136
2100	5.090	49.816	45.305	9.475	30.417	− .216	.022
2200	5.081	50.053	45.515	9.984	30.467	− 1.676	.166
2300	5.073	50.279	45.717	10.491	30.515	− 3.137	.298
2400	5.066	50.495	45.912	10.998	30.561	− 4.601	.419
2500	5.059	50.701	46.099	11.504	30.605	− 6.067	.530
2600	5.053	50.899	46.280	12.010	30.649	− 7.535	.633
2700	5.048	51.090	46.455	12.515	30.690	− 9.005	.729
2800	5.043	51.274	46.624	13.020	30.729	− 10.475	.818
2900	5.038	51.450	46.787	13.524	30.766	− 11.948	.900
3000	5.034	51.621	46.945	14.027	30.802	− 13.422	.978
3100	5.030	51.786	47.099	14.530	30.835	− 14.896	1.050
3200	5.027	51.946	47.248	15.033	30.867	− 16.372	1.118
3300	5.024	52.100	47.393	15.536	30.897	− 17.848	1.182
3400	5.021	52.250	47.533	16.038	30.926	− 19.325	1.242
3500	5.018	52.396	47.670	16.540	30.952	− 20.805	1.299
3600	5.015	52.537	47.803	17.042	30.978	− 22.283	1.353
3700	5.013	52.675	47.933	17.543	31.001	− 23.763	1.404
3800	5.011	52.808	48.060	18.044	31.023	− 25.244	1.452
3900	5.009	52.938	48.183	18.545	31.044	− 26.724	1.498
4000	5.007	53.065	48.304	19.046	31.063	− 28.206	1.541
4100	5.005	53.189	48.421	19.547	31.081	− 29.688	1.583
4200	5.004	53.309	48.536	20.047	31.097	− 31.171	1.622
4300	5.002	53.427	48.649	20.547	31.113	− 32.654	1.660
4400	5.001	53.542	48.758	21.048	31.128	− 34.136	1.696
4500	4.999	53.654	48.866	21.548	31.141	− 35.620	1.730
4600	4.998	53.764	48.971	22.047	31.154	− 37.104	1.763
4700	4.997	53.872	49.074	22.547	31.167	− 38.587	1.794
4800	4.996	53.977	49.176	23.047	31.178	− 40.073	1.825
4900	4.995	54.080	49.275	23.546	31.189	− 41.556	1.853
5000	4.994	54.181	49.372	24.046	31.200	− 43.041	1.881
5100	4.993	54.280	49.467	24.545	31.211	− 44.525	1.908
5200	4.992	54.377	49.560	25.044	31.221	− 46.010	1.934
5300	4.991	54.472	49.652	25.543	31.231	− 47.496	1.959
5400	4.990	54.565	49.742	26.042	31.240	− 48.982	1.982
5500	4.989	54.657	49.831	26.541	31.250	− 50.467	2.005
5600	4.989	54.747	49.918	27.040	31.259	− 51.954	2.028
5700	4.988	54.835	50.003	27.539	31.268	− 53.441	2.049
5800	4.987	54.922	50.087	28.038	31.277	− 54.925	2.070
5900	4.987	55.007	50.170	28.537	31.286	− 56.413	2.090
6000	4.986	55.091	50.251	29.035	31.295	− 57.898	2.109

March 31, 1961; June 30, 1972

CHLORINE MONATOMIC (Cl) (IDEAL GAS) GFW = 35.453

Ground State Configuration $^2P_{3/2}$ ΔHf°_0 = 28.587 ± 0.002 kcal/mol

$S^\circ_{298.15}$ = 39.454 ± 0.005 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 28.989 ± 0.002 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0.00	4
882.36	2

Heat of Formation

ΔHf° is the value adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). This value was obtained from $D_0(Cl_2)$ = 19997 ± 1 cm^{-1} derived by Leroy and Bernstein (2) from analysis of absorption bands observed near the dissociation limit by Douglas et al. (3). ΔHf° is 0.07 kcal/mol more positive than on the previous JANAF Table (4).

Heat Capacity and Entropy

Electronic levels are from Radziemski and Kaufman (5), who also give more than 200 levels with values greater than 71000 cm^{-1}. These excited levels are omitted since they do not change the calculated functions. The calculated entropy is the same as that adopted by CODATA (1).

References

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3. A. E. Douglas, C. K. Moeller and B. P. Stoicheff, Can. J. Phys. 41, 1174 (1963).
4. JANAF Thermochemical Tables, NSRDS-NBS 37, June, 1971; Cl(g) table dated Mar. 31, 1961.
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Sulfuryl Chloride Fluoride (SO_2ClF)

(Ideal Gas) GFW = 118.5142

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	− 3.514	− 131.234	− 131.234	INFINITE
100	4.299	58.314	85.223	− 2.691	− 131.964	− 129.068	282.076
200	13.849	66.173	73.825	− 1.530	− 132.406	− 125.903	137.579
298	17.111	72.356	72.356	.000	− 133.000	− 122.521	89.810
300	17.160	72.462	72.356	.032	− 133.006	− 122.456	89.209
400	19.375	77.722	73.058	1.865	− 133.782	− 118.879	64.952
500	20.916	82.221	74.452	3.884	− 134.262	− 115.094	50.307
600	22.012	86.137	76.080	6.034	− 134.575	− 111.228	40.515
700	22.804	89.592	77.768	8.277	− 134.775	− 107.296	33.499
800	23.348	92.678	79.443	10.588	− 134.963	− 104.631	28.584
900	23.825	95.459	81.070	12.949	− 134.736	− 99.227	24.096
1000	24.160	97.987	82.637	15.349	− 134.494	− 93.849	20.511
1100	24.420	100.302	84.140	17.779	− 134.241	− 88.499	17.583
1200	24.626	102.436	85.577	20.232	− 134.978	− 83.169	15.147
1300	24.790	104.414	86.951	22.703	− 136.712	− 77.861	13.090
1400	24.924	106.256	88.264	25.189	− 136.442	− 72.576	11.330
1500	25.035	107.980	89.522	27.687	− 136.172	− 67.310	9.807
1600	25.126	109.599	90.727	30.195	− 135.900	− 62.061	8.477
1700	25.203	111.124	91.882	32.712	− 135.628	− 56.828	7.306
1800	25.268	112.567	92.992	35.235	− 135.360	− 51.614	6.267
1900	25.324	113.934	94.058	37.765	− 135.093	− 46.411	5.338
2000	25.372	115.235	95.085	40.300	− 134.830	− 41.225	4.505
2100	25.414	116.474	96.074	42.839	− 134.570	− 36.053	3.752
2200	25.450	117.657	97.028	45.382	− 134.317	− 30.890	3.069
2300	25.482	118.789	97.950	47.929	− 134.066	− 25.741	2.446
2400	25.510	119.874	98.841	50.478	− 133.821	− 20.600	1.876
2500	25.534	120.916	99.703	53.031	− 133.582	− 15.472	1.353
2600	25.556	121.918	100.539	55.585	− 133.348	− 10.351	.870
2700	25.576	122.882	101.348	58.142	− 133.120	− 5.241	.424
2800	25.594	123.813	102.134	60.700	− 132.898	− .140	.011
2900	25.610	124.711	102.897	63.261	− 132.682	4.957	− .374
3000	25.624	125.580	103.639	65.822	− 132.474	10.044	− .732
3100	25.637	126.420	104.360	68.385	− 132.270	15.125	− 1.066
3200	25.649	127.234	105.062	70.950	− 132.074	20.197	− 1.379
3300	25.660	128.024	105.746	73.515	− 131.882	25.264	− 1.673
3400	25.670	128.790	106.413	76.082	− 131.698	30.329	− 1.950
3500	25.679	129.534	107.063	78.649	− 131.520	35.382	− 2.209
3600	25.687	130.258	107.697	81.217	− 131.346	40.438	− 2.455
3700	25.695	130.962	108.317	83.787	− 131.179	45.485	− 2.687
3800	25.702	131.647	108.922	86.356	− 131.017	50.529	− 2.906
3900	25.709	132.315	109.513	88.927	− 130.860	55.563	− 3.114
4000	25.715	132.966	110.091	91.498	− 130.709	60.601	− 3.311
4100	25.721	133.601	110.657	94.070	− 130.562	65.631	− 3.498
4200	25.726	134.221	111.210	96.642	− 130.420	70.657	− 3.677
4300	25.731	134.826	111.753	99.215	− 130.282	75.684	− 3.847
4400	25.735	135.418	112.284	101.788	− 130.150	80.704	− 4.009
4500	25.740	135.996	112.804	104.362	− 130.021	85.722	− 4.163
4600	25.744	136.562	113.315	106.936	− 129.895	90.739	− 4.311
4700	25.747	137.115	113.815	109.511	− 129.774	95.751	− 4.452
4800	25.751	137.657	114.306	112.086	− 129.656	100.760	− 4.588
4900	25.754	138.188	114.788	114.661	− 129.541	105.768	− 4.717
5000	25.757	138.709	115.261	117.237	− 129.430	110.769	− 4.842
5100	25.760	139.219	115.726	119.812	− 129.322	115.776	− 4.961
5200	25.763	139.719	116.183	122.389	− 129.215	120.776	− 5.076
5300	25.766	140.210	116.632	124.965	− 129.111	125.778	− 5.187
5400	25.768	140.692	117.073	127.542	− 129.012	130.770	− 5.293
5500	25.770	141.164	117.506	130.119	− 128.912	135.770	− 5.395
5600	25.773	141.629	117.933	132.696	− 128.818	140.761	− 5.493
5700	25.775	142.085	118.353	135.273	− 128.725	145.748	− 5.588
5800	25.777	142.533	118.766	137.851	− 128.633	150.745	− 5.680
5900	25.779	142.974	119.172	140.429	− 128.544	155.726	− 5.768
6000	25.780	143.407	119.573	143.006	− 128.458	160.720	− 5.854

June 30, 1971

SULFURYL CHLORIDE FLUORIDE (SO_2ClF) (IDEAL GAS) GFW = 118.5142 $ClFO_2S$

Point Group C_s ΔHf°_0 = [−131.2 ± 5] kcal/mol

$S^\circ_{298.15}$ = 72.36 ± 0.4 gibbs/mol $\Delta Hf^\circ_{298.15}$ = [−133 ± 5] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm⁻¹	ω, cm⁻¹	ω, cm⁻¹
1228 (1)	501 (1)	1467 (1)
824 (1)	423 (1)	474 (1)
629 (1)	300 (1)	308 (1)

Bond Distance: S-O = [1.404] Å S-F = [1.530] Å S-Cl = [2.011] Å

Bond Angle: O-S-O = [123.5°] Cl-S-F = [98.06°] σ = 1

Product of the Moments of Inertia: $I_A I_B I_C$ = [1.4037 × 10^{-113}] g^3 cm^6

Heat of Formation

ΔHf° is estimated as the mean of the ΔHf° values (1) for SO_2F_2(g) and SO_2Cl_2(g). This corresponds to use of the mean bond energies, D(S-F) = 74 and D(S-Cl) = 36 kcal/mol, from SO_2F_2 and SO_2Cl_2, respectively. The resulting values of ΔGf° are consistent with those methods of preparation for which thermodynamic tests are possible. Insufficient data preclude tests for preparation of SO_2ClF from AgF_2, CoF_3, MnF_3 and SbF_3. In other cases the tests are not stringent, since the calculated values of ΔGr are large and negative for the observed reactions.

Heat Capacity and Entropy

The point group and symmetry number are consistent with analysis of the spectral data, but the detailed structure is estimated from known coordinates of SO_2Cl in SO_2Cl_2 (1, 2) and SF in SO_2F_2 (1, 3). This estimate should be quite reliable since the SO_2 coordinates are almost identical in SO_2Cl_2 and SO_2F_2. The resulting structure has an O-S-Cl angle of 107.7°, an O-S-F angle of 108.4° and principal moments of inertia of I_A = 16.47 × 10^{-39}, I_B = 29.08 × 10^{-39} and I_C = 29.30 × 10^{-39} g cm^2.

Vibrational frequencies are based on infrared spectra of the vapor (4) and confirmed by Raman spectra of the liquid (5). Birchall and Gillespie (4) assigned δ(FSCl) to a weak Raman band at 195 cm^{-1}, but force-constant calculations based on SO_2Cl_2 and SO_2F_2 predict a value near 300 cm^{-1} (6, 7). It appears that the twist(FSCl) and δ(FSCl) are nearly accidentally degenerate, so we assign them arbitrarily to the Raman band at 308 cm^{-1} and the infrared band at 300 cm^{-1}. The adopted assignments are those of Toyuki and Shimizu (6) and Pfeiffer (7). All adopted values lie between the analogous modes for SO_2Cl_2 and SO_2F_2. δ(FSCl) = 195 cm^{-1} is unlikely since it would lie below δ(ClSCl) = 209 cm^{-1} in SO_2Cl_2; also the intensity of such bending modes should be strong not weak (7).

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Iron Dichloride ($FeCl_2$)

(Crystal) GFW = 126.753

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	= 3.889	= 82.320	= 82.320	INFINITE
100	12.164	10.703	43.476	= 3.277	= 82.507	= 78.916	172.471
200	16.906	21.138	29.828	= 1.738	= 82.116	= 75.452	82.450
298	18.393	28.190	28.190	= .000	= 81.700	= 72.270	52.975
300	18.340	28.303	28.190	.034	= 81.692	= 72.212	52.606
400	19.041	33.681	28.919	1.905	= 81.277	= 69.115	37.763
500	19.512	37.983	30.316	3.834	= 80.876	= 66.120	28.901
600	19.863	41.572	31.991	5.803	= 80.506	= 63.204	23.022
700	20.186	44.657	33.508	7.804	= 80.172	= 60.348	18.841
800	20.437	47.368	35.074	9.835	= 79.895	= 57.537	15.718
900	20.675	49.789	36.577	11.891	= 79.705	= 54.753	13.296
1000	20.878	51.976	38.009	13.969	= 79.678	= 51.985	11.361
1100	21.036	53.976	39.371	16.065	= 79.854	= 49.203	9.776
1200	21.165	55.812	40.666	18.175	= 79.807	= 46.424	8.455
1300	21.282	57.510	41.897	20.296	= 79.411	= 43.658	7.340
1400	21.340	59.089	43.069	22.427	= 79.023	= 40.922	6.388
1500	21.393	60.563	44.187	24.563	= 78.646	= 38.214	5.568
1600	21.435	61.945	45.254	26.705	= 78.281	= 35.530	4.853
1700	21.467	63.245	46.275	28.850	= 78.220	= 32.863	4.225
1800	21.488	64.473	47.252	30.998	= 77.974	= 30.202	3.667
1900	21.499	65.635	48.189	33.147	= 81.414	= 27.368	3.148
2000	21.500	66.738	49.089	35.297	= 81.235	= 24.530	2.681

June 30, 1965; Dec. 31, 1970

IRON DICHLORIDE ($FeCl_2$) (CRYSTAL) GFW = 126.753 Cl_2Fe

$S^\circ_{298.15}$ = 28.19 ± 0.8 gibbs/mol

Tm = 950°K

ΔHf°_0 = −82.3 ± 0.1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −81.7 ± 0.1 kcal/mol

ΔHm° = 10.28 ± 0.05 kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 48.0 ± 1 kcal/mol

$\Delta Hs^\circ_{298.15}$(to dimer) = 60.3 ± 1 kcal/mol dimer

Heat of Formation

Koehler and Coughlin (1) determined $\Delta Hr^\circ_{298.15}$ = −4.06 ± 0.05 kcal/mol for Fe(c) + 2HCl(12.731 H_2O) = $FeCl_2$(c) + H_2(g) by solution calorimetry. This leads to ΔHf°_{298}($FeCl_2$, c) = −81.7 ± 0.1 kcal/mol which is adopted in the tabulation. The value ΔHf°_{298}[HCl(12.731 H_2O)] = −38.812 kcal/mol (2) is used in the calculation.

Li and Gregory (3) also determined calorimetrically ΔHr°_{298} = −19.5 ± 0.2 kcal/mol for $FeCl_2$(c) → Fe^{++}(aq) + $2Cl^-$(aq) in aqueous solution at concentrations near 10^{-3} molal. Using ΔHf°_{298}($Fe^{++}\infty H_2O$, aq) = −21.3 kcal/mol (4) and ΔHf°_{298}($Cl^-\infty H_2O$, aq) = −39.952 kcal/mol (2), we have obtained ΔHf°_{298}($FeCl_2$, c) = −81.7 kcal/mol which is in excellent agreement with the adopted value.

Kangro and Petersen (5) determined the equilibrium constants for the reaction $FeCl_2$(c) + H_2(g) = Fe(c) + 2HCl(g) in the temperature range from 484-662°C. By use of second and third law analyses, the heat of reaction is evaluated as 37.81 and 38.24 kcal/mol respectively. Using the third law ΔHr°_{298}, we obtain ΔHf°_{298}($FeCl_2$, c) = −82.36 ± 0.5 kcal/mol which is in reasonable agreement with the value adopted.

Heat Capacity and Entropy

Kelley and Moore (6) measured the low temperature heat capacities in the temperature range from 53.2 - 295.0°K and made an extrapolation to 0°K which yielded an entropy of 5.19 ± 0.8 eu at 50.12°K. This value also includes the uncoupling energy of Fe^{++}(R$\ln$5 = 3.2 eu). We have adopted the measured heat capacities, but made a minor adjustment of the entropy at 53.2°K to 4.93 eu which is still within the limit of uncertainty, but yields the entropy at 298.15°K as 28.19 eu. The latter was found by E. F. Westrum (7).

Moore (8) measured high temperature enthalpy data from 670.5° to 941°K by drop calorimetry. The low temperature heat capacities and high temperature enthalpy data were smoothly joined at 298°K. The Cp values above 941°K were obtained by graphical extrapolation. Oetting and Gregory (9) measured high temperature heat capacities in the temperature range from 60° to 500°C in a constant heating adiabatic calorimeter. Their Cp values are in good agreement with those found by Moore (8).

Melting Data

Tm and ΔHm° were taken from Moore (8).

Heat of Sublimation

ΔHs°_{298} for the monomer and dimer are calculated from the adopted heats of formation of the crystal and the respective gaseous species.

References

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Iron Dichloride ($FeCl_2$)

(Liquid) GFW = 126.753

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	24.420	33.432	33.432	.000	= 74.411	= 66.544	48.778
300	24.420	33.583	33.432	.045	= 74.392	= 66.495	48.442
400	24.420	40.608	34.390	2.487	= 73.406	= 64.014	34.976
500	24.420	46.057	36.199	4.929	= 72.492	= 61.773	27.001
600	24.420	50.510	38.224	7.371	= 71.649	= 59.709	21.749
700	24.420	54.274	40.255	9.813	= 70.874	= 57.782	18.040
800	24.420	57.535	42.216	12.255	= 70.186	= 55.981	15.288
900	24.420	60.411	44.081	14.697	= 69.610	= 54.217	13.166
1000	24.420	62.984	45.845	17.139	= 69.219	= 52.532	11.481
1100	24.420	65.312	47.510	19.581	= 69.049	= 50.866	10.106
1200	24.420	67.436	49.084	22.023	= 68.670	= 49.236	8.967
1300	24.420	69.391	50.572	24.465	= 67.953	= 47.646	8.010
1400	24.420	71.201	51.981	26.907	= 67.254	= 46.109	7.198
1500	24.420	72.886	53.319	29.349	= 66.571	= 44.624	6.502
1600	24.420	74.462	54.592	31.791	= 65.906	= 43.182	5.898
1700	24.420	75.942	55.805	34.233	= 65.548	= 41.775	5.371
1800	24.420	77.338	56.963	36.675	= 65.008	= 40.393	4.904
1900	24.420	78.658	58.070	39.117	= 64.155	= 38.853	4.469
2000	24.420	79.911	59.131	41.559	= 67.684	= 37.325	4.079
2100	24.420	81.102	60.149	44.001	= 67.217	= 35.818	3.728
2200	24.420	82.238	61.128	46.443	= 66.757	= 34.334	3.411
2300	24.420	83.324	62.069	48.885	= 66.302	= 32.871	3.123
2400	24.420	84.363	62.977	51.327	= 65.853	= 31.427	2.862
2500	24.420	85.360	63.852	53.769	= 65.411	= 30.001	2.623
2600	24.420	86.318	64.698	56.211	= 64.974	= 28.594	2.404
2700	24.420	87.239	65.516	58.653	= 64.544	= 27.204	2.202
2800	24.420	88.127	66.308	61.095	= 64.121	= 25.826	2.016
2900	24.420	88.984	67.075	63.537	= 63.704	= 24.468	1.844
3000	24.420	89.812	67.819	65.979	= 63.294	= 23.121	1.684

June 30, 1965; Dec. 31, 1970

IRON DICHLORIDE ($FeCl_2$) (LIQUID) GFW = 126.753 Cl_2Fe

$S^\circ_{298.15}$ = 33.432 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -74.411 kcal/mol

Tm = 950°K

ΔHm° = 10.28 ± 0.05 kcal/mol

Tb(to equil. mixture) = 1297°K

ΔHv° = 26.27 ± 1 kcal/mol

Heat of Formation

The value of $\Delta Hf^\circ_{298.15}(\ell)$ = -74.411 kcal/mol is obtained from $\Delta Hf^\circ_{298.15}(c)$ by adding ΔHm° and the difference between $H^\circ_{950} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy

G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943), derived the constant heat capacity from enthalpy data measured in the temperature range from 950 to 1100°K in a drop calorimeter. The constant Cp is assumed for all the other temperatures. The entropy is obtained in a manner similar to the heat of formation.

Melting Data

Tm and ΔHm° were taken from G. E. Moore.

Vaporization Data

The boiling point Tb is the calculated temperature at which the sum of the partial pressures of $FeCl_2(g)$ and $Fe_2Cl_4(g)$ over $FeCl_2(\ell)$ reaches one atmosphere. At Tb, the mole fraction of the dimer is 0.1635. The heat of vaporization is calculated to be the difference between the heats of formation at 1297°K for one mole of $FeCl_2(\ell)$ vaporizing to the equilibrium mixture of 0.719 moles of $FeCl_2(g)$ and 0.1405 moles of $Fe_2Cl_4(g)$.

Iron Dichloride ($FeCl_2$)

(Ideal Gas) GFW = 126.753

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	− 3.412	− 33.843	− 33.843	INFINITE
100	14.926	57.953	83.048	− 2.509	− 33.739	− 34.873	76.215
200	12.844	66.181	72.737	− 1.311	− 33.689	− 36.034	39.376
298	13.759	71.503	71.503	.000	− 33.700	− 37.184	27.257
300	13.771	71.588	71.503	.025	− 33.701	− 37.206	27.104
400	14.210	75.617	72.050	1.427	− 33.755	− 38.367	20.963
500	14.442	78.816	73.094	2.861	− 33.849	− 39.509	17.289
600	14.574	81.462	74.274	4.312	− 33.997	− 40.628	14.799
700	14.673	83.716	75.466	5.775	− 34.201	− 41.718	13.025
800	14.750	85.681	76.623	7.246	− 34.464	− 42.776	11.686
900	14.823	87.422	77.728	8.725	− 34.871	− 43.789	10.633
1000	14.901	88.988	78.777	10.211	− 35.436	− 44.753	9.781
1100	14.984	90.412	79.771	11.705	− 36.214	− 45.642	9.068
1200	15.073	91.720	80.713	13.208	− 36.774	− 46.480	8.465
1300	15.166	92.930	81.607	14.720	− 36.987	− 47.260	7.949
1400	15.261	94.057	82.456	16.241	− 37.209	− 48.063	7.503
1500	15.354	95.113	83.265	17.772	− 37.437	− 48.831	7.115
1600	15.445	96.107	84.037	19.312	− 37.674	− 49.583	6.773
1700	15.532	97.046	84.775	20.861	− 38.209	− 50.313	6.468
1800	15.612	97.936	85.482	22.418	− 38.554	− 51.015	6.194
1900	15.686	98.782	86.160	23.983	− 42.576	− 51.517	5.925
2000	15.752	99.589	86.811	25.555	− 42.977	− 51.974	5.679
2100	15.816	100.359	87.438	27.133	− 43.374	− 52.413	5.455
2200	15.861	101.095	88.042	28.717	− 43.772	− 52.834	5.249
2300	15.904	101.801	88.625	30.305	− 44.171	− 53.238	5.059
2400	15.941	102.479	89.188	31.898	− 44.571	− 53.624	4.883
2500	15.970	103.130	89.733	33.493	− 44.976	− 53.992	4.720
2600	15.993	103.757	90.260	35.092	− 45.382	− 54.345	4.568
2700	16.010	104.361	90.772	36.692	− 45.794	− 54.683	4.426
2800	16.022	104.944	91.267	38.293	− 46.212	− 55.003	4.293
2900	16.029	105.506	91.749	39.896	− 46.634	− 55.311	4.168
3000	16.033	106.050	92.216	41.499	− 47.063	− 55.602	4.051
3100	16.032	106.575	92.671	43.102	− 47.499	− 55.879	3.939
3200	16.028	107.084	93.114	44.705	− 131.367	− 56.698	3.736
3300	16.022	107.577	93.545	46.308	− 131.354	− 52.303	3.484
3400	16.012	108.055	93.964	47.910	− 131.352	− 49.907	3.208
3500	16.001	108.519	94.374	49.510	− 131.363	− 47.515	2.967
3600	15.988	108.970	94.773	51.110	− 131.385	− 45.115	2.739
3700	15.974	109.408	95.162	52.708	− 131.419	− 42.719	2.523
3800	15.958	109.834	95.543	54.305	− 131.465	− 40.325	2.319
3900	15.942	110.248	95.915	55.900	− 131.524	− 37.920	2.125
4000	15.924	110.651	96.278	57.493	− 131.597	− 35.523	1.941
4100	15.906	111.044	96.634	59.084	− 131.681	− 33.118	1.765
4200	15.888	111.428	96.981	60.674	− 131.779	− 30.716	1.598
4300	15.869	111.801	97.322	62.262	− 131.889	− 28.307	1.439
4400	15.850	112.166	97.655	63.848	− 132.012	− 25.896	1.286
4500	15.831	112.522	97.981	65.432	− 132.149	− 23.486	1.141
4600	15.812	112.869	98.301	67.014	− 132.297	− 21.066	1.001
4700	15.793	113.209	98.615	68.594	− 132.460	− 18.646	.867
4800	15.774	113.542	98.922	70.173	− 132.634	− 16.223	.739
4900	15.755	113.867	99.224	71.749	− 132.823	− 13.795	.615
5000	15.736	114.185	99.520	73.324	− 133.023	− 11.367	.497
5100	15.716	114.496	99.811	74.896	− 133.236	− 8.929	.383
5200	15.700	114.801	100.096	76.467	− 133.462	− 6.489	.273
5300	15.682	115.100	100.376	78.036	− 133.701	− 4.047	.167
5400	15.665	115.393	100.652	79.604	− 133.952	− 1.598	.065
5500	15.648	115.680	100.922	81.169	− 134.216	.857	− .034
5600	15.631	115.962	101.188	82.733	− 134.492	3.312	− .129
5700	15.615	116.239	101.450	84.296	− 134.780	5.772	− .221
5800	15.599	116.510	101.707	85.856	− 135.081	8.248	− .311
5900	15.583	116.777	101.960	87.415	− 135.394	10.716	− .397
6000	15.566	117.038	102.210	88.973	− 135.718	13.200	− .481

June 30, 1965; Dec. 31, 1970

IRON DICHLORIDE ($FeCl_2$) (IDEAL GAS) GFW = 126.753 Cl_2Fe

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

$S^\circ_{298.15}$ = 71.50 ± 1.0 gibbs/mol

ΔHf°_0 = −33.8 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −33.7 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^5\Delta$	0	10
$^5\Pi$	4600	10
$^5\Sigma$	7140	5

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}	
[327]	(1)
88	(2)
492	(1)

Bond Distance: Fe-Cl = [2.17] Å

Bond Angle: Cl-Fe-Cl = [180°]

Rotational Constant: B_0 = [0.0505] cm^{-1}

σ = 2

Heat of Formation

Using the free energy functions of the monomeric and dimeric $FeCl_2(g)$ with the adopted heat of dimerization at 298°K, ΔH°_d = −35.7 kcal/mol (1), we have derived partial pressures of monomeric $FeCl_2$ from the reported pressure data (2-7). Schäfer (4) determined Kp for the equilibrium reaction C assuming the dimer concentration was insignificant at the equilibrium conditions. 2nd and 3rd law analyses for the vapor pressure data and the equilibrium constants are given below.

Investigator	Method	Reaction	Temp. Range(°K)	No. of Points	ΔHr°_{298} kcal/mol 3rd law	2nd law	Drift eu	$\Delta Hf^\circ_{298}(FeCl_2, g)^a$ kcal/mol
Beusman (2)	Static	A	1012-1179	29	40.61±0.11	41.3	−0.6±0.2	−33.80
Maier (3)	Static	A	972-1268	22	40.70±0.40	39.1	1.1±0.4	−33.71
Schäfer et al. (4)	Carrier gas	A	980-1106	6	40.71±0.27	41.7	−0.9±1.3	−33.70
Schoonmaker and Porter (5)	Mass spectrometric	B	621-701	8[b]	47.74±0.11	45.7	3.1±0.3	−33.96
Sime and Gregory (6)	Torsion Effusion	B	685-760	Equation	48.38±0.11	47.0	1.9	−33.32
Kana'an et al. (7)	Torsion Effusion	B	725-825	Equation	48.28±0.17	49.9	−2.2	−33.42
Kana'an et al. (7)	Mass Effusion (Mo Cell)	B	725-825	Equation	48.53±0.14	49.9	−1.7	−33.17
Kana'an et al. (7)	Mass Effusion (Fe Cell)	B	725-825	Equation	48.37±0.12	49.5	−1.5	−33.33
Hildenbrand (14)	Torsion Effusion	B	643-715	28	48.28±0.08	49.1	−1.1±0.3	−33.42
Schäfer et al. (4)	Equilibrium	C	1205-1375	9	≥10.47±0.50	5.1	4.2±0.1	≥−33.66

Reaction: A. $FeCl_2(\ell) \rightarrow FeCl_2(g)$; B. $FeCl_2(c) \rightarrow FeCl_2(g)$; C. $Fe(c) + 2HCl(g) \rightarrow FeCl_2(g) + H_2(g)$.

a: Derived from the 3rd law ΔHr°_{298} and $\Delta Hf^\circ_{298}(FeCl_2, \ell)$ = −74.411 kcal/mol, $\Delta Hf^\circ_{298}(FeCl_2, c)$ = −81.7 kcal/mol and $\Delta Hf^\circ_{298}(HCl, g)$ = −22.063 kcal/mol, all JANAF ΔHf° values. b: 1 point rejected due to failure of a statistical test.

The adopted value, $\Delta Hf^\circ_{298}(FeCl_2, g)$ = −33.7 kcal/mol, is in very good agreement with those derived from the reactions A and C. The adopted value is also between the more discrepant results for reaction B derived from mass spectrometry and from effusion studies. This implies that the total pressures calculated from the monomer and dimer tables fit the observed vapor pressures over liquid much better than those over solid. For the liquid, the ratio of the calculated to the observed vapor pressure is about 1.0 ± 0.1 and for the solid, the ratio is about 1.3 ± 0.2.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicated that other transition metal dichlorides are linear (8). The bond distance is estimated by comparison with that of $Fe_2Cl_6(g)$ reported by Zasorin (9). The ground state ($^5\Delta$), low lying electronic levels and the quantum weights were obtained from the work of DeKock and Gruen (10).

The asymmetric stretching frequency was observed in the infrared spectra of the vapor at 492 cm^{-1} by Leroi (11) and at 494 cm^{-1} in Ar matrices by Thompson (12) and Frey (13). Normal coordinate analysis yields the stretching force constant k_1 = 2.23 md/Å which leads to the stretching vibrational frequency, ν_1 = 327 cm^{-1}, by a valence force field model. The bending frequency, ν_2 = 88 cm^{-1} was observed in the matrix infrared spectra (12).

The drift, defined as the difference between ΔSr(JANAF functions) and ΔSr(2nd law), in the 3rd law analyses of the pressure data indicated that the entropy of $FeCl_2(g)$ is made more consistent by introducing two low lying electronic levels and a relatively low bending frequency. The heats derived by 2nd and 3rd law analyses are in good agreement.

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Sulfuryl Chloride (SO_2Cl_2)

(Ideal Gas) GFW = 134.9688

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	= 3.831	= 83.309	= 83.309	INFINITE
100	10.320	58.735	84.499	= 2.976	= 84.008	= 80.931	176.874
200	15.417	67.557	75.927	= 1.474	= 84.521	= 77.633	84.833
298	18.426	74.327	74.327	.000	= 84.800	= 74.187	54.380
300	18.469	74.441	74.327	.034	= 84.804	= 74.121	53.997
400	20.367	80.033	75.077	1.982	= 85.496	= 70.513	38.526
500	21.647	84.725	76.550	3.088	= 85.912	= 66.716	29.161
600	22.591	88.762	78.257	4.303	= 86.178	= 62.849	22.893
700	23.240	92.297	80.015	5.598	= 86.339	= 58.923	18.397
800	23.754	95.437	81.750	10.949	= 89.497	= 54.269	15.372
900	24.125	98.257	83.430	13.344	= 89.244	= 50.880	12.355
1000	24.409	100.815	85.043	15.772	= 88.978	= 45.520	9.948
1100	24.630	103.152	86.584	18.224	= 88.705	= 40.189	7.985
1200	24.805	105.303	88.056	20.694	= 88.425	= 34.881	6.353
1300	24.945	107.294	89.460	23.184	= 88.141	= 29.596	4.975
1400	25.059	109.147	90.801	25.684	= 87.856	= 24.334	3.799
1500	25.153	110.879	92.082	28.195	= 87.570	= 19.094	2.782
1600	25.231	112.505	93.308	30.714	= 87.284	= 13.871	1.895
1700	25.296	114.036	94.483	33.241	= 86.997	= 8.664	1.114
1800	25.352	115.486	95.610	35.773	= 86.715	= 3.478	.422
1900	25.399	116.856	96.692	38.311	= 86.434	1.697	= .195
2000	25.440	118.160	97.733	40.853	= 86.158	6.852	= .749
2100	25.475	119.402	98.736	43.398	= 85.885	11.995	= 1.248
2200	25.506	120.588	99.702	45.948	= 85.617	17.127	= 1.701
2300	25.533	121.722	100.635	48.500	= 85.353	22.245	= 2.114
2400	25.557	122.809	101.537	51.054	= 85.095	27.355	= 2.491
2500	25.578	123.853	102.409	53.611	= 84.843	32.449	= 2.837
2600	25.597	124.857	103.253	56.170	= 84.595	37.538	= 3.155
2700	25.614	125.823	104.071	58.730	= 84.355	42.614	= 3.449
2800	25.629	126.755	104.865	61.292	= 84.122	47.682	= 3.722
2900	25.643	127.654	105.635	63.856	= 83.894	52.743	= 3.975
3000	25.655	128.524	106.384	66.421	= 83.674	57.796	= 4.210
3100	25.666	129.365	107.111	68.987	= 83.459	62.842	= 4.430
3200	25.676	130.180	107.820	71.554	= 83.253	67.879	= 4.636
3300	25.686	130.971	108.509	74.122	= 83.052	72.910	= 4.829
3400	25.694	131.738	109.181	76.691	= 82.858	77.940	= 5.010
3500	25.702	132.482	109.836	79.261	= 82.671	82.958	= 5.180
3600	25.709	133.207	110.476	81.832	= 82.488	87.974	= 5.341
3700	25.715	133.911	111.099	84.403	= 82.314	92.985	= 5.492
3800	25.722	134.597	111.709	86.975	= 82.143	97.990	= 5.636
3900	25.727	135.265	112.304	89.547	= 81.979	102.989	= 5.771
4000	25.732	135.917	112.887	92.120	= 81.821	107.989	= 5.900
4100	25.737	136.552	113.456	94.694	= 81.666	112.981	= 6.022
4200	25.742	137.172	114.013	97.267	= 81.518	117.969	= 6.139
4300	25.746	137.778	114.559	99.842	= 81.372	122.957	= 6.249
4400	25.750	138.370	115.093	102.417	= 81.232	127.941	= 6.355
4500	25.753	138.949	115.617	104.992	= 81.096	132.920	= 6.455
4600	25.757	139.515	116.131	107.567	= 80.962	137.899	= 6.552
4700	25.760	140.069	116.634	110.143	= 80.832	142.872	= 6.644
4800	25.763	140.611	117.128	112.719	= 80.705	147.841	= 6.731
4900	25.766	141.142	117.613	115.296	= 80.580	152.811	= 6.816
5000	25.768	141.663	118.088	117.872	= 80.459	157.772	= 6.896
5100	25.771	142.173	118.556	120.449	= 80.339	162.743	= 6.974
5200	25.773	142.674	119.015	123.027	= 80.220	167.702	= 7.048
5300	25.776	143.165	119.466	125.604	= 80.104	172.662	= 7.120
5400	25.778	143.646	119.909	128.182	= 79.990	177.615	= 7.188
5500	25.780	144.119	120.345	130.760	= 79.876	182.575	= 7.255
5600	25.782	144.584	120.774	133.338	= 79.766	187.528	= 7.318
5700	25.783	145.040	121.195	135.916	= 79.657	192.468	= 7.380
5800	25.785	145.489	121.610	138.494	= 79.548	197.426	= 7.439
5900	25.787	145.930	122.019	141.073	= 79.440	202.365	= 7.496
6000	25.788	146.363	122.421	143.652	= 79.334	207.318	= 7.552

June 30, 1971

SULFURYL CHLORIDE (SO_2Cl_2) (IDEAL GAS) GFW = 134.9688 Cl_2O_2S

Point Group C_{2v} ΔHf°_0 = −83.3 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 74.33 ± 0.1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −84.8 ± 0.5 kcal/mol

Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies (ω, cm^{-1}, all singly degenerate)

1205 577 406 209 280 1434 388 586 363

Bond Distance: S-O = 1.404 ± 0.004 Å S-Cl = 2.011 ± 0.005 Å

Bond Angle: O-S-O = 123.5 ± 0.8° Cl-S-Cl = 100.0 ± 0.7° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 3.80493 \times 10^{-113}$ g^3 cm^6

Heat of Formation

The adopted ΔHf° = −84.8 ± 0.5 kcal/mol is based on Kp for dissociation to SO_2 and Cl_2 (see below). The relatively thorough study of Arii (2) gave similar values of Kp near the vapor pressure of SO_2Cl_2 and at reduced pressures. The entropy discrepancy is large (δS = −11 eu), but this may be due to the small temperature range and to uncertainties in absorption on the activated charcoal catalyst. Absorption uncertainties probably exist in all of the Kp studies, but the high-temperature data of Trautz (3) have an additional uncertainty; i.e., Kp is very sensitive to small systematic errors in the data since the SO_2Cl_2 is almost completely decomposed. Exclusion of data (3) above 416 K yields a third-law ΔHf° which agrees satisfactorily with Arii (2). Data of Londergan (1) yield a third-law ΔHf° which is smaller by about 0.4 kcal/mol; these data yield almost no entropy discrepancy, but the experimental method (1) appears to be less satisfactory.

The adopted ΔHf° is consistent with old calorimetric data of Thomsen (5) for hydrolysis of the liquid but inconsistent with recent data of Neale and Williams (4), on which the selections of NBS 270-3 (6) are probably based. Consistency tests require ΔHv; thus, we note that in the absence of a catalyst $SO_2Cl_2(g)$ persists to well above the boiling point even though it is unstable with respect to SO_2 and Cl_2. Evidence for this conclusion includes studies of catalysts (3, 7), vapor densities (8), boiling point and vapor pressures (9, 10, 7). The boiling point (69.5 ± 0.3°C) and ΔSv (20.8 gibbs/mol) are almost exactly those predicted by comparison with SO_2ClF (7.3°C and 20.6 gibbs/mol) and SO_2F_2 (−55.3°C and 21.1 gibbs/mol), which have normal vapors. Vapor pressure data (9) for SO_2Cl_2 yield ΔHv = 7.1 kcal/mol at 69.5°C and ΔHv° = 7.8 kcal/mol at 25°C. Trautz et al. (10) used a condensation method to measure ΔHv = 8.67 kcal/mol near Tb, but we dismiss this value since the resulting ΔSv (19.5 gibbs/mol) is too small for normal vapor and much too small for dissociating vapor.

Source	Data	Reaction[a]	T, K	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	δS, eu[b]	ΔHf°_{298}, kcal/mol[d] gas	ΔHf°_{298}, kcal/mol[d] liquid
Londergan (1)	Kp	A	340-373	13.08±0.05	13.41±0.3	−0.9±0.1	−84.36	(−92.1)
Arii (2)	Kp	A	303-323	10.41±0.13	13.84±0.2	−10.9±0.4	−84.79	(−92.6)
Trautz (3)	Kp	A	375-464	6.33±0.51	14.2 ±1.1	−19.2±1.2	−85.2	(−93.0)
			375-416	---	13.91±0.4	---	−84.86	(−92.7)
Neale (4)	ΔHr	B	295-296	---	−63.4 ±0.5[c]	---	(−86.1)	−93.9
Thomsen (5)	ΔHr	B	291-293	---	−63.6 ±0.5[c]	---	(−84.8)	−92.6
NBS 270-3 (6)	(4?)	B?	298?	---	−63.1	---	−87.0	−94.2

[a] Reactions: A) $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$; B) $SO_2Cl_2(\ell) + 2\ H_2O(\ell) \rightarrow [H_2SO_4 + 2HCl](nH_2O)$

[b] δS = ΔSr°(2nd Law) − ΔSr°(JANAF functions). [c] Calorimetric ΔHr adjusted to 25°C.

[d] Values in parentheses calculated from ΔHv° = 7.8 kcal/mol at 25°C.

Heat Capacity and Entropy

Bond lengths and bond angles are those derived from new electron-diffraction data by Hargittai (11). These differ significantly from early results of Palmer (12). Microwave spectra were reported by Abbar (13), but structural parameters were not derived from the data. The adopted structure has an O-S-Cl angle of 107.7° and principal moments of inertia of $I_A = 24.05 \times 10^{-39}$, $I_B = 36.07 \times 10^{-39}$ and $I_C = 43.86 \times 10^{-39}$ g cm^2.

The vibrational assignment is from force-constant calculations of Toyuki and Shimizu (14). Pfeiffer's assignment (15) is only slightly different and results in negligible change in the thermodynamic functions. Spectral data were summarized by Gillespie and Robinson (16) in their study of the liquid-phase Raman spectra. Only those frequencies above 500 cm^{-1} are based on gas-phase spectra. Trautz et al. (10) found Cp = 15.4 ± 0.3 gibbs/mol by calorimetry at 43 mmHg and 16 to 99°C; this Cp is too low, like ΔHv (10), and the error is almost 20%.

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Cl_2O_2S

Silicon Dichloride ($SiCl_2$)

(Ideal Gas) GFW = 98.992

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	− 3.004	− 40.043	− 40.043	INFINITE
100	9.196	55.703	77.416	− 2.172	− 39.969	− 40.932	89.457
200	11.103	62.685	68.450	− 1.153	− 39.957	− 41.905	45.792
298	12.269	67.360	67.360	.000	− 40.000	− 42.854	31.413
300	12.284	67.436	67.360	.023	− 40.001	− 42.872	31.232
400	12.893	71.063	67.850	1.285	− 40.076	− 43.818	23.941
500	13.224	73.979	68.794	2.592	− 40.166	− 44.743	19.557
600	13.420	76.408	69.868	3.925	− 40.270	− 45.649	16.828
700	13.543	78.487	70.953	5.274	− 40.384	− 46.536	14.529
800	13.626	80.301	72.011	6.633	− 40.511	− 47.408	12.951
900	13.684	81.910	73.023	7.998	− 40.646	− 48.261	11.719
1000	13.726	83.354	73.985	9.369	− 40.795	− 49.100	10.731
1100	13.757	84.664	74.897	10.743	− 40.953	− 49.923	9.919
1200	13.781	85.862	75.762	12.120	− 41.121	− 50.731	9.234
1300	13.804	86.966	76.581	13.499	− 41.299	− 51.525	8.667
1400	13.815	87.989	77.360	14.880	− 41.487	− 52.304	8.165
1500	13.827	88.942	78.101	16.262	− 41.686	− 53.070	7.732
1600	13.837	89.835	78.807	17.645	− 41.896	− 53.822	7.352
1700	13.845	90.674	79.480	19.029	− 54.109	− 54.458	7.001
1800	13.852	91.466	80.124	20.414	− 54.285	− 54.470	6.814
1900	13.858	92.215	80.741	21.800	− 54.461	− 54.474	6.266
2000	13.863	92.926	81.333	23.186	− 54.640	− 54.470	5.952
2100	13.868	93.602	81.901	24.572	− 54.819	− 54.458	5.666
2200	13.872	94.248	82.446	25.959	− 55.000	− 54.437	5.408
2300	13.875	94.864	82.974	27.347	− 55.181	− 54.407	5.170
2400	13.879	95.455	83.482	28.735	− 55.364	− 54.368	4.951
2500	13.882	96.021	83.972	30.123	− 55.550	− 54.324	4.749
2600	13.885	96.566	84.446	31.511	− 55.737	− 54.271	4.562
2700	13.889	97.090	84.905	32.900	− 55.926	− 54.212	4.388
2800	13.893	97.595	85.349	34.289	− 56.118	− 54.142	4.226
2900	13.897	98.083	85.780	35.678	− 56.312	− 54.070	4.075
3000	13.902	98.554	86.198	37.068	− 56.508	− 53.991	3.933
3100	13.907	99.010	86.604	38.458	− 56.707	− 53.904	3.800
3200	13.914	99.452	86.999	39.850	− 56.907	− 53.808	3.675
3300	13.921	99.880	87.382	41.241	− 57.111	− 53.708	3.557
3400	13.930	100.296	87.756	42.634	− 57.315	− 53.601	3.445
3500	13.940	100.700	88.120	44.027	− 57.523	− 53.492	3.340
3600	13.952	101.092	88.475	45.422	− 149.692	− 51.115	3.103
3700	13.965	101.475	88.821	46.818	− 149.803	− 48.374	2.857
3800	13.980	101.847	89.159	48.215	− 149.915	− 45.633	2.625
3900	13.996	102.211	89.489	49.614	− 150.029	− 42.887	2.403
4000	14.015	102.565	89.812	51.014	− 150.145	− 40.138	2.193
4100	14.035	102.912	90.127	52.417	− 150.260	− 37.390	1.993
4200	14.057	103.250	90.435	53.822	− 150.375	− 34.637	1.802
4300	14.083	103.581	90.737	55.229	− 150.489	− 31.879	1.620
4400	14.109	103.905	91.033	56.638	− 150.604	− 29.117	1.446
4500	14.138	104.223	91.323	58.050	− 150.717	− 26.353	1.280
4600	14.169	104.534	91.606	59.466	− 150.828	− 23.589	1.121
4700	14.202	104.839	91.885	60.884	− 150.936	− 20.820	.968
4800	14.237	105.138	92.158	62.306	− 151.042	− 18.054	.822
4900	14.274	105.432	92.426	63.732	− 151.145	− 15.279	.681
5000	14.313	105.721	92.689	65.161	− 151.245	− 12.509	.547
5100	14.353	106.005	92.947	66.594	− 151.341	− 9.727	.417
5200	14.396	106.284	93.201	68.032	− 151.433	− 6.950	.292
5300	14.441	106.558	93.450	69.474	− 151.521	− 4.173	.172
5400	14.487	106.829	93.695	70.920	− 151.606	− 1.393	.056
5500	14.534	107.095	93.937	72.371	− 151.686	1.390	.055
5600	14.583	107.357	94.174	73.827	− 151.761	4.174	.163
5700	14.633	107.616	94.408	75.288	− 151.832	6.959	.267
5800	14.685	107.871	94.637	76.754	− 151.898	9.748	.367
5900	14.736	108.122	94.864	78.225	− 151.960	12.530	.464
6000	14.791	108.371	95.087	79.701	− 152.017	15.320	.558

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

SILICON DICHLORIDE ($SiCl_2$) (IDEAL GAS) GFW = 98.992 Cl_2Si

Point Group C_{2v} ΔHf°_0 = -40.04 ± 1 kcal/mol

$S^\circ_{298.15}$ = 67.36 ± 1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -40.0 ± 1 kcal/mol

Electronic Levels and Quantum Weights

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

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
513 (1)
[190] (1)
502 (1)

Bond Distance: Si-Cl = [2.04] Å

Bond Angle: Cl-Si-Cl = [106°] σ = 2

Product of the Moments of Inertia: $I_A I_B I_C$ = [5.709 x 10^{-114}] g^3 cm^6

Heat of Formation

The adopted $\Delta Hf^\circ_{298}(SiCl_2, g)$ = -40.0 kcal/mol is calculated from $\Delta Hf^\circ_{298}(SiCl_4, g)$ = -158.4 kcal/mol (1) and ΔHr°_{298} = 78.5 ± 2 kcal/mol for Si(c) + $SiCl_4$(g) → 2$SiCl_2$(g). JANAF analyses of equilibrium data for this reaction are summarized below. Three sets of data (2, 3, 7) yield average values of ΔHr° (3rd law) which agree within 0.5 kcal/mol and values of ΔSr° (2nd law) which are in reasonable agreement with the JANAF functions. Two of the equilibrium studies used flow techniques while the third used a static technique. A median value of ΔHr° is adopted. Its uncertainty is estimated by assuming that the JANAF entropy for $SiCl_2$(g) may be too low by 0.7 gibbs/mol at 1400°K. The adopted value corresponds to ΔH°_0 atom = 203.8 kcal/mol and an average bond energy of 101.9 kcal/mol.

Two other flow studies (4, 5) yield large entropy errors, suggesting that there are temperature-dependent errors in Kp. The reported equilibrium constants are reasonable at the lower temperatures but deviate progressively at the higher temperatures. In contrast, the static study of Ishino (6) gave Kp values which differ by a factor of five from the adopted ones. These data yield a consistent entropy but ΔHr° (3rd law) is lower by 5 kcal/mol.

Source	Date	Method	No. of Points	Range T, °K	Entropy Test[a] δ, gibbs/mol	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law
Schäfer (2)	1967	Flow	Equation	1273-1473	1.6 ± 1	80.5 ± 1	78.35
Teichmann (3)	1966	Flow	Equation	1223-1573	1.7 ± 0.8	80.8 ± 1.1	78.49
Chechentsev (4)	1965	Flow	3	1473-1573	35 ± 6	132 ± 9	76.4
Antipin (5)	1954	Flow	5	1273-1673	26 ± 3	114 ± 4	75.4
Ishino (6)	1965	Static	27	1448-1573	-2.1 ± 1.4	70.2 ± 2.1	73.4
Schäfer (7)	1953	Static	Equation	1400-1593	0.6 ± 0.9	79.8 ± 1.4	78.84

[a] δ = ΔSr° (2nd law) − ΔSr° (JANAF functions); where equations are used as input, the uncertainties are those given by the original authors.

Heat Capacity and Entropy

The point group is assumed to be the same as that of CF_2 and SiF_2. The Si-Cl bond length and Cl-Si-Cl bond angle are estimated to be intermediate between those in HSiCl and H_2SiCl_2. Comparisons with CF_2, SiF_2, H_2CF_2 and H_2SiF_2 confirm that the estimated angle is reasonable. Further confirmation of the structure comes from analysis of isotopic splittings in the infrared spectra of matrix-isolated $SiCl_2$. Milligan and Jacox (8) deduced angles of 90 to 120° from alternative assignments for the two stretching vibrations. Observations on argon matrices gave 502 and 513 cm^{-1} for these vibrations, but it was not possible to decide which is the symmetric mode. Principal moments of inertia are I_A = 31.25 x 10^{-39}, I_B = 5.035 x 10^{-39}, and I_C = 35.29 x 10^{-39} g cm^2.

Milligan and Jacox (8) also observed an unstructured absorption in the ultraviolet spectrum. This is the region in which gas-phase emission studies (9) showed features tentatively ascribed to $SiCl_2$. Vibrational spacings of about 250 and 540 cm^{-1} were associated (9) with the ground state; however, this analysis should be reviewed in the light of the matrix spectra. Meanwhile, we estimate that the bending mode should be similar to that in H_2SiCl_2, probably 190 ± 40 cm^{-1}.

The ground state is assumed to be $^1A_1$ as suggested by Hückel-molecular-orbital calculations (10). Singlet excited states (9, 11) are included near 28000 and 30000 cm^{-1}, but the values are placed in brackets to emphasize the uncertainty in the analysis. Also tentatively adopted is the suggestion by Hastie et al. (11) that the continuous spectrum near 23000 cm^{-1} is due to a triplet excited state.

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Iron Dichloride Dimeric (Fe_2Cl_4)

(Ideal Gas) GFW = 253.506

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	= 7.134	= 103.696	= 103.696	INFINITE
100	23.353	81.171	136.431	= 5.526	= 103.686	= 102.480	223.970
200	28.443	99.276	113.700	= 2.885	= 103.341	= 101.413	110.819
298	30.084	110.990	110.990	.000	= 103.100	= 100.522	73.685
300	30.103	111.176	110.991	.056	= 103.096	= 100.506	73.219
400	30.795	119.944	112.182	3.105	= 102.959	= 99.667	54.455
500	31.140	126.857	114.450	6.203	= 102.917	= 98.849	43.207
600	31.337	132.553	117.006	9.328	= 102.990	= 98.031	35.708
700	31.467	137.394	119.581	12.469	= 103.183	= 97.191	30.344
800	31.567	141.602	122.077	15.620	= 103.540	= 96.316	26.312
900	31.656	145.326	124.457	18.782	= 104.110	= 95.378	23.161
1000	31.745	148.665	126.714	21.952	= 105.042	= 94.366	20.624
1100	31.836	151.695	128.849	25.131	= 106.407	= 93.222	18.521
1200	31.932	154.470	130.870	28.319	= 107.345	= 91.994	16.754
1300	32.029	157.029	132.785	31.517	= 107.597	= 90.704	15.249
1400	32.126	159.407	134.603	34.725	= 107.875	= 89.393	13.955
1500	32.225	161.626	136.331	37.943	= 108.175	= 88.064	12.831
1600	32.318	163.709	137.978	41.170	= 108.502	= 86.712	11.844
1700	32.407	165.671	139.550	44.406	= 109.434	= 85.324	10.969
1800	32.489	167.526	141.053	47.651	= 109.993	= 83.893	10.186
1900	32.564	169.284	142.493	50.904	= 117.918	= 82.055	9.438
2000	32.631	170.956	143.875	54.163	= 118.601	= 80.153	8.759
2100	32.691	172.550	145.203	57.430	= 119.284	= 78.213	8.140
2200	32.742	174.072	146.480	60.701	= 119.977	= 76.241	7.574
2300	32.787	175.528	147.712	63.978	= 120.674	= 74.238	7.054
2400	32.823	176.925	148.900	67.258	= 121.380	= 72.205	6.575
2500	32.853	178.265	150.048	70.542	= 122.096	= 70.139	6.132
2600	32.877	179.554	151.158	73.829	= 122.819	= 68.048	5.720
2700	32.895	180.795	152.233	77.117	= 123.555	= 65.929	5.337
2800	32.907	181.992	153.275	80.408	= 124.302	= 63.777	4.978
2900	32.915	183.147	154.285	83.699	= 125.061	= 61.606	4.643
3000	32.918	184.263	155.266	86.990	= 125.834	= 59.404	4.328
3100	32.916	185.342	156.219	90.282	= 126.620	= 57.174	4.031
3200	32.915	186.387	157.145	93.574	= 294.270	= 52.034	3.554
3300	32.908	187.400	158.047	96.865	= 294.159	= 44.467	2.945
3400	32.899	188.382	158.925	100.155	= 294.069	= 36.900	2.372
3500	32.888	189.336	159.780	103.445	= 294.001	= 29.344	1.832
3600	32.876	190.262	160.614	106.733	= 293.957	= 21.775	1.322
3700	32.861	191.163	161.427	110.020	= 293.934	= 14.216	.840
3800	32.846	192.039	162.222	113.305	= 293.935	= 6.665	.383
3900	32.830	192.892	162.997	116.589	= 293.959	.906	= .051
4000	32.812	193.723	163.755	119.871	= 294.009	8.461	= .462
4100	32.794	194.533	164.496	123.152	= 294.078	16.026	= .854
4200	32.776	195.323	165.220	126.430	= 294.176	23.585	= 1.227
4300	32.757	196.094	165.929	129.707	= 294.295	31.136	= 1.584
4400	32.739	196.847	166.623	132.982	= 294.438	38.727	= 1.924
4500	32.720	197.582	167.303	136.254	= 294.606	46.294	= 2.248
4600	32.701	198.301	167.969	139.525	= 294.797	53.870	= 2.560
4700	32.682	199.004	168.622	142.795	= 295.013	61.442	= 2.858
4800	32.663	199.692	169.262	146.062	= 295.252	69.049	= 3.144
4900	32.644	200.365	169.890	149.327	= 295.517	76.642	= 3.418
5000	32.625	201.025	170.506	152.591	= 295.803	84.234	= 3.682
5100	32.607	201.670	171.111	155.852	= 296.112	91.843	= 3.936
5200	32.589	202.303	171.705	159.112	= 296.446	99.454	= 4.180
5300	32.572	202.924	172.288	162.370	= 296.804	107.067	= 4.415
5400	32.554	203.533	172.861	165.626	= 297.186	114.690	= 4.642
5500	32.537	204.130	173.424	168.881	= 297.589	122.326	= 4.861
5600	32.521	204.716	173.978	172.134	= 298.016	129.958	= 5.072
5700	32.504	205.292	174.522	175.385	= 298.467	137.596	= 5.276
5800	32.488	205.857	175.058	178.635	= 298.939	145.267	= 5.474
5900	32.473	206.412	175.584	181.883	= 299.435	152.919	= 5.664
6000	32.457	206.958	176.103	185.129	= 299.953	160.598	= 5.850

Dec. 31, 1970

IRON DICHLORIDE DIMERIC (Fe_2Cl_4) (IDEAL GAS) GFW = 253.506 Cl_4Fe_2

Point Group [D_{2h}] ΔHf°_0 = -103.7 ± 1 kcal/mol

$S^\circ_{298.15}$ = [111.0 ± 3] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -103.1 ± 1 kcal/mol

Ground State Quantum Weight = [10]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[10]
[4600]	[10]
[7140]	[5]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[30] (1)	[90] (1)	[150] (1)	249 (1)
[50] (1)	110 (1)	[180] (1)	325 (1)
[80] (1)	[125] (1)	[200] (1)	438 (1)

Bond Distances: Fe-Cl = [2.17] Å Fe-Cl'$_{(bridge)}$ = [2.30] Å

Bond Angles: Fe-Cl'$_{(bridge)}$-Fe = [90°] Cl'$_{(bridge)}$-Fe-Cl'$_{(bridge)}$ = [90°] σ = [4]

Cl-Fe-Cl'$_{(bridge)}$ = [135°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.7005] x 10^{-111} g^3 cm^6

Heat of Formation

Beusman (1) reported the partial pressures of the monomer and dimer in the temperature range from 980-1167°K using both a static method to determine the total pressures of these two species and a transpiration method to determine the ratio of monomer to dimer. Schoonmaker and Porter (2) determined mass spectrometrically the partial pressures of the monomer and dimer in the temperature range from 521-658°K. Based on the combination of these two sets of partial pressure data, we have derived a smoothed equation log Kp(atm) = -7549/T + 6.506 for $Fe_2Cl_4(g) = 2FeCl_2(g)$. 2nd law analysis of the equilibrium constants gives the heat and the entropy of the dimerization at 298° as ΔH°_d = -35.7 kcal/mol and ΔS°_d = -32.0 eu which lead to the adopted $\Delta Hf^\circ_{298}(Fe_2Cl_4, g)$ = -103.1 kcal/mol and $S^\circ_{298}(Fe_2Cl_4, g)$ = 111.0 eu, using $\Delta Hf^\circ_{298}(FeCl_2, g)$ = -33.7 kcal/mol and $S^\circ_{298}(FeCl_2, g)$ = 71.50 eu (3).

The equilibrium constants derived from the two different experimental techniques are reasonably consistent considering the uncertainties inherent in the problems. Combination of these two sets of data leads to reliable 2nd law heat and entropy since the temperature ranges are different by 400°K.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was suggested by Leroi et al. (4), Thompson and Carlson (5). Two iron and two chlorine atoms form a square. The outer Fe-Cl distance is estimated to be the same as in $FeCl_2(g)$ and the square Fe-Cl' distance is assumed to be slightly larger. The Cl-Fe-Cl'$_{bridge}$ angle is estimated to be 135°. The three principal moments of inertia are: I_A = 31.13 x 10^{-39}, I_B = 218.68 x 10^{-39} g cm^2 and $I_C = I_A + I_B$. The electronic levels and quantum weights were arbitrarily estimated to be the same as in $FeCl_2(g)$.

There are only four vibrational frequencies observed in the matrix isolated infrared spectrum, ν_{10} = 110 cm^{-1} and ν_{12} = 436.2 cm^{-1} (5), ν_9 = 325 cm^{-1}, ν_{11} = 249 cm^{-1} and ν_{12} = 438 cm^{-1} (6). The other 8 fundamental vibrational frequencies were estimated by comparison with other dimer molecules and also adjusted so that they give $S^\circ_{298}(Fe_2Cl_4, g)$ = 111.0 eu which has been discussed in the earlier Heat of Formation part. The order of the frequencies listed above is arbitrary and not related to their species types.

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Silicon Tetrachloride ($SiCl_4$)

(Ideal Gas) GFW = 169.898

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	− 4.638	− 157.881	− 157.881	INFINITE
100	13.672	59.770	96.201	− 3.643	− 158.342	− 155.197	339.184
200	16.787	70.994	80.966	− 1.994	− 158.426	− 152.005	166.104
298	21.573	79.070	79.070	.000	− 158.400	− 148.858	109.115
300	21.610	79.204	79.071	.040	− 158.399	− 148.798	108.400
400	23.133	85.651	79.940	2.285	− 158.321	− 145.609	79.557
500	23.989	90.914	81.625	4.645	− 158.211	− 142.442	62.261
600	24.505	95.337	83.551	7.071	− 158.091	− 139.300	50.740
700	24.835	99.141	85.513	9.539	− 157.964	− 136.178	42.517
800	25.057	102.473	87.429	12.035	− 157.840	− 133.077	36.355
900	25.214	105.433	89.268	14.549	− 157.716	− 129.986	31.565
1000	25.328	108.096	91.020	17.076	− 157.603	− 126.913	27.737
1100	25.413	110.514	92.684	19.613	− 157.495	− 123.849	24.607
1200	25.479	112.728	94.263	22.158	− 157.395	− 120.795	22.000
1300	25.530	114.770	95.763	24.709	− 157.303	− 117.749	19.795
1400	25.571	116.663	97.189	27.264	− 157.221	− 114.709	17.907
1500	25.604	118.429	98.547	29.823	− 157.149	− 111.675	16.271
1600	25.632	120.082	99.842	32.384	− 157.089	− 108.646	14.840
1700	25.654	121.637	101.079	34.949	− 169.030	− 105.511	13.564
1800	25.674	123.104	102.262	37.515	− 168.936	− 101.779	12.358
1900	25.690	124.492	103.396	40.083	− 168.842	− 98.048	11.276
2000	25.704	125.810	104.484	42.653	− 168.752	− 94.325	10.307
2100	25.716	127.065	105.529	45.224	− 168.661	− 90.608	9.430
2200	25.726	128.261	106.536	47.796	− 168.575	− 86.894	8.632
2300	25.735	129.405	107.505	50.369	− 168.490	− 83.181	7.904
2400	25.743	130.501	108.441	52.943	− 168.408	− 79.472	7.237
2500	25.750	131.552	109.344	55.518	− 168.331	− 75.770	6.624
2600	25.756	132.562	110.218	58.093	− 168.256	− 72.068	6.058
2700	25.762	133.534	111.064	60.669	− 168.186	− 68.372	5.534
2800	25.767	134.471	111.883	63.245	− 168.122	− 64.672	5.048
2900	25.771	135.375	112.678	65.822	− 168.061	− 60.981	4.596
3000	25.775	136.249	113.449	68.400	− 168.005	− 57.292	4.174
3100	25.779	137.094	114.196	70.977	− 167.956	− 53.603	3.779
3200	25.782	137.912	114.926	73.555	− 167.912	− 49.913	3.409
3300	25.785	138.706	115.635	76.134	− 167.873	− 46.225	3.061
3400	25.788	139.476	116.325	78.712	− 167.839	− 42.537	2.734
3500	25.791	140.223	116.997	81.291	− 167.812	− 38.858	2.426
3600	25.793	140.950	117.652	83.871	− 259.749	− 32.913	1.998
3700	25.795	141.657	118.292	86.450	− 259.633	− 26.613	1.572
3800	25.797	142.345	118.916	89.030	− 259.520	− 20.320	1.169
3900	25.799	143.015	119.525	91.609	− 259.415	− 14.025	.786
4000	25.801	143.668	120.120	94.189	− 259.315	− 7.734	.423
4100	25.802	144.305	120.703	96.770	− 259.217	− 1.450	.077
4200	25.804	144.927	121.272	99.350	− 259.125	4.834	− .252
4300	25.805	145.534	121.829	101.930	− 259.035	11.118	− .565
4400	25.806	146.127	122.375	104.511	− 258.949	17.405	− .865
4500	25.807	146.707	122.909	107.091	− 258.867	23.684	− 1.150
4600	25.809	147.274	123.433	109.672	− 258.784	29.961	− 1.423
4700	25.810	147.829	123.946	112.253	− 258.706	36.241	− 1.685
4800	25.811	148.373	124.449	114.834	− 258.629	42.510	− 1.936
4900	25.811	148.905	124.943	117.415	− 258.554	48.789	− 2.176
5000	25.812	149.426	125.427	119.996	− 258.479	55.054	− 2.406
5100	25.813	149.938	125.903	122.578	− 258.403	61.333	− 2.628
5200	25.814	150.439	126.370	125.159	− 258.330	67.602	− 2.841
5300	25.815	150.931	126.829	127.741	− 258.257	73.864	− 3.046
5400	25.815	151.413	127.279	130.322	− 258.186	80.129	− 3.243
5500	25.816	151.887	127.722	132.904	− 258.119	86.396	− 3.433
5600	25.817	152.352	128.158	135.485	− 258.043	92.657	− 3.616
5700	25.817	152.809	128.587	138.067	− 257.973	98.916	− 3.793
5800	25.818	153.256	129.008	140.649	− 257.902	105.184	− 3.963
5900	25.818	153.699	129.423	143.230	− 257.834	111.434	− 4.128
6000	25.819	154.133	129.831	145.812	− 257.765	117.696	− 4.287

Dec. 31, 1960; Mar. 31, 1964; Sept. 30, 1967; Dec. 31, 1970

SILICON TETRACHLORIDE ($SiCl_4$) (IDEAL GAS) GFW = 169.898 Cl_4Si

Point Group T_d

$S^\circ_{298.15}$ = 79.07 ± 0.05 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = −157.9 ± 0.3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −158.4 ± 0.3 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
425 ± 1 (1)	620 ± 1 (3)
149 ± 2 (2)	220 ± 4 (3)

Bond Distance: Si-Cl = 2.0173 ± 0.0034 Å

Bond Angle: Cl-Si-Cl = 109°28' σ = 12

Product of the Moments of Inertia: $I_A I_B I_C = 2.60708 \times 10^{-112}$ g^3 cm^6

Heat of Formation

Gross et al. (1) measured the heat of formation of $SiCl_4(\ell)$ by the direct chlorination of silicon in a bomb calorimeter. Corrections for the difference in heat content between liquid and gaseous chlorine at 25°C and 1 atm led to the value of $\Delta Hf^\circ_{298}(SiCl_4, \ell)$ = −165.49 ± 0.16 kcal/mol. Combination of $\Delta Hf^\circ_{298}(\ell)$ with ΔHv°_{298} = 7.09 kcal/mol (see below) gives $\Delta Hf^\circ_{298}(SiCl_4, g)$ = −158.4 ± 0.3 kcal/mol which is adopted in the tabulation.

Schäfer and Heine (2) measured both heats of solution of Si(c) and $SiCl_4(\ell)$ in HF solution containing AgF which gave ΔHr°_{298} = 42.7 ± 0.4 kcal/mol for the overall reaction $SiCl_4(\ell) + 4Ag(c) = Si(c) + 4AgCl(c)$ and led to $\Delta Hf^\circ_{298}(SiCl_4, \ell)$ = −164.18 kcal/mol in agreement with the value adopted, using $\Delta Hf^\circ_{298}(AgCl, c)$ = −30.37 kcal/mol (3).

Wolf (4) determined the heats of solution of $SiCl_4(\ell)$ and $Na_2SiO_3 \cdot 8H_2O(c)$ in NaOH solution and derived ΔHr°_{298} = −129.3 kcal/mol for $SiCl_4(\ell) + 13NaOH(27.8\ H_2O) = Na_2SiO_3(c) + 4NaCl + 3H_2O(\ell) + 7NaOH(52.14\ H_2O)$ which leads to $\Delta Hf^\circ_{298}(SiCl_4, \ell)$ = −166.7 ± 2 kcal/mol, using all JANAF auxiliary data and heats of dilution of NaOH from Parker (5). However, Wolf's data are suspect due to uncertainties in how he converted his data from Na_2SiO_3(calorimetric solution) to $Na_2SiO_3(c)$. Beezer and Mortimer (6) measured the heat of solution ΔHr°_{298} = −97.0 kcal/mol for $SiCl_4(\ell) + 185\ HF(4.335\ H_2O) = 4HCl(11\ H_2O) + [H_2SiF_6, 179\ HF, 758\ H_2O]$ and combined with those of Good (7) for $[H_2SiF_6, 41\ HF, 174\ H_2O]$ solution by neglecting the unknown heats of dilution between the two calorimetric solutions and obtained $\Delta Hf^\circ_{298}(\ell)$ = −169.9 kcal/mol which is in poor agreement with the value adopted. In both the measurements of Wolf and Beezer, the final state of the calorimetric solution is not well defined or not well known, thus it leads to large uncertainties in their results.

Other calorimetric studies involving aqueous hydrolysis of $SiCl_4(\ell)$ to form SiO_2(colloidal solution) have been reviewed by Gross et al. (1). Since the SiO_2(colloidal solution) is an ill-defined state, the heat of formation of $SiCl_4(\ell)$ derived from hydrolysis data is quite unreliable.

Heat Capacity and Entropy

Morino and Murata (8) measured the adopted bond distance by electron diffraction. Their value was confirmed by Ryan and Hedberg (9). Morino et al. (10) observed the adopted vibrational frequencies from the infrared and Raman spectra from the vapor. Infrared data of Smith (11) confirm that ν_3 is about 12 cm^{-1} larger in the vapor than in the liquid. The moments of inertia are $I_A = I_B = I_C = 5.3883 \times 10^{-38}$ g cm^2.

Vaporization Data

Vapor pressure data ranging from 20° below Tm (supercooled liquid) to 10° above Tb are in reasonable agreement as summarized below. The analysis is based on fugacities calculated from vapor pressures by the approximation of Pitzer (19) using Tc = 506°K (20), Pc = 37.1 atm (21) and ω = 0.26. At 298.15°K the calculated f/P is 0.982 compared with 0.984 observed by Wood (22). The analysis also presumes a linear variation of the liquid phase Cp based on 33.3 gibbs/mol at 210°K and 34.2 at 300°K. The latter value is from data of Vold (17) since earlier data (77-294°K) of Latimer (18) appear to have a large positive bias below Tm. The Cp at 210°K assumes Latimer's value to have about 1 percent bias by analogy with his data for $CCl_4(\ell)$.

Source	No. of Points	Range, T°K	ΔSv°_{298}, eu	ΔHv°_{298}, kcal/mol
Combined 14, 15, 22	19	275-341	21.45 ± 0.04	7.09 ± 0.01
12. Balk (1964)	Equation	183-204	21.13	7.19
13. King (1962)	6	303-323	20.85 ± 0.13	6.89 ± 0.04
14. Nisel'son (1960)	12	298-341	21.48 ± 0.09	7.10 ± 0.03
15. Jenkins (1954)	6	275-330	21.40 ± 0.05	7.08 ± 0.01
16. Kearby (1936)	13	273-333	21.55 ± 0.08	7.13 ± 0.03

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Cl_4Si

Cobalt Trifluoride (CoF_3)

(Crystal) GFW = 115.9284

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	21.940	22.600	22.600	.000	- 188.900	- 171.831	125.955
300	22.101	22.736	22.600	.041	- 188.891	- 171.725	125.102
400	23.296	29.274	23.484	2.316	- 188.385	- 166.078	90.741
500	23.829	34.536	25.185	4.675	- 187.890	- 160.560	70.181
600	24.009	38.896	27.116	7.067	- 187.438	- 155.137	56.509
700	24.192	42.611	29.072	9.477	- 187.031	- 149.786	46.765
800	24.374	45.853	30.971	11.905	- 186.762	- 144.477	39.469
900	24.579	48.735	32.788	14.353	- 186.427	- 139.212	33.805
1000	24.825	51.338	34.515	16.823	- 186.139	- 133.982	29.282
1100	25.102	53.716	36.154	19.319	- 185.898	- 128.779	25.586
1200	25.398	55.913	37.710	21.843	- 185.707	- 123.594	22.509
1300	25.714	57.958	39.190	24.399	- 185.602	- 118.423	19.909
1400	26.036	59.876	40.600	26.986	- 185.607	- 113.255	17.680
1500	26.367	61.683	41.946	29.606	- 185.345	- 108.095	15.749

Dec. 31, 1970

COBALT TRIFLUORIDE (CoF_3) (CRYSTAL) GFW = 115.9284 CoF_3

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [22.6 ± 3.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -188.9 ± 3.0 kcal/mol

Tm = [1200 ± 200]°K

ΔHm = Unknown

Heat of Formation

Fowler et al. (1) determined calorimetrically the heat of fluorination of crystalline CoF_2 at 473.15°K. For the reaction

$$2\ CoF_2(c) + F_2(g) \rightarrow 2\ CoF_3(c)$$

they reported ΔH_r = -52.0 ± 3.0 kcal/mol which yields ΔHr_{298} = -52.4 ± 3.0 kcal/mol based upon our functions for $CoF_2(c)$ and $CoF_3(c)$. Combining this result with the heat of formation of $CoF_2(c)$ (2), we derive $\Delta Hf^\circ_{298}(CoF_3, c)$ = -186.7 ± 3.0 kcal/mol.

Jessup et al. (3) investigated calorimetrically this same fluorination reaction at 523.15°K and reported ΔH_r = -56.1 ± 2.0 kcal/mol. This result leads to $\Delta Hf^\circ_{298}(CoF_3, c)$ = -188.9 ± 2.0 kcal/mol. In the same investigation Jessup et al. (3) reported ΔHr_{608} = -74.0 ± 4.0 kcal/mol for the reduction reaction

$$2\ CoF_3(c) + H_2(g) \rightarrow 2\ CoF_2(c) + 2\ HF(g).$$

Corrected to 298.15°K we calculate ΔHr = -73.3 ± 4.0 kcal/mol. Combining this result with heat of formation data for $CoF_2(c)$ (2) and HF(g) (4), we derive $\Delta Hf^\circ_{298}(CoF_3, c)$ = -189.0 ± 4.0 kcal/mol. We note that the addition of these two results by Jessup et al. (3) leads to ΔH_r = -129.9 ± 6.0 kcal/mol for the reaction

$$H_2(g) + F_2(g) \rightarrow 2\ HF(g)$$

which is quite consistent with the result -130.28 ± 0.4 kcal/mol calculated from the selected value for the heat of formation of HF(g) (4). Thus, it is apparent that these two results are probably quite reliable, and we adopt $\Delta Hf^\circ_{298}(CoF_3, c)$ = -188.9 ± 3.0 kcal/mol.

Jellinek and Koop (5) reported equilibrium constants for the reduction reaction given above in the temperature range 470-595°K. Second and third law analyses of these equilibrium data are summarized below.

Range °K	Points	ΔHr°_{298} kcal/mol 2nd Law	3rd Law	Drift gibbs/mol
470-595	3	31.7	29.3 ± 0.6	-4.7 ± 1.5

We note that the second and third law values of ΔHr°_{298} for the reduction reaction are in considerable disagreement with the calorimetric value of -73.3 ± 4.0 kcal/mol given by Jessup et al. (3), and no weight is given to these equilibrium data.

Heat Capacity and Entropy

Heat capacity data for $CoF_3(c)$ are estimated by comparison with those for $FeF_2(c)$, $FeF_3(c)$, $TiF_3(c)$, and $CoF_2(c)$. S°_{298} is estimated to be 22.6 gibbs/mol from the ionic entropy contributions given by Kubaschewski, Evans, and Alcock (6). We note that this method leads to S°_{298} = 19.4 gibbs/mol for $CoF_2(c)$, which is in good agreement with the experimental value of 19.60 ± 0.10 gibbs/mol (2).

Melting Data

Tm is estimated by comparison with those for other transition metal halides. We note that Ruff and Ascher (7) reported $CoF_3(c)$ as being thermally unstable around 900°K, while Stewart (8) recently showed that $CoF_2(c)$ was formed by hydrolytic reactions and not by thermal decomposition. The derived ΔG°_f values for $CoF_3(c)$ indicate that it is thermodynamically more stable than $CoF_2(c)$ in agreement with the findings of Stewart (8). In the temperature range 298-900°K, the Gibbs energy changes for the decomposition reaction

$$2\ CoF_3(c) \rightarrow 2\ CoF_2(c) + F_2(g)$$

are in the range +10-20 kcal/mol.

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Cobalt Oxide (CoO)

(Crystal) GFW = 74.9326

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	= 2.255	= 56.898	= 56.898	INFINITE
100	4.550	2.177	23.194	= 2.102	= 57.216	= 55.180	120.596
200	10.845	7.386	13.954	= 1.314	= 57.233	= 53.105	58.030
298	13.212	12.666	12.666	.000	= 56.820	= 51.150	37.494
300	13.105	12.747	12.666	.024	= 56.813	= 51.115	37.237
400	12.651	16.419	13.169	1.300	= 56.507	= 49.264	26.917
500	12.890	19.271	14.114	2.578	= 56.248	= 47.484	20.755
600	12.981	21.629	15.176	3.872	= 56.024	= 45.753	16.665
700	13.029	23.634	16.244	5.173	= 55.838	= 44.056	13.755
800	13.102	25.378	17.279	6.479	= 55.791	= 42.369	11.575
900	13.220	26.927	18.267	7.794	= 55.682	= 40.698	9.883
1000	13.387	28.328	19.204	9.124	= 55.619	= 39.037	8.531
1100	13.596	29.614	20.093	10.473	= 55.607	= 37.380	7.427
1200	13.842	30.807	20.936	11.845	= 55.647	= 35.721	6.506
1300	14.116	31.926	21.739	13.243	= 55.774	= 34.057	5.725
1400	14.419	32.983	22.505	14.669	= 56.011	= 32.377	5.054
1500	14.740	33.989	23.237	16.127	= 55.981	= 30.690	4.472
1600	15.078	34.951	23.939	17.618	= 55.859	= 29.007	3.962
1700	15.430	35.875	24.615	19.143	= 55.681	= 27.334	3.514
1800	15.793	36.767	25.265	20.704	= 59.360	= 25.607	3.109
1900	16.166	37.631	25.893	22.302	= 59.177	= 23.731	2.730
2000	16.547	38.470	26.501	23.938	= 58.960	= 21.872	2.390
2100	16.935	39.287	27.091	25.612	= 58.706	= 20.023	2.084
2200	17.329	40.084	27.663	27.325	= 58.417	= 18.188	1.807
2300	17.726	40.863	28.220	29.078	= 58.090	= 16.367	1.555
2400	18.131	41.626	28.763	30.871	= 57.726	= 14.560	1.326
2500	18.536	42.374	29.293	32.704	= 57.325	= 12.770	1.116
2600	18.945	43.109	29.810	34.578	= 56.885	= 10.996	.924
2700	19.362	43.832	30.316	36.494	= 56.406	= 9.240	.748
2800	19.777	44.544	30.811	38.451	= 55.889	= 7.502	.586
2900	20.195	45.245	31.297	40.450	= 55.332	= 5.783	.436
3000	20.615	45.937	31.773	42.490	= 54.736	= 4.085	.298

Dec. 31, 1970

COBALT OXIDE (CoO) (CRYSTAL) GFW = 74.9326 CoO

ΔHf°_0 = −56.90 ± 0.10 kcal/mol

$S^\circ_{298.15}$ = 12.67 ± 0.08 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −56.82 ± 0.10 kcal/mol

Tm = 2078°K

ΔHm = Unknown

Heat of Formation

Boyle et al. (1) measured the heat of combustion of metallic cobalt at 303.16°K. Their analyses of the combustion products indicated that some overoxidation of the metal had occurred. Correction of their results to correspond to CoO was made on the assumption that the excess oxygen was combined as Co_3O_4. Also the analyses indicated that the combustion products had attacked the silica-glass capsules, used to hold the metal samples, resulting in appreciable amounts of silicate formation. Corrections for these two side reactions amounted to three percent of the total measured energy of combustion. From these data, we derive ΔHf°_{298}(CoO, c) = −57.0 ± 0.3 kcal/mol. Roth and Havekoss (2) also investigated calorimetrically the combustion of metallic cobalt and reported ΔHf°_{293}(CoO, c) = −57.2 ± 0.2 kcal/mol.

Second and third law analyses of several equilibrium studies (3-12), emf measurements (13), and mass-spectrometric studies (16) involving CoO(c) are summarized below.

Investigator	Method	Reaction	Temp. Range °K	No. of Points	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	*ΔHf°_{298}(CoO, c) kcal/mol
Chaudron (3)	Equilibrium	A	1073-1323	3	−3.61	−1.05±0.57	2.10±0.54	−56.75±0.57
Wöhler and Balz (4)	Equilibrium	A	723; 1023	2	3.32	0.78±1.24	−2.91	−58.58±1.24
Emmett and Shultz (5)	Equilibrium	A	723-843	3	−0.81	−1.07±0.04	−0.34±0.04	−56.73±0.04
Shibata and Mori (6)	Equilibrium	A	595-1194	6	0.17	−1.15±0.53	−1.40±0.14	−56.65±0.53
Kleppa (7)	Equilibrium	A	738-898	4	−0.93	−0.89±0.05	0.04±0.25	−56.91±0.05
Aubry and Gleitzer (8)	Equilibrium	A	1073-1498	5	−0.15	−1.01±0.27	−0.67±0.21	−56.79±0.27
Balakirev and Chufarov (9)	Equilibrium	A	773-1173	5	−2.20	−0.83±0.49	1.41±0.36	−56.97±0.50
Schenck and Wesselkoch (10)	Equilibrium	B	1173	1		−10.73		−56.91
Watanabe (11)	Equilibrium	B	836-1134	Equation	−11.58	−10.84±0.17	0.76	−56.79±0.22
Emmett and Shultz (12)	Equilibrium	B	723-843	3	−10.99	−10.81±0.03	0.24±0.03	−56.82±0.10
Kiukkola and Wagner (13)	emf	C	1173-1373	5	−6.26	−6.59±0.05	−0.27±0.12	−57.05±0.25
Grimley et al. (16)	mass. spec.	D	1578-1744	19	47.15	54.80±0.65	−4.59±1.19	−54.80±0.65

Reactions: A. $CoO(c) + H_2(g) \rightarrow Co(c) + H_2O(g)$ B. $CoO(c) + CO(g) \rightarrow Co(c) + CO_2(g)$

C. $0.947\ Fe(c) + CoO(c) \rightarrow Co(c) + Fe_{0.947}O(c)$ D. $CoO(c) \rightarrow Co(c) + 0.5\ O_2(g)$

*Third Law value based on JANAF ΔHf° data (14, 15) for $H_2O(g)$, CO(g), $CO_2(g)$, and $Fe_{0.947}O(c)$.

Emmett and Shultz (5) in their investigation of the H_2 reduction of CoO(c) clearly established by X-ray photographs that the only solid phases present during the equilibrium measurements were CoO(c) and Co(c), and they found no evidence for the formation of a solid solution between these two solids. Furthermore, we note that the third law values of ΔHr°_{298} calculated from their equilibrium data for the H_2 (5) and CO (12) reduction of CoO(c) leads to ΔHr°_{298} = +9.74 ± 0.07 kcal/mol for the reaction $H_2(g) + CO_2(g) \rightarrow CO(g) + H_2O(g)$, which is quite consistent with the value $\Delta H_{r\ 298}$ = +9.84 ± 0.05 kcal/mol calculated from JANAF heat of formation data (15) for CO(g), $CO_2(g)$, and $H_2O(g)$. The adopted heat of formation for CoO(c), ΔHf°_{298}(CoO, c) = −56.82 ± 0.10 kcal/mol, is the average of the ΔHf°_{298} values calculated from the results of Emmett and Shultz (5, 12) and Kleppa (7) and is in reasonable agreement within the uncertainties with the calorimetric work (1), other equilibrium studies (3, 6, 8, 9, 10, 11), and the emf results (13).

Heat Capacity and Entropy

The adopted heat capacities for CoO(c) in the temperature range 51-298°K are those of King (17). These data have a pronounced maximum at 287.3°K, at which point the heat capacity is greater than 17.6 gibbs/mol. Assayag and Bizette (18) also measured heat capacities for CoO(c) between 180-400°K and reported a maximum at 289.7°K. Presumably this anomaly is of the magnetic type. Heat capacity data above 300°K are calculated from the high temperature (400-1800°K) enthalpy data of King and Christensen (19). Both sets of data were smoothed by computer and joined at 298.15°K.

The value of $S^\circ_{298.15}$ is obtained from the low temperature heat capacity data of King (17) and is based on S_{51} = 0.42 eu.

Melting Data

Tm is the average of values reported to be 2083°K by Wartenberg and Prophet (20) and 2073°K by Wartenberg et al. (21).

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Cobalt Sulfate ($CoSO_4$)

(Crystal) GFW = 154.9948

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	- 4.120	- 210.078	- 210.078	INFINITE
100	10.625	9.022	46.029	- 3.701	- 211.335	- 203.477	444.699
200	19.188	19.309	30.146	- 2.167	- 212.043	- 195.310	213.424
298	24.670	28.054	28.054	.000	- 212.300	- 187.027	137.095
300	24.770	28.207	28.054	.046	- 212.301	- 186.871	136.135
400	28.510	35.864	29.073	2.716	- 212.766	- 178.377	97.461
500	31.440	42.555	31.114	5.720	- 212.816	- 169.768	74.205
600	33.620	48.489	33.525	8.978	- 212.617	- 161.173	58.707
700	35.200	53.796	36.049	12.423	- 212.254	- 152.603	47.645
800	36.340	58.572	38.571	16.003	- 224.955	- 145.368	39.712
900	37.140	62.904	41.038	19.680	- 226.143	- 135.465	32.895
1000	37.790	67.376	43.443	23.935	- 222.837	- 125.673	27.466
1100	38.340	71.006	45.786	27.742	- 222.068	- 115.996	23.046
1200	38.830	74.364	48.039	31.601	- 221.337	- 106.384	19.375
1300	39.270	77.484	50.177	35.506	- 220.687	- 96.831	16.279
1400	39.670	80.414	52.233	39.453	- 220.147	- 87.325	13.632
1500	40.050	83.168	54.205	43.439	- 219.343	- 77.867	11.345
1600	40.410	85.761	56.097	47.462	- 218.452	- 68.462	9.352
1700	40.750	88.221	57.915	51.520	- 217.514	- 59.116	7.600
1800	41.090	90.560	59.664	55.613	- 220.444	- 49.757	6.041
1900	41.410	92.790	61.349	59.738	- 219.527	- 40.297	4.635
2000	41.730	94.922	62.975	63.895	- 218.589	- 30.891	3.376

Dec. 31, 1971

COBALT SULFATE ($CoSO_4$) (CRYSTAL) GFW = 154.9948 CoO_4S

$S°_{298.15}$ = 28.05 ± 1.00 gibbs/mol

Tt(α → β) = 984 K

Td = 1413 K

$\Delta Hf°_0$ = -210.1 ± 0.3 kcal/mol

$\Delta Hf°_{298.15}$ = -212.3 ± 0.3 kcal/mol

ΔHt° = 0.51 ± 0.10 kcal/mol

Heat of Formation

Adami and King (1) determined calorimetrically the heats of solution of crystalline CoO and α-$CoSO_4$ in hydrochloric acid solution. From these measurements they derived the heat for the reaction $CoO(c) + H_2SO_4 \cdot 7.068\ H_2O(\ell) \rightarrow CoSO_4(c) + 8.068\ H_2O(\ell)$ as $\Delta Hr°_{298}$ = -14.280 ± 0.110 kcal/mol. Combining this result with heats of formation for CoO (2), H_2SO_4 7.068 H_2O (3), and H_2O (3), we derive $\Delta Hf°_{298}$(α-$CoSO_4$, c) = -212.3 ± 0.3 kcal/mol which is adopted.

The total pressures of $SO_3(g)$, $SO_2(g)$, and $O_2(g)$ over $CoSO_4(c)$ in the temperature range 1100-1300 K have been determined by manometric (4-7) and transpiration (8) methods. Previous investigators (4-6) analyzed these data solely in terms of two equilibria, namely (a) $CoSO_4(c) \rightleftharpoons CoO(c) + SO_3(g)$ and (b) $SO_3(g) \rightleftharpoons SO_2(g) + 0.5\ O_2(g)$. However, Warner (10) has shown that $CoSO_4$ takes part in three successive, univariant, decomposition equilibria as the temperature is increased. Co_3O_4 is the decomposition product at low temperatures (<1150 K), a mixture of Co_3O_4 and CoO at intermediate temperatures, and CoO at high temperatures. Second- and third-law analyses of those points involving only equilibria (a) and (b) are given below. The appearance of Co_3O_4 as a decomposition product was determined by comparing the oxygen partial pressures that were calculated from the total pressure data with those for the decomposition reaction (c) $Co_3O_4(c) \rightleftharpoons 3CoO(c) + 0.5\ O_2(g)$ (2). Espelund and Flengas (9) measured the free energy of reaction (a) in a high temperature solid electrolytic cell. Here, no Co_3O_4 was formed over the entire temperature range (827-1133 K), since the oxygen pressures in the cell were too low to oxidize the CoO. Results of an analysis of these data are also given below:

Investigator	Reaction	Method	No. of Points	Temp. Range K	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	*$\Delta Hf°_{298}$($CoSO_4$, c) kcal/mol
Marchal (4)	a	Manometric	17	1143-1303	54.5	60.4±0.5	4.9 ± 0.6	-211.8±0.8
Schenck and Raub (5)	a	Manometric	14	1099-1243	68.5	60.9±0.7	-6.3 ± 1.1	-212.3±1.0
Warner (6)	a	Manometric	2	1164 1175	56.9	59.3±0.3	2.1	-210.8±0.3
Ingraham (7)	a	Manometric	9	1144-1210	59.1	59.1±0.1	0.04± 0.91	-210.6±0.4
Alcock et al. (8)	d**	Transpiration	8	1131-1217	-191.1	-166.8±1.4	20.2 ± 5.5	-211.2±1.5
Espelund and Flengas (9)	a	emf	28	827-1177	59.5	59.5±0.3	0.08± 0.22	-211.0±0.6

* Third law value based on JANAF heats of formation (2).

** Reaction: (d) $2CoO(c) + 2SO_2(g) + O_2(g) \rightleftharpoons 2CoSO_4(c)$.

These results indicate that the Gibbs-energy functions and equilibrium data are in general consistent within experimental error.

Heat Capacity and Entropy

The low temperature (52-298 K) heat capacities are those reported by Weller (11). No anomalies appear in these data. Heat capacities in the temperature range 300-2000 K are estimated by comparison with those for $CuSO_4$ (2).

$S°_{298}$ *is determined from the Cp data based on* $S_{51.42}$ = 1.56 + 2.75 *eu. The 1.56 is a lattice contribution, while the 2.75* is the entropy associated with the ordering of the Co^{+2} spin moments. In assigning the magnetic entropy, it is assumed that all of the contribution remains to be extracted below the minimum temperature (52 K) of the heat capacity measurements (11).

Transition Data

The temperature (Tt) and the heat (ΔHt°) of the α-β transition for $CoSO_4$ are from the differential thermal analysis studies of Ingraham and Marier (12). Other temperatures reported for the transition are 890 (6) and 903 K (13).

Temperature of Decomposition

Td is the temperature at which the Gibbs energy change for the process $CoSO_4(c) \rightarrow CoO(c) + SO_3(g)$ is zero.

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CoO_4S

Tricobalt Tetraoxide (Co_3O_4)

(Crystal) GFW = 240.7972

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	− 4.295	− 214.228	− 214.228	INFINITE
100	6.214	7.526	47.350	− 3.982	− 215.675	− 207.597	453.703
200	20.936	17.218	29.767	− 2.510	− 216.966	− 198.970	217.425
298	29.410	27.315	27.315	.000	− 217.500	− 190.001	139.274
300	29.520	27.497	27.316	.055	− 217.504	− 189.830	138.291
400	34.096	36.725	28.543	3.273	− 217.550	− 180.591	98.670
500	36.532	44.596	30.986	6.805	− 217.442	− 171.360	74.902
600	38.912	51.464	33.838	10.575	− 217.258	− 162.161	59.067
700	41.498	57.654	36.805	14.594	− 216.973	− 153.000	47.769
800	44.281	63.375	39.773	18.882	− 216.861	− 143.843	39.296
900	47.216	68.759	42.697	23.456	− 216.312	− 134.746	32.721
1000	50.262	73.891	45.562	28.329	− 215.655	− 125.717	27.475
1100	53.390	78.827	48.363	33.511	− 214.902	− 116.760	23.198
1200	56.579	83.609	51.102	39.009	− 214.064	− 107.873	19.646
1300	59.814	88.266	53.782	44.828	− 213.247	− 99.060	16.653
1400	63.084	92.818	56.408	50.973	− 212.526	− 90.302	14.097
1500	66.382	97.282	58.985	57.446	− 210.771	− 81.631	11.894

Dec. 31, 1970; Dec. 31, 1971

TRICOBALT TETRAOXIDE (Co_3O_4) (CRYSTAL) GFW = 240.7972 Co_3O_4

Td = 1220 K

$S^\circ_{298.15}$ = 27.32 ± 1.00 gibbs/mol

ΔHf°_0 = −214.2 ± 1.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −217.5 ± 1.0 kcal/mol

Heat of Formation

Bugden and Pratt (1) measured free energies of reaction for (a) $2Cu(c) + Co_3O_4(c) \rightarrow 3CoO(c) + Cu_2O(c)$ and (b) $Ni(c) + Co_3O_4(c) \rightarrow 3CoO(c) + NiO(c)$ from high temperature solid electrolytic cells. These data were subjected to second- and third-law analyses with results summarized in the following table:

Investigator	Reaction	Method	Temp. Range K	No. of Points	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	*$\Delta Hf^\circ_{298}(Co_3O_4, c)$ kcal/mol
Bugden and Pratt (1)	a	emf	900-1150	Equn.	5.1	6.3±0.2	1.1	-217.5±0.8
	b	emf	850-1100	Equn.	-12.0	-10.6±0.2	1.3	-217.1±0.8
Foote and Smith (3)	c	Manometric	1073-1243	6	34.5	47.2±1.4	10.6±1.3	-217.7±1.5
Watanabe (4)	c	Manometric	1128-1233	4	38.1	47.9±0.7	8.3±0.8	-218.4±1.0
Chufarov et al. (5)	c	Manometric	973-1173	4	27.9	46.4±2.9	17.0±0.6	-216.9±3.0
Balakirev and Chufarov (6)	c	Manometric	923-1173	5	33.8	46.1±2.5	11.3±2.5	-216.6±3.0
Roiter and Paladino (7)	c	Manometric	1139-1220	5	36.4	47.1±0.6	9.0±2.0	-217.6±1.0
Ingraham (8) Set I	c	Manometric	1101-1159	6	41.4	46.8±0.2	4.5±0.4	-217.3±0.5
Set II	c	Manometric	1086-1219	19	35.6	46.9±0.8	9.7±0.2	-217.4±1.0
O'Bryan and Parravano (9)	c	X-ray & Wt. Loss	1073-1243	Equn.	40.3	47.3±0.8	5.9	-217.8±1.0

*Third law values based on $\Delta Hf^\circ_{298}(CoO, c)$ = −56.82 ± 0.1 kcal/mol (2).

Both sets of emf data are much more compatible with the adopted functions than the dissociation pressure data (see discussion below). The results obtained with the Cu/Cu_2O reference couple are judged to be more reliable and lead to the adopted heat of formation, $\Delta Hf^\circ_{298}(Co_3O_4, c)$ = −217.5 ± 1.0 kcal/mol, when used in conjunction with JANAF (2) heats of formation for CoO and Cu_2O.

Equilibrium oxygen pressures for the reaction (c) $Co_3O_4(c) \rightleftharpoons 3CoO(c) + 0.5\ O_2(g)$ have been determined by numerous investigators (3-9). Second- and third-law analyses of these data are given in the above table. Within each set the second- and third-law ΔHr_{298} values are not in agreement, and all sets contain large positive drifts. Warner (10) has suggested that these discrepancies arise as a result of an error in the measured standard entropy (11) for Co_3O_4. However, once the magnetic contribution is included (see entropy write-up) the real error in this value is probably no greater than one eu. The other possible source of error is lack of true equilibrium conditions. Recent thermogravimetric (9), X-ray (9), and kinetic (9, 12) studies of the Co_3O_4-CoO-O_2 system all point to an irreversible reaction. Therefore, no weight has been given to the dissociation pressure data in our evaluation.

Heat Capacity and Entropy

The low temperature heat capacities (54-298.3 K) are those reported by King (11). Heat capacities in the temperature range 300-1000 K are calculated from the high temperature enthalpy data of King and Christensen (13); a constrained curve fitting technique was used to join smoothly these data with the low temperature data at 298 K. No anomalies appear in either set of data.

Roth (14) observed a maximum in the magnetic susceptibility of Co_3O_4 at 40 K, while Mossbauer studies by Kündig et al. (15) indicated a Néel temperature of 33.0 ± 1.0 K. With the assumption that Co_3O_4 is a normal 2-3 spinel (16), this transition can be associated with the antiferromagnetic ordering of the Co^{+2} ion spin moments. Therefore, the entropy is based on S°_{51} = 1.36 + 2.75 = 4.11 eu, where 1.36 is a lattice contribution and 2.75 is the magnetic entropy. In assigning the magnetic entropy, it is assumed that all of the contribution remains to be extracted below the minimum temperature (54 K) of the heat capacity measurements.

Temperature of Decomposition

Td is the temperature at which the Gibbs energy change for the process $Co_3O_4(c) \rightarrow 3CoO(c) + 0.5\ O_2(g)$ approaches zero.

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Cesium Unipositive Ion (Cs^+)

(Ideal Gas) GFW = 132.90445

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	4.968	40.565	40.565	.000	109.596	102.082	- 74.826
300	4.968	40.596	40.565	.009	109.600	102.035	- 74.333
400	4.968	42.025	40.760	.506	109.332	99.642	- 54.442
500	4.968	43.133	41.128	1.003	109.577	97.192	- 42.482
600	4.968	44.039	41.540	1.500	109.829	94.692	- 34.491
700	4.968	44.805	41.953	1.996	110.081	92.148	- 28.770
800	4.968	45.468	42.352	2.493	110.335	89.569	- 24.469
900	4.968	46.054	42.731	2.990	110.590	86.958	- 21.116
1000	4.968	46.577	43.090	3.487	94.763	85.140	- 18.607
1100	4.968	47.050	43.429	3.984	95.261	84.154	- 16.720
1200	4.968	47.483	43.749	4.480	95.756	83.122	- 15.139
1300	4.968	47.880	44.052	4.977	96.253	82.049	- 13.794
1400	4.968	48.249	44.339	5.474	96.749	80.937	- 12.635
1500	4.968	48.591	44.611	5.971	97.246	79.791	- 11.626
1600	4.968	48.912	44.870	6.467	97.739	78.610	- 10.738
1700	4.968	49.213	45.110	6.964	98.233	77.400	- 9.950
1800	4.968	49.497	45.352	7.461	98.725	76.160	- 9.247
1900	4.968	49.766	45.577	7.958	99.215	74.894	- 8.615
2000	4.968	50.020	45.793	8.455	99.701	73.602	- 8.043
2100	4.968	50.263	46.000	8.951	100.188	72.284	- 7.523
2200	4.968	50.494	46.199	9.448	100.655	70.944	- 7.048
2300	4.968	50.715	46.391	9.945	101.124	69.584	- 6.612
2400	4.968	50.926	46.575	10.442	101.584	68.203	- 6.211
2500	4.968	51.129	46.754	10.939	102.034	66.802	- 5.840
2600	4.968	51.324	46.926	11.435	102.471	65.384	- 5.496
2700	4.968	51.511	47.092	11.932	102.897	63.949	- 5.176
2800	4.968	51.692	47.253	12.429	103.308	62.499	- 4.878
2900	4.968	51.866	47.409	12.926	103.703	61.035	- 4.600
3000	4.968	52.035	47.561	13.423	104.079	59.558	- 4.339
3100	4.968	52.198	47.708	13.919	104.432	58.067	- 4.094
3200	4.968	52.355	47.850	14.416	104.763	56.566	- 3.863
3300	4.968	52.508	47.989	14.913	105.069	55.055	- 3.646
3400	4.968	52.657	48.124	15.410	105.347	53.536	- 3.441
3500	4.968	52.801	48.256	15.907	105.593	52.009	- 3.248
3600	4.968	52.941	48.384	16.403	105.802	50.474	- 3.064
3700	4.968	53.077	48.509	16.900	105.976	48.935	- 2.890
3800	4.968	53.209	48.631	17.397	106.109	47.392	- 2.726
3900	4.968	53.338	48.750	17.894	106.197	45.846	- 2.569
4000	4.968	53.464	48.866	18.390	106.235	44.297	- 2.420
4100	4.968	53.587	48.980	18.887	106.224	42.748	- 2.279
4200	4.968	53.706	49.091	19.384	106.159	41.201	- 2.144
4300	4.968	53.823	49.200	19.881	106.035	39.655	- 2.016
4400	4.968	53.937	49.308	20.378	105.853	38.115	- 1.893
4500	4.968	54.049	49.410	20.874	105.607	36.578	- 1.776
4600	4.968	54.158	49.512	21.371	105.300	35.046	- 1.665
4700	4.968	54.265	49.612	21.868	104.929	33.523	- 1.559
4800	4.968	54.370	49.710	22.365	104.494	32.009	- 1.457
4900	4.968	54.472	49.806	22.862	103.995	30.504	- 1.361
5000	4.968	54.573	49.901	23.358	103.432	29.009	- 1.268
5100	4.968	54.671	49.993	23.855	102.811	27.527	- 1.180
5200	4.968	54.767	50.084	24.352	102.132	26.056	- 1.095
5300	4.968	54.862	50.174	24.849	101.400	24.601	- 1.014
5400	4.968	54.955	50.261	25.346	100.618	23.159	- .937
5500	4.968	55.046	50.347	25.842	99.790	21.732	- .864
5600	4.968	55.136	50.432	26.339	98.924	20.320	- .793
5700	4.968	55.223	50.515	26.836	98.024	18.925	- .726
5800	4.968	55.310	50.597	27.333	97.096	17.546	- .661
5900	4.968	55.395	50.678	27.830	96.145	16.182	- .599
6000	4.968	55.478	50.757	28.326	95.177	14.835	- .540

June 30, 1968; Dec. 31, 1970

CESIUM UNIPOSITIVE ION (Cs^+) (IDEAL GAS) GFW = 132.90445 Cs^+

Ground State Configuration $^1S_0$ ΔHf°_0 = 108.5 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 40.565 ± 0.0005 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 109.6 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

Heat of Formation

The ionization potential of Cs(g) was reported as 3.894 eV or 89.795 kcal/mol by Moore (1). Based on this data we derived $\Delta Hf^\circ_{298.15}$ = 109.6 ± 0.5 kcal/mol for Cs^+(g).

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights were reported by Moore (2). However, the lowest electronic level above ground state is given as 107392.33 cm^{-1} which is so high that the evaluated thermodynamic properties of Cs^+(g) will not be affected if we disregard all of these higher levels for calculation. Therefore we do not use them. The $H^\circ-H^\circ_{298}$ value at 0°K is -1.481 kcal/mol.

References

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Cesium Hydroxide (CsOH)

(Crystal) GFW = 149.912

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	16.220	23.600	23.600	.000	−99.600	−88.611	64.953
300	16.250	23.700	23.600	.030	−99.597	−88.543	64.503
400	17.780	28.589	24.257	1.733	−99.458	−84.797	46.292
500	19.700	36.467	25.727	5.370	−97.685	−81.077	35.438
600	20.000	40.102	27.828	7.364	−97.161	−77.803	28.340
700	20.000	43.185	29.807	9.364	−96.641	−74.618	23.297
800	20.000	45.855	31.650	11.364	−96.133	−71.508	19.535
900	20.000	48.211	33.362	13.364	−95.635	−68.459	16.624
1000	20.000	50.318	34.954	15.364	−111.228	−64.645	14.128

June 30, 1971

CESIUM HYDROXIDE (CsOH) (CRYSTAL) GFW = 149.912 CsHO

$S^\circ_{298.15}$ = [23.6 ± 1.0] gibbs/mol

Tt_1 = 410 K (α-β)

Tt_2 = 493 K (β-γ)

Tm = 588 K

ΔHf°_0 = Unknown

$\Delta Hf^\circ_{298.15}$ = −99.6 ± 0.2 kcal/mol

ΔHt°_1 = 0.31 ± 0.03 kcal/mol

ΔHt°_2 = 1.45 ± 0.15 kcal/mol

ΔHm° = 1.09 ± 0.10 kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 37.6 ± 3.0 kcal/mol

$\Delta Hs^\circ_{298.15}$(to dimer) = 34.8 ± 10.0 kcal/mol

Heat of Formation

The heat of formation of CsOH(c) is obtained from the heat of hydrolysis of metallic cesium, the heat of solution of the hydroxide in water, and appropriate auxiliary data.

Beketov (1) and de Forcrand (2) determined the heat of solution of crystalline CsOH in water. Parker (3) recently analyzed these data and selected $\Delta H^\circ_{soln.}$(CsOH, c) = −17.1 ± 0.2 kcal/mol. This value is adopted here.

Discordant values for the heat of hydrolysis of metallic cesium have been reported by Vorob'yev et al. (4) and Gunn (5). Data for the reaction Cs(c) + (n+1) $H_2O(\ell)$ = CsOH·n H_2O + 0.5 $H_2(g)$ are summarized below.

Investigator	n moles of H_2O	ΔHh°, kcal/mol*	ΔHf°(CsOH·∞ H_2O)** kcal/mol
Vorob'yev et al. (4)	1030	−46.50 ± 0.20	−114.82 ± 0.20
Gunn (5)	3000	−48.346 ± 0.020	−116.661 ± 0.020

*Dilution data estimated by comparison with similar data for the other alkali metal hydroxides tabulated by Parker (3).

**Based on $\Delta Hf^\circ_{298}(H_2O, \ell)$ = −68.315 kcal/mol (6).

In both investigations the possibility of hydroxide and oxide contamination of the metal samples was reduced by repeated distillation of the metal under vacuum, and spectroscopic analysis of each sample indicated low concentrations of the lighter alkali metals. Vorob'yev et al. (4) determined the amount of reaction by both weighing the metal sample and titrating the final hydroxide solution; both methods gave practically the same results. Gunn (5) determined the amount of reaction by both weighing the sample and recovering the hydrogen formed in the hydrolysis. The systematically high hydrogen yields (0.05-0.16%) obtained by Gunn (5) suggest the presence of lighter alkali metals in higher concentrations than indicated by the spectroscopic analysis of the cesium, and the flame-photometric analyses of the final hydroxide solutions. However, the presence of lighter alkali metals at these concentrations should not introduce any serious error in the heat of hydrolysis, since their heats (5) are quite similar to cesium.

The major difference between the two measurements lies in the instrumentation used to investigate the reaction. Vorob'yev et al. (4) used a hermetically sealed static calorimeter which was not stirred. In the absence of proper agitation, temperature gradients and chemical inhomogeneities are likely to arise in the final state. Without any indication of the performance of this calorimeter, the results of Vorob'yev et al. (4) are questionable. On the other hand, Gunn (5) carried out the hydrolysis reaction in a closed bomb calorimeter, agitation being effected by rocking the assembly through an angle of approximately 150°. This calorimeter has been used to investigate a variety of reactions (7), including the hydrolysis of the lighter alkali metals (5, 8). Where comparisons are possible, all indications are that the results are quite reliable. Therefore, we adopt ΔHf°_{298}(CsOH·∞ H_2O) = −116.661 ± 0.020 kcal/mol from the work of Gunn (5). Combining this result with the heat of solution of CsOH(c) given above, we derive ΔHf°_{298}(CsOH, c) = −99.6 ± 0.2 kcal/mol.

Heat Capacity and Entropy

Heat capacities for CsOH(c) over the entire temperature range 298 -1000 K are estimated by comparison with similar data for the other alkali metal hydroxides and halides (9). Likewise, $S^\circ_{298.15}$ is estimated to be 23.6 e.u. for CsOH(c) by comparison with similar data for the alkali metal halides and lighter hydroxides (9).

Transition and Melting Data

The temperatures and heats of the polymorphic transitions and melting of CsOH(c) are from the work of Reshetnikov and Baranskaya (10). These data were determined thermographically with ΔHm = 1.575 kcal/mol for NaOH(c) as a standard.

Heat of Sublimation

ΔHs°_{298} for the monomer and dimer are calculated from the adopted heats of formation of the crystal and the respective gaseous species.

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Cesium Hydroxide (CsOH)

(Liquid) GFW = 149.912

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	19.500	28.309	28.309	.000	−97.037	−87.452	64.104
300	19.500	28.430	28.310	.036	−97.028	−87.393	63.665
400	19.500	34.040	29.075	1.986	−97.042	−84.091	45.945
500	19.500	38.391	30.519	3.936	−96.556	−80.910	35.366
600	19.500	41.986	32.136	5.886	−96.076	−77.825	28.348
700	19.500	44.952	33.758	7.836	−95.606	−74.820	23.360
800	19.500	47.556	35.324	9.786	−95.148	−71.888	19.638
900	19.500	49.853	36.813	11.736	−94.700	−69.002	16.756
1000	19.500	51.908	38.221	13.686	−110.343	−65.350	14.282
1100	19.500	53.766	39.551	15.636	−109.672	−60.882	12.096
1200	19.500	55.463	40.808	17.586	−109.010	−56.476	10.286
1300	19.500	57.024	41.996	19.536	−108.357	−52.125	8.763
1400	19.500	58.469	43.122	21.486	−107.714	−47.824	7.466
1500	19.500	59.818	44.190	23.436	−107.080	−43.567	6.348
1600	19.500	61.073	45.206	25.386	−106.456	−39.355	5.376
1700	19.500	62.255	46.175	27.336	−105.841	−35.179	4.523
1800	19.500	63.369	47.099	29.286	−105.236	−31.040	3.769
1900	19.500	64.428	47.984	31.236	−104.640	−26.934	3.098
2000	19.500	65.428	48.831	33.186	−104.056	−22.860	2.498

June 30, 1971

CESIUM HYDROXIDE (CsOH) (LIQUID) GFW = 149.912 CsHO

$S^\circ_{298.15}$ = (28.31) gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −97.037 kcal/mol

Tm = 588 K

ΔHm = 1.09 ± 0.10 kcal/mol

Tb(to monomer) = 1263 K

ΔHv(to monomer) = 28.6 kcal/mol

Heat of Formation

The heat of formation of liquid CsOH at 298.15 K is obtained from that of the crystal by adding ΔHm and the difference between $H_{Tm}-H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

Cp for liquid CsOH is estimated to be 19.5 gibbs/mol by comparison with similar data for the other liquid alkali metal hydroxides (1). It is assumed constant in the temperature range 298-2000 K.

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

Melting Data

See CsOH(c) table for details.

Vaporization Data

Tb is calculated as the temperature at which ΔGr° for the vaporization process is zero. The difference in the heats of formation of CsOH(ℓ) and CsOH(g) at the boiling point is the heat of vaporization.

Reference

1. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan.

J. Phys. Chem. Ref. Data, Vol. 2, No. 2, 1973

Cesium Hydroxide (CsOH)

(Ideal Gas) GFW = 149.912

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	− 2.828	− 60.935	− 60.935	INFINITE
100	8.298	49.627	70.662	− 2.104	− 61.450	− 61.810	135.085
200	10.899	56.301	61.928	− 1.126	− 61.762	− 62.037	67.791
298	11.884	60.866	60.866	.000	− 62.000	− 62.122	45.537
300	11.895	60.940	60.866	.022	− 62.005	− 62.123	45.256
400	12.315	64.427	61.339	1.235	− 62.756	− 61.960	33.853
500	12.529	67.200	62.243	2.478	− 62.977	− 61.735	26.984
600	12.665	69.497	63.266	3.738	− 63.187	− 61.486	22.389
700	12.777	71.458	64.300	5.011	− 63.394	− 61.163	19.096
800	12.886	73.171	65.304	6.294	− 63.603	− 60.831	16.618
900	12.999	74.695	66.264	7.588	− 63.811	− 60.471	14.684
1000	13.116	76.071	67.177	8.894	− 80.099	− 59.288	12.953
1100	13.234	77.326	68.044	10.211	− 80.060	− 57.187	11.362
1200	13.350	78.483	68.866	11.540	− 80.019	− 55.109	10.037
1300	13.462	79.556	69.646	12.881	− 79.976	− 53.035	8.916
1400	13.568	80.557	70.391	14.232	− 79.931	− 50.965	7.956
1500	13.667	81.497	71.101	15.594	− 79.885	− 48.896	7.124
1600	13.759	82.382	71.778	16.966	− 79.840	− 46.833	6.397
1700	13.844	83.219	72.427	18.346	− 79.794	− 44.771	5.756
1800	13.921	84.012	73.049	19.734	− 79.751	− 42.712	5.186
1900	13.992	84.767	73.646	21.130	− 79.710	− 40.655	4.676
2000	14.057	85.486	74.220	22.532	− 79.673	− 38.601	4.218
2100	14.116	86.173	74.773	23.941	− 79.642	− 36.548	3.804
2200	14.169	86.831	75.306	25.355	− 79.618	− 34.497	3.427
2300	14.218	87.462	75.821	26.775	− 79.601	− 32.446	3.083
2400	14.263	88.068	76.319	28.199	− 79.596	− 30.395	2.768
2500	14.304	88.651	76.801	29.627	− 79.603	− 28.348	2.478
2600	14.341	89.213	77.267	31.059	− 79.622	− 26.295	2.210
2700	14.376	89.755	77.720	32.495	− 79.656	− 24.244	1.962
2800	14.407	90.278	78.159	33.934	− 79.708	− 22.192	1.732
2900	14.436	90.785	78.586	35.376	− 79.778	− 20.134	1.517
3000	14.462	91.278	79.001	36.821	− 79.870	− 18.077	1.317
3100	14.487	91.749	79.404	38.269	− 79.984	− 16.015	1.129
3200	14.509	92.209	79.797	39.719	− 80.125	− 13.950	.953
3300	14.530	92.656	80.180	41.171	− 80.293	− 11.880	.787
3400	14.550	93.090	80.553	42.625	− 80.492	− 9.804	.630
3500	14.568	93.512	80.918	44.081	− 80.726	− 7.721	.482
3600	14.584	93.923	81.273	45.538	− 80.997	− 5.632	.342
3700	14.600	94.323	81.621	46.997	− 81.308	− 3.533	.209
3800	14.614	94.712	81.960	48.458	− 81.662	− 1.425	.082
3900	14.628	95.092	82.292	49.920	− 82.064	.690	− .039
4000	14.640	95.462	82.617	51.384	− 82.516	2.817	− .154
4100	14.652	95.824	82.934	52.848	− 83.022	4.957	− .264
4200	14.663	96.177	83.245	54.314	− 83.586	7.109	− .370
4300	14.673	96.522	83.550	55.781	− 84.208	9.276	− .471
4400	14.683	96.860	83.849	57.249	− 84.892	11.457	− .569
4500	14.692	97.190	84.142	58.717	− 85.641	13.654	− .663
4600	14.701	97.513	84.429	60.187	− 86.455	15.873	− .754
4700	14.709	97.829	84.711	61.657	− 87.335	18.107	− .842
4800	14.716	98.139	84.987	63.129	− 88.281	20.360	− .927
4900	14.723	98.442	85.259	64.601	− 89.293	22.632	− 1.009
5000	14.730	98.740	85.525	66.073	− 90.369	24.926	− 1.089
5100	14.737	99.032	85.787	67.547	− 91.508	27.246	− 1.168
5200	14.743	99.318	86.045	69.021	− 92.706	29.582	− 1.243
5300	14.748	99.599	86.298	70.495	− 93.959	31.950	− 1.317
5400	14.754	99.875	86.547	71.970	− 95.264	34.333	− 1.390
5500	14.759	100.145	86.792	73.446	− 96.615	36.748	− 1.460
5600	14.764	100.411	87.032	74.922	− 98.008	39.183	− 1.529
5700	14.769	100.673	87.269	76.399	− 99.436	41.646	− 1.597
5800	14.773	100.930	87.503	77.876	− 100.895	44.136	− 1.663
5900	14.777	101.182	87.732	79.353	− 102.378	46.648	− 1.728
6000	14.781	101.431	87.959	80.831	− 103.877	49.187	− 1.792

June 30, 1971

CESIUM HYDROXIDE (CsOH) (IDEAL GAS) GFW = 149.912 CsHO

Point Group $C_{\infty v}$ ΔHf°_0 = −60.9 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = 60.87 ± 0.10 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −62.0 ± 3.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹
335.6 (1)
306 (2)
[3610] (1)

Bond Distance: Cs-O = 2.391 ± 0.002 Å O-H = [0.96 ± 0.01] Å

Bond Angle: Cs-O-H = 180° σ = 1

Rotational Constant: B_0 = 0.18479 cm⁻¹

Heat of Formation

Jensen and Padley (1) determined an equilibrium constant for the reaction Cs(g) + H_2O(g) = CsOH(g) + H(g) at 2475 K by atomic absorption spectroscopy in a hydrogen-oxygen-nitrogen flame. These workers pointed out that interference from ionization of the metal had introduced some uncertainity in their equilibrium datum. Using all JANAF functions (2), third law analysis of the equilibrium constant gives ΔHr_{298} = 27.4 kcal/mol. This leads to a heat of formation, ΔHf°_{298}(CsOH, g) = −64.2 ± 3.0 kcal/mol, and a corresponding bond dissociation energy, D_0(CsOH) = 91 kcal/mol. Cotton and Jenkins (3) investigated the same equilibrium in a fuel-rich hydrogen-oxygen-nitrogen flame and eliminated the ionization problem by working at a lower temperature (1570 K). Third law analysis of their equilibrium datum gives ΔHr_{298} = 28.9 kcal/mol which results in ΔHf°_{298}(CsOH, g) = −62.7 ± 2.0 kcal/mol corresponding to D_0(CsOH) = 89.6 kcal/mol. Smith and Sugden (4) had earlier reported a D_0(CsOH) = 91 ± 1 kcal/mol from flame studies. Electron impact studies (5, 6) have also led to values for the bond dissociation energy of CsOH(g). This method resulted in values of 82 ± 3 (5) and 86 ± 3 kcal/mol (6).

Cotton and Jenkins (3) also reported bond dissociation energies for LiOH(g), KOH(g), and NaOH(g) which are in good agreement with JANAF heat of formation data (7) for these hydroxides. Furthermore, the position of the hydroxides in the order of increasing bond dissociation energy established from their data, i.e. NaOH < KOH < RbOH < CsOH < LiOH, is that predicted by comparison with similar data on the stabilities of the alkali metal halides (8). However, trends within the bond dissociation energies for the halides suggest that the value D_0 = 89.6 kcal/mol for CsOH may be slightly high. The difference in D_0 for the potassium and sodium compounds is from 0.1 kcal/mol for the fluorides to 0.4 kcal/mol for the chlorides more than the difference in D_0 for the cesium and potassium compounds. Assuming this same trend in D_0 is prevalent in the hydroxides as well, then D_0(CsOH)−D_0(KOH) must be less than 3.9 kcal/mol (see NaOH(g) table). We adopt D_0(CsOH) = 89.0 ± 3.0 kcal/mol which results in the difference D_0(CsOH)−D_0(KOH) = 3.6 kcal/mol (7). This adopted bond dissociation energy corresponds to ΔHf°_{298}(CsOH, g) = −62.0 ± 3.0 kcal/mol.

Heat Capacity and Entropy

The microwave spectra of gaseous CsOH have been studied in a high temperature spectrometer by Kuczkowski et al. (9) and Lide et al. (10). The spectroscopic data were more consistent with patterns expected from a linear molecule, although a "quasilinear" structure could not be completely eliminated. Acquista et al. (11) observed the infrared spectra of CsOH and CsOD in a argon matrix at liquid hydrogen temperatures. The isotope shift of the bending mode, ν_2, was quite large (80 cm⁻¹), and the ratio of ν_2 for CsOH and CsOD was in excellent agreement with the value calculated for a linear molecule and a harmonic oscillator. The infrared results when used in combination with the microwave data indicate a linear equilibrium configuration for CsOH. We adopt this configuration along with the bond distances and angles determined by Lide et al. (10) from their microwave data.

The Cs-O stretching mode, ν_1, and the bending frequency, ν_2, are from the matrix isolation studies of Acquista et al. (11). The OH stretching frequency, ν_3, is an estimate from the recent work of Jensen (12). The principal moment of inertia is 15.147 × 10⁻³⁹ g cm².

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Cesium Hydroxide Unipositive Ion ($CsOH^+$)

(Ideal Gas) GFW = 149.9118

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	12,068	64,190	64,190	.000	106,000	103,400	= 75,794
300	12,077	64,265	64,190	.022	106,004	103,383	= 75,315
400	12,426	67,794	64,669	1,250	105,764	102,635	= 56,077
500	12,603	70,587	65,583	2,502	106,050	101,819	= 44,505
600	12,718	72,896	66,615	3,768	106,343	100,947	= 36,770
700	12,817	74,864	67,656	5,045	106,636	100,024	= 31,229
800	12,918	76,582	68,667	6,332	106,928	99,058	= 27,061
900	13,025	78,110	69,633	7,629	107,220	98,058	= 23,812
1000	13,138	79,488	70,550	8,937	91,432	97,045	= 21,384
1100	13,253	80,745	71,421	10,257	91,970	98,461	= 19,562
1200	13,367	81,903	72,247	11,588	92,509	99,027	= 18,035
1300	13,477	82,978	73,031	12,930	93,051	99,588	= 16,735
1400	13,582	83,980	73,778	14,283	93,594	100,027	= 15,615
1500	13,680	84,921	74,490	15,646	94,138	100,469	= 14,638
1600	13,770	85,807	75,170	17,019	94,680	100,871	= 13,778
1700	13,854	86,644	75,820	18,400	95,224	101,242	= 13,016
1800	13,931	87,438	76,444	19,789	95,765	101,580	= 12,334
1900	14,001	88,193	77,043	21,186	96,304	101,890	= 11,720
2000	14,065	88,913	77,618	22,589	96,839	102,169	= 11,165
2100	14,123	89,601	78,173	23,999	97,367	102,422	= 10,659
2200	14,176	90,259	78,707	25,414	97,888	102,650	= 10,197
2300	14,225	90,890	79,223	26,834	98,403	102,856	= 9,778
2400	14,269	91,496	79,722	28,259	98,906	103,040	= 9,383
2500	14,310	92,080	80,205	29,688	99,397	103,200	= 9,022
2600	14,347	92,642	80,672	31,120	99,874	103,343	= 8,687
2700	14,381	93,184	81,126	32,557	100,337	103,468	= 8,375
2800	14,412	93,707	81,566	33,996	100,783	103,575	= 8,084
2900	14,440	94,214	81,993	35,439	101,211	103,669	= 7,813
3000	14,467	94,704	82,409	36,884	101,616	103,746	= 7,558
3100	14,491	95,178	82,813	38,332	101,999	103,810	= 7,319
3200	14,513	95,639	83,207	39,783	102,355	103,862	= 7,093
3300	14,534	96,086	83,590	41,235	102,684	103,905	= 6,881
3400	14,553	96,520	83,964	42,689	102,982	103,937	= 6,681
3500	14,571	96,942	84,329	44,146	103,246	103,961	= 6,492
3600	14,588	97,353	84,685	45,604	103,472	103,978	= 6,312
3700	14,603	97,753	85,033	47,063	103,658	103,990	= 6,142
3800	14,618	98,142	85,373	48,524	103,801	103,999	= 5,981
3900	14,631	98,522	85,705	49,987	103,897	104,001	= 5,828
4000	14,644	98,893	86,030	51,450	103,940	104,002	= 5,682
4100	14,656	99,255	86,348	52,915	103,932	104,004	= 5,544
4200	14,667	99,608	86,660	54,382	103,866	104,007	= 5,412
4300	14,678	99,953	86,965	55,849	103,741	104,012	= 5,286
4400	14,688	100,291	87,264	57,317	103,554	104,019	= 5,167
4500	14,698	100,621	87,557	58,786	103,302	104,031	= 5,052
4600	14,707	100,944	87,845	60,257	102,986	104,054	= 4,944
4700	14,716	101,260	88,127	61,728	102,603	104,082	= 4,840
4800	14,724	101,570	88,404	63,200	102,155	104,118	= 4,741
4900	14,732	101,874	88,675	64,673	101,641	104,162	= 4,646
5000	14,740	102,172	88,942	66,146	101,062	104,217	= 4,555
5100	14,748	102,464	89,205	67,621	100,421	104,290	= 4,469
5200	14,755	102,750	89,462	69,096	99,721	104,369	= 4,387
5300	14,763	103,031	89,716	70,572	98,967	104,470	= 4,308
5400	14,770	103,307	89,965	72,048	98,160	104,577	= 4,232
5500	14,777	103,578	90,210	73,526	97,307	104,706	= 4,161
5600	14,783	103,845	90,451	75,004	96,413	104,846	= 4,092
5700	14,790	104,106	90,688	76,482	95,483	105,006	= 4,026
5800	14,797	104,364	90,922	77,962	94,524	105,183	= 3,963
5900	14,803	104,617	91,152	79,442	93,541	105,374	= 3,903
6000	14,810	104,866	91,378	80,922	92,540	105,583	= 3,846

Dec. 31, 1971

CESIUM HYDROXIDE UNIPOSITIVE ION ($CsOH^+$) (IDEAL GAS) GFW = 149.9118 $CsHO^+$

Point Group [$C_{\infty v}$] ΔHf°_0 = 105 ± 10 kcal/mol

$S^\circ_{298.15}$ = [64.2 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 106 ± 10 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[300] (1)
[275] (2)
[3600] (1)

Bond Distance: Cs-O = [2.40] Å O-H = [1.03] Å

Bond Angle: Cs-O-H = [180]° σ = 1

Rotational Constant: B_0 = [0.18258] cm^{-1}

Heat of Formation

The appearance potential of $CsOH^+$ has been determined by Emel'yanov et al. (1) as 7.21 ± 0.14 eV and by Gorokhov et al. (2) as 7.40 ± 0.15 eV. These values correspond to ΔHr_0 = 166.3 ± 3.0 kcal/mol and 170.7 ± 5 kcal/mol, respectively, for the process $e^- + CsOH(g) \rightarrow CsOH^+(g) + 2e^-$. Since there may be excess energy involved, we prefer the lower value. Combining this result with JANAF auxiliary data (3), we derive $\Delta Hf^\circ_0(CsOH^+, g)$ = 105 ± 10 kcal/mol.

Heat Capacity and Entropy

The correlation diagram of Walsh (4) for HAB molecules predicts that $CsOH^+$ (7 valence electrons) should be linear with the unpaired electron in a pi orbital. Therefore, we estimate the ground state of $CsOH^+$ to be $^2\Pi$. $CsOH^+$ is isoelectronic with OH (3) and SH (3). A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with these isoelectronic molecules. The bonding in $CsOH^+$ is assumed to be weakened relative to that in CsOH by the loss of the bonding electron from the neutral species. The vibrational frequencies are estimated from those for CsOH with somewhat lower values due to the weaker bonding. The Cs-O and O-H bond distances are increased slightly over those for CsOH.

The enthalpy at 0 K is -2.905 kcal/mol.

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Cesium Hydroxide, Dimeric ($Cs_2(OH)_2$)

(Ideal Gas) GFW = 299.8247

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	4.641	-161.254	-161.254	INFINITE
100	14.917	66.944	102.671	3.573	-162.665	-160.154	350.015
200	18.319	78.598	87.959	1.872	-163.545	-157.295	171.883
298	19.791	86.195	86.195	.000	-164.400	-154.048	112.920
300	19.818	86.317	86.195	.037	-164.417	-153.984	112.177
400	21.248	92.217	86.990	2.091	-166.292	-150.048	81.980
500	22.577	97.107	88.538	4.285	-167.026	-145.896	63.771
600	23.665	101.323	90.325	6.599	-167.651	-141.608	51.581
700	24.552	105.040	92.167	9.011	-168.199	-137.223	42.843
800	25.289	108.368	93.988	11.504	-168.690	-132.766	36.270
900	25.918	111.384	95.756	14.065	-169.133	-128.247	31.142
1000	26.467	114.144	97.458	16.685	-201.700	-122.041	26.672
1100	26.952	116.689	99.092	19.357	-201.585	-114.079	22.665
1200	27.384	119.053	100.658	22.074	-201.444	-106.129	19.329
1300	27.770	121.261	102.159	24.832	-201.281	-98.193	16.508
1400	28.116	123.332	103.598	27.627	-201.100	-90.272	14.092
1500	28.427	125.282	104.980	30.454	-200.904	-82.360	12.000
1600	28.704	127.126	106.307	33.311	-200.700	-74.466	10.172
1700	28.954	128.874	107.583	36.194	-200.486	-66.581	8.559
1800	29.178	130.535	108.812	39.101	-200.269	-58.712	7.129
1900	29.379	132.118	109.998	42.029	-200.050	-50.852	5.849
2000	29.560	133.630	111.142	44.976	-199.834	-43.006	4.699
2100	29.723	135.076	112.247	47.940	-199.625	-35.169	3.660
2200	29.871	136.462	113.317	50.920	-199.427	-27.344	2.716
2300	30.004	137.793	114.352	53.916	-199.238	-19.525	1.855
2400	30.125	139.073	115.356	56.920	-199.069	-11.713	1.067
2500	30.235	140.305	116.329	59.938	-198.922	-3.915	.342
2600	30.335	141.492	117.274	62.967	-198.795	3.886	-.327
2700	30.426	142.639	118.193	66.005	-198.698	11.679	-.945
2800	30.509	143.747	119.086	69.052	-198.633	19.468	-1.520
2900	30.586	144.819	119.955	72.107	-198.602	27.261	-2.054
3000	30.656	145.857	120.801	75.169	-198.613	35.048	-2.553
3100	30.720	146.863	121.625	78.238	-198.667	42.837	-3.020
3200	30.779	147.840	122.429	81.313	-198.774	50.627	-3.458
3300	30.834	148.788	123.214	84.393	-198.935	58.424	-3.869
3400	30.884	149.709	123.980	87.479	-199.155	66.225	-4.257
3500	30.931	150.605	124.728	90.570	-199.443	74.035	-4.623
3600	30.974	151.477	125.459	93.665	-199.805	81.853	-4.969
3700	31.015	152.326	126.173	96.765	-200.246	89.685	-5.297
3800	31.052	153.154	126.872	99.868	-200.772	97.530	-5.609
3900	31.087	153.961	127.557	102.975	-201.393	105.385	-5.906
4000	31.120	154.748	128.227	106.086	-202.114	113.260	-6.188
4100	31.150	155.517	128.883	109.199	-202.942	121.154	-6.458
4200	31.178	156.268	129.526	112.314	-203.883	129.069	-6.716
4300	31.205	157.002	130.157	115.435	-204.943	137.010	-6.964
4400	31.230	157.720	130.775	118.557	-206.125	144.974	-7.201
4500	31.253	158.422	131.381	121.681	-207.436	152.966	-7.429
4600	31.275	159.109	131.977	124.807	-208.876	160.997	-7.649
4700	31.296	159.782	132.561	127.936	-210.449	169.055	-7.861
4800	31.316	160.441	133.135	131.066	-212.153	177.147	-8.066
4900	31.334	161.087	133.699	134.199	-213.988	185.273	-8.263
5000	31.352	161.720	134.253	137.333	-215.952	193.438	-8.455
5100	31.368	162.341	134.798	140.469	-218.040	201.652	-8.641
5200	31.384	162.950	135.333	143.607	-220.246	209.896	-8.822
5300	31.398	163.548	135.860	146.746	-222.562	218.198	-8.998
5400	31.412	164.135	136.378	149.886	-224.983	226.528	-9.168
5500	31.426	164.712	136.888	153.028	-227.493	234.918	-9.335
5600	31.438	165.278	137.390	156.172	-230.088	243.344	-9.497
5700	31.450	165.835	137.884	159.316	-232.758	251.823	-9.655
5800	31.462	166.382	138.371	162.462	-235.479	260.351	-9.810
5900	31.472	166.920	138.850	165.608	-238.254	268.921	-9.961
6000	31.483	167.449	139.323	168.756	-241.061	277.542	-10.109

June 30, 1971

CESIUM HYDROXIDE, DIMERIC ($Cs_2(OH)_2$) (IDEAL GAS) GFW = 299.8247 $Cs_2H_2O_2$

Point Group C_{2h} ΔHf°_0 = -161.3 ± 10.0 kcal/mol

$S^\circ_{298.15}$ = [86.2 ± 3.0] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -164.4 ± 10.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹	ω, cm⁻¹
[200] (1)	[1250] (1)
[110] (1)	[1250] (1)
[210] (1)	[1250] (1)
[120] (1)	[1250] (1)
[220] (1)	[3700] (1)
[230] (1)	[3700] (1)

Bond Distance: Cs-O = [2.63] Å O-H = [0.96] Å

Bond Angle: Cs-O-Cs = [90°] Cs-O-H = [110°] σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [5.40115] x 10^{-112} g^3 cm^6

Heat of Formation

Schoonmaker and Porter (1) analyzed the vapors in equilibrium with liquid CsOH and mixed KOH-CsOH condensed phases with a mass spectrometer and reported the presence of appreciable concentrations of dimer in the temperature range 650-700 K. By applying the method of relative equilibrium constants, these workers calculated the difference in the free energies of dimerization for KOH-CsOH. A third law analysis of their free energy data for this pair leads to a difference in the heats of dimerization of 4.9 kcal/mol at 298.15 K for CsOH and KOH. Based upon the adopted value for KOH(g), ΔH_{298}(dimerization) = -45.3 ± 3.0 kcal/mol (2), we derive ΔH_{298}(dimerization) = -40.4 ± 4.0 kcal/mol for 2 CsOH(g) = $Cs_2(OH)_2$(g). Combining this result with the heat of formation for the gaseous monomer (3), that for the dimer is $\Delta Hf^\circ_{298}(Cs_2(OH)_2, g)$ = -164.4 ± 10.0 kcal/mol.

Heat Capacity and Entropy

Büchler et al. (4) investigated the geometries of several molecules containing cesium by the deflection of molecular beams in an inhomogeneous electric field. Their results for $Cs_2(OH)_2$(g) indicated that the molecule was nonpolar which implies a planar configuration for at least the Cs_2O_2 part of the molecule. Several structural models proposed for the dimers of the alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer et al. (5) calculated entropies of dimerization for NaOH(g) and KOH(g) with a dimer model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter (1) adopted the same alkali-oxygen configuration but did not allow for hydrogen bonding between the oxygens and hydrogens. Berkowitz et al. (6) relied on the apparent similarity of the alkali halides and hydroxides in forming dimeric species to propose a structural model for $Li_2(OH)_2$(g). This model consisted of a trans configuration with hydrogens above and below the plane of a rhombus formed by the lithium and oxygen atoms, the Li-O-Li bond angle being 100°. We adopt a structure for $Cs_2(OH)_2$(g) which is similar to the model of Berkowitz et al. (6) for $Li_2(OH)_2$(g) but with the Cs-O-Cs bond angle equal to 90°. The cesium and oxygen atoms form a square planar configuration. The Cs-O-H bond angle is assumed equal to 110°. The Cs-O bond distance is estimated as being 10% longer than that in CsOH(g). The O-H bond distance is estimated to be the same as in H_2O(g). The three principal moments of inertia are: I_A = [20.4289] x 10^{-39}, I_B = [152.908] x 10^{-39}, and I_C = [172.907] x 10^{-39} g cm^2.

Acquista et al. (7) observed the infrared spectra of matrix isolated CsOH and reported bands in the region 300-200 cm^{-1} whose relative intensities decreased with increasing temperature. Since the dimer to monomer ratio decreases with increasing temperature, these bands appeared to arise from polymeric species of CsOH, but no definite assignments could be made. Similar results have been reported for RbOH and NaOH from infrared studies (8) of these molecules trapped in inert matrices. Berkowitz et al. (6) estimated vibrational frequencies for $Li_2(OH)_2$(g) by comparison with those for dimeric Li_2F_2(g). The frequencies for Li_2F_2(g) had been estimated earlier by Berkowitz (9) using an ionic model and normal coordinate analysis. It has now been established experimentally that these estimated frequencies for Li_2F_2(g) are too low (See Li_2F_2(g) table for details). Until definite assignments for the dimeric hydroxides can be made from infrared studies, we tentatively adopt the six estimated frequencies for Cs_2F_2(g) (See CsF_2(g) table for details) and apply them directly to $Cs_2(OH)_2$(g). The remaining O-H stretching and bending frequencies are estimates from the work of Berkowitz et al. (6).

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Fluorine Uninegative Ion (F^-)

(Ideal Gas) GFW = 18.99895

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	4.968	34.767	34.767	.000	-61.082	-62.735	45.988
300	4.968	34.797	34.767	.009	-61.089	-62.748	45.712
400	4.968	36.227	34.962	.506	-61.474	-63.244	34.555
500	4.968	37.335	35.330	1.003	-61.878	-63.641	27.817
600	4.968	38.241	35.742	1.500	-62.294	-63.954	23.295
700	4.968	39.007	36.155	1.996	-62.719	-64.196	20.043
800	4.968	39.670	36.558	2.493	-63.152	-64.379	17.587
900	4.968	40.255	36.933	2.990	-63.590	-64.506	15.664
1000	4.968	40.779	37.292	3.487	-64.033	-64.584	14.115
1100	4.968	41.252	37.631	3.984	-64.479	-64.618	12.838
1200	4.968	41.684	37.951	4.480	-64.927	-64.610	11.767
1300	4.968	42.082	38.254	4.977	-65.378	-64.565	10.854
1400	4.968	42.450	38.540	5.474	-65.832	-64.486	10.067
1500	4.968	42.793	38.812	5.971	-66.288	-64.374	9.379
1600	4.968	43.114	39.071	6.467	-66.745	-64.231	8.774
1700	4.968	43.415	39.318	6.964	-67.204	-64.060	8.235
1800	4.968	43.699	39.554	7.461	-67.665	-63.863	7.754
1900	4.968	43.967	39.779	7.958	-68.127	-63.639	7.320
2000	4.968	44.222	39.995	8.455	-68.591	-63.390	6.927
2100	4.968	44.465	40.202	8.951	-69.055	-63.119	6.569
2200	4.968	44.696	40.401	9.448	-69.522	-62.825	6.241
2300	4.968	44.917	40.593	9.945	-69.989	-62.510	5.940
2400	4.968	45.128	40.777	10.442	-70.459	-62.175	5.662
2500	4.968	45.331	40.955	10.939	-70.929	-61.821	5.404
2600	4.968	45.526	41.127	11.435	-71.400	-61.446	5.165
2700	4.968	45.713	41.294	11.932	-71.873	-61.054	4.942
2800	4.968	45.894	41.455	12.429	-72.347	-60.646	4.734
2900	4.968	46.068	41.611	12.926	-72.822	-60.218	4.538
3000	4.968	46.237	41.762	13.423	-73.298	-59.778	4.355
3100	4.968	46.399	41.909	13.919	-73.775	-59.318	4.182
3200	4.968	46.557	42.052	14.416	-74.253	-58.844	4.019
3300	4.968	46.710	42.191	14.913	-74.733	-58.355	3.865
3400	4.968	46.858	42.326	15.410	-75.214	-57.852	3.719
3500	4.968	47.002	42.458	15.907	-75.696	-57.333	3.580
3600	4.968	47.142	42.586	16.403	-76.178	-56.801	3.448
3700	4.968	47.278	42.711	16.900	-76.662	-56.257	3.323
3800	4.968	47.411	42.833	17.397	-77.147	-55.698	3.203
3900	4.968	47.540	42.952	17.894	-77.634	-55.129	3.089
4000	4.968	47.666	43.068	18.390	-78.120	-54.544	2.980
4100	4.968	47.788	43.182	18.887	-78.609	-53.950	2.876
4200	4.968	47.908	43.293	19.384	-79.098	-53.342	2.776
4300	4.968	48.025	43.401	19.881	-79.589	-52.723	2.680
4400	4.968	48.139	43.508	20.378	-80.081	-52.093	2.587
4500	4.968	48.251	43.612	20.874	-80.573	-51.451	2.499
4600	4.968	48.360	43.714	21.371	-81.066	-50.799	2.413
4700	4.968	48.467	43.814	21.868	-81.561	-50.135	2.331
4800	4.968	48.571	43.912	22.365	-82.057	-49.461	2.252
4900	4.968	48.674	44.008	22.862	-82.554	-48.777	2.176
5000	4.968	48.774	44.103	23.358	-83.052	-48.082	2.102
5100	4.968	48.873	44.195	23.855	-83.551	-47.379	2.030
5200	4.968	48.969	44.286	24.352	-84.051	-46.663	1.961
5300	4.968	49.064	44.375	24.849	-84.552	-45.939	1.894
5400	4.968	49.157	44.463	25.346	-85.055	-45.208	1.830
5500	4.968	49.248	44.549	25.842	-85.557	-44.464	1.767
5600	4.968	49.337	44.634	26.339	-86.062	-43.712	1.706
5700	4.968	49.425	44.717	26.836	-86.568	-42.951	1.647
5800	4.968	49.512	44.799	27.333	-87.074	-42.182	1.589
5900	4.968	49.597	44.880	27.830	-87.581	-41.405	1.534
6000	4.968	49.680	44.959	28.326	-88.089	-40.617	1.479

June 30, 1965; Dec. 31, 1971

FLUORINE UNINEGATIVE ION (F^-) (IDEAL GAS) GFW = 18.99895

Ground State Configuration $^1S_0$ ΔHf°_0 = -60.03 ± 0.4 kcal/mol

$S^\circ_{298.15}$ = 34.767 ± 0.001 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -61.08 ± 0.4 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

Heat of Formation

Milstein and Berry (1) have recently concluded that the electron affinity reported by Berry and Reimann (2) was erroneous, the observed threshold being probably due to an A&F species. The new value reported by Milstein and Berry (1) is 3.398 eV in excellent agreement with a value 3.400 eV reported by Popp (3, 4). We adopt the electron affinity as 3.399 ± 0.002 eV (78.384 ± 0.050 kcal) which yields $\Delta Hf^\circ_0(F^-, g)$ = -60.027 ± 0.4 kcal/mol, or $\Delta Hf^\circ_{298}(F^-, g)$ = -61.082 ± 0.4 kcal/mol.

Heat Capacity and Entropy

The ground state configuration was assumed to be that of neon with which F^- is isoelectronic. The electronic levels were also assumed to be those of neon (5), and since the first excited state is above 100,000 cm^{-1}, only the ground state configuration is employed in the calculations. The enthalpy $H^\circ_0 - H^\circ_{298.15}$ is -1.481 kcal/mol.

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FHO_3S

Fluorosulfuric Acid (HSO_3F)

(ideal Gas) GFW = 100.0686

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	− 3.588	− 177.356	− 177.356	INFINITE
100	9.356	56.653	84.292	− 2.764	− 178.463	− 174.369	381.083
200	14.168	64.616	72.551	− 1.587	− 179.375	− 169.902	185.660
298	17.983	71.022	71.022	.000	− 180.000	− 165.109	121.028
300	18.045	71.133	71.022	.013	− 180.010	− 165.017	120.215
400	20.907	76.737	71.767	1.988	− 180.952	− 159.932	87.383
500	22.998	81.640	73.261	4.189	− 181.539	− 154.605	67.578
600	24.527	85.975	75.026	6.565	− 181.914	− 149.180	54.339
700	25.666	89.845	76.872	9.082	− 182.145	− 143.680	44.859
800	26.539	93.332	78.715	11.694	− 195.341	− 139.445	38.095
900	27.229	96.499	80.518	14.383	− 195.105	− 132.471	32.168
1000	27.787	99.398	82.263	17.135	− 194.836	− 125.524	27.433
1100	28.250	102.069	83.944	19.938	− 194.544	− 118.609	23.566
1200	28.639	104.544	85.558	22.783	− 194.230	− 111.718	20.347
1300	28.969	106.850	87.108	25.663	− 193.904	− 104.854	17.628
1400	29.253	109.007	88.596	28.575	− 193.566	− 98.018	15.301
1500	29.499	111.034	90.025	31.513	− 193.221	− 91.206	13.289
1600	29.712	112.945	91.399	34.474	− 192.870	− 84.416	11.531
1700	29.899	114.752	92.720	37.454	− 192.514	− 77.647	9.982
1800	30.063	116.466	93.992	40.453	− 192.158	− 70.902	8.609
1900	30.208	118.095	95.218	43.466	− 191.802	− 64.173	7.382
2000	30.336	119.648	96.401	46.494	− 191.447	− 57.467	6.280
2100	30.450	121.131	97.543	49.533	− 191.094	− 50.777	5.284
2200	30.552	122.550	98.648	52.583	− 190.746	− 44.103	4.381
2300	30.643	123.910	99.717	55.643	− 190.400	− 37.446	3.558
2400	30.725	125.216	100.752	58.712	− 190.060	− 30.800	2.805
2500	30.799	126.471	101.756	61.788	− 189.727	− 24.175	2.113
2600	30.866	127.681	102.730	64.871	− 189.397	− 17.557	1.476
2700	30.926	128.847	103.676	67.961	− 189.074	− 10.955	.887
2800	30.981	129.972	104.595	71.056	− 188.759	− 4.366	.341
2900	31.031	131.061	105.489	74.157	− 188.449	2.219	− .167
3000	31.077	132.113	106.359	77.262	− 188.148	8.787	− .640
3100	31.119	133.133	107.206	80.372	− 187.849	15.347	− 1.082
3200	31.157	134.122	108.032	83.486	− 187.561	21.895	− 1.495
3300	31.192	135.081	108.837	86.604	− 187.277	28.434	− 1.883
3400	31.225	136.013	109.623	89.724	− 187.002	34.969	− 2.248
3500	31.255	136.918	110.390	92.848	− 186.734	41.491	− 2.591
3600	31.282	137.799	111.139	95.975	− 186.470	48.011	− 2.915
3700	31.308	138.656	111.871	99.105	− 186.216	54.521	− 3.220
3800	31.332	139.492	112.587	102.237	− 185.965	61.027	− 3.510
3900	31.354	140.306	113.288	105.371	− 185.722	67.517	− 3.784
4000	31.375	141.100	113.973	108.507	− 185.486	74.010	− 4.044
4100	31.394	141.875	114.644	111.646	− 185.256	80.495	− 4.291
4200	31.412	142.632	115.302	114.786	− 185.031	86.974	− 4.526
4300	31.429	143.371	115.946	117.928	− 184.811	93.451	− 4.750
4400	31.444	144.094	116.577	121.072	− 184.600	99.915	− 4.963
4500	31.459	144.800	117.197	124.217	− 184.392	106.380	− 5.167
4600	31.473	145.492	117.804	127.364	− 184.189	112.844	− 5.361
4700	31.486	146.169	118.401	130.512	− 183.993	119.298	− 5.547
4800	31.498	146.832	118.986	133.661	− 183.801	125.749	− 5.725
4900	31.510	147.482	119.561	136.811	− 183.613	132.194	− 5.896
5000	31.521	148.118	120.126	139.963	− 183.432	138.632	− 6.060
5100	31.531	148.743	120.681	143.115	− 183.255	145.077	− 6.217
5200	31.541	149.355	121.226	146.269	− 183.082	151.510	− 6.368
5300	31.550	149.956	121.763	149.423	− 182.912	157.951	− 6.513
5400	31.559	150.546	122.290	152.579	− 182.748	164.371	− 6.652
5500	31.567	151.125	122.809	155.735	− 182.586	170.804	− 6.787
5600	31.575	151.694	123.320	158.892	− 182.432	177.224	− 6.916
5700	31.582	152.253	123.823	162.050	− 182.279	183.643	− 7.041
5800	31.589	152.802	124.318	165.209	− 182.130	190.068	− 7.162
5900	31.596	153.342	124.805	168.366	− 181.985	196.476	− 7.278
6000	31.602	153.873	125.285	171.528	− 181.844	202.896	− 7.390

June 30, 1972

FLUOROSULFURIC ACID (HSO_3F) (IDEAL GAS) GFW = 100.0686

Point Group [C_s] ΔHf°_0 = -177.4 ± 2 kcal/mol

$S^\circ_{298.15}$ = 71.0 ± 0.8 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -180 ± 2 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
3602 (1)	825 (1)	1486 (1)
1243 (1)	550 (1)	562 (1)
1150 (1)	410 (1)	390 (1)
896 (1)	390 (1)	265 (1)

Bond Distance: O=S = [1.405] Å S-OH = S-F = [1.53] Å O-H = [1.00] Å

Bond Angle: O=S=O = [124°] F-S-OH = S-O-H = [100°] σ = 1

Product of the Moments of Inertia: $I_A I_B I_C$ = [4.2733 x 10^{-114}] $g^3 cm^6$

Heat of Formation

ΔHf°(ℓ, 298.15 K) may be derived from calorimetric data of Richards and Woolf (1) which yield ΔHr_{298} = -14.94 ± 0.2 kcal/mol for $SO_3(\ell)$ + HF (real gas, 1 atm) → $HSO_3F(\ell)$. Using ΔHf°(SO_3, ℓ) = -105.41 (2) and ΔHf(HF, real gas) = -70.12 (3, 4) kcal/mol, we derive ΔHf° = -190.5 kcal/mol for $HSO_3F(\ell)$ and -180.3 ± 1.5 kcal/mol for the ideal gas. The latter value agrees well with -179.2 ± 3 kcal/mol estimated for $HSO_3F(g)$ from the related molecules SO_2F_2 and H_2SO_4 (4). We adopt ΔHf° = -180 ± 2 kcal/mol.

Derivation of ΔHf°(g) presumes that the heat of vaporization is 10.2 ± 1.0 kcal/mol at 25°C. Measurements of the heat of condensation (5) yield 12.8 ± 0.8 kcal/mol for the enthalpy difference between real gas at 164.4°C and the liquid at 25°C. Added to this value should be +0.2 kcal/mol (estimated correction for gas imperfection) and -2.8 kcal/mol (calculated enthalpy difference for the ideal gas between 25°C and 164.4°C, the approximate normal boiling point).

Other calorimetric data bearing on ΔHf° were reported by Lenskii et al. (5) and Woolf (6), but these results are much more uncertain (1) due to experimental error and to inadequate definition of the states of the reactants and products.

Heat Capacity and Entropy

Savoie and Giguere (7) reviewed possible molecular structures and preferred eclipsed (cis) forms, arbitrarily selecting one in which F-S-O-H is coplanar. We adopt this structure since the choice changes the thermodynamic functions very little. Possible structures all have σ = 1 (C_s or C_1 symmetry) and similar values of the product of the moments of inertia. Bond lengths and angles are estimated by comparison with SO_2ClF (8), SO_2F_2, SO_2Cl_2 and H_2SO_4 (4). These parameters yield O=S-F and O=S-OH angles of 107.56° and principal moments of inertia of I_A = 15.963 x 10^{-39}, I_B = 16.168 x 10^{-39}, I_C = 16.558 x 10^{-39} g cm^2.

Vibrational fundamentals are from the assignment of Savoie and Giguere (7) as modified by Chackalackal and Stafford (9). Data include Raman spectra of the liquid (10) and infrared spectra of all three phases (7) plus the superheated vapor (9). Spectra of the superheated vapor helped to clarify the vibrational distinction between the monomer and associated molecules. Savoie and Giguere derived a barrier of about 1.3 kcal/mol for hindered internal rotation of the OH group and used this to calculate Cp° = 17.64 and S° = 71.38 gibbs/mol at 298.15 K. We calculate Cp° = 17.98 and S° = 71.02 gibbs/mol using the OH-torsional frequency (265 cm^{-1}) instead of hindered rotation.

References

1. G. W. Richards and A. A. Woolf, J. Chem. Soc. A1967, 1118 (1967).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, Jan., 1968.
3. C. E. Vanderzee and W. W. Rodenburg, J. Chem. Thermodynamics 2, 461 (1970).
4. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Mich.; HF(g) dated Dec. 31, 1968; H_2SO_4(g) dated Dec. 31, 1966; SO_2F_2(g) and SO_2Cl_2(g) dated June 30, 1971.
5. A. S. Lenskii, A. D. Shaposhnikova and E. S. Sokolova, Russ. J. Inorg. Chem. 9, 626 (1964); 8, 1424 (1963).
6. A. A. Woolf, J. Inorg. Nucl. Chem. 14, 21 (1960).
7. R. Savoie and P. A. Giguere, Can. J. Chem. 42, 277 (1964).
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9. S. M. Chackalackal and F. E. Stafford, J. Amer. Chem. Soc. 88, 4815 (1966).
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FHO_3S

Potassium Bifluoride (KHF_2)

(Crystal) GFW = 78.10677

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	= 3.655	= 221.810	= 221.810	INFINITE
100	11.702	8.362	39.536	= 3.117	= 222.361	= 217.057	474.378
200	16.030	18.060	26.529	= 1.694	= 222.559	= 211.653	231.284
298	18.389	24.920	24.920	.000	= 222.570	= 206.295	151.218
300	18.430	25.034	24.920	.034	= 222.569	= 206.194	150.212
400	20.570	30.629	25.669	1.984	= 223.050	= 200.637	109.623
500	23.960	41.257	27.500	6.878	= 220.056	= 195.235	85.337
600	23.960	45.626	30.168	9.274	= 219.568	= 190.316	69.323
700	23.960	49.319	32.647	11.670	= 219.090	= 185.478	57.909
800	23.960	52.518	34.935	14.066	= 218.625	= 180.710	49.368
900	23.960	55.340	37.049	16.462	= 218.173	= 175.997	42.738
1000	23.960	57.865	39.006	18.858	= 217.742	= 171.335	37.445
1100	23.940	60.149	40.826	21.254	= 236.238	= 165.691	32.920
1200	23.940	62.233	42.525	23.650	= 235.603	= 159.304	29.013
1300	23.940	64.151	44.115	26.046	= 234.979	= 152.972	25.717
1400	23.940	65.927	45.611	28.442	= 234.364	= 146.686	22.899
1500	23.940	67.580	47.021	30.838	= 233.759	= 140.443	20.463
1600	23.960	69.126	48.355	33.234	= 233.164	= 134.243	18.337
1700	23.960	70.579	49.620	35.630	= 232.577	= 128.078	16.466
1800	23.960	71.948	50.822	38.026	= 232.000	= 121.950	14.807
1900	23.960	73.244	51.969	40.422	= 231.431	= 115.851	13.326
2000	23.960	74.473	53.063	42.818	= 230.869	= 109.780	11.996

June 30, 1962; Dec. 31, 1963; June 30, 1971

POTASSIUM BIFLUORIDE (KHF_2) (CRYSTAL) GFW = 78.10677 F_2HK

ΔHf°_0 = −221.41 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 24.92 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −222.57 ± 0.3 kcal/mol

Tt = 469.85 K

ΔHt° = 2.682 ± 0.01 kcal/mol

Tm = 511.95 K

ΔHm° = 1.582 ± 0.003 kcal/mol

Heat of Formation

Davis and Westrum (1) measured directly the enthalpy of the decomposition reaction $KHF_2(c) \rightarrow KF(c) + HF(g)$ in an adiabatic calorimeter as ΔHd° = 18.52 ± 0.05 kcal/mol at 500 K. Reducing to 298 K, we obtain ΔHd°_{298} = 21.533 ± 0.05 kcal/mol which leads to the heat of formation, $\Delta Hf^\circ_{298}(KHF_2, c)$ = −222.57 ± 0.3 kcal/mol, using all JANAF functions and $\Delta Hf^\circ_{298}(HF, g)$ = −65.14 ± 0.2 kcal/mol (2) and $\Delta Hf^\circ_{298}(KF, c)$ = −135.9 ± 0.1 kcal/mol (3). The value of −222.57 kcal/mol is adopted in the tabulation.

Westrum and Pitzer (4) measured the dissociation vapor pressures of $KHF_2(c, \ell)$ by a static method. Their pressure data have been analyzed by both 2nd law and 3rd law methods as given below. The heat of formation derived from the 3rd law analysis differs by about 0.3 kcal/mol from the value adopted, which is greater than the combined experimental errors.

Decomposition Reaction	Temp. K	No. of Points	ΔHd°_{298} kcal/mol 3rd law	ΔHd°_{298} kcal/mol 2nd law	Drift† (eu)	$\Delta Hf^\circ_{298}(KHF_2, c)$ (kcal/mol)
$KHF_2(c) \rightarrow KF(c) + HF(g)$	478-500	14	21.31 ± 0.01	21.21 ± 0.12	0.2 ± 0.2	−222.35*
$KHF_2(\ell) \rightarrow KF(c) + HF(g)$	504-577	5	17.73 ± 0.24	19.82 ± 0.08	−3.9 ± 0.2	−222.28**

† The drift is the difference between ΔSr°(JANAF functions) and ΔSr°(2nd law)

* *3rd law ΔHd°_{298} is used in calculation.*

** This value is derived from the adopted heat of melting, ΔHm°_{298} = 3.504 kcal/mol and $\Delta Hf^\circ_{298}(KHF_2, \ell)$ = −218.773 kcal/mol. The latter is calculated from the 3rd law ΔHd°_{298}.

Heat Capacity and Entropy

Westrum and Pitzer (4) measured both low temperature Cp data (16-315 K) in an adiabatic calorimeter and high temperature enthalpy data (321.6 - 465 K for α phase and 471.3 - 505.9 K for β phase) in a drop calorimeter. We use their experimental Cp data to derive S°_{298} = 24.92 ± 0.1 eu, based on S° = 0.0643 eu at 15 K. The low temperature Cp and high temperature enthalpy data for the α phase are smoothly joined at 298 K by a polynomial curve fitting method. The deviations of the observed enthalpy data from the adopted values are 0.68% at 321.6 K and 0.09% at 463.7 K. The constant heat capacity, 23.96 gibbs/mol, in the β phase is derived from the measured enthalpy data (4), and is assumed to be the same when the temperature is above the melting point.

Transition and Melting Data

Davis and Westrum (1) measured the heat of the α-β transition, ΔHt° = 2.682 ± 0.01 kcal/mol at 196.7°C, and the heat of melting, ΔHm° = 1.582 ± 0.003 kcal/mol at 238.8°C in an adiabatic calorimeter. Their data are adopted in the tabulation. Based on the drop calorimetric measurements (4), we have derived ΔHm° = 1.554 kcal/mol which is in good agreement with the value adopted.

References

1. M. L. Davis and E. F. Westrum, Jr., J. Phys. Chem. 65, 338 (1961).
2. JANAF HF(g) table dated Dec. 31, 1968.
3. JANAF KF(c) table dated June 30, 1969.
4. E. F. Westrum, Jr. and K. S. Pitzer, J. Amer. Chem. Soc. 71, 1940 (1949).

J. Phys. Chem. Ref. Data, Vol. 3, No. 3, 1974

Potassium Bifluoride (KHF_2)

(Liquid) GFW = 78.10677

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	18.390	31.731	31.731	.000	− 219.066	− 204.821	150.137
300	18.430	31.845	31.731	.034	− 219.065	− 204.733	149.147
400	25.000	38.744	32.634	2.444	− 219.086	− 199.919	109.230
500	25.000	44.323	34.434	4.944	− 218.486	− 195.198	85.321
600	25.000	48.881	36.474	7.444	− 217.894	− 190.595	69.424
700	25.000	52.735	38.529	9.944	− 217.312	− 186.091	58.100
800	25.000	56.073	40.518	12.444	− 216.743	− 181.672	49.630
900	25.000	59.018	42.413	14.944	− 216.187	− 177.321	43.059
1000	25.000	61.652	44.207	17.444	− 215.652	− 173.032	37.816
1100	25.000	64.034	45.903	19.944	− 234.044	− 167.771	33.333
1200	25.000	66.210	47.506	22.444	− 233.305	− 161.778	29.464
1300	25.000	68.211	49.023	24.944	− 232.577	− 155.848	26.200
1400	25.000	70.063	50.460	27.444	− 231.858	− 149.971	23.412
1500	25.000	71.788	51.825	29.944	− 231.149	− 144.146	21.002
1600	25.000	73.402	53.124	32.444	− 230.450	− 138.370	18.900
1700	25.000	74.917	54.362	34.944	− 229.759	− 132.636	17.051
1800	25.000	76.346	55.544	37.444	− 229.078	− 126.944	15.413
1900	25.000	77.698	56.675	39.944	− 228.405	− 121.288	13.951
2000	25.000	78.980	57.758	42.444	− 227.739	− 115.666	12.639

June 30, 1962; Dec. 31, 1963; June 30, 1971

POTASSIUM BIFLUORIDE (KHF_2) (LIQUID) GFW = 78.10677 F_2HK

$S^\circ_{298.15}$ = 31.731 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -219.066 kcal/mol

Tm = 511.95 K ΔHm° = 1.582 ± 0.003 kcal/mol

Td = [750] K

Heat of Formation

The heat of formation is calculated from that of the crystal by adding ΔHm° and the difference between $H_{511.95} - H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy

Westrum and Pitzer (1) measured high temperature enthalpy data by drop calorimetry in a narrow range of 510.6-523.2 K and derived a constant heat capacity of approximately 25 gibbs/mol which is adopted in the tabulation.

A glass transition is assumed at 314 K. Below 314 K, the heat capacities are assumed to be the same as those of the crystal. Between 314 K and the melting point, the Cp is assumed to be the same as that of the liquid.

The entropy is calculated from that of the crystal in a manner similar to the heat of formation.

Melting Data

See JANAF KHF_2(c) table.

Decomposition

The decomposition temperature, Td = 750 K, is calculated as the temperature at which ΔGf = 0 for $KHF_2(\ell) \rightarrow KF(c) + HF(g)$. At Td, the vapor pressure of HF(g) reaches one atmosphere.

Westrum and Pitzer (1) determined the decomposition vapor pressures of KHF_2(c, ℓ) by a static method. Their data lead to the decomposition temperature, 700 K when the pressure of HF reaches one atmosphere. JANAF analyses of their data are given in KHF_2(c) table. Their data over the crystal phase are suspected to be high by approximatley 11.5%; and the data over the liquid phase are probably in error as indicated by the third law drift (3.9 eu) in the JANAF analyses.

Reference

1. E. F. Westrum, Jr. and K. S. Pitzer, J. Amer. Chem. Soc. 71, 1940 (1949).

Thionyl Fluoride (SOF_2)

(Ideal Gas) GFW = 86.0602

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	- 3.017	- 128.817	- 128.817	INFINITE
100	8.495	55.011	77.142	- 2.213	- 129.219	- 128.284	280.364
200	11.272	61.718	67.864	- 1.229	- 129.676	- 127.164	138.959
298	13.648	66.687	66.687	.000	- 130.000	- 125.858	92.256
300	13.686	66.772	66.687	.025	- 130.005	- 125.832	91.669
400	15.362	70.954	67.246	1.483	- 130.772	- 124.383	67.960
500	16.506	74.513	68.352	3.080	- 131.285	- 122.725	53.643
600	17.295	77.556	69.642	4.772	- 131.660	- 120.975	44.065
700	17.853	80.306	70.976	6.531	- 131.941	- 119.147	37.199
800	18.255	82.718	72.296	8.338	- 145.224	- 118.572	32.392
900	18.553	84.886	73.576	10.179	- 145.104	- 115.247	27.986
1000	18.778	86.853	74.807	12.046	- 144.976	- 111.936	24.464
1100	18.951	88.651	75.985	13.933	- 144.844	- 108.641	21.585
1200	19.087	90.306	77.110	15.835	- 144.707	- 105.354	19.188
1300	19.196	91.839	78.185	17.749	- 144.569	- 102.079	17.161
1400	19.284	93.264	79.212	19.674	- 144.431	- 98.816	15.426
1500	19.356	94.597	80.194	21.606	- 144.293	- 95.563	13.924
1600	19.416	95.849	81.133	23.544	- 144.156	- 92.319	12.610
1700	19.466	97.027	82.034	25.489	- 144.020	- 89.082	11.452
1800	19.508	98.141	82.898	27.437	- 143.888	- 85.857	10.424
1900	19.544	99.197	83.728	29.390	- 143.757	- 82.634	9.505
2000	19.575	100.200	84.527	31.346	- 143.629	- 79.421	8.679
2100	19.602	101.156	85.296	33.305	- 143.504	- 76.216	7.932
2200	19.626	102.068	86.038	35.266	- 143.384	- 73.013	7.253
2300	19.646	102.941	86.754	37.230	- 143.266	- 69.817	6.634
2400	19.664	103.778	87.446	39.195	- 143.153	- 66.625	6.067
2500	19.680	104.581	88.116	41.163	- 143.043	- 63.440	5.546
2600	19.694	105.353	88.764	43.131	- 142.938	- 60.257	5.065
2700	19.707	106.096	89.392	45.101	- 142.836	- 57.079	4.620
2800	19.718	106.813	90.002	47.073	- 142.738	- 53.907	4.208
2900	19.729	107.505	90.593	49.045	- 142.644	- 50.733	3.823
3000	19.738	108.174	91.168	51.018	- 142.557	- 47.567	3.465
3100	19.746	108.822	91.727	52.993	- 142.470	- 44.402	3.130
3200	19.754	109.449	92.271	54.968	- 142.390	- 41.240	2.817
3300	19.761	110.057	92.801	56.943	- 142.312	- 38.082	2.522
3400	19.767	110.647	93.317	58.920	- 142.239	- 34.923	2.245
3500	19.773	111.220	93.821	60.897	- 142.171	- 31.768	1.984
3600	19.778	111.777	94.312	62.874	- 142.105	- 28.613	1.737
3700	19.783	112.319	94.791	64.852	- 142.045	- 25.461	1.504
3800	19.788	112.847	95.259	66.831	- 141.987	- 22.310	1.283
3900	19.792	113.361	95.717	68.810	- 141.934	- 19.166	1.074
4000	19.796	113.862	96.164	70.789	- 141.883	- 16.014	.875
4100	19.800	114.351	96.602	72.769	- 141.837	- 12.870	.686
4200	19.803	114.828	97.030	74.749	- 141.794	- 9.724	.506
4300	19.806	115.294	97.450	76.730	- 141.754	- 6.578	.334
4400	19.809	115.749	97.860	78.711	- 141.719	- 3.437	.171
4500	19.812	116.194	98.263	80.692	- 141.687	- .294	.014
4600	19.814	116.630	98.657	82.673	- 141.657	2.848	- .135
4700	19.817	117.056	99.044	84.654	- 141.632	5.988	- .278
4800	19.819	117.473	99.424	86.636	- 141.608	9.130	- .416
4900	19.821	117.882	99.797	88.618	- 141.589	12.272	- .547
5000	19.823	118.282	100.162	90.600	- 141.573	15.408	- .673
5100	19.825	118.675	100.521	92.583	- 141.560	18.547	- .795
5200	19.827	119.060	100.874	94.565	- 141.550	21.689	- .912
5300	19.828	119.438	101.221	96.548	- 141.541	24.831	- 1.024
5400	19.830	119.808	101.562	98.531	- 141.538	27.964	- 1.132
5500	19.831	120.172	101.897	100.514	- 141.535	31.106	- 1.236
5600	19.833	120.530	102.226	102.497	- 141.538	34.246	- 1.337
5700	19.834	120.881	102.551	104.481	- 141.543	37.383	- 1.433
5800	19.836	121.226	102.870	106.464	- 141.549	40.525	- 1.527
5900	19.837	121.565	103.184	108.448	- 141.558	43.657	- 1.617
6000	19.838	121.898	103.493	110.432	- 141.571	46.802	- 1.705

Dec. 31, 1960; Sept. 30, 1965; June 30, 1972

THIONYL FLUORIDE (SOF_2) (IDEAL GAS) GFW = 86.0602

Point Group C_s ΔHf°_0 = [-129 ± 25] kcal/mol

$S^\circ_{298.15}$ = 66.69 ± 0.1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-130 ± 25] kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1330 (1)	377.8 (1)
808.2 (1)	747.0 (1)
530.4 (1)	392.5 (1)

Bond Distance: O-S = 1.412 Å S-F = 1.585 Å

Bond Angle: O-S-F = 106.82° F-S-F = 92.82° σ = 1

Product of the Moments of Inertia: $I_A I_B I_C$ = 1.6550 x 10^{-114} $g^3 cm^6$

Heat of Formation

The increment in ΔHf° at 298.15 K between gaseous SOF_2 and SO_2F_2 is estimated from increments for the four pairs a) S and SO, b) SO and SO_2, c) SO_2 and SO_3, and d) $SOCl_2$ and SO_2Cl_2. Based on ΔHf°= -181.3 kcal/mol for SO_2F_2 (1), we derive a) -116, b) -109, c) -158, and d) -148 for ΔHf° of $SOF_2(g)$. *The derivation is based on $\Delta Hf(SOCl_2, g)$ from (2)* and other values from (1). Giving lesser weight to c) which involves SO_3, we adopt an average of -130 ± 25 kcal/mol.

Heat Capacity and Entropy

The molecular structure is from the microwave study of Ferguson (3). Principal moments of inertia are I_A = 9.736 x 10^{-39}, I_B = 10.039 x 10^{-39}, and I_C = 16.932 x 10^{-39} g cm^2. Vibrational frequencies are those assigned by Pace and Samuelson (4) from their gas-phase infrared spectra. These authors also measured Raman spectra of liquid and gas and summarized earlier spectral studies. We adopt ν_1 as the lower wave number of the Fermi resonance doublet at 1330 and 1340 cm^{-1}. Uncertainty is greatest for the overlapping bands near 378 and 392 cm^{-1}.

Pace and Turnbull (5) derived S° = 63.56 ± 0.15 gibbs/mol for the ideal gas at Tb = 228.84 K from calorimetric measurements of heat capacity (12 to 230 K), ΔHm, and ΔHv. Spectroscopic data of this table yield the corresponding value of S° = 63.29 which is 0.27 gibbs/mol smaller than observed. Pace and Turnbull attributed the minor discrepancy to bias in the measurements of ΔHv.

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J. Phys. Chem. Ref. Data, Vol. 3, No. 4, 1974

Sulfuryl Fluoride (SO_2F_2)

(Ideal Gas) GFW = 102.0596

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	= 3.226	= 179.288	= 179.288	INFINITE
100	8.574	55.144	79.354	= 2.421	= 180.036	= 177.045	386.930
200	12.335	62.170	69.097	= 1.385	= 180.789	= 173.747	189.861
298	15.732	67.761	67.761	.000	= 181.300	= 170.173	124.739
300	15.787	67.858	67.761	.029	= 181.308	= 170.104	123.920
400	18.287	72.762	68.413	1.740	= 182.177	= 166.293	90.858
500	20.070	77.046	69.720	3.663	= 182.730	= 162.256	70.922
600	21.349	80.824	71.262	5.737	= 183.100	= 158.123	57.598
700	22.276	84.189	72.873	7.921	= 183.345	= 153.915	48.054
800	22.960	87.210	74.480	10.184	= 196.571	= 150.968	41.242
900	23.474	89.946	76.049	12.507	= 196.376	= 145.279	35.278
1000	23.866	92.440	77.565	14.875	= 196.161	= 139.612	30.512
1100	24.172	94.730	79.023	17.278	= 195.932	= 133.970	26.617
1200	24.413	96.844	80.421	19.707	= 195.692	= 128.346	23.375
1300	24.607	98.806	81.760	22.159	= 195.445	= 122.742	20.635
1400	24.764	100.635	83.044	24.627	= 195.195	= 117.160	18.289
1500	24.894	102.348	84.274	27.111	= 194.941	= 111.596	16.259
1600	25.002	103.958	85.455	29.606	= 194.686	= 106.047	14.485
1700	25.092	105.477	86.588	32.110	= 194.431	= 100.514	12.922
1800	25.169	106.913	87.678	34.623	= 194.179	= 94.999	11.534
1900	25.234	108.276	88.727	37.144	= 193.927	= 89.494	10.298
2000	25.291	109.572	89.737	39.670	= 193.679	= 84.004	9.180
2100	25.339	110.807	90.711	42.202	= 193.434	= 78.528	8.173
2200	25.382	111.987	91.651	44.738	= 193.195	= 73.061	7.258
2300	25.419	113.116	92.560	47.278	= 192.959	= 67.606	6.424
2400	25.452	114.198	93.439	49.821	= 192.729	= 62.160	5.660
2500	25.482	115.238	94.291	52.368	= 192.504	= 56.726	4.959
2600	25.508	116.238	95.116	54.918	= 192.283	= 51.298	4.312
2700	25.531	117.201	95.916	57.470	= 192.068	= 45.879	3.714
2800	25.552	118.130	96.693	60.024	= 191.859	= 40.471	3.159
2900	25.570	119.027	97.448	62.580	= 191.656	= 35.064	2.643
3000	25.587	119.894	98.181	65.138	= 191.460	= 29.670	2.161
3100	25.603	120.733	98.895	67.697	= 191.267	= 24.280	1.712
3200	25.617	121.546	99.591	70.258	= 191.082	= 18.897	1.291
3300	25.629	122.335	100.268	72.821	= 190.900	= 13.521	.895
3400	25.641	123.100	100.928	75.384	= 190.726	= 8.146	.524
3500	25.652	123.844	101.572	77.949	= 190.557	= 2.780	.174
3600	25.662	124.566	102.201	80.514	= 190.392	2.585	= .157
3700	25.671	125.270	102.815	83.081	= 190.234	7.944	= .469
3800	25.679	125.954	103.415	85.649	= 190.079	13.300	= .765
3900	25.687	126.621	104.002	88.217	= 189.931	18.643	= 1.045
4000	25.694	127.272	104.575	90.786	= 189.787	23.994	= 1.311
4100	25.701	127.906	105.137	93.356	= 189.648	29.336	= 1.564
4200	25.707	128.526	105.688	95.926	= 189.514	34.675	= 1.804
4300	25.713	129.131	106.224	98.497	= 189.383	40.015	= 2.034
4400	25.718	129.722	106.752	101.069	= 189.259	45.345	= 2.252
4500	25.723	130.300	107.269	103.641	= 189.138	50.676	= 2.461
4600	25.728	130.865	107.775	106.213	= 189.021	56.006	= 2.661
4700	25.732	131.419	108.273	108.786	= 188.909	61.330	= 2.852
4800	25.736	131.960	108.761	111.360	= 188.799	66.655	= 3.035
4900	25.740	132.491	109.239	113.933	= 188.695	71.975	= 3.210
5000	25.744	133.011	109.710	116.508	= 188.594	77.290	= 3.378
5100	25.747	133.521	110.172	119.082	= 188.498	82.608	= 3.540
5200	25.751	134.021	110.625	121.657	= 188.404	87.924	= 3.695
5300	25.754	134.512	111.071	124.232	= 188.313	93.242	= 3.845
5400	25.757	134.993	111.510	126.808	= 188.227	98.545	= 3.988
5500	25.759	135.466	111.941	129.383	= 188.143	103.860	= 4.127
5600	25.762	135.930	112.366	131.960	= 188.064	109.168	= 4.260
5700	25.764	136.386	112.783	134.536	= 187.988	114.472	= 4.389
5800	25.767	136.834	113.194	137.112	= 187.914	119.783	= 4.514
5900	25.769	137.274	113.598	139.689	= 187.843	125.079	= 4.633
6000	25.771	137.708	113.996	142.266	= 187.776	130.389	= 4.749

Dec. 31, 1960; Mar. 31, 1963; June 30, 1971

SULFURYL FLUORIDE (SO_2F_2) (IDEAL GAS) GFW = 102.0596 F_2O_2S

Point Group C_{2v} ΔHf°_0 = -179.3 ± 2 kcal/mol

$S^\circ_{298.15}$ = 67.76 ± 0.1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -181.3 ± 2 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm⁻¹	ω, cm⁻¹
1269 (1)	1502 (1)
848 (1)	553 (1)
544 (1)	885 (1)
384 (1)	539 (1)
388 (1)	

Bond Distance: S-O = 1.405 ± 0.003 Å S-F = 1.530 ± 0.003 Å

Bond Angle: O-S-O = 123.97 ± 0.20° F-S-F = 96.12 ± 0.17° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 4.4894 \times 10^{-114}$ g³ cm⁶

Heat of Formation

Ruh, Davis and Allswede (1) reported percent conversions for the reaction $SO_2(g) + Cl_2(g) + 2HF(g) \rightarrow SO_2F_2(g) + 2HCl(g)$ at 110 to 700°C and at pressures slightly above atmospheric. The data allow calculation of apparent values of Kp from the assumption of exact stoichiometry. Two temperatures may be excluded, namely 110°C for failure to approach equilibrium and 597°C due to power failure. The remaining values (503 to 973 K) yield ΔHr°(3rd law) = -24.15 ± 2 and ΔHr°(2nd law) = -20.7 ± 1.6 kcal/mol at 298.15 K. The third-law values show a minor trend with temperature, corresponding to ΔSr°(2nd law) − ΔSr°(3rd law) = 5.4 ± 2.5 gibbs/mol, but this inconsistency is small enough to suggest that there was reasonable approach to equilibrium. An example given in the text of the patent (1) reveals that the actual recovery of SO_2 was somewhat less than that predicted on the assumption of stoichiometry. Use of this actual recovery of SO_2 would make ΔHr°(3rd law) more negative by less than 0.4 kcal/mol. We adopt ΔHr° = -24.15 kcal/mol and ΔHf° = -181.3 ± 2 kcal/mol at 298.15 K.

Reese, Dibeler and Franklin (2) derived ΔHf° = -205 kcal/mol from electron-impact studies. They measured potentials of 12.44 ± 0.1 and 18.9 ± 0.3 eV for the appearance of SO_2^+ from SO_2 and SO_2F_2, respectively. Combination of these values implies that ΔHf° of SO_2F_2 should be about 1.0 eV more negative than the adopted value. This discrepancy could reasonably arise from neglect of the unknown excess energies of the products of the two reactions. Bond-energy comparisons tend to confirm this view. Average values of D(S-F) may be calculated from $\Delta Hr^\circ/2$ for $SF_6 \rightarrow SF_4 + 2F$ and $SO_2F_2 \rightarrow SO_2 + 2F$. D(S-F) = 72 kcal/mol from SF_6 is much more consistent with D(S-F) = 74 kcal/mol from the adopted ΔHf° than with D(S-F) = 86 kcal/mol from the electron-impact value.

Heat Capacity and Entropy

Bond lengths and bond angles are from the microwave study of Lide, Mann and Fristrom (3). The resulting O-S-F angle is 108.3° and the principal moments of inertia are $I_A = 16.345 \times 10^{-39}$, $I_B = 16.571 \times 10^{-39}$ and $I_C = 16.574 \times 10^{-39}$ g cm². An early electron-diffraction study (4) is in reasonable agreement.

Vibrational frequencies are those assigned by Lide, Mann and Comeford (5) based on additional microwave and infrared data for the gaseous and matrix-isolated phases. Assignment of the three fundamentals near 544 cm⁻¹ and the two near 388 cm⁻¹ is supported by gas-phase Raman spectra (6), by combination and overtones in the infrared (6) and by force-field calculations (7).

Calculated values of Cp° agree within 0.1% with those derived by Gehri (8) from measurements of Cp at temperatures of 273 to 323 K and pressures up to 1 atm. The calculated entropy, S° = 63.25 gibbs/mol at the normal boiling point of 217.78 K, may be compared with 62.66 ± 0.15 gibbs/mol derived from low-temperature calorimetric data by Bockhoff, Petrella and Pace (9). The discrepancy is 0.59 gibbs/mol; it was attributed (9) to randomness in the solid at absolute zero. Bockhoff and Pace (10) later reported an entropy discrepancy of 1.48 gibbs/mol, but this value resulted from an incorrect vibrational assignment (5-7).

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F_2O_2S

Tungsten Oxytetrafluoride (WOF_4)

(Crystal) GFW = 275.843

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	31.926	42.000	42.000	.000	-336.259	-310.260	227.426
300	32.000	42.198	42.001	.059	-336.285	-310.099	225.907
400	36.000	51.951	43.304	3.459	-335.330	-301.513	164.739
500	39.800	60.410	45.896	7.257	-334.113	-293.195	128.155
600	42.700	67.937	48.954	11.390	-332.632	-285.145	103.864
700	44.600	74.670	52.156	15.760	-330.974	-277.359	86.595
800	45.900	80.715	55.354	20.266	-329.210	-269.822	73.712
900	46.800	86.177	58.481	24.927	-327.372	-262.507	63.785
1000	47.300	91.137	61.502	29.635	-325.502	-255.400	55.818

June 30, 1962; Mar. 31, 1967; Dec. 31, 1971

TUNGSTEN OXYTETRAFLUORIDE (WOF_4) (CRYSTAL) GFW = 275.843

$\Delta Hf°_0$ = Unknown

$S°_{298.15}$ = 42.0 ± 1.0 gibbs/mol

$\Delta Hf°_{298.15}$ = -333.26 ± 15.00 kcal/mol

Tm = 379 K

$\Delta Hm°$ = 1.20 ± 1.00 kcal/mol

Heat of Formation

The heat of formation, $\Delta Hf°_{298}(WOF_4, c)$ = -333.26 kcal/mol, is calculated from the heat of formation of $WOF_4(g)$ less the heat of sublimation, $\Delta Hs°_{298}$ = 16.80 kcal/mol. This latter quantity is calculated by the third-law method from the vapor pressure equation determined by Cady and Hargreaves (1). The second-law value is $\Delta Hs°_{298}$ = 16.94 kcal/mol.

Heat Capacity and Entropy

The heat capacities are estimated from those of $WOCl_4(c)$, $WO_3(c)$, $WO_2(c)$, $WCl_6(c)$, and $WF_6(c, \ell)$ (3).

The entropy, $S°_{298}$ = 42.0 gibbs/mol is calculated from the vapor pressure equation of Cady and Hargreaves (1) using a second law analysis.

This entropy is larger than the corresponding value for $WOCl_4(c)$ (2). In both cases the entropies of the condensed phases are derived from gas phase values using second law analysis of sublimation and vaporization data. The entropy of melting for $WOCl_4$ is an order of magnitude larger than that of WOF_4. This suggests some inconsistency in the data for $WOCl_4$ since all values for $WOF_4(c, \ell, g)$ appear internally reasonable.

Melting Data

Tm is calculated as the temperature at which the Gibbs energy of reaction $WOF_4(c) \rightarrow WOF_4(\ell)$ approaches zero. The difference between the heats of formation for the crystal and liquid at the melting point is $\Delta Hm°$.

Ruff, Eisner, and Heller (3) reported the melting point as 383 K. Cady and Hargreaves (1) calculated the melting point as 378 K, and the heat of fusion as 2.26 kcal/mol from vapor pressure equations for the crystal and liquid. This second law value of $\Delta Hm°$, when corrected for ΔCp of vaporization and sublimation, is in good agreement with the value adopted in this table.

References

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Tungsten Oxytetrafluoride (WOF_4)

(Liquid) GFW = 275.843

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	43,500	42,600	42,800	.000	= 335,838	= 310,077	227,293
300	43,500	43,069	42,801	.080	= 335,803	= 309,918	225,775
400	43,500	55,583	44,507	4,430	= 333,938	= 301,573	164,772
500	43,500	65,290	47,729	8,780	= 332,168	= 293,690	128,372
600	43,500	73,221	51,337	13,130	= 330,471	= 286,156	104,231
700	43,500	79,927	54,954	17,480	= 328,833	= 278,897	87,075
800	43,500	85,735	58,447	21,830	= 327,247	= 271,875	74,273
900	43,500	90,859	61,769	26,180	= 325,698	= 265,045	64,362
1000	43,500	95,442	64,911	30,530	= 324,185	= 258,388	56,471

June 30, 1962; Mar. 31, 1967; Dec. 31, 1971

TUNGSTEN OXYTETRAFLUORIDE (WOF_4) (LIQUID) GFW = 275.843 F_4OW

$S^\circ_{298.15}$ = 42.8 ± 1.0 gibbs/mol

Tm = 379 K

Tb = 460 K

$\Delta Hf^\circ_{298.15}$ = -335.84 ± 15.00 kcal/mol

ΔHm° = 1.20 ± 1.00 kcal/mol

ΔHv° = 13.41 ± 2.00 kcal/mol

Heat of Formation

The heat of formation, $\Delta Hf^\circ_{298}(WOF_4, \ell)$ = -335.84 kcal/mol is calculated from that of the gas less the heat of vaporization, ΔHv°_{298} = 16.38 kcal/mol. This latter value was calculated by the third law method from the vapor pressure equation determined by Cady and Hargreaves (1). The second law value is ΔHv°_{298} = 16.50 kcal/mol.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom as suggested by Kubaschewski and Evans (2). The entropy, S°_{298} = 42.8 gibbs/mol is calculated by a second law analysis of the vapor pressure equation given by Cady and Hargreaves (1) for the system $WOF_4(\ell) \rightarrow WOF_4(g)$.

Melting Data

See $WOF_4(c)$ table (3).

Vaporization Data

Tb is calculated as the temperature at which the Gibbs energy of reaction $WOF_4(\ell) \rightarrow WOF_4(g)$ approaches zero. The difference between the heats of formation for the liquid and gas at the boiling point is ΔHv°.

Ruff, Eisner and Heller (4) reported the boiling point of $WOF_4(\ell)$ as 459 K. Cady and Hargreaves (1) calculated the boiling point as 459 K, and the heat of vaporization as 14.23 kcal/mol from the vapor pressure equation for the liquid. This second law value of ΔHv°, when corrected for ΔCp of vaporization, is in good agreement with the value adopted in the tabulation.

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Tungsten Oxytetrafluoride (WOF_4)

(Ideal Gas) GFW = 275.843

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	− 4.603	− 317.616	− 317.616	INFINITE
100	12.863	60.923	97.292	− 3.637	− 318.543	− 314.197	686.677
200	18.633	71.678	81.938	− 2.052	− 319.187	− 309.570	338.283
298	22.909	79.969	79.969	.000	− 319.460	− 304.781	223.411
300	22.974	80.111	79.969	.042	− 319.463	− 304.691	221.967
400	25.762	87.138	80.908	2.490	− 319.500	− 299.755	163.779
500	27.504	93.084	82.764	5.160	− 319.410	− 294.829	128.870
600	28.622	98.205	84.921	7.970	− 319.253	− 289.926	105.605
700	29.369	102.676	87.185	10.872	− 319.063	− 285.052	88.997
800	29.887	106.634	89.338	13.837	− 318.862	− 280.210	76.550
900	30.259	110.177	91.460	16.845	− 318.655	− 275.389	66.874
1000	30.533	113.380	93.495	19.885	− 318.452	− 270.593	59.138
1100	30.742	116.300	95.437	22.949	− 318.256	− 265.818	52.813
1200	30.903	118.982	97.289	26.032	− 318.066	− 261.057	47.545
1300	31.030	121.461	99.054	29.129	− 317.890	− 256.313	43.090
1400	31.132	123.764	100.738	32.237	− 317.724	− 251.584	39.274
1500	31.215	125.915	102.345	35.355	− 317.572	− 246.863	35.968
1600	31.284	127.932	103.882	38.480	− 317.435	− 242.155	33.077
1700	31.341	129.830	105.353	41.611	− 317.312	− 237.452	30.527
1800	31.389	131.623	106.763	44.747	− 317.206	− 232.761	28.261
1900	31.430	133.321	108.117	47.888	− 317.113	− 228.071	26.234
2000	31.465	134.934	109.418	51.033	− 317.037	− 223.384	24.410
2100	31.495	136.470	110.670	54.181	− 316.979	− 218.706	22.761
2200	31.521	137.936	111.876	57.332	− 316.939	− 214.030	21.262
2300	31.544	139.338	113.040	60.485	− 316.914	− 209.350	19.893
2400	31.564	140.681	114.164	63.641	− 316.907	− 204.673	18.638
2500	31.582	141.970	115.250	66.798	− 316.920	− 199.999	17.484
2600	31.598	143.209	116.302	69.957	− 316.949	− 195.320	16.418
2700	31.612	144.401	117.321	73.118	− 317.000	− 190.639	15.431
2800	31.625	145.551	118.309	76.280	− 317.083	− 185.958	14.515
2900	31.636	146.661	119.267	79.443	− 317.209	− 181.272	13.661
3000	31.647	147.734	120.198	82.607	− 317.383	− 176.585	12.864
3100	31.656	148.772	121.103	85.772	− 317.613	− 171.890	12.118
3200	31.665	149.777	121.984	88.938	− 317.910	− 167.188	11.418
3300	31.672	150.752	122.841	92.105	− 318.279	− 162.469	10.760
3400	31.679	151.697	123.676	95.272	− 318.728	− 157.739	10.139
3500	31.686	152.616	124.490	98.441	− 319.271	− 152.993	9.553
3600	31.692	153.508	125.283	101.610	− 319.932	− 148.233	8.999
3700	31.697	154.377	126.058	104.779	− 329.046	− 143.808	8.471
3800	31.702	155.222	126.814	107.949	− 329.158	− 138.385	7.959
3900	31.707	156.046	127.553	111.120	− 329.278	− 133.369	7.474
4000	31.711	156.848	128.276	114.290	− 329.401	− 128.342	7.012
4100	31.715	157.631	128.982	117.462	− 329.531	− 123.315	6.573
4200	31.719	158.396	129.673	120.633	− 329.666	− 118.283	6.155
4300	31.722	159.142	130.350	123.806	− 329.804	− 113.243	5.756
4400	31.726	159.871	131.013	126.978	− 329.951	− 108.210	5.375
4500	31.729	160.584	131.662	130.151	− 330.101	− 103.172	5.011
4600	31.731	161.282	132.298	133.324	− 330.255	− 98.125	4.662
4700	31.734	161.964	132.922	136.497	− 330.417	− 93.075	4.328
4800	31.737	162.632	133.534	139.670	− 330.581	− 88.020	4.008
4900	31.739	163.287	134.135	142.844	− 330.752	− 82.968	3.701
5000	31.741	163.928	134.724	146.018	− 330.927	− 77.910	3.405
5100	31.743	164.557	135.303	149.192	− 331.108	− 72.854	3.122
5200	31.745	165.173	135.872	152.367	− 331.292	− 67.782	2.849
5300	31.747	165.778	136.430	155.542	− 331.481	− 62.709	2.586
5400	31.749	166.371	136.979	158.716	− 331.677	− 57.646	2.333
5500	31.750	166.954	137.519	161.891	− 331.874	− 52.564	2.089
5600	31.752	167.526	138.050	165.066	− 332.079	− 47.483	1.853
5700	31.753	168.088	138.572	168.242	− 332.288	− 42.402	1.626
5800	31.755	168.640	139.085	171.417	− 332.499	− 37.312	1.406
5900	31.756	169.183	139.591	174.593	− 332.716	− 32.223	1.194
6000	31.757	169.717	140.089	177.768	− 526.842	− 25.045	.912

June 30, 1962; Mar. 31, 1967; Dec. 31, 1971

TUNGSTEN OXYTETRAFLUORIDE (WOF_4) (IDEAL GAS) GFW = 275.843 F_4OW

Point Group [C_{4v}] ΔHf°_0 = −317.62 ± 15.00 kcal/mol

$S^\circ_{298.15}$ = 79.97 ± 1.00 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −319.46 ± 15.00 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm⁻¹	ω, cm⁻¹	ω, cm⁻¹
1055 (1)	620 (1)	700 (2)
[300] (1)	[300] (1)	560 (2)
735 (1)	[200] (1)	[250] (2)

Bond Distance : W-O = [1.64] Å W-F = [1.82] Å

Bond Angle: O-W-F = [90°] F-W-F = [90°] σ = [4]

Product of Moment of Inertia: $I_AI_BI_C$ = [3.1909] x 10^{-113} g^3cm^6

Heat of Formation

The heat of formation, $\Delta Hf^\circ_{298.15}(WOF_4, g)$ = −319.46 kcal/mol, was calculated from the heat of reaction data of Zmbov, Uy, and Margrave (1). This data came from a mass spectrometric study of the equilibrium in the reaction:

$$2TaF_5(g) + WO_3(c) = 2TaOF_3(g) + WOF_4(g).$$

Heat Capacity and Entropy

The infrared spectra of WOF_4 and $MoOF_4$ in the vapor state are very similar (2, 3, 4) and have been interpreted on the basis of a monomeric unit with C_{4v} symmetry (5) by comparison with the spectrum of X_eOF_4 (6). Thus, as with X_eOF_4 and $MoOF_4$, gaseous WOF_4 is assumed to be C_{4v} symmetry with a square-pyramidal structure.

Blanchard (5) *and Reynes* (10) *reported the following vibrational assignments and frequencies, the Q frequency being adopted in this tabulation:*

ν_1 = 1064(R), 1055(Q), 1047(P); ν_7 = 705(R), 700(Q), 690(P); ν_3 = 745(R), 735(Q), 720(P); ν_8 = 560 cm⁻¹

Similar frequencies, as well as additional frequencies, have been reported by Ward and Stafford (4), Edwards et al. (3), and Edwards and Jones (2). The remaining frequencies and assignments are estimated with regard to the preceding references, the data for X_eOF_4 (6), and results for $MoOF_4$ (7).

There exists some controversy as to the crystallographic structure of WOF_4. Beattie et al. (8) suggest fluorine-bridged tetramers as in $MoOF_4$ (9) rather than an oxygen-bridged structure as suggested by Edwards and Jones (2). This leads to significantly different bond lengths for W-F and W-O. Due to the similarities in the melt, solid, and vapor phase infrared spectra of $MoOF_4$ and WOF_4, one would suspect similar structures (4, 8). The assumption is made that the structures are similar and thus the bond lengths are taken to be the same as those of $MoOF_4$. Further support for the bond length assumption is the similarity of bond lengths in MoO_3 and WO_3 and in MoF_6 and WF_6 (7).

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Potassium Hydroxide (KOH)

(Crystal) GFW = 56.10937

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	− 2.907	− 100.675	− 100.675	INFINITE
100	8.150	5.702	31.113	− 2.541	− 101.449	− 97.879	213.915
200	12.890	12.815	20.264	− 1.490	− 101.667	− 94.199	102.936
298	15.510	18.859	18.859	.000	− 101.510	− 90.567	66.387
300	15.538	18.955	18.860	.029	− 101.507	− 90.499	65.928
400	17.130	23.636	19.487	1.660	− 101.893	− 86.747	47.396
500	19.020	27.656	20.727	3.465	− 101.546	− 82.997	36.278
600	10.800	34.080	22.596	6.891	− 99.573	− 79.578	28.986
700	10.800	36.979	24.449	8.771	− 99.149	− 76.279	23.815
800	10.800	39.489	26.175	10.651	− 98.733	− 73.082	19.954
900	10.800	41.703	27.780	12.531	− 98.326	− 69.854	16.963
1000	10.800	43.684	29.273	14.411	− 97.942	− 66.712	14.580
1100	10.800	45.476	30.666	16.291	− 116.481	− 62.583	12.434
1200	10.800	47.112	31.969	18.171	− 115.889	− 57.708	10.510
1300	10.800	48.616	33.193	20.051	− 115.307	− 52.884	8.891
1400	10.800	50.010	34.345	21.931	− 114.733	− 48.103	7.509
1500	10.800	51.307	35.433	23.811	− 114.168	− 43.363	6.318

Dec. 31, 1961; Mar. 31, 1962; June 30, 1962; Mar. 31, 1966; Dec. 31, 1970

POTASSIUM HYDROXIDE (KOH) (CRYSTAL) GFW = 56.10937 HKO

$S^\circ_{298.15}$ = 18.86 ± 0.20 gibbs/mol

T_t = 516°K

T_m = 679°K

ΔHf°_0 = -100.7 ± 0.1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -101.5 ± 0.1 kcal/mol

ΔHt° = 1.54 ± 0.15 kcal/mol

ΔHm° = 2.06 ± 0.15 kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 45.9 ± 3.0 kcal/mol

$\Delta Hs^\circ_{298.15}$(to dimer) = 46.6 ± 3.0 kcal/mol

Heat of Formation

The heat of formation of KOH(c) is obtained from its heat of solution in water, the heat of hydrolysis of metallic potassium, and appropriate auxiliary data.

Reshetnikov (1) determined calorimetrically the heat of solution of KOH(c) in 650 H_2O as -13.665 ± 0.009 kcal/mol. Combining this result with heat of dilution data for KOH reported by Parker (2), we derive ΔH°soln.(KOH, c) = -13.77 ± 0.01 kcal/mol.

The heat of hydrolysis of metallic potassium has been determined by various investigators (3-5). The data are summarized below for the reaction

$$K(c) + (n + 1)H_2O(\ell) \rightarrow KOH{\cdot}nH_2O + 0.5\ H_2(g).$$

Investigator	n moles of H_2O	ΔHr°_{298} kcal/mol	ΔHf°_{298}(KOH(∞ H_2O))* kcal/mol	ΔHf°_{298}(KOH, c) kcal/mol
Gunn and Green (3a, 3b)	∞	-46.958±0.022	-115.273±0.022	-101.50±0.02
Messer et al. (4)	∞	-47.02 ±0.15	-115.34 ±0.15	-101.57±0.16
Ketchen and Wallace (5)	∞	-46.89 ±0.24	-115.21 ±0.24	-101.44±0.25

*Based on ΔHf°_{298}(H_2O, ℓ) = -68.315 kcal/mol (6).

The values of ΔHf°_{298}(KOH, c) given in the last column are calculated from ΔHf°_{298}(KOH,∞ H_2O) and the heat of solution of KOH(c) at infinite dilution given above. The adopted value for ΔHf°_{298}(KOH, c) is from the work of Gunn and Green (3a, 3b).

Earlier investigations pertaining to the determination of ΔHf°_{298}(KOH, c) have been reviewed by Bichowsky and Rossini (7) and Messer et al. (4) and are only of historical interest.

Heat Capacity and Entropy

The low temperature heat capacities for KOH(c) in the temperature range 20-298°K are from the recent work of Stull et al. (8). These data contain a broad lambda type transition with a heat capacity peak at 227.5°K. Powers and Blalock (9) measured high temperature enthalpy data for KOH(c) in both the α and β phases in a Bunsen ice calorimeter. Their enthalpy data are scattered and not precise enough to accurately define the heat capacities for the α phase. Therefore, the selected heat capaciites between 298° and 516°K are estimated by graphical extrapolation of the low temperature heat capacity data. Heat capacities for the β phase are from Powers and Blalock (9).

$S^\circ_{298.15}$ is calculated from the smoothed Cp data and is based on an extrapolation of S°_{20} = 0.129 gibbs/mol.

Transition and Melting Data

Several values for the heat of the α-β transition and the heat of melting of KOH have been reported in the literature. These data are summarized below.

Investigator	Method	Tt°K	ΔHt° kcal/mol	Tm°K	ΔHm° kcal/mol
Powers and Blalock (9)	Calorimetric	522	1.346	673	2.244
Seward and Martin (10)	Freezing Point			683	1.830
Kelley (11)	Freezing Point			633	1.980
Reshetnikov and Baranskaya (12)	Thermographic	515	1.540±0.15	679	1.980±0.15
Maurice (13)	Freezing Point	517		678	2.13 ±0.07

The selected values are from the work of Reshetnikov and Baranskaya (12) and Maurice (13).

Heat of Sublimation

ΔHs°_{298} for the monomer and dimer are calculated from the selected heats of vaporization and the heat of melting at 298.15°K. See KOH(g) table for details.

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HKO

Potassium Hydroxide (KOH)

(Liquid) GFW = 56.10937

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	19.863	23.085	23.085	.000	− 98.644	− 88.960	65.210
300	19.863	23.208	23.085	.037	− 98.633	− 88.900	64.764
400	19.863	28.922	23.864	2.023	− 98.663	− 85.632	46.787
500	19.863	33.354	25.335	4.009	− 98.135	− 82.435	36.032
600	19.863	36.976	26.983	5.996	− 97.602	− 79.344	28.901
700	19.863	40.037	28.635	7.982	− 97.072	− 76.343	23.835
800	19.863	42.690	30.229	9.968	− 96.550	− 73.419	20.057
900	19.863	45.029	31.746	11.955	− 96.038	− 70.558	17.134
1000	19.863	47.122	33.181	13.941	− 95.545	− 67.753	14.807
1100	19.863	49.015	34.536	15.927	− 113.979	− 63.973	12.710
1200	19.863	50.743	35.816	17.913	− 113.280	− 59.457	10.829
1300	19.863	52.333	37.026	19.900	− 112.592	− 55.001	9.247
1400	19.863	53.805	38.172	21.886	− 111.911	− 50.596	7.898
1500	19.863	55.176	39.261	23.872	− 111.240	− 46.239	6.737
1600	19.863	56.458	40.296	25.859	− 110.579	− 41.928	5.727
1700	19.863	57.662	41.282	27.845	− 109.925	− 37.658	4.841
1800	19.863	58.797	42.224	29.831	− 109.280	− 33.425	4.058
1900	19.863	59.871	43.125	31.818	− 108.644	− 29.229	3.362
2000	19.863	60.890	43.988	33.804	− 108.015	− 25.065	2.739

Dec. 31, 1961; Mar. 31, 1962; Sept. 30, 1962; Mar. 31, 1966; Dec. 31, 1970

POTASSIUM HYDROXIDE (KOH) (LIQUID) GFW = 56.10937 HKO

$S^\circ_{298.15}$ = 23.08 ± 0.50 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −98.644 ± 0.5 kcal/mol

Tm = 679°K

ΔHm° = 2.06 ± 0.15 kcal/mol

Tb(to monomer) = 1596°K

ΔHv°(to monomer) = 34.1 kcal/mol

Heat of Formation

The heat of formation of KOH(ℓ) at 298.15°K is obtained from that of the crystal by adding ΔHm and the difference between $H_{679}-H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid phase is obtained from the high temperature enthalpy measurements of Powers and Blalock (1). The constant Cp is extrapolated below the melting point and up to 2000°K.

$S^\circ_{298.15}$ is obtained in a manner analogous to that of the heat of formation.

Melting Data

See KOH(c) table for details.

Vaporization Data

Tb is calculated as the temperature at which the free energies of formation of KOH(ℓ) and KOH(g) are equal. The difference in the heats of formation of KOH(ℓ) and KOH(g) at the boiling point is the heat of vaporization. If $K_2(OH)_2(g)$ is also considered a minor component in the vapor mixture (approximately 2% of the total vapor pressure at the boiling point) the calculated boiling point is unchanged.

Wartenberg and Albrecht (2) reported a boiling point of 1597°K for KOH from static vapor pressure measurements, while very recently Dubois and Millet (3) determined a boiling point of 1540°K from transpiration vapor pressure measurements.

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HKO

Potassium Hydroxide (KOH)

(Ideal Gas) GFW = 56.10937

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.730	-54.588	-54.588	INFINITE
100	7.874	45.729	45.898	-2.017	-55.015	-55.448	121.181
200	10.439	52.052	57.500	-1.090	-55.357	-55.737	60.906
298	11.599	56.469	56.469	.000	-55.600	-55.870	40.954
300	11.613	56.541	56.469	.021	-55.605	-55.872	40.703
400	12.136	59.962	56.932	1.212	-55.830	-55.815	30.496
500	12.407	62.703	57.822	2.440	-55.660	-55.634	24.318
600	12.576	64.981	58.830	3.690	-55.464	-55.400	20.183
700	12.712	66.930	59.851	4.955	-55.255	-55.151	17.219
800	12.835	68.635	60.845	6.232	-55.042	-54.868	14.989
900	12.959	70.154	61.796	7.522	-54.827	-54.559	13.249
1000	13.083	71.526	62.702	8.824	-54.618	-54.230	11.852
1100	13.207	72.779	63.562	10.139	-54.423	-52.858	10.502
1200	13.327	73.933	64.379	11.465	-54.485	-50.689	9.232
1300	13.442	75.004	65.155	12.804	-54.644	-48.526	8.158
1400	13.551	76.005	65.895	14.154	-54.800	-46.364	7.238
1500	13.652	76.943	66.601	15.514	-54.955	-44.205	6.441
1600	13.746	77.827	67.275	16.884	-54.510	-42.050	5.744
1700	13.832	78.663	67.920	18.263	-54.463	-39.898	5.129
1800	13.911	79.456	68.539	19.650	-54.417	-37.749	4.583
1900	13.983	80.210	69.134	21.045	-54.373	-35.602	4.095
2000	14.048	80.929	69.706	22.446	-54.329	-33.457	3.656
2100	14.108	81.616	70.257	23.854	-54.287	-31.314	3.259
2200	14.162	82.274	70.788	25.268	-54.251	-29.173	2.898
2300	14.212	82.904	71.301	26.686	-54.217	-27.035	2.569
2400	14.257	83.510	71.798	28.110	-54.188	-24.896	2.267
2500	14.299	84.093	72.278	29.538	-54.166	-22.762	1.990
2600	14.336	84.654	72.743	30.970	-54.148	-20.623	1.733
2700	14.371	85.196	73.194	32.405	-54.140	-18.489	1.497
2800	14.403	85.719	73.632	33.844	-54.140	-16.355	1.277
2900	14.432	86.225	74.058	35.285	-54.148	-14.216	1.071
3000	14.459	86.715	74.472	36.730	-54.166	-12.083	.880
3100	14.483	87.190	74.874	38.177	-54.196	-9.945	.701
3200	14.506	87.650	75.266	39.626	-54.237	-7.807	.533
3300	14.527	88.096	75.648	41.078	-54.292	-5.670	.375
3400	14.547	88.530	76.021	42.532	-54.362	-3.530	.227
3500	14.565	88.952	76.384	43.987	-54.448	-1.386	.087
3600	14.582	89.363	76.739	45.445	-54.552	.762	.046
3700	14.597	89.763	77.086	46.904	-54.677	2.910	.172
3800	14.612	90.152	77.425	48.364	-54.823	5.063	.291
3900	14.625	90.532	77.756	49.826	-54.993	7.219	.405
4000	14.638	90.902	78.080	51.289	-55.190	9.381	.513
4100	14.650	91.264	78.397	52.754	-55.416	11.549	.616
4200	14.661	91.617	78.708	54.219	-55.674	13.722	.714
4300	14.671	91.962	79.012	55.686	-55.966	15.903	.808
4400	14.681	92.300	79.310	57.153	-56.296	18.087	.898
4500	14.690	92.630	79.602	58.622	-56.669	20.283	.985
4600	14.699	92.953	79.889	60.092	-57.085	22.488	1.068
4700	14.707	93.269	80.170	61.562	-57.549	24.701	1.149
4800	14.715	93.578	80.447	63.033	-58.062	26.926	1.226
4900	14.722	93.882	80.718	64.505	-58.629	29.159	1.301
5000	14.729	94.179	80.984	65.977	-59.251	31.402	1.373
5100	14.735	94.471	81.246	67.451	-59.933	33.658	1.443
5200	14.741	94.757	81.503	68.924	-60.675	35.938	1.510
5300	14.747	95.038	81.755	70.399	-61.479	38.229	1.576
5400	14.753	95.314	82.004	71.874	-62.348	40.528	1.640
5500	14.758	95.585	82.248	73.349	-63.280	42.850	1.703
5600	14.763	95.851	82.489	74.825	-64.278	45.188	1.764
5700	14.768	96.112	82.726	76.302	-65.338	47.544	1.823
5800	14.772	96.369	82.959	77.779	-66.463	49.921	1.881
5900	14.776	96.621	83.188	79.256	-67.646	52.319	1.938
6000	14.780	96.870	83.414	80.734	-68.892	54.738	1.994

Mar. 31, 1962; June 30, 1962; Mar. 31, 1966; Dec. 31, 1970

POTASSIUM HYDROXIDE (KOH) (IDEAL GAS) GFW = 56.10937 HKO

Point Group $C_{\infty v}$ ΔHf°_0 = -54.6 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = [56.47 ± 0.30] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -55.6 ± 3.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹
408 (1)
[340] (2)
[3610] (1)

Bond Distance: K-O = 2.18 ± 0.01 Å O-H = [0.97 ± 0.05] Å

Bond Angle: K-O-H = 180° σ = 1

Rotational Constant: B_0 = 0.27989 cm⁻¹

Heat of Formation

Mass spectrometric studies (1-5) of the equilibrium gases over pure KOH(c, ℓ) and mixed KOH-NaOH condensed phases have unequivocally identified the vapor species as monomer and dimer in the temperature range 600-700°K. Absolute partial pressures for KOH(g) and $K_2(OH)_2$(g) have been determined from peak intensity data by Porter and Schoonmaker (3) and Gusarov and Gorokhov (5). These data are analyzed by the third law method with JANAF free energy functions (6) in order to evaluate a heat of dimerization at 298°K. The adopted value is ΔH_{298} = -45.3 ± 3.0 kcal/mol for the reaction 2KOH(g) = $K_2(OH)_2$(g).

Vapor pressures for liquid KOH have been determined by static (1443-1600°K) (7) and transpiration (873-1323°K) (8) methods. In order to evaluate ΔHv°_{298}(KOH, ℓ), we have used a trial and error variation of ΔHv°_{298} for the monomer and dimer, such that these values are in accordance with the adopted heat of dimerization given above, and the sum of the calculated partial pressures for KOH(g) and $K_2(OH)_2$(g) is in good agreement with the experimental vapor pressure data. Since the dimer to monomer ratio decreases with increasing temperature, more weight is given to the static data of Wartenberg and Albrecht (7). The selected values are: ΔHv°_{298}(to monomer) = 43.0 ± 3.0 kcal/mol and ΔHv°_{298}(to dimer) = 40.8 ± 3.0 kcal/mol. From these results we derive ΔHf°_{298} (KOH, g) = -55.6 ± 3.0 kcal/mol with ΔHf°_{298}(KOH, ℓ) = -98.64 ± 0.50 kcal/mol (6). This value is adopted here and when used in combination with the heat of dimerization results in ΔHf°_{298}($K_2(OH)_2$, g) = -156.5 ± 3.0 kcal/mol.

The bond dissociation energies of the alkali metal hydroxides have been determined by several workers from flame studies (9-11) and by mass spectrometry (12). The data for KOH are summarized below.

Investigator	Method	Reaction	ΔHr°_{298}, kcal/mol 3rd Law	D_0(K-OH) kcal/mol
Smith and Sugden (9)	Flame	A		86 ± 1
Jensen and Padley (10)	Flame	A	36.4	82 ± 2
Cotton and Jenkins (11)	Flame	A	32.5	86 ± 2
Gorokhov et al. (12)	Mass Spec.			80 ± 3

Reaction: (A) K(g) + H_2O(g) ⇌ KOH(g) + H(g)

Our adopted heat of formation for KOH(g) leads to D_0 = 85.4 ± 3.0 kcal/mol, which is in reasonable agreement with the results of the flame studies (9-11), particularly when one considers the difficulties inherent in this method.

Heat Capacity and Entropy

Kuczkowski et al. (13) observed the microwave spectra of gaseous KOH and interpreted the results in terms of a linear geometry. Very recently, microwave studies of gaseous CsOH (14a) and RbOH (14b), along with infrared spectra of matrix-isolated CsOH (15a), RbOH (15b), and NaOH (15b) have been reported and interpreted in terms of linear structures for all these molecules. We adopt a linear configuration for KOH(g), along with the bond distances determined by Kuczkowski et al. (13) from their microwave studies.

Acquista and Abramowitz (15b) attempted to measure the infrared spectrum of matrix-isolated monomeric KOH but observed bands which could only be ascribable to polymeric species. Spinar and Margrave (16) investigated the infrared spectrum of the equilibrium gases over liquid KOH at temperatures up to 1000°K. An absorption band at 408 ± 10 cm⁻¹ was assigned to the K-OH stretching by these workers, and this assignment is adopted here. The doubly degenerate bending and O-H stretching frequencies are estimates taken from the recent work of Jensen (17). The principal moment of inertia is 10.001 x 10^{-39} g cm².

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HKO

Potassium Hydroxide Unipositive Ion (KOH^+)

(Ideal Gas) GFW = 56.1088

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	11,826	59,804	59,804	,000	119,000	116,248	= 85,212
300	11,838	59,877	59,804	,022	119,005	116,231	= 84,674
400	12,277	63,350	60,274	1,230	118,694	115,375	= 63,038
500	12,503	66,117	61,176	2,470	118,973	114,513	= 50,054
600	12,647	68,410	62,196	3,728	119,274	113,594	= 41,377
700	12,764	70,368	63,227	4,999	119,585	112,622	= 35,162
800	12,877	72,080	64,229	6,281	119,900	111,605	= 30,489
900	12,993	73,603	65,187	7,575	120,216	110,550	= 26,845
1000	13,111	74,978	66,099	8,880	120,524	109,459	= 23,922
1100	13,231	76,238	66,964	10,197	101,919	109,362	= 21,728
1200	13,349	77,390	67,785	11,526	102,456	110,016	= 20,037
1300	13,461	78,463	68,566	12,866	102,996	110,623	= 18,597
1400	13,568	79,464	69,309	14,218	103,538	111,190	= 17,358
1500	13,668	80,404	70,017	15,580	104,082	111,719	= 16,277
1600	13,760	81,289	70,695	16,951	104,625	112,209	= 15,327
1700	13,845	82,126	71,343	18,331	105,169	112,666	= 14,484
1800	13,922	82,919	71,964	19,720	105,714	113,091	= 13,731
1900	13,993	83,674	72,560	21,116	106,256	113,486	= 13,054
2000	14,058	84,394	73,134	22,518	106,798	113,853	= 12,441
2100	14,117	85,081	73,687	23,927	107,337	114,193	= 11,884
2200	14,171	85,739	74,220	25,342	107,871	114,507	= 11,375
2300	14,220	86,370	74,735	26,761	108,403	114,796	= 10,908
2400	14,265	86,976	75,232	28,185	108,930	115,064	= 10,478
2500	14,305	87,559	75,714	29,614	109,449	115,306	= 10,080
2600	14,343	88,121	76,180	31,046	109,963	115,533	= 9,711
2700	14,377	88,663	76,632	32,482	110,470	115,735	= 9,368
2800	14,408	89,186	77,071	33,922	110,967	115,921	= 9,048
2900	14,437	89,692	77,498	35,364	111,456	116,092	= 8,749
3000	14,464	90,182	77,913	36,809	111,936	116,242	= 8,468
3100	14,488	90,657	78,316	38,257	112,403	116,378	= 8,205
3200	14,511	91,117	78,709	39,707	112,859	116,500	= 7,957
3300	14,532	91,564	79,092	41,159	113,302	116,605	= 7,722
3400	14,551	91,998	79,465	42,613	113,729	116,697	= 7,501
3500	14,569	92,420	79,829	44,069	114,140	116,779	= 7,292
3600	14,586	92,831	80,185	45,527	114,533	116,851	= 7,094
3700	14,601	93,231	80,532	46,986	114,905	116,909	= 6,905
3800	14,616	93,620	80,871	48,447	115,257	116,959	= 6,727
3900	14,630	94,000	81,203	49,909	115,584	116,998	= 6,556
4000	14,642	94,371	81,528	51,373	115,884	117,030	= 6,394
4100	14,654	94,733	81,845	52,838	116,155	117,056	= 6,240
4200	14,666	95,086	82,156	54,304	116,394	117,076	= 6,092
4300	14,677	95,431	82,461	55,771	116,600	117,091	= 5,951
4400	14,687	95,769	82,760	57,239	116,766	117,098	= 5,816
4500	14,696	96,099	83,052	58,708	116,890	117,105	= 5,687
4600	14,706	96,422	83,340	60,178	116,973	117,110	= 5,564
4700	14,715	96,738	83,621	61,649	117,007	117,113	= 5,446
4800	14,723	97,048	83,898	63,121	116,992	117,117	= 5,332
4900	14,731	97,352	84,169	64,594	116,922	117,119	= 5,224
5000	14,739	97,649	84,436	66,067	116,797	117,119	= 5,119
5100	14,747	97,941	84,698	67,542	116,613	117,134	= 5,020
5200	14,754	98,228	84,955	69,017	116,369	117,143	= 4,923
5300	14,762	98,509	85,208	70,492	116,063	117,163	= 4,831
5400	14,769	98,785	85,457	71,969	115,693	117,182	= 4,743
5500	14,776	99,056	85,702	73,446	115,259	117,214	= 4,658
5600	14,782	99,322	85,943	74,924	114,760	117,253	= 4,576
5700	14,789	99,584	86,180	76,403	114,199	117,302	= 4,498
5800	14,796	99,841	86,413	77,882	113,573	117,363	= 4,422
5900	14,802	100,094	86,643	79,362	112,888	117,436	= 4,350
6000	14,809	100,343	86,869	80,842	112,142	117,521	= 4,281

Dec. 31, 1971

POTASSIUM HYDROXIDE UNIPOSITIVE ION (KOH^+) (IDEAL GAS) GFW = 56.1088

Point Group [$C_{\infty v}$] ΔHf°_0 = 118 ± 10 kcal/mol

$S^\circ_{298.15}$ = [59.8 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 119 ± 10 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[375] (1)
[300] (2)
[3600] (1)

Bond Distance: K-O = [2.20] Å O-H = [1.03] Å

Bond Angle: Na-O-H = [180]° σ = 1

Rotational Constant: B_0 = [0.27367] cm^{-1}

Heat of Formation

Porter and Schoonmaker (1) obtained an appearance potential curve near threshold for KOH^+ which extrapolates to 7.8 eV at zero ion current. They presented evidence which indicated that a large fraction of KOH^+ was formed by dissociative ionization of the dimer. In a later study, these same workers (2) rejected their earlier results, since it was found that the presence of magnesia in their cell had reduced the activity of the hydroxide. Gusarov and Gorokhov (3) in a similar mass spectrometric study of the evaporation products of KOH have shown that KOH^+ is formed primarily from direct ionization of the hydroxide. Very recently, Gorokhov et al. (4) reported the appearance potential of KOH^+ from KOH as 7.5 ± 0.2 eV. We adopt this result as ΔHr_0 for the process $e^- + KOH(g) \rightarrow KOH^+(g) + 2e^-$, since it is consistent with the expected mode of ionization. This value leads to $\Delta Hf^\circ_0(KOH^+, g)$ = 118 ± 10 kcal/mol when used in conjunction with $\Delta Hf^\circ_0(KOH, g)$ = −54.6 ± 3.0 kcal/mol (5).

Heat Capacity and Entropy

The configuration of KOH^+ is predicted to be linear by Walsh (6), since it has seven valence electrons. The same correlation predicts that the unpaired electron is in a pi orbital, thus, the ground state of KOH^+ is $^2\Pi$. A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with the isoelectronic molecules OH (5) and SH (5). The vibrational frequencies are estimated from those for KOH with somewhat lower values to account for the effect of weaker bonding predicted for the positive ion. Similarly, the K-O and O-H bond distances are increased slightly over those for KOH.

The enthalpy at 0 K is −2.811 kcal/mol.

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J. Phys. Chem. Ref. Data, Vol. 3, No. 2, 1974

Lithium Hydroxide (LiOH)

(Crystal) GFW = 23.9464

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	− 1.772	− 114.518	− 114.518	INFINITE
100	3.500	2.046	18.436	− 1.639	− 115.230	− 111.970	244.709
200	8.599	6.126	11.229	− 1.021	− 115.701	− 108.504	118.547
298	11.853	10.235	10.234	.000	− 115.900	− 104.920	76.908
300	11.893	10.308	10.235	.022	− 115.902	− 104.853	76.385
400	13.875	14.024	10.728	1.319	− 115.929	− 101.161	55.272
500	15.212	17.271	11.719	2.776	− 114.605	− 97.400	42.574
600	16.302	20.143	12.888	4.353	− 114.468	− 93.570	34.083
700	17.275	22.730	14.112	6.032	− 114.229	− 89.772	28.028
800	18.185	25.096	15.339	7.806	− 115.899	− 86.015	23.498
900	19.060	27.249	16.547	9.668	− 115.491	− 82.303	19.986
1000	19.911	29.341	17.725	11.617	− 115.005	− 78.640	17.187
1100	20.749	31.278	18.869	13.650	− 114.442	− 75.030	14.907
1200	21.576	33.119	19.981	15.766	− 113.805	− 71.475	13.017
1300	22.396	34.879	21.060	17.965	− 113.093	− 67.977	11.428
1400	23.211	36.548	22.107	20.245	− 112.306	− 64.535	10.074
1500	24.022	38.197	23.126	22.607	− 111.446	− 61.152	8.910

Dec. 31, 1950; Mar. 31, 1966; June 30, 1971

LITHIUM HYDROXIDE (LiOH) (CRYSTAL) GFW = 23.9464 HLiO

$S^\circ_{298.15}$ = 10.23 ± 0.05 gibbs/mol

Tm = 744.3 K

ΔHf°_0 = −114.5 ± 0.1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −115.9 ± 0.1 kcal/mol

ΔHm° = 4.99 ± 0.05 kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 59.9 ± 1.5 kcal/mol

$\Delta Hs^\circ_{298.15}$(to dimer) = 61.8 ± 8.0 kcal/mol

Heat of Formation

The heat of formation of crystalline LiOH is determined from calorimetric studies on the heat of hydrolysis of metallic lithium and the heat of solution of the hydroxide in water.

Reshetnikov (1) determined the heat of solution of LiOH(c) in 400 H_2O as −5.479 ± 0.007 kcal/mol. Combining this result with heat of dilution data for LiOH tabulated by Parker (2), we derive ΔH°_{soln}(LiOH, c) = −5.632 ± 0.020 kcal/mol, which is essentially the value recommended by Parker (2). Lower values by some 600-650 cal/mol for the heat of solution of LiOH(c) are summarized by Parker (2). The discrepancy in these values probably arises from carbonate and water impurities in the LiOH samples. Since their presence would tend to reduce the heat of solution, we adopt the higher results of Reshetnikov (1).

Gunn and Green (3a, 3b) and Messer et al. (4) measured the heat of hydrolysis of metallic lithium. Their results for the reaction

$$Li(c) + (n+1)\ H_2O \rightarrow LiOH{\cdot}n\ H_2O + 0.5\ H_2(g)$$

are summarized below.

Investigator	n Moles of H_2O	ΔHh°_{298}* kcal/mol	ΔHf°_{298}(LiOH∞ H_2O)** kcal/mol	ΔHf°_{298}(LiOH, c) kcal/mol
Gunn and Green (3a, 3b)	1000	−53.210±0.040	−121.525±0.040	−115.893±0.060
Messer et al. (4)	70	−53.05 ±0.20	−121.37 ±0.20	−115.74 ±0.20

* Dilution data from Parker (2)

** Based on $\Delta Hf^\circ_{298}(H_2O, \ell)$ = −68.315 kcal/mol (5).

Combination of the ΔHf°_{298}(LiOH∞ H_2O) values with the heat of solution of LiOH(c) given above results in the values for ΔHf°_{298}(LiOH, c) given in the last column. The adopted value is from the work of Gunn and Green (3a, 3b) with minor adjustments in the uncertainty interval to include possible errors in some of the auxiliary data used in the calculations.

Heat Capacity and Entropy

Heat capacities for LiOH(c) in the temperature range 15-300 K are those of Bauer et al. (6). Heat capacities above 300 K are calculated from the high temperature (418-878 K) enthalpy data of Shomate and Cohen (7). Both sets of data were smoothed by computer and joined at 298.15 K. The rapid rise in the enthalpy data of Shomate and Cohen (7) near the melting point is attributed to premelting and data in the temperature range 725-732 K were not used in the fit. Powers and Blalock (8) also measured high temperature (397-1213 K) enthalpy data for LiOH(c) in a Bunsen ice calorimeter. Although their results are less precise than those of Shomate and Cohen (7), the two sets of measurements are in reasonable agreement.

$S^\circ_{298.15}$ is determined from the smoothed Cp data of Bauer et al. (6) and is based on an extrapolation of S°_{15} = 0.027 gibbs/mol.

Transition and Melting Data

The adopted heat of melting and melting point for LiOH are from the enthalpy measurements of Shomate and Cohen (7). Powers and Blalock (8) reported ΔHm° = 5.029 kcal/mol at 746 K from their enthalpy measurements on LiOH. Very recently, Reshetnikov and Baranskaya (9) reported a slightly higher value of 5.29 kcal/mol at 747 K which was determined by a thermographic method.

Heat of Sublimation

ΔHs°_{298} values for the monomer and dimer are calculated from the adopted heats of formation for the gaseous species and the crystal.

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HLiO

Lithium Hydroxide (LiOH)

(Liquid) GFW = 23.9464

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	20.814	11.488	11.488	.000	-113.393	-102.787	75.345
300	20.814	11.617	11.488	.039	-113.378	-102.722	74.833
400	20.814	17.604	12.305	2.120	-112.621	-99.285	54.287
500	20.814	22.249	13.846	4.201	-112.672	-95.957	41.943
600	20.814	26.044	15.572	6.283	-112.031	-92.674	33.756
700	20.814	29.252	17.303	8.364	-111.390	-89.499	27.943
800	20.814	32.031	18.975	10.446	-110.752	-86.416	23.608
900	20.814	34.483	20.564	12.527	-110.125	-83.411	20.255
1000	20.814	36.676	22.068	14.608	-109.506	-80.476	17.588
1100	20.814	38.660	23.487	16.690	-108.895	-77.603	15.418
1200	20.814	40.471	24.828	18.771	-108.293	-74.785	13.620
1300	20.814	42.137	26.096	20.853	-107.698	-72.017	12.107
1400	20.814	43.679	27.298	22.934	-107.111	-69.294	10.817
1500	20.814	45.115	28.438	25.015	-106.531	-66.613	9.706
1600	20.814	46.459	29.523	27.097	-105.958	-63.971	8.738
1700	20.814	47.720	30.557	29.178	-140.438	-60.035	7.718
1800	20.814	48.910	31.544	31.260	-139.696	-55.326	6.715
1900	20.814	50.036	32.488	33.341	-138.963	-50.658	5.827
2000	20.814	51.103	33.392	35.422	-138.237	-46.031	5.030
2100	20.814	52.119	34.260	37.504	-137.519	-41.439	4.313
2200	20.814	53.087	35.094	39.585	-136.809	-36.880	3.664
2300	20.814	54.012	35.896	41.667	-136.105	-32.354	3.074
2400	20.814	54.898	36.670	43.748	-135.412	-27.857	2.537
2500	20.814	55.748	37.416	45.829	-134.726	-23.391	2.045

Dec. 31, 1960; Mar. 31, 1965; June 30, 1971

LITHIUM HYDROXIDE (LiOH) (LIQUID) GFW = 23.9464 HLiO

$S^\circ_{298.15}$ = 11.49 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -113.393 kcal/mol

Tm = 744.3 K

ΔHm° = 4.99 ± 0.05 kcal/mol

Tb(to monomer) = 1899 K

ΔHv°(to monomer) = 44.9 kcal/mol

Heat of Formation

The heat of formation of LiOH(ℓ) at 298.15 K is obtained from that of the crystal by adding ΔHm and the difference between $H_{Tm}-H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid phase is obtained from the high temperature enthalpy measurements (750-875 K) of Shomate and Cohen (1). We derive a constant Cp of 20.814 gibbs/mol for LiOH(ℓ) from these enthalpy data. The average percent deviation of the linear fit of the data was 0.2%. Powers and Blalock (2) also determined a constant Cp (22.03 gibbs/mol) for LiOH(ℓ) from enthalpy data (746-1200 K) determined by drop calorimetry.

$S^\circ_{298.15}$ is obtained in a manner analogous to that of the heat of formation.

Melting Data

See LiOH(c) table for details.

Vaporization Data

Dissociation pressures for LiOH(c, ℓ) have been measured by static (4), effusion (5, 6), and transpiration (6) methods. These data are combined with the equilibrium studies of Berkowitz et al. (3) to give either ΔHs°_{298}, or ΔHv°_{298}. An analysis of the data is summarized below, and further discussion of these results is presented on the LiOH(g) table under Heat of Formation.

Investigator	Reaction	Method	Temp. Range K	No. of Points	ΔHr, kcal/mol 2nd Law	ΔHr, kcal/mol 3rd Law	Drift gibbs/mol	ΔHs°_{298} [a] kcal/mol	ΔHv°_{298} [a] kcal/mol
Berkowitz et al. (3)	A	Mass. Spec.	1120-1450	18	82.3	82.9±1.9	0.5±2.6		
Johnston (4)	B	Static	793-1176	9[b]	34.7	25.9±2.1	-8.5±0.4		54.4±5.0
Ditmars and	C	Effusion	648-736	11	37.8	39.5±1.0	2.6±5.4	61.2±3.0	
Johnston (5)	B	Effusion	752-795	7	35.5	34.3±0.9	-1.9±12.9		58.6±3.0
Gregory and Mohr (6)	C	Transpiration and Effusion	525-675	Equation	32.1	32.7±0.1	0.9±0.1	57.8±2.0	

(A) $Li_2O(c) + H_2O(g) = 2LiOH(g)$ (B) $2LiOH(\ell) = Li_2O(c) + H_2O(g)$ (C) $2LiOH(c) = Li_2O(c) + H_2O(g)$

[a] Third Law Values.

[b] One point rejected due to failure of a statistical test.

The boiling point is determined as the temperature at which the free energies of formation for LiOH(g) and LiOH(ℓ) become equal. The difference in their heats of formation at the boiling point is the heat of vaporization.

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Lithium Hydroxide (LiOH)

(Ideal Gas) GFW = 23.9464

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	2.600	55.445	55.445	INFINITE
100	7.570	40.233	59.174	1.894	55.585	56.143	122.701
200	9.728	46.168	51.294	1.025	55.808	56.817	61.868
298	11.095	50.321	50.321	.000	56.000	56.972	41.762
300	11.042	50.389	50.321	.020	56.008	56.979	41.509
400	11.731	53.671	50.764	1.163	56.185	57.276	31.294
500	12.116	56.333	51.620	2.357	57.124	57.451	25.112
600	12.361	58.565	52.597	3.581	57.340	57.495	20.943
700	12.543	60.485	53.590	4.827	57.538	57.506	17.958
800	12.698	62.170	54.559	6.089	57.716	57.491	15.706
900	12.843	63.674	55.490	7.366	57.893	57.451	13.951
1000	12.983	65.035	56.377	8.657	58.064	57.393	12.543
1100	13.119	66.279	57.222	9.963	58.229	57.318	11.388
1200	13.248	67.426	58.025	11.281	58.390	57.228	10.423
1300	13.371	68.491	58.789	12.612	58.545	57.125	9.604
1400	13.486	69.486	59.518	13.955	58.697	57.010	8.900
1500	13.593	70.420	60.214	15.309	58.844	56.884	8.288
1600	13.691	71.301	60.880	16.673	58.988	56.749	7.751
1700	13.781	72.134	61.518	18.047	59.126	55.276	7.106
1800	13.864	72.924	62.130	19.429	59.134	52.988	6.434
1900	13.939	73.675	62.718	20.819	59.091	50.707	5.832
2000	14.008	74.392	63.284	22.217	59.049	48.421	5.291
2100	14.070	75.077	63.829	23.621	59.009	46.141	4.802
2200	14.127	75.733	64.355	25.031	58.971	43.862	4.357
2300	14.179	76.362	64.864	26.446	58.933	41.586	3.952
2400	14.226	76.966	65.355	27.866	58.900	39.316	3.580
2500	14.270	77.548	65.832	29.291	58.871	37.037	3.238
2600	14.309	78.109	66.293	30.720	58.844	34.764	2.922
2700	14.345	78.649	66.741	32.153	58.823	32.493	2.630
2800	14.379	79.172	67.175	33.589	58.805	30.222	2.359
2900	14.409	79.677	67.598	35.029	58.795	27.949	2.106
3000	14.437	80.166	68.009	36.471	58.789	25.679	1.871
3100	14.463	80.640	68.408	37.916	58.791	23.408	1.650
3200	14.487	81.099	68.798	39.363	58.798	21.139	1.444
3300	14.509	81.545	69.177	40.813	58.818	18.868	1.250
3400	14.529	81.979	69.548	42.265	58.837	16.596	1.067
3500	14.548	82.400	69.909	43.719	58.867	14.325	.894
3600	14.546	82.810	70.262	45.175	58.907	12.051	.732
3700	14.582	83.210	70.606	46.632	58.956	9.777	.578
3800	14.598	83.599	70.943	48.091	59.014	7.497	.431
3900	14.612	83.978	71.272	49.552	59.081	5.221	.293
4000	14.625	84.348	71.595	51.014	59.159	2.943	.161
4100	14.638	84.709	71.910	52.477	59.248	.660	.035
4200	14.649	85.062	72.219	53.941	59.347	1.622	.084
4300	14.660	85.407	72.522	55.407	59.457	3.909	.199
4400	14.670	85.746	72.818	56.873	59.579	6.198	.308
4500	14.680	86.078	73.109	58.341	59.714	8.489	.412
4600	14.689	86.397	73.395	59.809	59.860	10.787	.512
4700	14.697	86.713	73.675	61.278	59.021	13.083	.608
4800	14.706	87.022	73.950	62.749	59.195	15.384	.700
4900	14.713	87.326	74.219	64.219	59.384	17.688	.789
5000	14.720	87.623	74.485	65.691	59.587	19.999	.874
5100	14.727	87.914	74.745	67.164	59.808	22.316	.956
5200	14.733	88.200	75.001	68.637	59.045	24.632	1.035
5300	14.740	88.481	75.253	70.110	59.300	26.956	1.112
5400	14.745	88.757	75.500	71.584	59.573	29.281	1.185
5500	14.751	89.027	75.744	73.059	59.866	31.618	1.256
5600	14.756	89.293	75.983	74.535	57.180	33.951	1.325
5700	14.761	89.554	76.219	76.010	57.516	36.298	1.392
5800	14.766	89.811	76.451	77.487	57.875	38.651	1.456
5900	14.770	90.064	76.680	78.964	58.256	41.007	1.519
6000	14.774	90.312	76.905	80.441	58.664	43.372	1.580

Dec. 31, 1980; Mar. 31, 1966; June 30, 1971

HLiO

LITHIUM HYDROXIDE (LiOH) (IDEAL GAS) GFW = 23.9464

Point Group $C_{\infty v}$ ΔHf°_0 = −55.4 ± 1.5 kcal/mol

$S^\circ_{298.15}$ = [50.32 ± 0.50] gibbs/mol $\Delta Hf^\circ_{298.15}$ = −55.0 ± 1.5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies ω, cm^{-1}

[630] (1) [362] (2) [3666] (1)

Bond Distance: Li-O = 1.582 Å O-H = [0.97] Å σ = 1

Bond Angle: Li-O-H = 180° Rotational Constant: B_0 = 1.1923 cm^{-1}

Heat of Formation

Smith and Sugden (1) provided the first information on the stability of gaseous LiOH by studying its formation in hydrogen-air flames. Very recently, other flame photometric studies (3 - 5) have been reported on LiOH(g), primarily in connection with establishing its bond dissociation energy. Mass spectrometry (6 - 7) has also provided additional information on the stability of this species. These investigations have resulted in a wealth of equilibrium data involving this compound. Second and third law analyses of these data are presented in tabular form below. Vapor pressure data for LiOH(c, ℓ) are analyzed under Heat of Vaporization (see LiOH(ℓ) table); these data lead to ΔHf°_{298}(LiOH, g) values of −59.0, −54.7, −54.8 and −58.1 kcal/mol.

Investigator	Reaction	Method	Temp. Range K	No. of Points	ΔHr_{298} kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	ΔHf°_{298}(LiOH, g)[a] kcal/mol
Smith and Sugden (1)	A	Flame	2200	1		99.8		-51.7
James and Sugden (2)	A	Flame	2200	1		100.0		-53.2
Jensen and Padley (3)	B	Flame	2475	1		15.9		-55.6 ± 2.0
Cotton and Jenkins (4)	B	Flame	2370	1		15.1		-56.4 ± 1.5
McEwan and Phillips (5)	B	Flame	1400-2600	4	15.8	16.7±0.6	0.5 ± 0.2	-54.8 ± 1.6

Reaction: (A) LiOH(g) = Li(g) + OH(g) (B) Li(g) + H_2O(g) = LiOH(g) + H(g)

[a] Third law values based on JANAF heat of formation data; Li(g) 8-30-62; OH(g) 12-31-70; H_2O(g) 3-31-61; H(g) 9-30-65.

The equilibrium data of Sugden and co-workers (1, 2) are likely to contain significant errors, since the dissociation constants were calculated with OH concentrations determined from measured flame temperatures and known gas compositions. It is now well established (8, 9) that flame radical concentrations vary greatly with the distance from the reaction zone of the flame. The dissociation pressure data of Johnston and Ditmars and Johnston (see LiOH(ℓ) table) show excessive drifts which usually are indications of nonequilibrium measurements. However, even the remaining flame work (3 - 5) and vapor pressure data still show a scatter of over 3 kcal/mol in ΔHf°_{298} of LiOH(g). Cotton and Jenkins (4) investigated the other alkali metal hydroxides, and their data lead to ΔHf°_{298} values for these compounds which are quite consistent with JANAF data (10). On the other hand, the flame studies of McEwan and Phillips (5) as a function of temperature do not show significant drift; yet, the discrepancy between their ΔHf°_{298} value and that of Cotton and Jenkins (4) is 1.6 kcal/mol. We choose to adopt for ΔHf°_{298}(LiOH, g) a weighted average of the results from the flame work (3 - 5) and the vapor pressure data. The adopted value ΔHf°_{298}(LiOH, g) = −56.0 ± 1.5 kcal/mol corresponds to a bond dissociation energy of D_0(LiOH) = 102.8 ± 1.5 kcal/mol.

Heat Capacity and Entropy

Freund et al. (11) measured the molecular beam electric resonance spectra of LiOH and calculated molecular constants on the basis of a linear equilibrium structure. Linear structures for the other alkali metal hydroxides have been proposed from microwave and infrared studies on these molecules. (See the respective tables for details) We adopt a linear configuration for LiOH and calculate a Li-O bond length from the rotational constant given by Freund et al. (11). The O-H bond length is estimated to be the same as for H_2O. The principal moment of inertia is 2.348 x 10^{-39} g cm^2.

Experimental vibrational frequencies for LiOH have not been reported in the literature at the present time. Acquista and Abramowitz (12) have made matrix-isolation studies of monomeric CsOH, RbOH, and NaOH and provided assignments for the metal-oxygen stretch (ν_1) and the bending modes (ν_2) of these molecules. A Valence Force Treatment of the frequencies by these workers led to metal-oxygen (F_{11}), O-H (F_{33}), and bending (F_{22}) force constants. We extrapolate their data to LiOH with the result; F_{11} = 1.15 mdyn/Å, F_{33} assumed equal to 7.5 mdyn/Å with the interaction constant F_{13} = 0, and F_{22} = 0.060 mdyn·Å. These estimated force constants are used to calculate the adopted frequencies by the Valence Force Treatment. Our adopted frequencies when used in an analysis of the equilibrium data from McEwan and Phillips (5) and Berkowitz et al. (7) (see LiOH(ℓ) table) lead to reasonable agreement between the second and third law ΔHr_{298} values.

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HLiO

Lithium Hydroxide Unipositive Ion ($LiOH^+$)

(Ideal Gas) GFW = 23.9458

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.238	53.532	53.532	.000	186.000	182.583	= 133.837
300	11.253	53.601	53.532	.021	186.006	182.561	= 132.996
400	11.874	56.933	53.982	1.180	186.339	181.364	= 99.092
500	12.218	59.623	54.850	2.387	185.909	180.159	= 78.747
600	12.438	61.871	55.838	3.620	186.199	178.982	= 65.194
700	12.605	63.801	56.841	4.872	186.507	177.754	= 55.497
800	12.752	65.494	57.819	6.140	186.828	176.481	= 48.212
900	12.893	67.004	58.757	7.423	187.154	175.169	= 42.537
1000	13.030	68.370	59.651	8.719	187.484	173.820	= 37.988
1100	13.163	69.618	60.501	10.028	187.820	172.437	= 34.260
1200	13.291	70.769	61.310	11.351	188.160	171.023	= 31.147
1300	13.412	71.837	62.079	12.686	188.506	169.580	= 28.509
1400	13.525	72.836	62.812	14.033	188.856	168.112	= 26.244
1500	13.630	73.772	63.512	15.391	189.209	166.619	= 24.276
1600	13.727	74.655	64.181	16.759	189.565	165.100	= 22.552
1700	13.815	75.490	64.822	18.136	154.877	164.889	= 21.198
1800	13.896	76.282	65.437	19.522	155.420	165.464	= 20.090
1900	13.970	77.035	66.027	20.915	155.963	166.008	= 19.095
2000	14.037	77.754	66.596	22.316	156.505	166.521	= 18.197
2100	14.098	78.440	67.144	23.722	157.044	167.008	= 17.381
2200	14.153	79.097	67.672	25.135	157.581	167.470	= 16.637
2300	14.204	79.727	68.183	26.553	158.119	167.907	= 15.955
2400	14.250	80.333	68.676	27.976	158.651	168.323	= 15.328
2500	14.292	80.916	69.154	29.403	159.180	168.713	= 14.749
2600	14.330	81.477	69.618	30.834	159.705	169.084	= 14.213
2700	14.365	82.018	70.067	32.269	160.225	169.434	= 13.715
2800	14.397	82.541	70.503	33.707	160.741	169.766	= 13.251
2900	14.427	83.047	70.927	35.148	161.250	170.081	= 12.818
3000	14.454	83.537	71.339	36.592	161.755	170.377	= 12.412
3100	14.479	84.011	71.740	38.039	162.251	170.656	= 12.031
3200	14.502	84.471	72.131	39.488	162.742	170.918	= 11.673
3300	14.524	84.918	72.512	40.939	163.225	171.167	= 11.336
3400	14.544	85.352	72.883	42.393	163.701	171.401	= 11.018
3500	14.562	85.773	73.245	43.848	164.168	171.620	= 10.716
3600	14.579	86.184	73.599	45.305	164.626	171.826	= 10.431
3700	14.595	86.584	73.945	46.764	165.075	172.019	= 10.161
3800	14.610	86.973	74.282	48.224	165.516	172.205	= 9.904
3900	14.624	87.353	74.613	49.686	165.947	172.374	= 9.660
4000	14.637	87.723	74.936	51.149	166.366	172.531	= 9.427
4100	14.649	88.085	75.252	52.613	166.775	172.682	= 9.205
4200	14.661	88.438	75.562	54.078	167.174	172.820	= 8.993
4300	14.672	88.783	75.865	55.545	167.562	172.952	= 8.790
4400	14.682	89.120	76.163	57.013	167.939	173.073	= 8.597
4500	14.692	89.450	76.454	58.482	168.301	173.183	= 8.411
4600	14.702	89.773	76.740	59.951	168.653	173.291	= 8.233
4700	14.711	90.090	77.021	61.422	168.990	173.386	= 8.062
4800	14.719	90.399	77.297	62.893	169.315	173.475	= 7.899
4900	14.728	90.703	77.567	64.366	169.624	173.558	= 7.741
5000	14.736	91.001	77.833	65.839	169.918	173.635	= 7.590
5100	14.744	91.293	78.094	67.313	170.196	173.710	= 7.444
5200	14.751	91.579	78.350	68.788	170.458	173.774	= 7.304
5300	14.759	91.860	78.603	70.263	170.702	173.837	= 7.168
5400	14.766	92.136	78.851	71.739	170.928	173.890	= 7.038
5500	14.773	92.407	79.095	73.216	171.133	173.946	= 6.912
5600	14.780	92.673	79.335	74.694	171.318	173.991	= 6.790
5700	14.787	92.935	79.571	76.172	171.482	174.039	= 6.673
5800	14.793	93.192	79.804	77.651	171.623	174.085	= 6.560
5900	14.800	93.445	80.033	79.131	171.741	174.125	= 6.450
6000	14.807	93.694	80.259	80.611	171.833	174.166	= 6.344

Dec. 31, 1971

LITHIUM HYDROXIDE UNIPOSITIVE ION ($LiOH^+$) (IDEAL GAS) GFW = 23.9458

Point Group [$C_{\infty v}$] ΔHf°_0 = [185 ± 25] kcal/mol

$S^\circ_{298.15}$ = [53.5 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [186 ± 25] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[600] (1)
[325] (2)
[3600] (1)

Bond Distance: Li-O = [1.50] Å O-H = [1.03] Å

Bond Angle: Li-O-H = [180]° σ = 1

Rotational Constant: B_0 = [1.15435] cm^{-1}

Heat of Formation

The heat of formation, $\Delta Hf^\circ_{298}(LiOH^+,g)$ = 186 ± 25 kcal/mol, is calculated from the ionization potential for LiOH and $\Delta Hf^\circ_{298}(LiOH,g)$ = -56.0 ± 1.5 kcal/mol (1). The ionization potential is estimated to be 10.5 ± 1.0 eV for LiOH by comparison with similar data (2) for the isoelectronic molecules LiF and LiCl. We note that this estimated value is in accord with the ionization potential of LiO (IP = 9.0 eV) (3), which should be less than LiOH since the electron in the monoxide is unpaired.

Heat Capacity and Entropy

The correlation diagram of Walsh (4) for HAB molecules predicts a linear configuration for $LiOH^+$ (seven valence electrons) with the unpaired electron in a pi orbital. Therefore, the electronic ground state of $LiOH^+$ should be $^2\Pi$. A first excited state ($^2\Sigma$) is estimated at 32000 cm^{-1} by analogy with the isoelectronic molecules OH (1) and SH (1). The ionization of LiOH is assumed to lead to weaker bonding in $LiOH^+$, since the electron lost is a bonding one. The Li-O and O-H bond distances are increased slightly over those for LiOH to account for this weaker bonding. Similarly, the vibrational frequencies are estimated from those for LiOH with somewhat lower values.

The enthalpy at 0 K is -2.662 kcal/mol.

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Imidogen (NH)

(Ideal Gas) GFW = 15.01467

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	-2.060	90.150	90.150	INFINITE
100	6.961	35.687	49.484	-1.380	90.104	89.663	-195.959
200	6.963	40.512	43.930	-.684	90.151	89.200	-97.473
298	6.966	43.293	43.293	.000	90.162	88.730	-65.041
300	6.966	43.336	43.293	.013	90.162	88.721	-64.633
400	6.973	45.341	43.566	.710	90.163	88.240	-48.212
500	6.994	46.899	44.083	1.408	90.160	87.759	-38.359
600	7.041	48.178	44.662	2.109	90.156	87.279	-31.792
700	7.119	49.268	45.244	2.817	90.149	86.801	-27.100
800	7.222	50.226	45.808	3.534	90.141	86.323	-23.582
900	7.343	51.083	46.347	4.262	90.134	85.846	-20.846
1000	7.471	51.863	46.860	5.003	90.128	85.370	-18.658
1100	7.601	52.581	47.348	5.756	90.125	84.894	-16.867
1200	7.727	53.248	47.812	6.523	90.124	84.419	-15.375
1300	7.847	53.871	48.255	7.302	90.125	83.943	-14.112
1400	7.961	54.457	48.677	8.092	90.128	83.467	-13.030
1500	8.066	55.010	49.081	8.893	90.132	82.992	-12.092
1600	8.164	55.534	49.468	9.705	90.137	82.515	-11.271
1700	8.255	56.032	49.840	10.526	90.143	82.040	-10.547
1800	8.339	56.506	50.197	11.356	90.149	81.562	-9.903
1900	8.418	56.959	50.541	12.194	90.158	81.086	-9.327
2000	8.492	57.392	50.873	13.039	90.167	80.608	-8.808
2100	8.562	57.808	51.193	13.892	90.176	80.129	-8.339
2200	8.628	58.208	51.503	14.751	90.187	79.651	-7.913
2300	8.692	58.593	51.803	15.618	90.199	79.171	-7.523
2400	8.753	58.965	52.094	16.490	90.212	78.692	-7.166
2500	8.812	59.323	52.376	17.368	90.225	78.211	-6.837
2600	8.869	59.670	52.650	18.252	90.241	77.731	-6.534
2700	8.924	60.005	52.916	19.142	90.258	77.249	-6.253
2800	8.978	60.331	53.175	20.037	90.276	76.766	-5.992
2900	9.032	60.647	53.427	20.937	90.296	76.285	-5.749
3000	9.084	60.954	53.673	21.843	90.318	75.801	-5.522
3100	9.135	61.253	53.913	22.754	90.341	75.315	-5.310
3200	9.185	61.544	54.147	23.670	90.367	74.830	-5.111
3300	9.235	61.827	54.375	24.591	90.393	74.345	-4.924
3400	9.284	62.103	54.598	25.517	90.422	73.858	-4.748
3500	9.332	62.373	54.817	26.448	90.453	73.370	-4.581
3600	9.380	62.637	55.030	27.383	90.485	72.882	-4.425
3700	9.427	62.894	55.239	28.324	90.519	72.393	-4.276
3800	9.474	63.146	55.444	29.269	90.555	71.903	-4.135
3900	9.520	63.393	55.645	30.218	90.592	71.412	-4.002
4000	9.565	63.635	55.841	31.173	90.632	70.919	-3.875
4100	9.610	63.871	56.034	32.131	90.673	70.425	-3.754
4200	9.655	64.104	56.224	33.095	90.716	69.932	-3.639
4300	9.699	64.331	56.410	34.062	90.761	69.436	-3.529
4400	9.742	64.555	56.592	35.034	90.807	68.939	-3.424
4500	9.786	64.774	56.772	36.011	90.855	68.440	-3.324
4600	9.829	64.990	56.948	36.992	90.906	67.944	-3.228
4700	9.871	65.202	57.121	37.977	90.958	67.444	-3.136
4800	9.913	65.410	57.292	38.966	91.012	66.943	-3.048
4900	9.955	65.615	57.460	39.959	91.068	66.440	-2.963
5000	9.996	65.816	57.625	40.957	91.125	65.937	-2.882
5100	10.037	66.015	57.787	41.958	91.184	65.432	-2.804
5200	10.078	66.210	57.947	42.964	91.246	64.927	-2.729
5300	10.119	66.402	58.105	43.974	91.309	64.421	-2.656
5400	10.159	66.592	58.261	44.988	91.374	63.911	-2.587
5500	10.199	66.778	58.414	46.006	91.440	63.404	-2.519
5600	10.238	66.963	58.565	47.028	91.509	62.892	-2.454
5700	10.278	67.144	58.714	48.053	91.579	62.383	-2.392
5800	10.317	67.323	58.861	49.083	91.651	61.869	-2.331
5900	10.356	67.500	59.006	50.117	91.724	61.355	-2.273
6000	10.394	67.674	59.149	51.154	91.800	60.838	-2.216

Dec. 31, 1960; Dec. 31, 1965; Dec. 31, 1971

IMIDOGEN (NH) (IDEAL GAS) GFW = 15.01467 HN

Ground State Configuration $^3\Sigma^-$ ΔHf°_0 = 90.15 ± 5.00 kcal/mol

$S^\circ_{298.15}$ = 43.29 ± 0.20 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 90.16 ± 5.00 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^3\Sigma^-$	0	3
$a^1\Delta$	[12000]	2
$b^1\Sigma^-$	[12000] + 8502	1
$A^3\Pi$	29772	6

ω_e = 3316.5 cm^{-1} $\omega_e x_e$ = 95.4 cm^{-1} σ = 1

B_e = 16.668 cm^{-1} α_e = 0.646 cm^{-1} r_e = 1.038 Å

Heat of Formation

Herzberg (2), referring only to literature prior to 1940, suggests a value of 3.8 eV for the dissociation energy of NH(g). An examination of the dissociation energies of the first and second row hydrides as tabulated by Gaydon (1) would suggest a value in the range 3.47-4.40 eV.

Pannetier and Gaydon (17) calculated a value of 4.0 eV by a two point linear Birge-Sponer extrapolation. This value was adjusted to 3.26 eV using an ionic character correction factor as suggested by Hildenbrand (23), Franklin et al. (3) and Reed and Sneddon (4) determined the dissociation energy by electron impact to be 3.6 eV and 3.70 eV, respectively. These latter two values should be considered as upper limits since electron impact measurements usually involve excess energy. Using a shock tube technique and published transition probabilities, Seal and Gaydon (5) calculated a value of 3.21 ± 0.16 eV, a value which Gaydon adopts in his tabulation (1). Stedman (14), using reactions of rare gas metastables with NH-containing compounds, deduced values of 3.04-3.64 eV and 3.17-3.47 eV.

On the theoretical side many calculations have been made:

Companion and Ellison (7) - semiempirical interpolative method	3.61 eV
Jordan and Longuet-Higgins (8) - semiempirical method	3.52 eV
Cade and Huo (10), Claxton (11) - Hartree-Fock method	2.10 eV
Kouba and Öhrn (12) - natural-orbital valence-shell configuration interaction	2.42 eV
O'Neil and Schaeffer (13) - configuration interaction	2.858 eV.

Finally, Wilkinson (6) and Vedeneyev et al (15) suggest values of 3.76 eV and 3.60 eV, respectively. Both references are based on spectroscopic data, the latter arising from a linear Birge-Sponer extrapolation for the $X^3\Sigma$ state.

The value chosen as the dissociation energy of NH(g) is 3.21 ± 0.20 eV. The reason for the choice is that it is consistent with all the experimental data. Theoretically, the early results are above the accepted value whereas recent results are below but increasing. The accepted value leads to a heat of formation, ΔHf°_0 = 90.15 ± 5.00 kcal/mol.

Heat Capacity and Entropy

The spectroscopic constants for the ground state were obtained from Dixon (16).

The electronic states of NH(g) are well-known but the energy separation of the ground state and the $a^1\Delta$ state is uncertain. Hurley (18) calculates the splitting as 1.74 eV using ab initio calculations with empirical atomic correlation corrections, whereas Huo (19) calculates 1.83 eV via single configuration SCF calculations. Kouba and Öhrn (12) and O'Neil and Schaeffer (13) using configuration interaction studies calculated the splitting to be 1.9 eV and 1.47 eV respectively. Cade (20) predicts 1.63 eV using relationships between the united atom and the diatomic hydride. Jordan and Longuet-Higgins (8) calculated a value of 1.51 eV by a semiempirical technique.

On the experimental side, Stedman (14) with rare gas metastables suggests a value no less than 0.68 eV. Okabe and Lenzi (21) examined the photo-dissociation of NH_3. Using the current value ΔHf°_0(NH, g) = 90.15 kcal/mol, their data (21) predicts an upper limit of 1.21 eV. Foner and Hudson (22) produced NH by short-duration pulsed electric discharges and calculated a splitting of 1.6 to 2.2 eV.

The value chosen as the $X^3\Sigma^-$-$a^1\Delta$ splitting is 1.44 eV or approximately 12000 cm^{-1}. This value is roughly an average of the experimental data and a lower limit on the theoretical calculations.

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HN

Sodium Hydroxide (NaOH)

(Crystal) GFW = 39.9972

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	−2.507	−100.716	−100.716	INFINITE
100	6.631	3.705	26.262	−2.255	−101.511	−98.024	214.231
200	11.850	10.179	16.636	−1.292	−101.784	−94.401	103.157
298	14.220	15.403	15.403	.000	−101.800	−90.768	66.535
300	14.260	15.491	15.403	.026	−101.799	−90.699	66.074
400	15.520	19.775	15.979	1.518	−102.353	−86.961	47.513
500	17.963	23.464	17.112	3.176	−102.152	−83.131	36.336
600	20.560	30.040	18.609	6.858	−99.018	−79.454	28.941
700	20.560	33.209	20.474	8.914	−99.308	−76.099	23.757
800	20.560	35.954	22.242	10.970	−98.699	−72.817	19.893
900	20.560	38.376	23.902	13.026	−98.096	−69.618	16.906
1000	20.560	40.542	25.460	15.082	−97.502	−66.485	14.530
1100	20.560	42.502	26.922	17.138	−96.925	−63.414	12.599
1200	20.560	44.291	28.296	19.194	−119.600	−59.934	10.916
1300	20.560	45.936	29.590	21.250	−119.841	−54.993	9.245
1400	20.560	47.460	30.813	23.306	−118.091	−50.110	7.823
1500	20.560	48.879	31.970	25.362	−117.351	−45.280	6.597

Dec. 31, 1960; Mar. 31, 1966; Dec. 31, 1970

SODIUM HYDROXIDE (NaOH) (CRYSTAL) GFW = 39.9972 HNaO

$S^\circ_{298.15}$ = 15.40 ± 0.20 gibbs/mol

Tt = 572°K

Tm = 596°K

ΔHf°_0 = −100.7 ± 0.1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −101.8 ± 0.1 kcal/mol

ΔHt = 1.72 ± 0.20 kcal/mol

ΔHm = 1.58 ± 0.20 kcal/mol

ΔHs°_{298}(to monomer) = 54.5 ± 3.0 kcal/mol

ΔHs°_{298}(to dimer) = 58.4 ± 6.0 kcal/mol

Heat of Formation

The heat of formation of NaOH(c) is obtained from its heat of solution in water, the heat of hydrolysis of metallic sodium, and appropriate auxiliary data.

Reshetnikov (1) determined calorimetrically the heat of solution of NaOH in 400 H_2O as −10.445 ± 0.015 kcal/mol. Combining this result with heat of dilution data for aqueous sodium hydroxide solutions tabulated by Parker (2), we derive ΔH°_{soln}(NaOH, c) = −10.56 ± 0.02 kcal/mol. Murch and Giauque (3) measured the heats of solution in water of a series of solids which contained various amounts of water in the range NaOH·(0.1 to 1) H_2O. Their data indicated a linear relationship between the heat of solution and the ratio of the moles of water to the moles of sodium hydroxide. Upon extrapolation their data gave ΔH°_{soln}(NaOH, c) = −10.637 ± 0.010 kcal/mol (2). This latter value is adopted here, since the extrapolation to zero moles of water tends to eliminate its effect on the heat of solution.

The heat of hydrolysis of metallic sodium has been determined by various investigators (4–6). For the reaction Na(c) + (n+1)H_2O → NaOH·n H_2O + 0.5 H_2(g) data are summarized below.

Investigator	n moles of H_2O	ΔHh°_{298} kcal/mol	ΔHf°_{298}(NaOH·∞H_2O)* kcal/mol	ΔHf°_{298}(NaOH, c) kcal/mol
Gunn and Green (4a, 4b)	∞	−44.124 ± 0.015	−112.439	−101.80
Messer et al. (5)	∞	−44.22 ± 0.20	−112.53	−101.88
Ketchen and Wallace (6)	∞	−44.05 ± 0.20	−112.37	−101.72

*Based on ΔHf°_{298}(H_2O, ℓ) = −68.315 kcal/mol (7).

Combination of the ΔHf°_{298}(NaOH·∞ H_2O) values with the heat of solution of NaOH(c) at infinite dilution given above, results in the ΔHf°_{298}(NaOH, c) values given in the last column. The value determined from the work of Gunn and Green (4a, 4b) is adopted.

Earlier determinations of ΔHf°_{298}(NaOH, c) have been summarized by Bichowsky and Rossini (8) and are not listed here.

Heat Capacity and Entropy

Murch and Giauque (3) determined low temperature heat capacities for NaOH·0.04014 H_2O and NaOH·0.97776 H_2O from 15° to 320°K. From these data Cp's for anhydrous NaOH(c) were calculated and joined smoothly at 298.15°K with the high temperature (273°–973°K) enthalpy data of Douglas and Dever (9). These smoothed Cp's given by Murch and Giauque are adopted. Low temperature heat capacity data for NaOH(c) in the temperature range 60° to 300°K have also been reported by Kelley and Snyder (10a, 10b). The deviations of their data from the adopted values range from a few tenths of a percent (150°–300°K) to up to about 30% at the lowest temperatures investigated (60°K). Popov and Ginzburg (11a, 11b) also determined high temperature enthalpy data (293°–1016°K) for NaOH by drop calorimetry. Their reported value $H_{500}-H_{298}$ = 3.112 kcal/mol (11b) is in very good agreement with the tabulated value of 3.176 kcal/mol.

S°_{298} is based upon an extrapolation of 0.020 gibbs/mol at 15°K.

Transition and Melting Data

The adopted heats of the polymorphic transformation and melting of NaOH are mean values from the work of Douglas and Dever (9), Popov and Ginzburg (11a, 11b), and Reshetnikov and Baranskaya (12). Tt and Tm are from Reshetnikov and Baranskaya (12).

Heat of Sublimation

ΔHs°_{298} for the monomer and dimer are calculated from the adopted heats of formation of the crystal and the respective gaseous species.

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Sodium Hydroxide (NaOH)

(Liquid) GFW = 39.9972

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	20.990	18.130	18.130	.000	− 99.641	− 89.422	65.548
300	20.988	18.280	18.130	.039	− 99.627	− 89.358	65.098
400	20.844	24.278	18.952	2.130	− 99.582	− 85.991	46.983
500	20.710	28.915	20.898	4.208	− 98.960	− 82.665	36.133
600	20.570	32.682	22.225	6.274	− 98.383	− 79.464	28.945
700	20.430	35.843	23.951	8.328	− 97.739	− 76.367	23.843
800	20.290	38.562	25.611	10.360	− 97.150	− 73.354	20.039
900	20.150	40.983	27.185	12.382	− 96.581	− 70.413	17.099
1000	20.010	43.059	28.669	14.390	− 96.035	− 67.535	14.760
1100	19.870	44.960	30.065	16.384	− 95.520	− 64.712	12.857
1200	19.730	46.683	31.379	18.364	− 118.271	− 61.475	11.196
1300	19.590	48.256	32.617	20.330	− 117.602	− 56.770	9.544
1400	19.450	49.703	33.787	22.282	− 116.956	− 52.115	8.136
1500	19.310	51.040	34.893	24.220	− 116.334	− 47.505	6.921
1600	19.170	52.282	35.942	26.144	− 115.734	− 42.936	5.865
1700	19.030	53.440	36.937	28.054	− 115.155	− 38.403	4.937
1800	18.910	54.524	37.884	29.951	− 114.598	− 33.905	4.117
1900	18.795	55.543	38.787	31.836	− 114.060	− 29.436	3.386
2000	18.690	56.505	39.649	33.711	− 113.541	− 24.997	2.732
2100	18.595	57.414	40.474	35.575	− 113.039	− 20.582	2.142
2200	18.515	58.277	41.264	37.430	− 112.553	− 16.191	1.608
2300	18.447	59.099	42.021	39.278	− 112.081	− 11.822	1.123
2400	18.393	59.883	42.749	41.120	− 111.623	− 7.470	.680
2500	18.346	60.633	43.450	42.957	− 111.176	− 3.144	.275

Dec. 31, 1960; Mar. 31, 1966; Dec. 31, 1970

SODIUM HYDROXIDE (NaOH) (LIQUID) GFW = 39.9972 HNaO

$S^\circ_{298.15}$ = 18.13 ± 0.50 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −99.641 ± 0.5 kcal/mol

Tm = 596°K

ΔHm° = 1.58 ± 0.20 kcal/mol

Tb(to monomer) = 1830°K

ΔHv°(to monomer) = 41.9 kcal/mol

Heat of Formation

The heat of formation of liquid NaOH at 298.15°K is obtained from that of the crystal by adding ΔHm and the difference between $H_{596}-H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The adopted heat capacities for NaOH(ℓ) in the temperature range 596° to 1000°K are from the enthalpy measurements of *Douglas and Dever* (1). *The heat capacities below the melting point and above 1000°K are extrapolated from the experimental* heat capacity curve. Powers and Blalock (2) reported Cp(ℓ) = 19.6 gibbs/mol from enthalpy measurements, in a short temperature range, by drop calorimetry. The smoothed enthalpy data for NaOH(ℓ) reported by Popov and Ginzburg (3a, 3b) are from 0.2 to 0.5 kcal/mol less than the adopted values in the temperature range 700° to 1000°K.

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

Melting Data

See NaOH(c) table for details.

Vaporization Data

Tb is calculated as the temperature at which the free energies of formation of NaOH(ℓ) and NaOH(g) are equal. The difference in the heats of formation of NaOH(ℓ) and NaOH(g) at the boiling point is the heat of vaporization.

Wartenberg and Albrecht (4) reported a boiling point of 1661°K from their static vapor pressure data. However, these workers observed the presence of water after each experiment which may indicate some decomposition of the sample. (See NaOH(g) table for further discussion).

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Sodium Hydroxide (NaOH)

(Ideal Gas) GFW = 39.9972

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	-2.721	-46.395	-46.395	INFINITE
100	7.855	43.879	63.960	-2.008	-46.729	-47.259	103.284
200	10.386	50.174	55.599	-1.085	-47.043	-47.659	52.079
298	11.561	54.572	54.572	.000	-47.265	-47.911	35.120
300	11.575	54.644	54.572	.021	-47.269	-47.915	34.906
400	12.110	58.056	55.034	1.209	-48.128	-48.048	26.252
500	12.384	60.791	55.921	2.435	-48.357	-48.001	20.981
600	12.563	63.067	56.928	3.683	-48.558	-47.910	17.451
700	12.698	65.014	57.947	4.947	-48.740	-47.788	14.920
800	12.822	66.717	58.939	6.223	-48.911	-47.641	13.015
900	12.944	68.235	59.889	7.511	-49.076	-47.471	11.528
1000	13.067	69.605	60.793	8.811	-49.238	-47.284	10.334
1100	13.190	70.856	61.652	10.124	-49.404	-47.082	9.358
1200	13.310	72.009	62.468	11.449	-72.810	-46.406	8.452
1300	13.425	73.079	63.243	12.786	-72.770	-44.207	7.432
1400	13.534	74.078	63.982	14.134	-72.728	-42.012	6.558
1500	13.635	75.015	64.686	15.493	-72.685	-39.819	5.807
1600	13.729	75.898	65.360	16.861	-72.642	-37.629	5.140
1700	13.816	76.733	66.005	18.238	-72.595	-35.441	4.554
1800	13.895	77.525	66.623	19.624	-72.549	-33.258	4.038
1900	13.968	78.278	67.217	21.017	-72.504	-31.075	3.574
2000	14.034	78.996	67.788	22.417	-72.459	-28.897	3.158
2100	14.094	79.683	68.338	23.824	-72.414	-26.721	2.781
2200	14.149	80.339	68.869	25.236	-72.372	-24.546	2.438
2300	14.199	80.970	69.381	26.653	-72.330	-22.374	2.126
2400	14.245	81.575	69.877	28.076	-72.291	-20.200	1.839
2500	14.287	82.157	70.356	29.502	-72.255	-18.034	1.577
2600	14.326	82.718	70.821	30.933	-72.221	-15.863	1.333
2700	14.361	83.260	71.272	32.367	-72.191	-13.697	1.109
2800	14.393	83.783	71.709	33.805	-72.166	-11.533	.900
2900	14.423	84.288	72.134	35.246	-72.143	-9.364	.706
3000	14.450	84.778	72.548	36.689	-72.126	-7.201	.525
3100	14.475	85.252	72.950	38.136	-72.112	-5.038	.355
3200	14.498	85.712	73.342	39.584	-72.104	-2.874	.196
3300	14.520	86.158	73.723	41.035	-72.103	-.711	.047
3400	14.539	86.592	74.095	42.488	-72.107	1.451	.093
3500	14.558	87.014	74.458	43.943	-72.118	3.618	.226
3600	14.575	87.424	74.813	45.400	-72.137	5.781	.351
3700	14.591	87.824	75.159	46.858	-72.165	7.944	.469
3800	14.606	88.213	75.498	48.318	-72.199	10.113	.582
3900	14.620	88.592	75.829	49.779	-72.245	12.276	.688
4000	14.632	88.963	76.152	51.242	-72.300	14.445	.789
4100	14.645	89.324	76.469	52.706	-72.367	16.617	.886
4200	14.656	89.677	76.779	54.171	-72.446	18.786	.978
4300	14.666	90.022	77.083	55.637	-72.537	20.961	1.065
4400	14.676	90.359	77.381	57.104	-72.644	23.133	1.149
4500	14.686	90.689	77.673	58.572	-72.767	25.314	1.229
4600	14.695	91.012	77.960	60.041	-72.906	27.495	1.306
4700	14.703	91.328	78.241	61.511	-73.064	29.679	1.380
4800	14.711	91.638	78.517	62.982	-73.242	31.866	1.451
4900	14.718	91.941	78.788	64.453	-73.443	34.059	1.519
5000	14.725	92.239	79.054	65.925	-73.667	36.254	1.585
5100	14.732	92.531	79.315	67.398	-73.919	38.458	1.648
5200	14.738	92.817	79.572	68.871	-74.197	40.660	1.709
5300	14.744	93.097	79.825	70.346	-74.506	42.876	1.768
5400	14.749	93.373	80.073	71.820	-74.849	45.090	1.825
5500	14.755	93.644	80.317	73.295	-75.227	47.315	1.880
5600	14.760	93.910	80.558	74.771	-75.644	49.545	1.934
5700	14.765	94.171	80.794	76.247	-76.098	51.785	1.986
5800	14.769	94.428	81.027	77.724	-76.595	54.034	2.036
5900	14.774	94.680	81.256	79.201	-77.138	56.292	2.085
6000	14.778	94.929	81.482	80.679	-77.726	58.558	2.133

Dec. 31, 1960; Mar. 31, 1966; Dec. 31, 1970

SODIUM HYDROXIDE (NaOH) (IDEAL GAS) GFW = 39.9972 HNaO

Point Group $C_{\infty v}$

ΔHf°_0 = -46.4 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = 54.57 ± 0.10 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -47.3 ± 3.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
431 (1)
337 (2)
[3650] (1)

Bond Distance: Na-O = [1.93] Å O-H = [0.97] Å

Bond Angle: Na-O-H = 180°

Rotational Constant: B_0 = 0.42670 cm^{-1}

σ = 1

Heat of Formation

The bond dissociation energies of the alkali metal hydroxides have been the subject of a number of investigations (1-4) in recent years. The majority of this work has involved equilibrium studies on the reaction $A(g) + H_2O(g) = AOH(g) + H(g)$, where A is an alkali metal, in hydrogen-oxygen-nitrogen flames containing water. In the case of NaOH, data are summarized below.

Investigator	Method	Reaction	No. of Points	Temp. °K	ΔHr°, kcal/mol 3rd Law	D_0(Na-OH) kcal/mol
Jensen and Padley (2a)	Flames	A	1	2475	40.5	77.9
Cotton and Jenkins (4)	Flames	A	1	2030	36.6	81.8

Reaction: (A) $Na(g) + H_2O(g) = NaOH(g) + H(g)$

We note that Cotton and Jenkins (4) in the same paper reported bond dissociation energies for LiOH(g) and KOH(g) which are in reasonable agreement with JANAF values (5) for the heat of formation of these two compounds. Furthermore, bond dissociation data for the alkali metal halides (6) clearly establish the sodium compound as the least stable within each halide series. The potassium and sodium compounds differ by from 4.3 kcal/mol for the fluorides and bromides to 3.6 kcal/mol for the chlorides. It seems most likely that this same trend in the bond dissociation energies would apply to the hydroxides as well. Based upon these correlations, we adopt D_0(Na-OH) = 81.5 ± 3.0 kcal/mol with D_0(K-OH) - D_0(Na-OH) = 3.9 kcal/mol. This value corresponds to ΔHf°_{298}(NaOH, g) = -47.3 ± 3.0 kcal/mol.

Wartenberg and Albrecht (7) determined vapor pressures for NaOH(ℓ) in the temperature range 1283-1581°K by a static method. In order to evaluate ΔHv°_{298}(NaOH, ℓ), we have used a trial and error variation of ΔHv°_{298} for the monomer and dimer, such that these values are in accordance with the adopted heat of dimerization (See $Na_2(OH)_2$(g) table), and the sum of the calculated partial pressures for NaOH(g) and $Na_2(OH)_2$(g) is in good agreement with the experimental vapor pressure data. The resulting values are: ΔHv°_{298}(to monomer) = 48.25 kcal/mol and ΔHv°_{298}(to dimer) = 45.8 kcal/mol. From the heat of vaporization of the monomer, we derive ΔHf°_{298}(NaOH, g) = -51.4 kcal/mol. This value corresponds to a bond dissociation energy for NaOH(g) that is slightly greater than the adopted value for KOH(g) (5), and thus not in line with the established trends in D_0 discussed above. Büchler and Berkowitz-Mattuck (8) in their review on gaseous ternary compounds of the alkali metals point to the decomposition of NaOH in the condensed phase with a resulting change in composition as the major problem in the interpretation of thermodynamic measurements on this system. Until the nature of the condensed phase and the relationship between the vapor and condensed phase composition for NaOH(ℓ) are established, an accurate heat of vaporization will remain undetermined.

Heat Capacity and Entropy

The infrared spectra of matrix-isolated NaOH and NaOD have been recently observed by Acquista and Abramowitz (9). The alkali-metal-oxygen stretching frequency, ν_1, and the bending mode, ν_2, for NaOH were assigned as 431 and 337 cm^{-1}, respectively, by these workers. The isotope shift of ν_2 was consistent with a linear structure for NaOH having bond lengths of 1.93 and 0.97 A for the Na-O and O-H bonds. We have adopted a linear configuration for NaOH with the bond lengths and frequencies given above. Spinar and Margrave (10) assigned ν_1 as 437 ± 10 cm^{-1} for NaOH which is in good agreement with the adopted value. The O-H stretching frequency, ν_3, was estimated by Jensen (2b). The principal moment of inertia is 6.5599 x 10^{-39} g cm^2.

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HNaO

Sodium Hydroxide Unipositive Ion ($NaOH^+$)

(Ideal Gas) GFW = 39.9966

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.772	57.962	57.962	.000	162.000	158.856	- 116.444
300	11.785	58.035	57.962	.022	162.006	158.836	- 115.712
400	12.243	61.496	58.431	1.226	161.660	157.785	- 86.210
500	12.480	64.256	59.329	2.463	161.939	156.785	- 68.531
600	12.630	66.545	60.387	3.719	162.243	155.726	- 56.723
700	12.751	68.502	61.375	4.988	162.562	154.613	- 48.272
800	12.867	70.212	62.375	6.269	162.893	153.455	- 41.922
900	12.985	71.734	63.332	7.562	163.230	152.256	- 36.973
1000	13.105	73.108	64.242	8.866	163.569	151.019	- 33.005
1100	13.226	74.363	65.106	10.183	163.904	149.746	- 29.752
1200	13.344	75.519	65.926	11.511	164.997	148.901	- 27.119
1300	13.457	76.592	66.706	12.851	141.537	149.538	- 25.140
1400	13.565	77.593	67.448	14.203	142.079	150.133	- 23.437
1500	13.665	78.532	68.156	15.564	142.622	150.691	- 21.956
1600	13.757	79.417	68.832	16.935	143.165	151.210	- 20.654
1700	13.842	80.254	69.480	18.315	143.711	151.697	- 19.502
1800	13.920	81.047	70.101	19.704	144.257	152.151	- 18.474
1900	13.992	81.802	70.697	21.099	144.802	152.576	- 17.550
2000	14.056	82.521	71.270	22.502	145.346	152.969	- 16.716
2100	14.116	83.208	71.822	23.910	145.889	153.336	- 15.958
2200	14.169	83.866	72.355	25.325	146.430	153.678	- 15.267
2300	14.219	84.497	72.869	26.744	146.971	153.995	- 14.633
2400	14.263	85.103	73.367	28.168	147.509	154.292	- 14.050
2500	14.304	85.686	73.848	29.597	148.044	154.560	- 13.512
2600	14.342	86.248	74.314	31.029	148.575	154.812	- 13.013
2700	14.376	86.790	74.766	32.465	149.103	155.040	- 12.550
2800	14.407	87.314	75.205	33.904	149.628	155.250	- 12.118
2900	14.436	87.820	75.631	35.346	150.149	155.445	- 11.715
3000	14.463	88.309	76.046	36.791	150.664	155.618	- 11.337
3100	14.487	88.784	76.449	38.239	151.175	155.773	- 10.982
3200	14.510	89.244	76.842	39.689	151.681	155.914	- 10.648
3300	14.531	89.691	77.224	41.141	152.181	156.038	- 10.334
3400	14.550	90.125	77.597	42.595	152.675	156.146	- 10.037
3500	14.568	90.547	77.961	44.051	153.161	156.245	- 9.756
3600	14.585	90.958	78.317	45.508	153.639	156.325	- 9.490
3700	14.601	91.358	78.664	46.968	154.110	156.391	- 9.238
3800	14.615	91.747	79.003	48.429	154.574	156.450	- 8.998
3900	14.629	92.127	79.335	49.891	155.026	156.490	- 8.769
4000	14.642	92.498	79.659	51.354	155.467	156.522	- 8.552
4100	14.654	92.860	79.977	52.819	155.899	156.546	- 8.345
4200	14.665	93.213	80.288	54.285	156.318	156.554	- 8.146
4300	14.676	93.558	80.592	55.752	156.724	156.558	- 7.957
4400	14.686	93.895	80.891	57.220	157.115	156.546	- 7.776
4500	14.696	94.226	81.183	58.689	157.490	156.530	- 7.602
4600	14.705	94.549	81.471	60.160	157.849	156.505	- 7.436
4700	14.714	94.865	81.752	61.631	158.189	156.472	- 7.276
4800	14.723	95.175	82.029	63.102	158.509	156.432	- 7.123
4900	14.731	95.479	82.300	64.575	158.807	156.387	- 6.975
5000	14.739	95.776	82.567	66.049	159.079	156.332	- 6.833
5100	14.747	96.068	82.828	67.523	159.326	156.278	- 6.697
5200	14.754	96.355	83.086	68.998	159.546	156.212	- 6.565
5300	14.761	96.636	83.339	70.474	159.736	156.151	- 6.439
5400	14.768	96.912	83.588	71.950	159.892	156.078	- 6.317
5500	14.775	97.183	83.832	73.427	160.012	156.006	- 6.199
5600	14.782	97.449	84.073	74.905	160.095	155.931	- 6.085
5700	14.789	97.711	84.310	76.384	160.140	155.857	- 5.976
5800	14.796	97.968	84.543	77.863	160.142	155.783	- 5.870
5900	14.802	98.221	84.773	79.343	160.099	155.710	- 5.768
6000	14.809	98.470	84.999	80.824	160.010	155.634	- 5.669

Dec. 31, 1971

SODIUM HYDROXIDE UNIPOSITIVE ION ($NaOH^+$) (IDEAL GAS) GFW = 39.9966

Point Group [$C_{\infty v}$] ΔHf°_0 = [161 ± 25] kcal/mol

$S^\circ_{298.15}$ = [58.0 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [162 ± 25] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[400] (1)
[300] (2)
[3600] (1)

Bond Distance: Na-O = [2.00] Å O-H = [1.03] Å

Bond Angle: Na-O-H = [180]° σ = 1

Rotational Constant: B_0 = [0.39635] cm^{-1}

Heat of Formation

Beckett and Cassidy (1) selected the ionization potential of NaOH as 9.0 ± 1.0 eV (207.6 ± 23 kcal/mol). A measured value of roughly 9 eV has been reported by Schoonmaker and Porter (2). Combining this result with JANAF auxiliary data (3), we derive ΔHf°_0 ($NaOH^+$, g) = 161 ± 25 kcal/mol, which is tentatively adopted.

Heat Capacity and Entropy

$NaOH^+$ has seven valence electrons. According to the correlation diagram of Walsh (4) for HAB type molecules, $NaOH^+$ should be linear with the unpaired electron in a pi orbital. Therefore, we assume the ground state to be $^2\Pi$. A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with the isoelectronic molecules OH (3) and SH (3). The removal of a bonding electron from NaOH to form $NaOH^+$ should lead to weaker bonding in the positive ion. Consequently, the vibrational frequencies are estimated to be somewhat lower than those for NaOH. Similarly, the Na-O and O-H bond distances are increased slightly over those for NaOH.

The enthalpy at 0 K is -2.795 kcal/mol.

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Hydroxyl (OH)

(Ideal Gas) GFW = 17.0074

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	− 2.192	9.349	9.349	INFINITE
100	7.798	35.726	50.398	− 1.467	9.348	9.064	− 19.810
200	7.356	40.985	44.541	− .711	9.454	8.731	− 9.541
298	7.147	43.881	43.880	.000	9.492	8.367	− 6.133
300	7.145	43.925	43.881	.013	9.492	8.360	− 6.090
400	7.087	45.974	44.160	.725	9.502	7.980	− 4.360
500	7.055	47.551	44.687	1.432	9.494	7.600	− 3.322
600	7.057	48.837	45.275	2.137	9.471	7.223	− 2.631
700	7.090	49.927	45.863	2.845	9.439	6.851	− 2.139
800	7.150	50.877	46.432	3.556	9.398	6.488	− 1.771
900	7.233	51.724	46.974	4.275	9.354	6.122	− 1.487
1000	7.332	52.491	47.488	5.003	9.310	5.766	− 1.260
1100	7.439	53.195	47.975	5.742	9.266	5.413	− 1.076
1200	7.544	53.847	48.437	6.491	9.224	5.065	− .923
1300	7.659	54.456	48.877	7.252	9.184	4.720	− .794
1400	7.766	55.027	49.296	8.023	9.146	4.378	− .683
1500	7.867	55.566	49.696	8.805	9.110	4.039	− .589
1600	7.963	56.077	50.079	9.596	9.074	3.703	− .506
1700	8.053	56.563	50.447	10.397	9.040	3.368	− .433
1800	8.137	57.025	50.799	11.207	9.007	3.035	− .368
1900	8.214	57.467	51.139	12.024	8.974	2.704	− .311
2000	8.286	57.891	51.466	12.849	8.941	2.374	− .259
2100	8.353	58.296	51.782	13.681	8.909	2.047	− .213
2200	8.415	58.687	52.087	14.520	8.875	1.721	− .171
2300	8.472	59.062	52.382	15.364	8.842	1.396	− .133
2400	8.526	59.424	52.668	16.214	8.808	1.075	− .098
2500	8.576	59.773	52.945	17.069	8.771	.751	− .066
2600	8.622	60.110	53.214	17.929	8.735	.432	− .038
2700	8.665	60.436	53.476	18.794	8.697	.114	− .009
2800	8.706	60.752	53.730	19.662	8.658	− .204	.016
2900	8.744	61.058	53.977	20.535	8.617	− .518	.039
3000	8.780	61.355	54.218	21.411	8.575	− .834	.061
3100	8.814	61.644	54.453	22.291	8.532	− 1.147	.081
3200	8.846	61.924	54.682	23.174	8.487	− 1.458	.100
3300	8.876	62.197	54.906	24.060	8.441	− 1.768	.117
3400	8.905	62.462	55.124	24.949	8.393	− 2.078	.134
3500	8.933	62.721	55.338	25.841	8.343	− 2.385	.149
3600	8.956	62.973	55.546	26.735	8.292	− 2.690	.163
3700	8.984	63.219	55.750	27.633	8.239	− 2.992	.177
3800	9.009	63.458	55.950	28.532	8.185	− 3.296	.190
3900	9.032	63.693	56.145	29.434	8.129	− 3.599	.202
4000	9.054	63.922	56.337	30.339	8.072	− 3.899	.213
4100	9.076	64.146	56.525	31.245	8.013	− 4.197	.224
4200	9.097	64.365	56.709	32.154	7.952	− 4.494	.234
4300	9.117	64.579	56.889	33.064	7.890	− 4.789	.243
4400	9.137	64.789	57.066	33.977	7.827	− 5.085	.253
4500	9.156	64.994	57.240	34.892	7.762	− 5.378	.261
4600	9.175	65.196	57.411	35.808	7.697	− 5.666	.269
4700	9.194	65.393	57.579	36.727	7.629	− 5.956	.277
4800	9.212	65.587	57.744	37.647	7.562	− 6.245	.284
4900	9.229	65.777	57.906	38.569	7.493	− 6.533	.291
5000	9.247	65.964	58.065	39.493	7.422	− 6.821	.298
5100	9.264	66.147	58.222	40.419	7.351	− 7.102	.304
5200	9.281	66.327	58.376	41.346	7.279	− 7.387	.310
5300	9.296	66.504	58.528	42.275	7.207	− 7.668	.316
5400	9.314	66.678	58.677	43.205	7.133	− 7.948	.322
5500	9.331	66.849	58.824	44.138	7.059	− 8.225	.327
5600	9.347	67.017	58.969	45.071	6.983	− 8.504	.332
5700	9.363	67.183	59.111	46.007	6.906	− 8.780	.337
5800	9.379	67.346	59.252	46.944	6.832	− 9.053	.341
5900	9.395	67.506	59.390	47.883	6.755	− 9.327	.345
6000	9.411	67.664	59.527	48.823	6.678	− 9.599	.350

Dec. 31, 1960; Mar. 31, 1968; Dec. 31, 1970

HYDROXYL (OH) (IDEAL GAS) GFW = 17.0074 HO

Ground State Configuration $^2\Pi$ ΔHf°_0 = 9.35 ± 0.04 kcal/mol

$S^\circ_{298.15}$ = 43.88 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 9.492 ± 0.04 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{3/2}$	0	2
$X^2\Pi_{1/2}$	139.7	2
$A^2\Sigma^+$	32440.6	2

ω_e = 3735.21 cm^{-1} $\omega_e x_e$ = 82.81 cm^{-1} σ = 1

B_e = 18.871 cm^{-1} α_e = 0.714 cm^{-1} r_e = 0.9706 Å

Heat of Formation

P. Gray (1) has summarized the determinations of the heat of formation of OH and concludes that the short extrapolation, by Barrow (2), of the vibrational levels of the $A^2\Sigma^+$ state gives the most reliable value. This value D°_0 = 101.35 ± 0.3 kcal/mol corresponds to ΔHf°_{298}(OH, g) = 9.41 ± 0.3 kcal/mol. Recently Carlone and Dalby (3) have restudied the spectrum under higher resolution and have revised the value to D°_0 = 101.27 ± 0.04 kcal/mol or ΔHf°_{298}(OH, g) = 9.492 kcal/mol, which is adopted.

Heat Capacity and Entropy

The molecular constants were all listed by Herzberg (4). The present calculation is in excellent agreement with the calculations of Haar et al. (5), and with those of Johnston et al. (6) to 4000°K. Above 4000°K there are discrepancies due to the use of different fundamental constants and a different ground state splitting constant as well as the inclusion of the $A^2\Sigma$ state.

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HO

Hydroxyl Unipositive Ion (OH^+)

(Ideal Gas) GFW = 17.0068

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	0.966	43.658	43.658	.000	314.800	312.254	- 228.888
300	0.968	43.701	43.658	.013	314.809	312.238	- 227.465
400	0.977	45.706	43.931	.710	315.301	311.306	- 170.090
500	7.006	47.266	44.448	1.409	315.781	310.252	- 135.911
600	7.066	48.546	45.027	2.112	314.254	309.102	- 112.590
700	7.160	49.644	45.610	2.823	316.721	307.872	- 96.122
800	7.279	50.607	46.176	3.545	317.186	306.576	- 83.753
900	7.412	51.472	46.717	4.280	317.657	305.222	- 74.118
1000	7.550	52.260	47.233	5.028	318.129	303.815	- 66.309
1100	7.686	52.986	47.723	5.790	318.606	302.361	- 60.074
1200	7.817	53.661	48.190	6.565	319.046	300.862	- 54.795
1300	7.939	54.291	48.635	7.353	319.570	299.324	- 50.321
1400	8.052	54.884	49.061	8.152	320.058	297.749	- 46.481
1500	8.156	55.443	49.468	8.963	320.547	296.139	- 43.147
1600	8.252	55.973	49.858	9.783	321.036	294.494	- 40.226
1700	8.339	56.478	50.233	10.613	321.528	292.821	- 37.645
1800	8.419	56.954	50.593	11.451	322.020	291.118	- 35.347
1900	8.492	57.412	50.940	12.296	322.512	289.389	- 33.287
2000	8.560	57.849	51.274	13.149	323.004	287.632	- 31.431
2100	8.622	58.268	51.596	14.008	323.495	285.851	- 29.749
2200	8.679	58.671	51.910	14.873	323.985	284.047	- 28.217
2300	8.733	59.058	52.212	15.744	324.475	282.221	- 26.817
2400	8.783	59.430	52.505	16.620	324.963	280.375	- 25.532
2500	8.830	59.790	52.790	17.500	325.449	278.505	- 24.347
2600	8.875	60.137	53.066	18.384	325.935	276.618	- 23.252
2700	8.918	60.473	53.334	19.275	326.419	274.712	- 22.236
2800	8.958	60.796	53.595	20.169	326.902	272.788	- 21.292
2900	8.996	61.113	53.848	21.067	327.384	270.848	- 20.412
3000	9.036	61.419	54.096	21.969	327.864	268.890	- 19.589
3100	9.073	61.715	54.337	22.874	328.343	266.915	- 18.818
3200	9.109	62.004	54.572	23.783	328.821	264.926	- 18.094
3300	9.145	62.285	54.801	24.696	329.298	262.922	- 17.413
3400	9.181	62.558	55.025	25.612	329.774	260.903	- 16.771
3500	9.216	62.825	55.244	26.532	330.250	258.871	- 16.165
3600	9.252	63.085	55.459	27.456	330.724	256.825	- 15.591
3700	9.287	63.339	55.668	28.382	331.197	254.766	- 15.048
3800	9.323	63.587	55.873	29.313	331.671	252.695	- 14.533
3900	9.358	63.830	56.074	30.247	332.144	250.610	- 14.044
4000	9.395	64.067	56.271	31.185	332.616	248.512	- 13.578
4100	9.431	64.300	56.464	32.126	333.088	246.404	- 13.135
4200	9.468	64.528	56.653	33.071	333.561	244.285	- 12.712
4300	9.506	64.751	56.839	34.020	334.035	242.154	- 12.308
4400	9.544	64.970	57.021	34.972	334.506	240.011	- 11.921
4500	9.583	65.185	57.200	35.928	334.981	237.856	- 11.552
4600	9.622	65.396	57.376	36.889	335.456	235.696	- 11.198
4700	9.662	65.603	57.549	37.853	335.931	233.522	- 10.859
4800	9.702	65.807	57.719	38.821	336.408	231.338	- 10.533
4900	9.743	66.007	57.886	39.793	336.887	229.143	- 10.220
5000	9.785	66.205	58.051	40.770	337.365	226.937	- 9.919
5100	9.826	66.399	58.212	41.750	337.846	224.727	- 9.630
5200	9.871	66.590	58.372	42.735	338.329	222.501	- 9.351
5300	9.914	66.778	58.529	43.724	338.813	220.274	- 9.083
5400	9.958	66.964	58.683	44.718	339.300	218.028	- 8.824
5500	10.003	67.147	58.835	45.716	339.788	215.780	- 8.574
5600	10.048	67.328	58.985	46.719	340.278	213.519	- 8.333
5700	10.094	67.506	59.133	47.726	340.771	211.251	- 8.100
5800	10.140	67.682	59.279	48.737	341.266	208.976	- 7.874
5900	10.186	67.856	59.423	49.754	341.764	206.691	- 7.656
6000	10.233	68.027	59.565	50.775	342.263	204.396	- 7.445

Mar. 31, 1966; Dec. 31, 1970

HYDROXYL UNIPOSITIVE ION (OH^+) (IDEAL GAS) GFW = 17.0068 HO^+

Ground State Configuration $^3\Sigma^-$ ΔHf°_0 = 313.3 ± 2.5 kcal/mol

$S^\circ_{298.15}$ = 43.66 ± 0.05 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 314.8 ± 2.5 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^3\Sigma^-$	0	3
$a^1\Delta$	[17700]	2
$A^3\Pi$	22949	6
$b^1\Sigma^+$	29150	1

ω_e = [3135 ± 100] cm^{-1} $\omega_e x_e$ = [89.3 ± 50] cm^{-1} σ = 1

B_e = 16.776 cm^{-1} α_e = 0.728 cm^{-1} r_e = 1.0289 Å

Heat of Formation

The ionization potential of hydroxyl has been determined by Mann et al. (1) as 13.6 eV and by Foner and Hudson (2) as 13.18 ± 0.1 eV, both by electron impact methods. These values correspond to $\Delta Hf^\circ_0(OH^+, g)$ = 322.97 kcal/mol and 313.28 ± 2.5 kcal/mol respectively. Metzger and Cook (3) have reported the photoionization onset of the process $H_2O(g) + h\nu \rightarrow OH^+ + H + e^-$ as 18.3 eV, with JANAF auxiliary data (4) this gives $\Delta Hf^\circ_0(OH^+, g)$ = 313.3 kcal/mol, which is adopted.

Heat Capacity and Entropy

The measured electronic levels are those reported by Merer et al. (5), the rotational constants are derived from this analysis also. The estimated electronic level is from the Hartree-Fock calculations of Cade (6).

The vibrational constants are estimated so that $\Delta G_{1/2}$ is equal to that reported by Merer et al. (5). The anharmonicity, $\omega_e x_e$, is estimated by comparison with OH and NH. Calculations of $\omega_e x_e$ based on the Morse potential curve and the relation $\omega_e^2 = 4B_e^3/D_e$, or $\omega_o^2 = 4\omega_o x_o D_o$ (7) do not appear to yield values which are preferable to our estimates; this is due to the inexactness of the potential for ionic molecules.

The value of H_T-H_{298} at 0°K is -2.06 kcal/mol.

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Hydroxyl Uninegative Ion (OH^-)

(Ideal Gas) GFW = 17.0079

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	6.965	41.194	41.194	.000	-34.320	-33.157	24.305
300	6.965	41.237	41.194	.013	-34.329	-33.150	24.150
400	6.968	43.241	41.467	.710	-34.832	-32.681	17.856
500	6.977	44.797	41.984	1.407	-35.347	-32.085	14.024
600	7.000	46.071	42.562	2.105	-35.873	-31.383	11.431
700	7.044	47.153	43.142	2.807	-34.407	-30.592	9.551
800	7.110	48.098	43.704	3.515	-36.948	-29.725	8.121
900	7.196	48.940	44.240	4.230	-37.493	-28.790	6.991
1000	7.295	49.703	44.748	4.955	-38.036	-27.793	6.074
1100	7.403	50.403	45.231	5.689	-38.583	-26.743	5.313
1200	7.514	51.052	45.690	6.435	-39.124	-25.642	4.670
1300	7.624	51.658	46.126	7.192	-39.664	-24.497	4.118
1400	7.731	52.227	46.541	7.960	-40.202	-23.310	3.639
1500	7.833	52.764	46.938	8.738	-40.740	-22.084	3.218
1600	7.929	53.273	47.319	9.526	-41.275	-20.823	2.844
1700	8.019	53.756	47.683	10.324	-41.809	-19.528	2.510
1800	8.103	54.217	48.033	11.130	-42.343	-18.203	2.210
1900	8.181	54.657	48.371	11.944	-42.876	-16.847	1.938
2000	8.253	55.079	48.695	12.766	-43.409	-15.464	1.690
2100	8.320	55.483	49.009	13.595	-43.941	-14.052	1.462
2200	8.382	55.871	49.312	14.430	-44.475	-12.617	1.253
2300	8.440	56.245	49.606	15.271	-45.008	-11.157	1.060
2400	8.493	56.606	49.890	16.118	-45.543	-9.673	.881
2500	8.543	56.953	50.165	16.970	-46.079	-8.170	.714
2600	8.589	57.289	50.433	17.826	-46.615	-6.640	.558
2700	8.632	57.618	50.693	18.687	-47.153	-5.093	.412
2800	8.673	57.929	50.946	19.553	-47.693	-3.526	.275
2900	8.711	58.238	51.192	20.422	-48.234	-1.938	.146
3000	8.747	58.530	51.432	21.295	-48.776	-.334	.024
3100	8.780	58.817	51.665	22.171	-49.316	1.291	-.091
3200	8.812	59.096	51.893	23.051	-49.864	2.932	-.200
3300	8.842	59.366	52.116	23.933	-50.411	4.590	-.304
3400	8.871	59.633	52.333	24.819	-50.959	6.264	-.403
3500	8.898	59.890	52.545	25.708	-51.509	7.955	-.497
3600	8.923	60.141	52.753	26.599	-52.059	9.663	-.587
3700	8.946	60.386	52.956	27.492	-52.613	11.385	-.673
3800	8.972	60.625	53.154	28.388	-53.168	13.123	-.755
3900	8.994	60.858	53.349	29.286	-53.725	14.873	-.833
4000	9.016	61.086	53.539	30.187	-54.282	16.640	-.909
4100	9.037	61.309	53.726	31.090	-54.842	18.420	-.982
4200	9.057	61.527	53.909	31.994	-55.403	20.213	-1.052
4300	9.076	61.740	54.089	32.901	-55.966	22.021	-1.119
4400	9.095	61.949	54.265	33.809	-56.531	23.839	-1.184
4500	9.113	62.154	54.438	34.720	-57.096	25.672	-1.247
4600	9.131	62.354	54.608	35.632	-57.662	27.521	-1.308
4700	9.148	62.551	54.775	36.546	-58.232	29.378	-1.366
4800	9.164	62.744	54.939	37.462	-58.801	31.248	-1.423
4900	9.180	62.933	55.100	38.379	-59.372	33.128	-1.478
5000	9.196	63.118	55.259	39.298	-59.943	35.021	-1.531
5100	9.212	63.301	55.415	40.218	-60.517	36.929	-1.583
5200	9.227	63.480	55.568	41.140	-61.091	38.842	-1.632
5300	9.241	63.656	55.719	42.063	-61.666	40.773	-1.681
5400	9.256	63.828	55.868	42.988	-62.242	42.707	-1.728
5500	9.270	63.998	56.014	43.914	-62.818	44.659	-1.775
5600	9.284	64.166	56.158	44.842	-63.397	46.616	-1.819
5700	9.297	64.330	56.300	45.771	-63.976	48.586	-1.863
5800	9.310	64.492	56.440	46.701	-64.556	50.567	-1.905
5900	9.324	64.651	56.578	47.633	-65.137	52.556	-1.947
6000	9.337	64.808	56.713	48.566	-65.717	54.556	-1.987

Mar. 31, 1966; Dec. 31, 1970

HYDROXYL UNINEGATIVE ION (OH^-) (IDEAL GAS) GFW = 17.0079 HO^-

Ground State Configuration $^1\Sigma^+$ ΔHf°_0 = -32.85 ± 0.9 kcal/mol

$S^\circ_{298.15}$ = [41.19 ± 0.2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -34.32 ± 0.9 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = [3770] cm^{-1} $\omega_e x_e$ = [74.7] cm^{-1} σ = 1

B_e = [19.2] cm^{-1} α_e = [0.65] cm^{-1} r_e = [0.9628] Å

Heat of Formation

Branscomb (1) has obtained an electron affinity of OH of 1.83 ± 0.04 eV (42.2 ± 0.9 kcal) from the photodetachment spectrum of OH^-. The vibrational state was identified as the ground state since no other absorption sequence could be detected by a thorough search. Kay and Page (2) have also determined the electron affinity by the magnetron method and report 49.1 at 1820°K, which reduces to 40 ± 2.7 kcal at 0°K. They also disclaim prior papers, Page (3) and Page and Sugden (4), which supported higher values. Feugier and Queraud (5) have reported an electron affinity at 2250°K of 2.13 eV (49.1 kcal) which reduces to 37.7 kcal at 0°K. We adopt the value reported by Branscomb (1) which yields $\Delta Hf_0(OH^-, g)$ = -32.85 kcal/mol.

Heat Capacity and Entropy

Branscomb (1) deduced from his photodetachment spectra that ω_e, B_e and r_e are very close to the values for OH(g). Our adopted values are from the calculations of Cade (6) corrected for the mean deviations in OH and HF. The values of $\omega_e x_e$ and α_e were estimated by comparison with OH(g) and other related hydrides. The ground state configuration was assumed to be that of HF(g) with which OH^- is isoelectronic.

The value of H_T-H_{298} at 0°K is -2.057 kcal/mol.

References

1. L. M. Branscomb, Phys. Rev. 148, 11 (1966).
2. J. Kay and F. M. Page, Trans. Faraday Soc. 62, 3081 (1966).
3. F. M. Page, Discussions Faraday Soc. 19, 87 (1955).
4. F. M. Page and T. M. Sugden, Trans. Faraday Soc. 53, 1092 (1957).
5. A. Feugier and A. Queraud, Elec. MHD, Proc. Symp. 4, 2129 (1968).
6. P. E. Cade, unpublished calculations, quoted in ref. 1.

Silicon Monohydride Unipositive Ion (SiH^+)

(Ideal Gas) GFW = 29.09342

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.975	44.617	44.617	.000	274.300	265.504	- 194.619
300	6.976	44.660	44.617	.013	274.306	265.449	- 193.379
400	7.033	46.673	44.891	.713	274.649	262.443	- 143.392
500	7.156	48.254	45.411	1.422	274.962	259.356	- 113.364
600	7.326	49.574	45.998	2.146	275.265	256.206	- 93.323
700	7.513	50.717	46.592	2.887	275.566	253.005	- 78.992
800	7.698	51.732	47.172	3.648	275.871	249.761	- 68.231
900	7.868	52.649	47.731	4.427	276.179	246.480	- 59.854
1000	8.021	53.486	48.265	5.221	276.487	243.164	- 53.143
1100	8.155	54.257	48.775	6.030	276.795	239.816	- 47.687
1200	8.272	54.972	49.262	6.852	277.101	236.440	- 43.062
1300	8.374	55.638	49.727	7.684	277.403	233.039	- 39.177
1400	8.464	56.262	50.172	8.526	277.700	229.616	- 35.845
1500	8.542	56.849	50.598	9.376	277.989	226.173	- 32.953
1600	8.611	57.402	51.006	10.234	278.269	222.707	- 30.420
1700	8.673	57.926	51.398	11.098	266.549	219.333	- 28.197
1800	8.728	58.423	51.774	11.969	266.868	216.547	- 26.292
1900	8.777	58.897	52.137	12.844	267.187	213.742	- 24.586
2000	8.822	59.348	52.486	13.724	267.506	210.922	- 23.048
2100	8.863	59.779	52.823	14.608	267.825	208.084	- 21.656
2200	8.901	60.193	53.149	15.496	268.144	205.231	- 20.388
2300	8.935	60.589	53.466	16.388	268.463	202.365	- 19.229
2400	8.967	60.970	53.769	17.283	268.782	199.486	- 18.166
2500	8.997	61.337	54.064	18.182	269.100	196.590	- 17.186
2600	9.026	61.690	54.351	19.083	269.417	193.684	- 16.281
2700	9.053	62.031	54.629	19.987	269.734	190.764	- 15.441
2800	9.078	62.361	54.899	20.893	270.051	187.835	- 14.661
2900	9.103	62.680	55.162	21.802	270.368	184.894	- 13.934
3000	9.126	62.989	55.418	22.714	270.685	181.939	- 13.254
3100	9.149	63.289	55.667	23.627	271.000	178.974	- 12.618
3200	9.172	63.579	55.910	24.543	271.316	176.003	- 12.020
3300	9.194	63.862	56.146	25.462	271.632	173.021	- 11.459
3400	9.215	64.137	56.377	26.382	271.948	170.027	- 10.929
3500	9.237	64.404	56.603	27.305	272.263	167.024	- 10.429
3600	9.259	64.665	56.823	28.230	180.617	166.270	- 10.094
3700	9.281	64.919	57.039	29.157	181.030	165.866	- 9.797
3800	9.303	65.167	57.249	30.086	181.444	165.451	- 9.516
3900	9.326	65.408	57.455	31.017	181.857	165.024	- 9.248
4000	9.349	65.645	57.657	31.951	182.269	164.587	- 8.993
4100	9.372	65.876	57.855	32.887	182.681	164.138	- 8.749
4200	9.396	66.102	58.048	33.825	183.093	163.681	- 8.517
4300	9.421	66.324	58.238	34.766	183.507	163.214	- 8.295
4400	9.446	66.540	58.425	35.710	183.920	162.737	- 8.083
4500	9.472	66.753	58.607	36.655	184.332	162.253	- 7.880
4600	9.498	66.961	58.787	37.604	184.747	161.758	- 7.685
4700	9.526	67.166	58.963	38.555	185.162	161.255	- 7.498
4800	9.554	67.367	59.136	39.509	185.578	160.740	- 7.319
4900	9.582	67.564	59.306	40.466	185.995	160.220	- 7.146
5000	9.612	67.758	59.473	41.426	186.413	159.685	- 6.980
5100	9.642	67.949	59.637	42.388	186.832	159.151	- 6.820
5200	9.673	68.136	59.799	43.354	187.253	158.603	- 6.666
5300	9.705	68.321	59.958	44.323	187.675	158.050	- 6.517
5400	9.737	68.502	60.114	45.295	188.098	157.484	- 6.374
5500	9.770	68.681	60.269	46.270	188.522	156.912	- 6.235
5600	9.804	68.858	60.420	47.249	188.949	156.335	- 6.101
5700	9.838	69.032	60.570	48.231	189.377	155.752	- 5.972
5800	9.873	69.203	60.717	49.217	189.805	155.157	- 5.846
5900	9.908	69.372	60.863	50.206	190.236	154.553	- 5.725
6000	9.944	69.539	61.006	51.198	190.667	153.943	- 5.607

Dec. 31, 1971

SILICON MONOHYDRIDE UNIPOSITIVE ION (SiH^+) (IDEAL GAS) GFW = 29.09342

Ground State Configuration $^1\Sigma^+$ ΔHf°_0 = 272.5 ± 2.7 kcal/mol

$S^\circ_{298.15}$ = 44.617 ± 0.001 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 274.3 ± 2.7 kcal/mol

Electronic Levels and Degeneracies

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$A^1\Pi$	25025.2	2

ω_e = 2157.1 cm^{-1} $\omega_e x_e$ = 34.21 cm^{-1} σ = 1

B_e = 7.8603 cm^{-1} α_e = 0.2096 cm^{-1} r_e = 1.499 Å

Heat of Formation

According to Douglas and Lutz (1) the A state must have an extremely shallow potential curve since the observed *first vibrational quantum is only* $\Delta G'_{1/2}$ = 390.2 cm^{-1}. Since no other levels were observed they estimated ω'_e and $\omega_e x'_e$ for the A state from $\Delta G'_{1/2}$, α'_e and B'_e. From the estimated ω'_e and $\omega_e x'_e$ they obtained a dissociation limit of 1180 cm^{-1}. Thus, the dissociation limit of the A state is likely to lie between 390 and 1180 cm^{-1}, on this basis Douglas and Lutz select D'_0 = 780 ± 600 cm^{-1}. Since SiH^+ can correlate with normal products $Si^+(^2P)$ and $H(^2S)$ in both the X and A states these are assumed to be the products. Thus, the dissociation energy of the ground state to these products is 25805 ± 600 cm^{-1} (73.78 ± 1.7 kcal). With $\Delta Hf^\circ_0(H, g)$ = 51.631 ± 0.001 kcal/mol (2) and $\Delta Hf^\circ_0(Si^+, g)$ = 294.626 ± 1.0 kcal/mol (2) we obtain $\Delta Hf^\circ_0(SiH^+, g)$ = 272.5 ± 2.7 kcal/mol, which is adopted. This gives an ionization potential of 182.9 kcal (7.93 eV) with the JANAF value for SiH (2).

Heat Capacity and Entropy

The electronic levels and vibrational and rotational constants are all from Douglas and Lutz (1).

References

1. A. E. Douglas and B. L. Lutz, Can. J. Phys. 48, 247 (1970).
2. JANAF Thermochemical Tables. H(g) 9-30-65; Si(g) 3-31-67; SiH(g) 12-31-69; Si^+(g) 12-31-71.

Potassium Hydroxide, Dimeric ($K_2O_2H_2$)

(Ideal Gas) GFW = 112.2187

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	− 4.415	− 153.430	− 153.430	INFINITE
100	13.560	60.002	94.314	− 3.431	− 154.727	− 152.447	333.173
200	17.684	70.956	80.092	− 1.877	− 155.662	− 149.792	163.685
298	19.465	78.366	78.366	.000	− 156.500	− 146.733	107.558
300	19.496	78.487	78.366	.036	− 156.516	− 146.672	106.850
400	21.073	84.315	79.150	2.066	− 158.519	− 143.044	78.156
500	22.452	89.170	80.682	4.244	− 159.257	− 139.088	60.795
600	23.578	93.366	82.454	6.548	− 159.860	− 134.994	49.172
700	24.486	97.072	84.283	8.952	− 160.368	− 130.808	40.840
800	25.239	100.392	86.092	11.440	− 160.808	− 126.557	34.574
900	25.879	103.403	87.851	13.997	− 161.201	− 122.250	29.686
1000	26.435	106.159	89.546	16.613	− 161.572	− 117.903	25.768
1100	26.925	108.702	91.173	19.281	− 199.743	− 111.471	22.147
1200	27.362	111.063	92.733	21.996	− 199.604	− 103.450	18.841
1300	27.751	113.269	94.229	24.752	− 199.443	− 95.446	16.046
1400	28.106	115.339	95.664	27.545	− 199.262	− 87.451	13.652
1500	28.412	117.288	97.041	30.371	− 199.067	− 79.470	11.579
1600	28.692	119.131	98.365	33.226	− 198.861	− 71.504	9.767
1700	28.943	120.876	99.638	36.108	− 198.644	− 63.552	8.170
1800	29.168	122.539	100.865	39.014	− 198.420	− 55.612	6.752
1900	29.370	124.122	102.047	41.941	− 198.194	− 47.685	5.485
2000	29.552	125.633	103.189	44.887	− 197.963	− 39.768	4.346
2100	29.716	127.079	104.293	47.851	− 197.732	− 31.863	3.316
2200	29.864	128.464	105.360	50.830	− 197.507	− 23.970	2.381
2300	29.996	129.795	106.394	53.823	− 197.283	− 16.089	1.529
2400	30.119	131.074	107.396	56.829	− 197.066	− 8.213	.748
2500	30.230	132.306	108.367	59.847	− 196.861	− .354	.031
2600	30.330	133.494	109.311	62.875	− 196.661	7.510	− .631
2700	30.422	134.640	110.228	65.912	− 196.477	15.354	− 1.243
2800	30.505	135.748	111.120	68.959	− 196.308	23.195	− 1.810
2900	30.582	136.820	111.988	72.013	− 196.154	31.038	− 2.339
3000	30.652	137.858	112.833	75.075	− 196.017	38.865	− 2.831
3100	30.717	138.864	113.656	78.143	− 195.902	46.695	− 3.292
3200	30.776	139.840	114.459	81.218	− 195.809	54.520	− 3.724
3300	30.831	140.788	115.243	84.298	− 195.742	62.338	− 4.128
3400	30.881	141.709	116.008	87.384	− 195.704	70.155	− 4.510
3500	30.928	142.605	116.755	90.474	− 195.697	77.976	− 4.869
3600	30.972	143.477	117.485	93.569	− 195.725	85.800	− 5.209
3700	31.012	144.326	118.199	96.669	− 195.792	93.618	− 5.530
3800	31.050	145.154	118.898	99.772	− 195.902	101.442	− 5.834
3900	31.085	145.961	119.581	102.879	− 196.059	109.265	− 6.123
4000	31.117	146.748	120.251	105.989	− 196.269	117.099	− 6.398
4100	31.146	147.517	120.906	109.102	− 196.537	124.937	− 6.660
4200	31.176	148.268	121.549	112.218	− 196.869	132.782	− 6.909
4300	31.203	149.002	122.179	115.337	− 197.267	140.638	− 7.148
4400	31.228	149.719	122.797	118.459	− 197.743	148.496	− 7.376
4500	31.252	150.421	123.403	121.583	− 198.300	156.375	− 7.595
4600	31.274	151.108	123.998	124.709	− 198.944	164.266	− 7.804
4700	31.295	151.781	124.582	127.838	− 199.683	172.170	− 8.006
4800	31.314	152.440	125.155	130.968	− 200.521	180.094	− 8.200
4900	31.333	153.086	125.719	134.100	− 201.467	188.029	− 8.386
5000	31.350	153.719	126.272	137.234	− 202.523	195.981	− 8.566
5100	31.367	154.340	126.817	140.370	− 203.697	203.975	− 8.741
5200	31.382	154.950	127.352	143.508	− 204.991	211.973	− 8.909
5300	31.397	155.547	127.878	146.647	− 206.409	220.011	− 9.072
5400	31.411	156.135	128.396	149.787	− 207.956	228.059	− 9.230
5500	31.424	156.711	128.906	152.929	− 209.630	236.151	− 9.384
5600	31.437	157.277	129.407	156.072	− 211.434	244.270	− 9.533
5700	31.449	157.834	129.901	159.216	− 213.364	252.424	− 9.678
5800	31.460	158.381	130.387	162.362	− 215.421	260.615	− 9.820
5900	31.471	158.919	130.866	165.508	− 217.600	268.845	− 9.959
6000	31.482	159.448	131.338	168.656	− 219.897	277.114	− 10.094

June 30, 1962; Mar. 31, 1966; Dec. 31, 1970

POTASSIUM HYDROXIDE, DIMERIC ($K_2O_2H_2$) (IDEAL GAS) GFW = 112.2187 $H_2K_2O_2$

Point Group C_{2h} ΔHf°_0 = −153.4 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = [78.4 ± 2.0] gibbs/mol $\Delta Hf^\circ_{298.15}$ = −156.5 ± 3.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹	ω, cm⁻¹
[273] (1)	[3700] (1)
[150] (1)	[3700] (1)
[235] (1)	[1250] (1)
[150] (1)	[1250] (1)
[255] (1)	[1250] (1)
[258] (1)	[1250] (1)

Bond Distance: K-O = [2.43] Å O-H = [0.96] Å

Bond Angle: K-O-K = [90°] K-O-H = [110°] σ = 2

Product of the Moments of Inertia: $I_A I_B I_C$ = [3.7587] x 10^{-113} g^3 cm^6

Heat of Formation

ΔHf°_{298} ($K_2(OH)_2$, g) is calculated from the heat of dimerization, ΔH_{298}(dimerization) = −45.3 ± 3.0 kcal/mol, and the heat of formation of the monomer, ΔHf°_{298} (KOH, g) = −55.6 ± 3.0 kcal/mol. See KOH(g) table for details.

Heat Capacity and Entropy

A key to the molecular structure of $K_2(OH)_2$(g) is provided by the work of Büchler et al. (1) which involves the electric deflection of molecular beams of $Cs_2(OH)_2$(g) and $Na_2(OH)_2$(g). Their results indicate that these dimers are nonpolar which implies a planar structure for at least the H_2O_2 part of the molecule. The three models proposed thus far for the dimeric alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer et al. (2) proposed a model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter (3) adopted the square planar model for the H_2O_2 configuration but did not allow for hydrogen bonding. Berkowitz et al. (4) proposed a model for $Li_2(OH)_2$(g) which consisted of a trans configuration with hydrogens above and below the plane of a rhombus formed by the lithium and oxygen atoms, the O-Li-O bond angle being 100°. The adopted molecular structure for $K_2(OH)_2$(g) is similar to the model of Berkowitz et al. (4) but with the O-K-O bond angle equal to 90°. The K-O-H bond angle is assumed equal to 110°. The K-O bond distance is estimated as being 10% longer than that in KOH(g). The O-H bond distance is estimated to be the same as in H_2O(g). The three principal moments of inertia are: I_A = [17.5202] x 10^{-39}, I_B = [38.5534] x 10^{-39}, and I_C = [55.6452] x 10^{-39} g cm^2.

The first six vibrational frequencies are taken equal to those for dimeric K_2F_2(g) (See K_2F_2(g) table), and the remaining O-H stretching and bending modes are estimates taken from the work of Berkowitz et al. (4).

References

1. A. Büchler, J. L. Stauffer, and W. Klemperer, J. Chem. Phys., 46, 605 (1967).
2. S. H. Bauer, R. H. Diner, and R. F. Porter, J. Chem. Phys., 29, 991 (1958).
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).

Lithium Hydroxide, Dimeric ($(LiOH)_2$)

(Ideal Gas) GFW = 47.8927

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	− 3.866	− 167.157	− 167.157	INFINITE
100	8.982	50.643	77.175	− 2.653	− 168.035	− 166.170	363.163
200	13.685	58.325	65.911	− 1.517	− 169.078	− 163.899	179.100
298	17.092	64.453	64.453	.000	− 170.000	− 161.155	118.130
300	17.075	64.558	64.453	.032	− 170.016	− 161.101	117.382
400	19.542	69.825	65.154	1.868	− 170.827	− 158.002	86.328
500	21.815	74.396	66.556	3.920	− 173.041	− 154.560	67.558
600	22.835	78.432	68.205	6.136	− 173.706	− 150.798	54.928
700	23.931	82.038	69.928	8.476	− 174.246	− 146.937	45.876
800	24.808	85.293	71.649	10.915	− 174.695	− 143.006	39.067
900	25.535	88.258	73.332	13.433	− 175.085	− 139.020	33.759
1000	26.154	90.981	74.963	16.018	− 175.425	− 134.998	29.503
1100	26.693	93.500	76.535	18.661	− 175.723	− 130.936	26.015
1200	27.166	95.843	78.047	21.355	− 175.987	− 126.853	23.103
1300	27.584	98.034	79.501	24.093	− 176.222	− 122.750	20.636
1400	27.955	100.092	80.899	26.870	− 176.433	− 118.627	18.519
1500	28.286	102.032	82.244	29.682	− 176.624	− 114.491	16.681
1600	28.581	103.867	83.539	32.526	− 176.797	− 110.343	15.072
1700	28.844	105.608	84.786	35.397	− 247.049	− 103.528	13.309
1800	29.080	107.264	85.989	38.294	− 246.832	− 95.090	11.545
1900	29.291	108.842	87.151	41.212	− 246.609	− 86.664	9.969
2000	29.480	110.349	88.273	44.151	− 246.381	− 78.255	8.551
2100	29.651	111.792	89.359	47.108	− 246.151	− 69.855	7.270
2200	29.805	113.175	90.410	50.081	− 245.922	− 61.464	6.106
2300	29.944	114.503	91.429	53.068	− 245.690	− 53.086	5.044
2400	30.070	115.780	92.417	56.069	− 245.464	− 44.715	4.072
2500	30.184	117.009	93.377	59.082	− 245.242	− 36.358	3.178
2600	30.288	118.195	94.309	62.106	− 245.022	− 28.006	2.354
2700	30.382	119.340	95.215	65.139	− 244.812	− 19.665	1.592
2800	30.469	120.447	96.096	68.182	− 244.607	− 11.330	.884
2900	30.548	121.517	96.954	71.233	− 244.414	− 2.999	.226
3000	30.620	122.554	97.790	74.291	− 244.229	5.323	− .388
3100	30.687	123.559	98.606	77.357	− 244.056	13.639	− .962
3200	30.748	124.535	99.401	80.428	− 243.895	21.947	− 1.499
3300	30.804	125.482	100.177	83.506	− 243.748	30.252	− 2.004
3400	30.857	126.402	100.935	86.589	− 243.615	38.555	− 2.478
3500	30.905	127.297	101.675	89.677	− 243.496	46.850	− 2.925
3600	30.950	128.168	102.399	92.770	− 243.394	55.145	− 3.348
3700	30.991	129.017	103.107	95.867	− 243.310	63.435	− 3.747
3800	31.030	129.844	103.800	98.968	− 243.242	71.733	− 4.126
3900	31.066	130.650	104.478	102.073	− 243.193	80.018	− 4.484
4000	31.099	131.437	105.142	105.181	− 243.165	88.302	− 4.825
4100	31.131	132.206	105.793	108.293	− 243.156	96.591	− 5.149
4200	31.160	132.956	106.431	111.407	− 243.170	104.875	− 5.457
4300	31.188	133.690	107.056	114.525	− 243.203	113.164	− 5.752
4400	31.213	134.407	107.670	117.645	− 243.259	121.452	− 6.033
4500	31.238	135.109	108.272	120.767	− 243.342	129.741	− 6.301
4600	31.260	135.796	108.863	123.892	− 243.447	138.038	− 6.558
4700	31.282	136.468	109.443	127.019	− 243.580	146.327	− 6.804
4800	31.302	137.127	110.013	130.148	− 243.739	154.623	− 7.040
4900	31.321	137.773	110.573	133.280	− 243.927	162.922	− 7.267
5000	31.339	138.406	111.123	136.413	− 244.144	171.228	− 7.484
5100	31.356	139.026	111.664	139.547	− 244.396	179.546	− 7.694
5200	31.372	139.635	112.196	142.684	− 244.679	187.855	− 7.895
5300	31.387	140.233	112.719	145.822	− 244.998	196.179	− 8.090
5400	31.401	140.820	113.234	148.961	− 245.354	204.499	− 8.277
5500	31.415	141.396	113.741	152.102	− 245.749	212.840	− 8.457
5600	31.428	141.962	114.240	155.244	− 246.186	221.172	− 8.632
5700	31.440	142.519	114.731	158.387	− 246.665	229.527	− 8.801
5800	31.452	143.066	115.215	161.532	− 247.191	237.889	− 8.964
5900	31.463	143.603	115.692	164.678	− 247.762	246.255	− 9.122
6000	31.474	144.132	116.161	167.825	− 248.384	254.636	− 9.275

Dec. 31, 1960; Mar. 31, 1966; June 30, 1971

LITHIUM HYDROXIDE, DIMERIC ($Li_2O_2H_2$) (IDEAL GAS) GFW = 47.8927 $H_2Li_2O_2$

Point Group [C_{2h}] ΔHf°_0 = −167.2 ± 8.0 kcal/mol

$S^\circ_{298.15}$ = [64.45 ± 2.0] gibbs/mol ΔHf°_{298} = −170.0 ± 8.0 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies (ω, cm^{-1}, all singly degenerate)

[400] [400] [500] [500] [450] [350] [3700] [3700] [1250] [1250] [1250] [1250]

Bond Distance: Li-O = [1.74] Å O-H = [0.97] Å

Bond Angle: Li-O-Li = [90]° Li-O-H = [110]° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.2833 x 10^{-115}] g^3 cm^6

Heat of Formation

The reaction between water vapor and condensed lithium oxide has been investigated as a function of temperature and water pressure by means of such techniques as mass spectrometry (1, 2) and transpiration (3). At low water pressures (<0.01 Torr) in the temperature range 780-900 K, Schoonmaker and Porter (1) observed only Li^+ and $LiOH^+$ ion species in the mass spectrum of the reaction products. The precursor of these two ions was assumed to be monomeric LiOH. Berkowitz et al. (2) in a more extensive mass spectrometric study of the $Li_2O(c)$-$H_2O(g)$ equilibrium detected not only monomeric and dimeric LiOH in the vapor phase, but also trace amounts of trimer ($Li_3(OH)_3$). Their work covered the temperature range 1100-1400 K at water pressures of 0.04 and 0.16 Torr. Absolute equilibrium constants were determined for the dimerization reaction, $2LiOH(g) = Li_2(OH)_2(g)$, by calibrating the mass spectrometer in units of pressure. This was accomplished by measuring the water pressure externally and simultaneously monitoring the intensity of the H_2O^+ peak. In an attempt to investigate the same equilibrium at water pressures inaccessible to mass spectrometry, Berkowitz-Mattuck and Büchler (3) used the transpiration method. Their work covered water pressures of 4.58 and 19.5 Torr at 1095 and 1145 K. An analysis of these equilibrium data are summarized below.

Investigator	Reaction	Method	Temp. Range K	No. of Points	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol	$\Delta Hf^\circ_{298}(Li_2(OH)_2, g)$[a] kcal/mol
Berkowitz et al. (2)	A	Mass Spec.	1119-1352	9[b]	−57.2	−63.8±1.4	−5.4±2.8	−175.8±4.0
Berkowitz-Mattuck and Büchler (3)	B	Transpiration	1095 and 1145	2		12.7		−188.2±4.0

Reaction: A $2LiOH(g) = Li_2(OH)_2(g)$ B $H_2O(g) + Li_2O(c) = Li_2(OH)_2(g)$

[a] Third Law values based upon JANAF ΔHf°_{298} data for LiOH(g) and $Li_2O(c)$ (4).

[b] One point rejected due to failure of a statistical test.

It seems most likely that the equilibrium data of Berkowitz-Mattuck and Büchler (3) are in error, since no satisfactory compromise in the flow rates of the inert carrier gas could be found such that saturation was achieved while eliminating thermal diffusion effects. Under these conditions the simple equations relating partial pressures to the masses transported during the transpiration experiment are no longer valid. Furthermore, the authors assumed that under the conditions of their experiment only dimeric LiOH would be formed. The work of Berkowitz et al. (2) clearly establishes the existence of a trimer at water pressures some 100 times lower than those employed by Berkowitz-Mattuck and Büchler (3).

Trends in the dimerization energies for the higher alkali metal hydroxides, as well as for the dimeric alkali fluorides and chlorides, suggest that the heat of dimerization for LiOH from the work of Berkowitz et al. (2) may be slightly high. Such a comparison results in ΔH_{298}(dimerization) values in the range −(52-61) kcal/mol. Further support for a lower value comes from the mass spectral work of Porter and Schoonmaker (1). They investigated the reaction of $H_2O(g)$ with a mixture of condensed Li_2O-Na_2O. From the reported ion current intensities for the various ions found in the reaction products we calculate, ΔH_{298}(dimerization, NaOH(g)) − ΔH_{298}(dimerization, LiOH(g)) = 5.3 kcal/mol. This value yields ΔH_{298}(dimerization) = −56.0 ± 5.0 kcal/mol for LiOH(g) when used in combination with the adopted value for NaOH(g) (4). A high heat of dimerization from the mass spectral work of Berkowitz et al. (2) is easily reconciled in terms of nonequilibrium measurements. Based upon these findings, we adopt ΔH_{298}(dimerization) = −58.0 ± 5.0 kcal/mol for LiOH(g). Combining this result with the heat of formation for LiOH(g) (4), that for the dimer is $\Delta Hf^\circ_{298}(Li_2(OH)_2, g)$ = −170.0 ± 8.0 kcal/mol.

Heat Capacity and Entropy

The molecular structure of $Li_2(OH)_2(g)$ is assumed identical to that adopted for the higher alkali metal hydroxide dimers. It consists of a planar configuration for the lithium and oxygen atoms with the O-Li-O bond angle equal to 90°. The hydrogen atoms are placed in a trans configuration above and below the plane of the rhombus formed by the lithium and oxygen atoms. The Li-O-H bond angle is assumed equal to 110°. The Li-O bond distance is estimated as being 10% longer than in LiOH(g). The O-H bond distance is estimated to be the same as in $H_2O(g)$. The principal moments of inertia are: I_A = [9.2484 x 10^{-39}], I_B = [3.7005 x 10^{-39}], and I_C = [12.5184 x 10^{-38}] g cm^2.

The first six vibrational frequencies are estimated by comparison with calculated (5) and experimental (4, 6) frequencies for $Li_2F_2(g)$. In the estimation it is assumed that the bulkier OH group would tend to reduce the frequencies of $Li_2(OH)_2(g)$ relative to those for $Li_2F_2(g)$. The remaining OH stretching and bending frequencies are estimates from the work of Berkowitz et al. (2).

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$H_2Li_2O_2$

Sodium Hydroxide, Dimeric ($Na_2O_2H_2$)

(Ideal Gas) GFW = 79.9943

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	-4.135	-142.154	-142.154	INFINITE
100	11.924	56.308	88.609	-3.230	-143.342	-141.257	308.716
200	16.732	66.319	75.110	-1.758	-144.383	-138.769	151.640
298	16.949	73.442	73.442	.000	-145.200	-135.848	99.579
300	16.985	73.559	73.442	.035	-145.215	-135.789	98.922
400	20.765	79.272	74.209	2.025	-147.318	-132.423	72.352
500	22.248	84.070	75.714	4.178	-148.077	-128.607	56.214
600	23.434	88.236	77.461	6.465	-148.687	-124.654	45.405
700	24.381	91.922	79.269	8.857	-149.187	-120.609	37.656
800	25.157	95.230	81.061	11.335	-149.603	-116.497	31.825
900	25.813	98.232	82.804	13.884	-149.960	-112.335	27.279
1000	26.381	100.981	84.486	16.495	-150.274	-108.137	23.633
1100	26.881	103.520	86.103	19.158	-150.568	-103.913	20.646
1200	27.324	105.878	87.654	21.869	-197.319	-98.744	17.984
1300	27.720	108.081	89.141	24.622	-197.161	-90.535	15.220
1400	28.073	110.148	90.569	27.412	-196.983	-82.341	12.854
1500	28.386	112.096	91.939	30.235	-196.791	-74.157	10.805
1600	28.671	113.938	93.257	33.088	-196.587	-65.989	9.014
1700	28.924	115.683	94.526	35.968	-196.368	-57.830	7.435
1800	29.151	117.343	95.748	38.872	-196.144	-49.689	6.033
1900	29.355	118.925	96.926	41.798	-195.913	-41.557	4.780
2000	29.538	120.435	98.064	44.742	-195.680	-33.442	3.654
2100	29.704	121.881	99.164	47.705	-195.440	-25.337	2.637
2200	29.853	123.266	100.228	50.683	-195.202	-17.242	1.713
2300	29.986	124.596	101.259	53.675	-194.961	-9.160	.870
2400	30.110	125.875	102.258	56.680	-194.723	-1.081	.098
2500	30.221	127.106	103.228	59.696	-194.488	6.974	-.610
2600	30.322	128.294	104.169	62.724	-194.254	15.034	-1.264
2700	30.414	129.440	105.084	65.761	-194.026	23.076	-1.868
2800	30.496	130.547	105.974	68.806	-193.805	31.110	-2.428
2900	30.575	131.619	106.840	71.860	-193.587	39.147	-2.950
3000	30.646	132.657	107.683	74.921	-193.379	47.165	-3.436
3100	30.711	133.663	108.505	77.989	-193.176	55.179	-3.890
3200	30.771	134.639	109.306	81.063	-192.984	63.187	-4.315
3300	30.826	135.586	110.088	84.143	-192.803	71.189	-4.715
3400	30.877	136.507	110.852	87.228	-192.632	79.183	-5.090
3500	30.924	137.403	111.598	90.318	-192.475	87.182	-5.444
3600	30.966	138.275	112.327	93.413	-192.331	95.169	-5.778
3700	31.008	139.124	113.040	96.512	-192.203	103.150	-6.093
3800	31.046	139.951	113.737	99.614	-192.090	111.138	-6.392
3900	31.081	140.758	114.420	102.721	-191.997	119.109	-6.675
4000	31.114	141.546	115.088	105.831	-191.923	127.086	-6.944
4100	31.145	142.314	115.743	108.943	-191.872	135.066	-7.200
4200	31.173	143.065	116.384	112.059	-191.844	143.035	-7.443
4300	31.200	143.799	117.013	115.178	-191.840	151.012	-7.675
4400	31.225	144.517	117.630	118.299	-191.867	158.979	-7.897
4500	31.249	145.219	118.236	121.423	-191.924	166.958	-8.109
4600	31.271	145.906	118.830	124.549	-192.014	174.935	-8.311
4700	31.292	146.578	119.413	127.677	-192.142	182.912	-8.505
4800	31.312	147.237	119.986	130.808	-192.309	190.892	-8.692
4900	31.331	147.883	120.548	133.940	-192.521	198.880	-8.870
5000	31.348	148.516	121.102	137.074	-192.781	206.867	-9.042
5100	31.365	149.137	121.645	140.209	-193.094	214.870	-9.208
5200	31.380	149.746	122.180	143.347	-193.460	222.865	-9.367
5300	31.395	150.344	122.706	146.485	-193.889	230.884	-9.521
5400	31.409	150.931	123.223	149.626	-194.383	238.895	-9.669
5500	31.423	151.508	123.732	152.767	-194.946	246.924	-9.812
5600	31.435	152.074	124.233	155.910	-195.588	254.960	-9.950
5700	31.447	152.631	124.726	159.054	-196.306	263.014	-10.085
5800	31.459	153.178	125.212	162.200	-197.109	271.081	-10.215
5900	31.470	153.715	125.691	165.346	-198.002	279.164	-10.341
6000	31.480	154.244	126.162	168.493	-198.986	287.258	-10.463

Mar. 31, 1966; Dec. 31, 1970

SODIUM HYDROXIDE, DIMERIC ($Na_2O_2H_2$) (IDEAL GAS) GFW = 79.9943 $H_2Na_2O_2$

Point Group C_{2h}

ΔHf°_0 = -142.2 ± 6.0 kcal/mol

$S^\circ_{298.15}$ = [73.4 ± 2.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -145.2 ± 6.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹	ω, cm⁻¹
[350] (1)	[3700] (1)
[209] (1)	[3700] (1)
[270] (1)	[1250] (1)
[201] (1)	[1250] (1)
[294] (1)	[1250] (1)
[313] (1)	[1250] (1)

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

Bond Angle: Na-O-Na = [90°] Na-O-H = [110°] σ = 2

Product of the Moments of Inertia: $I_A I_B I_C$ = [8.1568] x 10^{-114} g^3 cm^6

Heat of Formation

Mass spectrometric studies of the vapors in equilibrium with NaOH(ℓ) (1, 2) and mixed NaOH-KOH condensed phases (3, 4), along with a study of the vapor composition by a molecular beam velocity analysis technique (5), have established the importance of monomeric and dimeric species in the temperature range 573°-1050°K. Absolute partial pressures for the monomer and dimer calculated from peak intensity data by Porter and Schoonmaker (3) are analyzed by the third law method with JANAF free energy functions (6) to give a heat of dimerization of -50.0 kcal/mol at 298.15°K. Schoonmaker and Porter (4) also calculated differences in the free energies of dimerization for several alkali metal hydroxide pairs from peak intensity data on mixed systems. A third law analysis of the free energy data for the NaOH-KOH system leads to a difference in their heats of dimerization of -6.0 kcal/mol at 298.15°K. Based upon the adopted value for KOH(g), ΔH(dimerization) = -45.3 ± 3.0 kcal/mol (7), we derive ΔH(dimerization) = -51.3 kcal/mol for NaOH(g). For the reaction 2NaOH(g) = $Na_2(OH)_2$(g), we adopt a mean of these two results, ΔH_{298}(dimerization) = -50.7 ± 3.0 kcal/mol. Combining this result with the adopted heat of formation for NaOH(g) (6), that for the dimer is ΔHf°_{298} ($Na_2(OH)_2$, g) = -145.2 ± 6.0 kcal/mol.

Heat Capacity and Entropy

A key to the molecular structure of $Na_2(OH)_2$(g) is provided by the work of Büchler et al. (8) which involves the electric deflection of molecular beams of $Cs_2(OH)_2$(g) and $Na_2(OH)_2$(g). Their results indicate that these dimers are nonpolar which implies a planar structure for at least the M_2O_2 part of the molecule. The three models proposed thus far for the dimeric alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer et al. (9) proposed a model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter (4) adopted the square planar model for the M_2O_2 configuration but did not allow for hydrogen bonding. Berkowitz et al. (10) proposed a model for $Li_2(OH)_2$(g) which consisted of a trans configuration with hydrogens above and below the plane of a rhombus formed by the lithium and oxygen atoms, the O-Li-O bond angle being 100°. The adopted molecular structure for $Na_2(OH)_2$(g) is similar to the model of Berkowitz et al. (10) but with the O-Na-O bond angle equal to 90°. The Na-O-H bond angle is assumed equal to 110°. The Na-O bond distance is estimated as being 12% longer than that in NaOH(g). The O-H bond distance is estimated to be the same as in H_2O(g). The three principal moments of inertia are: I_A = [14.083] x 10^{-39}, I_B = [18.188] x 10^{-39}, and I_C = [31.845] x 10^{-39} g cm^2.

The first six vibrational frequencies are estimated by comparison with those for other alkali metal fluorides and hydroxides. The remaining O-H stretching and bending modes are estimates taken from the work of Berkowitz et al. (10).

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Orthophosphoric Acid (H_3PO_4)

(Crystal) GFW = 97.9953

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	.000	.000	INFINITE	- 4.058	- 298.810	- 298.810	INFINITE
100	10.240	8.252	43.876	- 3.562	- 300.932	- 289.671	633.075
200	18.130	17.829	28.506	- 2.135	- 302.119	- 277.918	303.695
298	25.350	26.421	26.421	.000	- 302.800	- 265.874	194.891
300	25.480	26.578	26.421	.047	- 302.807	- 265.645	193.522
400	32.720	34.900	27.507	2.957	- 302.893	- 253.228	138.357
500	39.960	42.979	29.796	6.591	- 302.341	- 240.862	105.281
600	47.200	50.904	32.656	10.949	- 301.144	- 228.669	83.293
700	54.440	58.724	35.822	16.031	- 299.304	- 216.725	67.665
800	61.680	66.466	39.169	21.837	- 317.236	- 210.403	57.480
900	68.920	74.149	42.630	28.367	- 313.838	- 197.244	47.897
1000	76.160	81.785	46.164	35.621	- 309.754	- 184.502	40.323

June 30, 1962; Dec. 31, 1971

ORTHOPHOSPHORIC ACID (H_3PO_4) (CRYSTAL) GFW = 97.9953 H_3O_4P

$S^\circ_{298.15}$ = 26.42 ± 0.1 gibbs/mol

Tm = 315.5 ± 5 K

ΔHf°_0 = -298.8 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -302.8 ± 0.5 kcal/mol

ΔHm^* = 3.2 ± 0.2 kcal/mol

Heat of Formation

Recent calorimetric measurements (1, 2, 3) indicate the National Bureau of Standards' selected value quoted in reference (4), $\Delta Hf^\circ_{298}(H_3PO_4, c)$ = -305.7 ± 0.3 kcal/mol, is probably in error. The value was taken from Holmes' work (5). The data are summarized below, with heat values based on white phosphorus reference state.

Investigator	Method	n Moles of H_2O	$\Delta Hf^\circ_{298}(H_3PO_4, aq)$ kcal/mol	$\Delta Hf^\circ_{298}(H_3PO_4, c)$ kcal/mol
Head (1)	a & b	40	-309.34 ± 0.38	-307.0 ± 0.4
Birley (2)	a	100	-309.8 ± 0.35	-307.18 ± 0.5
Irving (3)	a	0.6416	-305.9 ± 0.5	-307.36 ± 0.5
Holmes (5)	a & b	----	----	-307.4 ± 0.5*

a = solution calorimetry; b = combustion calorimetry

* see text

Head and Lewis (1) determined the heat of combustion of phosphorus and heats of hydrolysis of combustion products which led to $\Delta Hf^\circ_{298}(H_3PO_4 \cdot 40\ H_2O, aq)$ = -309.34 ± 0.38 kcal/mol. Birley and Skinner (2) measured the heat of hydrolysis of PCl_5 and derived $\Delta Hf^\circ_{298}(H_3PO_4 \cdot 100\ H_2O, aq)$ = -309.8 ± 0.35 kcal/mol based on $\Delta Hf^\circ_{298}(PCl_5, c)$ = -105.0 kcal/mol obtained by direct chlorination of phosphorus (4). Irving and McKerrell (3) measured the heat of solution of P_4O_{10} from which they derived $\Delta Hf^\circ_{298}(H_3PO_4 \cdot 0.6416\ H_2O, aq)$ = -305.9 ± 0.5 kcal/mol. Using heat of solution data for $H_3PO_4(c) \rightarrow H_3PO_4(363\ H_2O, aq)$ (5) and heat of dilution data for $H_3PO_4(363\ H_2O, aq) \rightarrow H_3PO_4(n\ H_2O, aq)$ (6), we obtain heat of formation of $H_3PO_4(c)$ listed in the last column of the table. (These values are based on white phosphorus as the references state.) Holmes (5) determined $\Delta Hf^\circ_{298}(H_3PO_4, c)$ = -305.7 ± 0.3 kcal/mol based on his heat of combustion of white phosphorus and related heat of solution data which were combined to form a thermal cycle. Using the white phosphorus based $\Delta Hf^\circ_{298}(P_4O_{10}, c)$ = -719.4 kcal/mol (7) (instead of his value -713.2 kcal/mol), we have recalculated his thermal cycle and find $\Delta Hf^\circ_{298}(H_3PO_4, c)$ = -307.4 ± 0.5 kcal/mol which is in good agreement with the recent calorimetric measurements (1, 2, 3).

The value, -307.0 ± 0.5 kcal/mol, is tentatively selected for the heat of formation of $H_3PO_4(c)$, based on white phosphorus as references state. The adopted $\Delta Hf^\circ_{298}(H_3PO_4, c)$ = -302.8 ± 0.5 kcal/mol is recalculated based on the P (red, V, c) as reference state.

Heat Capacity and Entropy

Low temperature heat capacity from 10 to 300 K were measured by Egan and Wakefield (8). Their smooth Cp are adopted in the tabulation. Heat capacities above 300 K are estimated graphically based on the measured Cp curve.

The entropy S°_{298} is derived from heat capacity data, using S°_{10} = 0.04 eu.

Melting Data

Egan and Wakefield (8) measured calorimetrically the heat of fusion ΔHm^* = 3.1 ± 0.2 kcal/mol, but failed to determine the exact melting point due to continuous fusion between 301 to 319 K in their measurements. They suggested the melting point 315.5 K which was found by Ross and Jones (9).

Holmes (5) derived the heat of fusion ΔHm_{298} = 3.2 ± 0.5 kcal/mol from his heat-of-solution data for crystalline and liquid H_3PO_4 in water and in aq. $HClO_4$ solution, which corresponds to ΔHm^* = 3.36 kcal/mol. We adopt an intermediate value of ΔHm^* = 3.2 ± 0.2 kcal/mol.

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7. JANAF $P_4O_{10}(c)$ table dated Dec. 31, 1965.
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Orthophosphoric Acid (H_3PO_4)

(Liquid) GFW = 97.9953

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	34.667	36.036	36.036	.000	− 299.762	− 265.703	194.766
300	34.800	36.251	36.037	.064	− 299.752	− 265.492	193.411
400	42.000	47.248	37.488	3.904	− 298.908	− 254.182	138.879
500	49.200	57.394	40.465	8.464	− 297.430	− 243.159	106.285
600	56.400	67.000	44.093	13.744	− 295.311	− 232.493	84.686
700	63.600	76.235	48.029	19.744	− 292.553	− 222.232	69.384
800	70.800	85.198	52.117	26.464	− 309.571	− 217.724	59.479
900	78.000	93.953	56.281	33.904	− 305.263	− 206.493	50.143
1000	85.200	102.543	60.479	42.064	− 300.273	− 195.779	42.787

June 30, 1962; Dec. 31, 1971

ORTHOPHOSPHORIC ACID (H_3PO_4) (LIQUID) GFW = 97.9953 H_3O_4P

$S^\circ_{298.15}$ = [36 ± 1] gibbs/mol

ΔHf°_{298} = −299.762 ± 0.5 kcal/mol

Tm = 315.5 K

ΔHm° = 3.2 ± 0.2 kcal/mol

Heat of Formation

The heat of formation of H_3PO_4(ℓ) at 298.18 K is calculated from that of the crystal by adding ΔHm° and the difference between $H_{315.5} - H_{298.15}$ for the crystal and liquid.

Heat Capacity and Entropy

Heat capacities of the liquid are estimated by comparison with those of H_2SO_4(c, ℓ) (1) and H_3PO_4(c). The value S°_{298} is obtained in a manner similar to that of the heat of formation.

Melting Data

See H_3PO_4(c) table dated Dec. 30, 1971.

Decomposition

The phosphoric acid tends to be dehydrated to pyro- and meta-phosphoric acids when it is heated.

Reference

1. W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, J. Am. Chem. Soc. 82, 62 (1960).

J. Phys. Chem. Ref. Data Vol. 3, No. 3, 1974

Potassium Superoxide (KO_2)

(Crystal) GFW = 71.1008

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	= 4.000	= 68.232	= 68.232	INFINITE
100	12.524	11.048	45.136	= 3.409	= 68.749	= 64.663	141.758
200	16.600	23.124	30.916	= 1.742	= 68.418	= 61.043	66.704
298	18.530	29.276	29.276	.000	= 68.000	= 57.510	42.156
300	18.550	29.393	29.278	.034	= 67.992	= 57.445	41.849
400	20.050	34.949	30.026	1.969	= 68.082	= 53.892	29.445
500	20.950	39.525	31.482	4.022	= 67.503	= 50.410	22.034
600	21.550	43.401	33.153	6.148	= 66.858	= 47.050	17.138
700	21.970	46.795	34.862	8.325	= 66.175	= 43.802	13.676
800	22.280	49.710	36.537	10.538	= 65.472	= 40.656	11.107
900	22.520	52.349	38.150	12.779	= 64.757	= 37.596	9.130
1000	22.680	54.730	39.691	15.039	= 64.045	= 34.616	7.565
1100	22.800	56.898	41.158	17.314	= 82.246	= 30.684	6.096
1200	22.880	58.885	42.554	19.598	= 81.307	= 26.037	4.742
1300	22.940	60.719	43.882	21.889	= 80.370	= 21.470	3.609
1400	22.980	62.421	45.146	24.185	= 79.435	= 16.974	2.650
1500	23.000	64.007	46.351	26.484	= 78.504	= 12.544	1.828

June 30, 1962; June 30, 1971

POTASSIUM SUPEROXIDE (KO_2) (CRYSTAL) GFW = 71.1008 KO_2

$S^\circ_{298.15}$ = 29.3 ± 1 gibbs/mol

Tt_1 = 193.5 K

Tt_2 = 230.9 K

Tm = 782 ± 20 K

ΔHf°_0 = −68.2 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −68.0 ± 0.5 kcal/mol

ΔHt_1 = 0.0721 kcal/mol

ΔHt_2 = 0.0375 kcal/mol

ΔHm° = Unknown

Heat of Formation

D'Orazio and Wood (1) measured the heat of solution, $\Delta H^\circ_{soln}(25^\circ C)$ = −13.0 ± 0.4 kcal/mol for $KO_2(c) + 1/2\ H_2O(\ell) \rightarrow KOH(12{,}000\ H_2O,\ aq.) + 3/4\ O_2(g)$ which leads to $\Delta Hf^\circ_{298}(KO_2,\ c)$ = −68.09 ± 0.4 kcal/mol, using the following auxiliary data, $\Delta Hf^\circ_{298}(KOH\cdot 12{,}000\ H_2O,\ aq.)$ = −115.243 kcal/mol (2) and $\Delta Hf^\circ_{298}(H_2O,\ \ell)$ = −68.315 kcal/mol (3). Gilles and Margrave (4) also measured the heat of solution as −13.2 ± 0.8 kcal/mol from which we obtain $\Delta Hf^\circ_{298}(KO_2,\ c)$ = −67.88 ± 0.8 kcal/mol. Both ΔH°_{soln} values have been corrected for impurities present in their samples. The value $\Delta Hf^\circ_{298}(KO_2,\ c)$ = −68.0 ± 0.5 kcal/mol is adopted in the tabulation.

Kazarnovskaya and Kazarnovskii (5) and deforcrand (6) determined the heat of solution in $H_2SO_4(aq.)$ and derived the heat of formation of $KO_2(c)$ as −67.9 kcal/mol and −66.8 kcal/mol, respectively. The former is reliable since their sample was well characterized and corrections for the impurities were included in the ΔH°_{soln} data (5). The latter did not give enough experimental details to check their derivation.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range from 52-298 K are obtained from Todd's measurements (7). Two peaks at 193.5 K and 230.9 K were found in his heat capacity data. Below 50 K, the heat capacities were extrapolated using a combination of 1 Debye (θ = 139) and 2 Einstein (θ = 260) functions as suggested by Todd. This extrapolation yields the entropy from lattice contribution as 3.278 eu at 50 K. By neutron diffraction, Smith et al. (8) found an antiferromagnetic transition at 7 K which indicates the existence of an unpaired electron in $KO_2(c)$. We tentatively adopt S°_{50} = 4.656 ± 1 eu which includes both lattice (3.278 eu) and unpaired electron (Rℓn2) contributions. Heat capacities above 298 K are estimated graphically.

The entropy at 298 K is calculated from the Cp data and is based on an extrapolation of S°_{50} = 4.656 eu.

Transition Data

Todd (7) observed two anomalies in the heat capacity at 193.5 and 230.9 K which are adopted as two phase transitions in the tabulation. The heats of transition are calculated from the total heats of absorption given by Todd between 180 and 208 K for transition 1 and 217-240 K for transition 2 with extrapolated Cp below 176 K and above 250 K.

Smith et al. (8) confirmed these two transitions in the neutron diffraction measurements. In addition, they found an antiferromagnetic transition at 7.1 ± 0.5 K and an unusually low temperature phase transition at 12 K. Neuman (9) observed a color change at −75.5 ± 15°C in the warming and cooling curves for $KO_2(c)$. This color change represents a phase transition which is in good agreement with Todd's observation.

Melting Data

Firsova et al. (10) studied the thermograms of $KO_2(c)$ and found the melting point 509 ± 20°C under atmospheric pressure which is adopted in the tabulation. Earlier melting point data were reported as 380°C by Blumental (11) and 440°C by deforcrand (6).

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3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
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6. M. R. deForcrand, Comp. Rend. 158, 843 (1914).
7. S. S. Todd, J. Amer. Chem. Soc. 75, 1229 (1953).
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9. E. W. Neuman, J. Chem. Phys. 3, 243 (1935).
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Potassium Metasilicate (K_2SiO_3)

(Crystal) GFW = 154.288

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 5.227	- 367.959	- 367.959	INFINITE
100	15.120	11.220	56.510	- 4.529	- 369.194	- 362.314	791.836
200	23.470	24.630	37.365	- 2.547	- 369.777	- 355.166	388.108
298	28.300	34.930	34.930	.000	- 370.000	- 347.940	255.047
300	28.400	35.105	34.931	.052	- 370.002	- 347.804	253.375
400	32.400	43.847	36.095	3.101	- 371.155	- 340.181	185.866
500	35.400	51.412	38.419	6.497	- 370.886	- 332.462	145.319
600	37.700	58.079	41.151	10.157	- 370.378	- 324.821	- 118.316
700	39.400	64.022	44.002	14.014	- 369.705	- 317.279	99.059
800	40.800	69.378	46.845	18.027	- 368.913	- 309.846	84.646
900	41.900	74.249	49.623	22.163	- 368.034	- 302.512	73.460
1000	42.800	78.712	52.312	26.400	- 367.104	- 295.281	64.534
1100	43.500	82.824	54.901	30.715	- 403.956	- 286.098	56.842
1200	44.200	86.640	57.389	35.101	- 402.481	- 275.447	50.166
1300	44.800	90.202	59.778	39.552	- 400.965	- 264.924	44.538
1400	45.300	93.540	62.071	44.057	- 399.415	- 254.516	39.732
1500	45.800	96.683	64.275	48.612	- 397.835	- 244.220	35.583
1600	46.300	99.655	66.394	53.217	- 396.225	- 234.030	31.967
1700	46.800	102.476	68.434	57.872	- 406.577	- 223.840	28.777
1800	47.300	105.166	70.401	62.577	- 404.851	- 213.139	25.879
1900	47.800	107.736	72.299	67.332	- 403.089	- 202.538	23.297
2000	48.300	110.201	74.133	72.137	- 401.284	- 192.028	20.984
2100	48.800	112.570	75.907	76.992	- 399.440	- 181.608	18.900
2200	49.300	114.851	77.626	81.897	- 397.563	- 171.281	17.015

June 30, 1972

POTASSIUM METASILICATE (K_2SiO_3) (CRYSTAL) GFW = 154.288

$\Delta Hf°_0$ = -367.96 ± 2 kcal/mol

$S°_{298.15}$ = 34.93 ± 0.2 gibbs/mol

$\Delta Hf°_{298.15}$ = -370.0 ± 2 kcal/mol

Tm = 1249 K

$\Delta Hm°$ = [12 ± 3] kcal/mol

Heat of Formation

Hatton et al (1) conducted heat of solution measurements on K_2SiO_3(c) and KOH(c) in HF(aq) at 50°C to determine the heat of formation of the silicate. The results of this work gave a ΔHr_{298} = -17.5 ± 0.5 kcal/mol for the process 2KOH(c) + SiO_2(c, quartz) → K_2SiO_3(c) + H_2O(ℓ). When combined with the auxiliary data for H_2O(ℓ) KOH(c) and SiO_2(c) (2, 3) we calculate $\Delta Hf°_{298}$(K_2SiO_3, c) = -369.9 ± 1 kcal/mol.

Urusov (4) summarized the various methods of estimating the heats of formation of silicates using the Born-Haber cycle and energies of atomization. His estimate for $\Delta Hf°_{298}$(K_2SiO_3, c) is -369 kcal/mol.

An earlier estimate by Wilcox and Bromley (5) based upon ionic contributions to crystal lattice energies gave $\Delta Hf°_{298}$(K_2SiO_3, c) = -367 ± 15 kcal/mol.

An attempt to calculate the $\Delta Hf°_{298}$(K_2SiO_3, c) from HF solution experiments on higher potassium silicates ($K_2Si_2O_5$, $K_2Si_3O_7$) and sodium silicates (6) yielded a value of -383.8 kcal/mol which is discrepant with the former values.

A value for $\Delta Hf°_{298}$(K_2SiO_3, c) = -370 ± 2 kcal/mol has been selected.

Heat Capacity and Entropy

The low temperature heat capacity of K_2SiO_3(c) has been measured and reported by Stull et al. (7) in the range 15-298 K. They report $S°_{298\ K}$ = 34.93 gibbs/mol, which is derived from $C°_p$ and an extrapolation of S_{15} = 0.18 gibbs/mol.

Heat capacities above 298 K have been estimated by analogy with other alkali metal silicates and borates.

Melting Data

A melting temperature of 1249 K for K_2SiO_3 was measured by Morey and Bowen (8). The heat of fusion ΔHm = 12 ± 3 kcal/mol was estimated by comparison with other silicates.

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K_2O_3Si

Potassium Metasilicate (K_2SiO_3)

(Liquid) GFW = 154.288

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	28.300	44.029	44.029	.000	− 358.349	− 339.002	248.495
300	28.400	44.204	44.030	.052	− 358.351	− 338.882	246.875
400	32.400	52.946	45.194	3.101	− 359.504	− 332.169	181.489
500	35.400	60.511	47.518	6.497	− 359.235	− 325.361	142.215
600	37.700	67.178	50.250	10.157	− 358.727	− 318.629	116.061
700	39.400	73.125	53.101	14.017	− 358.051	− 311.997	97.410
800	43.000	78.867	55.971	18.317	− 356.972	− 305.496	83.458
900	43.000	83.931	58.802	22.617	− 355.929	− 299.122	72.637
1000	43.000	88.462	61.545	26.917	− 354.936	− 292.864	64.005
1100	43.000	92.560	64.181	31.217	− 391.803	− 284.655	56.556
1200	43.000	96.302	66.704	35.517	− 390.414	− 274.975	50.080
1300	43.000	99.744	69.115	39.817	− 389.049	− 265.412	44.620
1400	43.000	102.930	71.418	44.117	− 387.704	− 255.951	39.956
1500	43.000	105.897	73.619	48.417	− 386.379	− 246.585	35.927
1600	43.000	108.672	75.724	52.717	− 385.074	− 237.307	32.415
1700	43.000	111.279	77.740	57.017	− 395.781	− 228.008	29.312
1800	43.000	113.737	79.672	61.317	− 394.460	− 218.176	26.490
1900	43.000	116.062	81.526	65.617	− 393.153	− 208.420	23.974
2000	43.000	118.267	83.309	69.917	− 391.853	− 198.729	21.716
2100	43.000	120.365	85.024	74.217	− 390.564	− 189.103	19.680
2200	43.000	122.366	86.676	78.517	− 389.292	− 179.541	17.836
2300	43.000	124.277	88.270	82.817	− 388.030	− 170.037	16.157
2400	43.000	126.107	89.808	87.117	− 386.783	− 160.583	14.623
2500	43.000	127.862	91.296	91.417	− 385.555	− 151.189	13.217
2600	43.000	129.549	92.735	95.717	− 384.339	− 141.832	11.922
2700	43.000	131.172	94.128	100.017	− 383.144	− 132.532	10.728
2800	43.000	132.735	95.480	104.317	− 381.971	− 123.270	9.622
2900	43.000	134.244	96.790	108.617	− 380.817	− 114.047	8.595
3000	43.000	135.702	98.063	112.917	− 379.684	− 104.871	7.640

June 30, 1972

POTASSIUM METASILICATE (K_2SiO_3) (LIQUID) GFW = 154.288

$S^\circ_{298.15}$ = [44.03] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [−358.35 ± 5] kcal/mol

Tm = 1249 K

ΔHm° = [12 ± 3] kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298}(K_2SiO_3, \ell)$ = −358.35 ± 2 kcal/mol has been calculated by adding the estimated heat of fusion, reduced to 298 K with the present functions, to the heat of formation of $K_2SiO_3(c)$.

Heat Capacity and Entropy

The heat capacity of $K_2SiO_3(\ell)$ has been estimated. A constant Cp of 43 gibbs/mol for $K_2SiO_3(\ell)$ was selected above a hypothetical glass transition temperature of 700 K. Below this temperature the heat capacity was taken as that of the crystal.

Melting Data

See $K_2SiO_3(c)$ for details.

Potassium Sulfate (K_2SO_4)

(Crystal) GFW = 174.2656

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	= 6.079	= 341.030	= 341.030	INFINITE
100	18.900	14.744	66.294	= 5.155	= 342.486	= 333.683	729.264
200	26.449	30.450	44.675	= 2.845	= 343.201	= 324.565	354.668
298	31.362	41.965	41.965	.000	= 343.540	= 315.339	231.149
300	31.443	42.159	41.966	.058	= 343.544	= 315.163	229.596
400	35.351	51.764	43.249	3.406	= 345.345	= 305.442	166.886
500	38.278	59.982	45.793	7.094	= 345.543	= 295.438	129.136
600	40.757	67.178	48.770	11.045	= 345.411	= 285.422	103.965
700	44.108	73.688	51.870	15.272	= 344.972	= 275.430	85.993
800	50.444	79.941	54.988	19.962	= 357.127	= 266.821	72.892
900	45.698	87.946	58.205	26.767	= 353.812	= 255.722	62.098
1000	45.791	92.745	61.423	31.321	= 352.795	= 244.677	53.518
1100	47.884	97.195	64.475	35.992	= 389.519	= 232.091	46.112
1200	51.339	101.502	67.381	40.945	= 387.700	= 217.855	39.677
1300	55.753	105.781	70.170	46.293	= 385.595	= 203.788	34.260
1400	60.663	110.096	72.868	52.120	= 382.847	= 189.905	29.646
1500	66.489	114.485	75.496	58.483	= 379.668	= 176.232	25.677
1600	72.506	118.966	78.072	65.430	= 375.917	= 162.787	22.236
1700	78.825	123.550	80.612	72.995	= 371.561	= 149.599	19.232
1800	85.382	128.240	83.127	81.203	= 366.577	= 136.682	16.595
1900	92.126	133.036	85.627	90.077	= 360.943	= 124.061	14.270
2000	99.022	137.937	88.120	99.634	= 354.637	= 111.754	12.212

Dec. 31, 1971

POTASSIUM SULFATE (K_2SO_4) (CRYSTAL) GFW = 174.2656 K_2O_4S

$\Delta Hf°_0$ = -341.03 ± 0.2 kcal/mol

$S°_{298.15}$ = 41.96 ± 0.3 gibbs/mol

$\Delta Hf°_{298.15}$ = -343.54 ± 0.2 kcal/mol

Tt = 857 ± 1 K (orthorhombic → hexagonal)

$\Delta Ht°$ = 1.787 ± 0.03 kcal/mol

Tm = 1342 K

$\Delta Hm°$ = 8.479 ± 0.06 kcal/mol

Heat of Formation

The heat of formation of $K_2SO_4(c)$ is calculated from the cell measurements of Shibata et al. (1) who studied the reaction at 25°C.

$$2K\ (Hg\ amalgam\ 0.22\%) + Hg_2SO_4(sat'd) \rightarrow K_2SO_4(sat'd) + 2Hg(\ell).$$

After correcting the observed voltage for the formation of the K-amalgam and conversion to absolute volts we have E_{cell} = 3.591725 volts for the reaction at 25°C.

$$2\ K(c) + Hg_2SO_4(c) \rightarrow K_2SO_4(c) + 2Hg(\ell).$$

From this voltage we calculate $\Delta Gr°_{298}$ = -165.656 kcal/mol. Taking $\Delta Gf°_{298}(Hg_2SO_4, c)$ = -149.589 kcal/mol (2) and reference entropies from (3) we calculate $\Delta Hf°_{298}(K_2SO_4, c)$ = -343.446 kcal/mol.

Mischenko and Pronina (10) and Tsvetkov and Rabinovich (11) have determined the heat of solution, $\Delta Hs°_{298}$ = 5.68 kcal/mol for the process $K_2SO_4(c) + 2K^+(\infty, aq.) + SO_4 = (\infty, aq.)$. When this is combined with the heats of formation of the infinitely dilute ions (2) we obtain $\Delta Hf°_{298}(K_2SO_4, c)$ = -343.64 kcal/mol.

We adopt a median value for $\Delta Hf°_{298}(K_2SO_4, c)$ = -343.54 ± 0.2 kcal/mol.

Heat Capacity and Entropy

Low temperature heat capacities have been measured by Moore and Kelley (4) from 52.7 - 295 K and by Paukov (5) from 12.5 - 299.5 K. *The heat capacities reported by Moore and Kelley are systematically lower by about 0.5% than those of* Paukov, however the $S°_{298}$ = 41.96 gibbs/mol calculated from the Paukov data agrees well with the Moore and Kelley value (42 ± 0.6 eu).

Heat capacity data measured by adiabatic calorimetry in the range 298.5 - 773.7 K has been reported by Shmidt (6). In addition, drop calorimetric measurements have been reported by the following workers; Shomate and Naylor (7), Dworkin and Bredig (8), and Rubinchik et al. (9). The latter three workers detected and measured a heat of transition at 857 K where K_2SO_4 exhibits an orthorhombic to hexagonal crystal structure change. The heat capacity and enthalpy curve between 298 K and 857 K was established by orthogonal polynomial curve-fitting of all the data listed above. These data were in good agreement except for those of Shomate and Naylor whose values were systematically high by about 0.6%.

In the hexagonal crystal phase region (857 → Tm) a similar enthalpy data comparison was made using the data from references 7, 8, and 9. The smoothed curves agreed well but the values from reference 7 were high by 0.6% as in the lower temperature phase.

Transition Data

The orthorhombic to hexagonal transition temperature for K_2SO_4 was selected as 857 ± 1 K from the recently reported calorimetric work of Dworkin and Bredig (8) and Rubinchik et al. (9). The enthalpy of transition was determined by taking the difference between the adopted enthalpy curves extrapolated to 857 K.

Melting Data

The adopted melting point of 1342 K was determined by Shomate and Naylor (7) and Rubinchik et al. (9). The heat of fusion, 8.479 kcal/mol is calculated from the difference between the smoothed relative enthalpy of the liquid (see liquid table) and the adopted enthalpy value for the crystal at Tm.

References

1. F. L. E. Shibata, S. Oda and S. Furukawa, J. Sci. Hiroshima Univ. (Japan) 3A, 227 (1933).
2. U. S. Natl. Bur. Std. Tech. Note 270-3 (1968).
3. JANAF Thermochemical Tables; K(ref. st) 12-31-61; S(ref. st) 12-31-65; O_2(ref. st) 9-30-65.
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5. I. E. Paukov, Russ. J. Phys. Chem. (Eng. Transl.) 43, 1134 (1969).
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10. K. P. Mischenko and M. Z. Pronina, J. Gen. Chem. USSR 6, 85 (1936).
11. V. G. Tsvetkov and I. B. Rabinovich, Russian J. Phys. Chem. (Eng. Transl.) 43, 675 (1969).

K_2O_4S

Potassium Sulfate (K_2SO_4)

(Liquid) GFW = 174.2656

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	31.362	51.587	51.587	.000	-331.848	-306.515	224.682
300	31.483	51.781	51.588	.058	-331.852	-306.358	223.182
400	35.351	61.386	52.871	3.406	-333.653	-297.599	162.601
500	38.278	69.604	55.415	7.094	-333.851	-288.557	126.128
600	40.757	76.800	58.392	11.045	-333.719	-279.504	101.809
700	44.108	83.310	61.492	15.272	-333.280	-270.473	84.446
800	50.484	89.565	64.610	19.964	-345.433	-262.827	71.801
900	47.050	95.107	67.697	24.669	-344.218	-252.573	61.333
1000	47.050	100.064	70.690	29.374	-343.050	-242.452	52.988
1100	47.050	104.548	73.568	34.079	-379.740	-230.401	45.776
1200	47.050	108.642	76.322	38.784	-378.169	-216.892	39.501
1300	47.050	112.408	78.955	43.489	-376.617	-203.516	34.214
1400	47.050	115.895	81.471	48.194	-375.081	-190.257	29.701
1500	47.050	119.141	83.875	52.899	-373.560	-177.110	25.805
1600	47.050	122.178	86.175	57.604	-372.051	-164.060	22.410
1700	47.050	125.030	88.378	62.309	-370.555	-151.109	19.426
1800	47.050	127.720	90.490	67.014	-369.074	-138.243	16.785
1900	47.050	130.263	92.517	71.719	-367.609	-125.458	14.431
2000	47.050	132.677	94.465	76.424	-366.155	-112.752	12.321
2100	47.050	134.972	96.339	81.129	-364.716	-100.117	10.419
2200	47.050	137.161	98.146	85.834	-363.297	-87.549	8.697
2300	47.050	139.253	99.888	90.539	-361.891	-75.050	7.131
2400	47.050	141.255	101.570	95.244	-360.503	-62.605	5.701
2500	47.050	143.176	103.196	99.949	-359.137	-50.226	4.391
2600	47.050	145.021	104.769	104.654	-357.786	-37.890	3.185
2700	47.050	146.797	106.293	109.359	-356.459	-25.616	2.073
2800	47.050	148.508	107.771	114.064	-355.157	-13.388	1.045
2900	47.050	150.159	109.204	118.769	-353.877	-1.199	.090
3000	47.050	151.754	110.596	123.474	-352.622	10.939	.797

Dec. 31, 1971

POTASSIUM SULFATE (K_2SO_4) (LIQUID) GFW = 174.2656 K_2O_4S

$S^\circ_{298.15}$ = 51.59 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -331.85 kcal/mol

Tm = 1342 K ΔHm° = 8.479 kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298}(K_2SO_4, \ell)$ is calculated from $\Delta Hf^\circ_{298}(K_2SO_4, c)$ = -343.45 kcal/mol by adding the heat of fusion and the difference between $H_{1342} - H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

Thermal properties of $K_2SO_4(\ell)$ were derived from the data of Shomate and Naylor (1) and a single datum at 1344.8 K by Rubinchik et al. (2). A constant heat capacity of 47.05 gibbs/mol was selected above a hypothetical glass transition at 800 K. Below the glass transition the heat capacity was taken as that of the orthorhombic crystal. The $S^\circ_{298}(K_2SO_4, \ell)$ = 51.587 gibbs/mol was calculated in a manner analogous to that of the heat of formation.

Melting Data

See $K_2SO_4(c)$ for details.

References

1. C. H. Shomate and B. F. Naylor, J. Amer. Chem Soc. 67, 72 (1945).
2. S. M. Rubinchik, E. I. Barashek, V. A. Sokolov and A. I. Fomin, Zhur. Fiz. Khim. 45, 1069 (1971).

Magnesium Unipositive Ion (Mg^+)

(Ideal Gas) GFW = 24.31145

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	4.968	36.879	36.879	.000	213.087	202.934	- 148.755
300	4.968	36.910	36.879	.009	213.094	202.871	- 147.791
400	4.968	38.339	37.074	.506	213.474	199.404	- 108.949
500	4.968	39.448	37.442	1.003	213.826	195.847	- 85.605
600	4.968	40.353	37.854	1.500	214.151	192.219	- 70.016
700	4.968	41.119	38.267	1.996	214.450	188.540	- 58.865
800	4.968	41.782	38.666	2.493	214.719	184.820	- 50.490
900	4.968	42.368	39.045	2.990	214.952	181.068	- 43.969
1000	4.968	42.891	39.404	3.487	213.027	177.474	- 38.787
1100	4.968	43.365	39.743	3.984	213.219	173.908	- 34.552
1200	4.968	43.797	40.063	4.480	213.384	170.326	- 31.021
1300	4.968	44.194	40.366	4.977	213.525	166.732	- 28.030
1400	4.968	44.563	40.653	5.474	183.275	163.608	- 25.540
1500	4.968	44.905	40.925	5.971	183.772	162.186	- 23.631
1600	4.968	45.226	41.184	6.467	184.267	160.729	- 21.955
1700	4.968	45.527	41.430	6.964	184.764	159.244	- 20.472
1800	4.968	45.811	41.666	7.461	185.261	157.729	- 19.151
1900	4.968	46.080	41.891	7.958	185.759	156.186	- 17.965
2000	4.968	46.335	42.107	8.455	184.256	154.616	- 16.896
2100	4.968	46.577	42.314	8.951	186.751	153.021	- 15.925
2200	4.968	46.808	42.513	9.448	187.248	151.405	- 15.041
2300	4.968	47.029	42.705	9.945	187.745	149.765	- 14.231
2400	4.968	47.240	42.889	10.442	188.242	148.102	- 13.486
2500	4.968	47.443	43.068	10.939	188.738	146.418	- 12.800
2600	4.968	47.638	43.240	11.435	189.232	144.717	- 12.165
2700	4.968	47.825	43.406	11.932	189.727	142.995	- 11.575
2800	4.968	48.006	43.567	12.429	190.222	141.254	- 11.025
2900	4.968	48.180	43.723	12.926	190.716	139.498	- 10.513
3000	4.968	48.349	43.875	13.423	191.208	137.723	- 10.033
3100	4.968	48.512	44.022	13.919	191.697	135.931	- 9.583
3200	4.968	48.669	44.164	14.416	192.186	134.124	- 9.160
3300	4.968	48.822	44.303	14.913	192.673	132.302	- 8.762
3400	4.968	48.971	44.438	15.410	193.157	130.468	- 8.386
3500	4.968	49.115	44.570	15.907	193.638	128.615	- 8.031
3600	4.969	49.255	44.698	16.403	194.113	126.751	- 7.695
3700	4.969	49.391	44.823	16.900	194.586	124.874	- 7.376
3800	4.969	49.523	44.945	17.397	195.055	122.985	- 7.073
3900	4.970	49.652	45.064	17.894	195.519	121.079	- 6.785
4000	4.970	49.778	45.180	18.391	195.976	119.165	- 6.511
4100	4.971	49.901	45.294	18.888	196.427	117.239	- 6.249
4200	4.972	50.021	45.405	19.386	196.873	115.302	- 6.000
4300	4.973	50.138	45.514	19.883	197.310	113.354	- 5.761
4400	4.975	50.252	45.620	20.380	197.740	111.399	- 5.533
4500	4.976	50.364	45.724	20.878	198.161	109.431	- 5.315
4600	4.978	50.473	45.826	21.376	198.574	107.456	- 5.105
4700	4.981	50.580	45.926	21.873	198.977	105.470	- 4.904
4800	4.983	50.685	46.025	22.372	199.371	103.478	- 4.711
4900	4.986	50.788	46.121	22.870	199.754	101.476	- 4.526
5000	4.989	50.889	46.215	23.369	200.126	99.466	- 4.348
5100	4.993	50.988	46.308	23.868	200.487	97.446	- 4.176
5200	4.996	51.085	46.399	24.368	200.837	95.424	- 4.011
5300	5.002	51.180	46.488	24.868	201.175	93.396	- 3.851
5400	5.008	51.274	46.576	25.368	201.500	91.356	- 3.697
5500	5.013	51.365	46.662	25.869	201.811	89.314	- 3.549
5600	5.020	51.456	46.747	26.371	202.110	87.265	- 3.406
5700	5.027	51.545	46.830	26.873	202.395	85.216	- 3.267
5800	5.034	51.632	46.912	27.376	202.666	83.153	- 3.133
5900	5.042	51.718	46.993	27.880	202.922	81.094	- 3.004
6000	5.051	51.803	47.072	28.385	203.163	79.022	- 2.878

Dec. 31, 1967; Dec. 31, 1970

MAGNESIUM UNIPOSITIVE ION (Mg^+) (IDEAL GAS) GFW = 24.31145 Mg^+

Ground State Configuration $^2S_{1/2}$ ΔHf°_0 = 211.3 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 36.879 ± 0.005 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 213.1 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
35669.42	2
35760.97	4
69805.19	2

Heat of Formation

We derive the heat of formation at 0°K from the reaction $Mg(g) - e^-(g) \rightarrow Mg^+(g)$ using the JANAF auxiliary value for Mg(g) and an ionization potential of 176.325 kcal/mol from Moore (1).

Heat Capacity and Entropy

We adopt the electronic levels and quantum weights given by Moore (2). Levels above 70,000 cm^{-1} are not included since they have no effect on the thermodynamic functions. $H^\circ_0 - H^\circ_{298}$ = -1.481 kcal/mol at 0°K.

References

1. C. E. Moore, NSRDS-NBS 34, 1970.
2. C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, 1949.

Magnesium Sulfide (MgS)

(Crystal) GFW = 56.376

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	= 1.992	= 81.443	= 81.443	INFINITE
100	5.420	2.610	20.666	= 1.806	= 81.575	= 81.312	177.707
200	9.590	7.910	12.988	= 1.016	= 81.740	= 81.091	88.612
298	10.890	12.030	12.030	.000	= 81.700	= 80.682	59.141
300	10.910	12.097	12.030	.020	= 81.701	= 80.675	58.772
400	11.429	15.314	12.465	1.139	= 82.295	= 80.305	43.877
500	11.700	17.897	13.302	2.298	= 82.716	= 79.757	34.862
600	11.900	20.048	14.252	3.478	= 83.062	= 79.133	28.824
700	12.100	21.898	15.215	4.678	= 83.355	= 78.430	24.487
800	12.300	23.526	16.154	5.898	= 96.685	= 78.976	21.575
900	12.500	24.987	17.056	7.138	= 96.644	= 76.765	18.641
1000	12.700	26.314	17.916	8.398	= 98.784	= 74.375	16.255
1100	12.900	27.534	18.736	9.678	= 98.709	= 71.943	14.294
1200	13.100	28.665	19.517	10.978	= 98.680	= 69.510	12.660
1300	13.300	29.721	20.261	12.298	= 98.658	= 67.079	11.277
1400	13.500	30.714	20.973	13.638	= 129.009	= 64.171	10.018
1500	13.700	31.652	21.654	14.998	= 128.594	= 59.556	8.677
1600	13.900	32.543	22.307	16.378	= 128.159	= 54.967	7.508
1700	14.100	33.392	22.934	17.778	= 127.705	= 50.406	6.480
1800	14.300	34.203	23.538	19.198	= 127.232	= 45.873	5.570
1900	14.500	34.982	24.120	20.638	= 126.738	= 41.365	4.758
2000	14.700	35.731	24.682	22.098	= 126.226	= 36.885	4.031
2100	14.900	36.453	25.225	23.578	= 125.695	= 32.434	3.375
2200	15.100	37.150	25.751	25.078	= 125.144	= 28.002	2.782
2300	15.300	37.826	26.262	26.598	= 124.574	= 23.600	2.242
2400	15.500	38.481	26.757	28.138	= 123.984	= 19.223	1.750
2500	15.700	39.118	27.239	29.698	= 123.375	= 14.871	1.300

Dec. 31, 1960; Dec. 31, 1971

MAGNESIUM SULFIDE (MgS) (CRYSTAL) GFW = 56.376

ΔHf°_0 = -81.4 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 12.03 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -81.7 ± 0.5 kcal/mol

Tm > [2273] K

Heat of Formation

Wartenberg (1) measured the heat of solution of MgS in hydrochloric acid solution as ΔHr = -33.9 ± 1 kcal/mol for MgS(c) + 2HCl(30 H_2O, aq) → $MgCl_2$(30 H_2O, aq) + H_2S(g). We derive ΔHf°_{298}(MgS, c) = -82.0 ± 1 kcal/mol, using the following data: ΔHf°_{298}(HCl · 30 H_2O, aq) = -39.357 kcal/mol (2), ΔHf°_{298}(H_2S, g) = -4.88 kcal/mol (3), and ΔHf°_{298}($MgCl_2$ · 30 H_2O, aq) = -189.80 kcal/mol (4).

JANAF analyses of equilibrium studies (5, 8) of MgS(c) + H_2O(g) → MgO(c) + H_2S(g) are listed below. The pressure data of Curlook (5) and Dewing (8) are in reasonable agreement. The heat of formation derived from the third law ΔHr°_{298} is in very good agreement with the value determined by solution calorimetry (1). The assigned uncertainty is ± 0.5 kcal/mol since the free energy functions of MgS employed in the calculations are partially based on estimated high temperature Cp values.

Investigator	Temp (K)	No. of Points	ΔHr°_{298} kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(MgS, c)* (kcal/mol)
Curlook (5)	1180-1483	6	-8.49±0.59	-9.19±0.24	-0.60±0.45	-81.59
Dewing (8)	1267-1768	6	-5.53±0.38	-8.73±1.01	-2.23±0.22	-82.06

* 3rd law ΔHr°_{298} is used to derive ΔHf°_{298}(MgS, c).

Heats of formation derived from solution calorimetry (1) and equilibrium studies are in good agreement. A weighted average, ΔHf°_{298}(MgS, c) = -81.7 ± 0.5 kcal/mol, is selected for the tabulation.

Heat Capacity and Entropy

Stull et al. (6) measured adiabatically the low temperature heat capacities from 15 - 320 K. Their smooth values are adopted in the tabulation. The entropy, S°_{298} = 12.03 ± 0.1 eu, is based on S° = 0.010 eu at 15 K. The Cp values above 320 K are estimated by graphical extrapolation.

Melting Data

MgS melts above 2000°C (7) and no other literature melting data is available.

References

1. H. V. Wartenberg, Z. Anorg. Chem. 252, 136 (1943).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. JANAF H_2S(g) table dated Dec. 31, 1965.
4. The value, ΔHf°_{298}($MgCl_2$ · 30 H_2O, aq) = -189.80 ± 0.1 kcal/mol, is extrapolated from ΔHf°_{298} values for aq. $MgCl_2$ selected by V. B. Parker, U. S. Natl. Bur. Std. Rept. 9803, p. 120, Jan. 1, 1968.
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Magnesium Sulfide (MgS)

(Ideal Gas) GFW = 56.376

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	= 2.207	62.042	62.042	INFINITE
100	7.020	45.650	60.757	= 1.511	62.420	58.379	= 127.587
200	7.656	50.692	54.590	= .780	62.196	54.289	= 59.324
298	8.182	53.856	53.856	.000	62.000	50.548	= 37.052
300	8.190	53.907	53.856	.015	61.994	50.477	= 36.772
400	8.487	56.308	54.182	.850	61.116	46.708	= 25.520
500	8.658	58.222	54.805	1.708	60.394	43.191	= 18.879
600	8.765	59.811	55.511	2.580	59.740	39.812	= 14.501
700	8.837	61.167	56.224	3.460	59.127	36.564	= 11.416
800	8.890	62.351	56.918	4.347	45.464	32.113	= 8.773
900	8.934	63.401	57.581	5.238	45.156	30.463	= 7.397
1000	8.977	64.344	58.211	6.134	42.692	29.030	= 6.345
1100	9.026	65.202	58.808	7.034	42.347	27.678	= 5.499
1200	9.088	65.990	59.374	7.939	41.981	26.361	= 4.801
1300	9.171	66.720	59.911	8.852	41.596	25.076	= 4.216
1400	9.279	67.404	60.422	9.774	10.827	24.300	= 3.793
1500	9.416	68.049	60.909	10.709	10.817	25.261	= 3.681
1600	9.582	68.661	61.375	11.658	10.821	26.224	= 3.582
1700	9.776	69.248	61.821	12.626	10.843	27.187	= 3.495
1800	9.997	69.813	62.249	13.614	10.884	28.147	= 3.417
1900	10.239	70.360	62.662	14.626	10.950	29.105	= 3.348
2000	10.499	70.892	63.060	15.663	11.039	30.058	= 3.285
2100	10.769	71.410	63.445	16.726	11.153	31.004	= 3.227
2200	11.046	71.918	63.819	17.817	11.295	31.949	= 3.174
2300	11.322	72.415	64.182	18.935	11.463	32.884	= 3.125
2400	11.592	72.902	64.535	20.081	11.659	33.810	= 3.079
2500	11.852	73.381	64.879	21.253	11.880	34.728	= 3.036
2600	12.097	73.851	65.216	22.451	12.126	35.639	= 2.996
2700	12.324	74.311	65.544	23.672	12.394	36.537	= 2.957
2800	12.531	74.763	65.865	24.915	12.683	37.423	= 2.921
2900	12.717	75.206	66.180	26.178	12.991	38.304	= 2.887
3000	12.879	75.640	66.488	27.458	13.313	39.172	= 2.854
3100	13.018	76.065	66.790	28.753	13.650	40.028	= 2.822
3200	13.134	76.480	67.086	30.060	13.995	40.872	= 2.791
3300	13.229	76.886	67.377	31.379	14.351	41.705	= 2.762
3400	13.302	77.282	67.663	32.705	14.710	42.533	= 2.734
3500	13.357	77.668	67.943	34.039	15.073	43.341	= 2.706
3600	13.393	78.045	68.218	35.376	15.436	44.146	= 2.680
3700	13.413	78.412	68.489	36.717	15.797	44.940	= 2.655
3800	13.419	78.770	68.755	38.058	16.155	45.722	= 2.630
3900	13.411	79.119	69.016	39.400	16.508	46.492	= 2.605
4000	13.393	79.458	69.273	40.740	16.853	47.261	= 2.582
4100	13.365	79.788	69.525	42.078	17.189	48.016	= 2.559
4200	13.329	80.110	69.774	43.413	17.515	48.763	= 2.537
4300	13.286	80.423	70.018	44.744	17.829	49.502	= 2.516
4400	13.237	80.728	70.258	46.070	18.130	50.237	= 2.495
4500	13.184	81.025	70.494	47.391	18.417	50.966	= 2.475
4600	13.127	81.314	70.726	48.707	18.690	51.685	= 2.456
4700	13.067	81.596	70.954	50.016	18.947	52.398	= 2.437
4800	13.005	81.870	71.179	51.320	19.187	53.107	= 2.418
4900	12.942	82.138	71.400	52.617	19.410	53.815	= 2.400
5000	12.878	82.399	71.617	53.908	19.615	54.513	= 2.383
5100	12.814	82.653	71.831	55.193	19.802	55.206	= 2.366
5200	12.750	82.901	72.041	56.471	19.970	55.901	= 2.349
5300	12.687	83.143	72.249	57.743	20.120	56.592	= 2.334
5400	12.624	83.380	72.452	59.008	20.249	57.277	= 2.318
5500	12.562	83.611	72.653	60.268	20.359	57.962	= 2.303
5600	12.501	83.837	72.851	61.521	20.447	58.645	= 2.289
5700	12.442	84.058	73.046	62.768	20.515	59.329	= 2.275
5800	12.384	84.274	73.237	64.009	20.562	60.005	= 2.261
5900	12.328	84.485	73.426	65.245	20.588	60.686	= 2.248
6000	12.273	84.691	73.612	66.475	20.592	61.365	= 2.235

Dec. 31, 1960; June 30, 1971

MAGNESIUM SULFIDE (MgS) (IDEAL GAS) GFW = 56.376 MgS

Ground State Configuration $^1\Sigma^+$ ΔHf°_0 = 62.0 ± 8.0 kcal/mol

$S^\circ_{298.15}$ = 53.86 ± 1.0 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 62.0 ± 8.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$a[^3\Pi]$	[8000]	[6]
$A[^1\Pi]$	[10000]	[2]
$B'[^1\Delta]$	[15000]	[2]
$b[^3\Sigma]$	[19000]	[3]
$B^1\Sigma^+$	23037	1

ω_e = 526.34 cm^{-1} $\omega_e x_e$ = 2.682 cm^{-1} σ = 1

B_e = 0.26563 cm^{-1} α_e = 0.00174 cm^{-1} r_e = 2.1425 Å

Heat of Formation

Marcano and Barrow (1) experimentally conducted a rotational analysis of bands in the $B^1\Sigma$-$X^1\Sigma$ system of gaseous MgS. Their data was used to calculate a dissociation energy of 73.1 kcal/mol by means of a linear Birge-Sponer extrapolation. We adjusted this value to 65.2 kcal/mol using an ionic character correction factor as suggested by Hildenbrand (2).

Gaydon (3) references two values of the dissociation energy. A value of 66.9 kcal/mol was obtained by a linear Birge-Sponer extrapolation of older data. The other value, also referenced by Marcano and Barrow (1), is based on a Knudsen effusion-mass spectrometry study. This study was unsuccessful in searching for gaseous MgS but sets a limit for D°_0(MgS) ≤ 55 kcal/mol.

The value of 65.2 kcal/mol for the dissociation energy is accepted as the best value. The reason is that it is based on the most recent positive data and an ionic correction factor which has been shown to be quite dependable.

The $^1\Sigma$ ground state of MgS cannot dissociate into ground state atoms. It is assumed that the ground state of MgS dissociates into Mg($^1S_0$) and S($^1D_2$). The heat of formation adopted is calculated to be ΔHf°_{298}(MgS, g) = 62.0 ± 8.0 kcal/mol using JANAF values for the products (6).

Heat Capacity and Entropy

The spectroscopic constants, taken from Marcano and Barrow (1) for the isotopic species $Mg^{24}S^{32}$, were corrected to account for the natural abundances of the elements.

To date the literature suggests that all gaseous alkaline earth sulfides have a $^1\Sigma^+$ ground state - BeS (7, 8), MgS (1), CaS (10), SrS (5), and BaS (9). However, assuming an analogy with the gaseous alkaline earth oxides, such a ground state is uncertain due to the suspected presence of low-lying triplet states. Triplet states have been observed directly in BeS and indirectly (through perturbative effects) in BaS. In the other three sulfides, there is, as yet, no evidence for the presence of triplet states.

A $^1\Pi$ state is predicted for MgS at 10000 cm^{-1} based on experimentally based $^1\Pi$ states for C_2 (6), BeO (4), and BeS (7, 8) at ~8000 cm^{-1} and MgO (12) at ~3500 cm^{-1}. Marcano and Barrow (1) searched for this state but could not find it above 11700 cm^{-1}. The corresponding triplet, $^3\Pi$, is assumed to lie 2000 cm^{-1} lower in energy. In BaS the $^3\Pi$ state is known (through perturbative effects) to lie below 14500 cm^{-1}.

In C_2, SiC, and Si_2 a $^1\Delta$ state is predicted to lie in the range 10000-15000 cm^{-1} (6). In BeS a study of perturbations reveals a $^1\Delta$ state below 13048 cm^{-1} (7). By analogy a $^1\Delta$ state for MgS is predicted to lie at 15000 cm^{-1}. A $^3\Sigma$ state, assumed to lie between the $A[^1\Pi]$ and the $B[^1\Sigma]$ is estimated at 19000 cm^{-1}. This estimation is based on energy level calculations for BeO (4), BeS, and the energy level scheme of C_2, Si_2, and SiC.

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MgS

Nitrogen Dioxide Uninegative Ion (NO_2^-)

(Ideal Gas) GFW = 46.0060

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	9.002	56.521	56.521	.000	−48.450	−42.381	31.066
300	9.018	56.577	56.521	.017	−48.462	−42.343	30.847
400	9.928	59.296	56.886	.964	−49.071	−40.210	21.970
500	10.739	61.602	57.604	1.999	−49.616	−37.931	16.579
600	11.386	63.619	58.442	3.106	−50.116	−35.546	12.948
700	11.882	65.414	59.312	4.271	−50.590	−33.079	10.328
800	12.259	67.026	60.177	5.479	−51.048	−30.547	8.345
900	12.547	68.487	61.021	6.720	−51.498	−27.957	6.789
1000	12.770	69.821	61.835	7.986	−51.943	−25.317	5.533
1100	12.944	71.047	62.617	9.272	−52.386	−22.634	4.497
1200	13.083	72.179	63.368	10.574	−52.829	−19.909	3.626
1300	13.195	73.231	64.086	11.888	−53.275	−17.148	2.883
1400	13.286	74.212	64.775	13.212	−53.722	−14.353	2.241
1500	13.361	75.131	65.435	14.544	−54.172	−11.525	1.679
1600	13.424	75.996	66.068	15.884	−54.624	−8.666	1.184
1700	13.477	76.811	66.677	17.229	−55.079	−5.779	.743
1800	13.521	77.583	67.261	18.579	−55.540	−2.867	.348
1900	13.560	78.315	67.824	19.933	−56.004	.073	−.008
2000	13.593	79.011	68.366	21.291	−56.472	3.035	−.332
2100	13.621	79.675	68.889	22.651	−56.944	6.023	−.627
2200	13.646	80.310	69.394	24.015	−57.422	9.032	−.897
2300	13.669	80.917	69.882	25.380	−57.904	12.063	−1.146
2400	13.689	81.499	70.354	26.748	−58.391	15.117	−1.377
2500	13.707	82.058	70.811	28.118	−58.883	18.187	−1.590
2600	13.724	82.596	71.254	29.490	−59.378	21.282	−1.789
2700	13.740	83.114	71.683	30.863	−59.880	24.394	−1.975
2800	13.755	83.614	72.101	32.238	−60.385	27.524	−2.148
2900	13.769	84.097	72.506	33.614	−60.895	30.674	−2.312
3000	13.784	84.564	72.900	34.992	−61.410	33.840	−2.465
3100	13.799	85.016	73.284	36.371	−61.927	37.024	−2.610
3200	13.814	85.455	73.657	37.751	−62.449	40.223	−2.747
3300	13.830	85.880	74.021	39.134	−62.975	43.438	−2.877
3400	13.847	86.293	74.376	40.517	−63.504	46.672	−3.000
3500	13.865	86.695	74.722	41.903	−64.036	49.918	−3.117
3600	13.884	87.086	75.060	43.290	−64.569	53.184	−3.229
3700	13.905	87.466	75.391	44.680	−65.106	56.462	−3.335
3800	13.927	87.837	75.713	46.071	−65.644	59.755	−3.437
3900	13.951	88.199	76.029	47.465	−66.183	63.060	−3.534
4000	13.976	88.553	76.338	48.862	−66.724	66.381	−3.627
4100	14.003	88.898	76.640	50.261	−67.266	69.716	−3.716
4200	14.032	89.236	76.936	51.662	−67.809	73.063	−3.802
4300	14.063	89.567	77.226	53.067	−68.351	76.426	−3.884
4400	14.096	89.890	77.510	54.475	−68.894	79.796	−3.963
4500	14.130	90.208	77.788	55.886	−69.435	83.183	−4.040
4600	14.166	90.519	78.062	57.301	−69.976	86.585	−4.114
4700	14.204	90.824	78.330	58.720	−70.516	89.992	−4.185
4800	14.244	91.123	78.593	60.142	−71.055	93.414	−4.253
4900	14.286	91.417	78.852	61.568	−71.592	96.839	−4.319
5000	14.328	91.706	79.106	62.999	−72.125	100.284	−4.383
5100	14.373	91.990	79.356	64.434	−72.658	103.739	−4.446
5200	14.418	92.270	79.602	65.874	−73.188	107.201	−4.506
5300	14.465	92.545	79.843	67.318	−73.715	110.679	−4.564
5400	14.513	92.816	80.081	68.767	−74.239	114.158	−4.620
5500	14.562	93.083	80.315	70.221	−74.758	117.657	−4.675
5600	14.612	93.345	80.545	71.679	−75.276	121.156	−4.728
5700	14.663	93.605	80.772	73.143	−75.790	124.669	−4.780
5800	14.714	93.860	80.996	74.612	−76.300	128.194	−4.830
5900	14.766	94.112	81.216	76.086	−76.807	131.720	−4.879
6000	14.819	94.361	81.433	77.565	−77.308	135.262	−4.927

Dec. 31, 1965; June 30, 1972

NITROGEN DIOXIDE UNINEGATIVE ION (NO_2^-) (IDEAL GAS) GFW = 46.0060 NO_2^-

Point Group C_{2v} ΔHf°_0 = −46.30 ± 1.38 kcal/mol

$S^\circ_{298.15}$ = 58.52 ± 0.50 gibbs/mol $\Delta Hf^\circ_{298.15}$ = −48.45 ± 1.38 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
[$^1A_1$]	[0]	[1]
[$^3B_1$]	[22000]	[3]
[$^1B_1$]	[27000]	[1]

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[1320] (1)
[750] (1)
1244 (1)

Bond Distance: N-O = [1.23 ± 0.04] Å

Bond Angle: O-N-O = 115° ± 3° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [25.9543 x 10^{-117}] g^3cm^6

Heat of Formation

The recent literature concerning the electron affinity of NO_2(g) is summarized in the following table.

reference	technique	electron affinity NO_2(g), eV
1.	magnetron technique, direct electron-capture process	3.99 ± 0.16
2.	endothermic charge transfer reaction	>2.04, >3.063
3.	endothermic charge transfer reaction	2.30 ± 0.15
4.	photodetachment of e^- from NO_2^- in argon matrix	<3.9
5.	reaction of NO_2^- with HCl and HBr in flowing after glow system	<2.6
6.	correlation between heats of hydration and heterolytic bond dissociation energies	2.5
7.	charge transfer reactions, flowing after glow system	2.38 ± 0.06

The early literature on the electron affinity of NO_2(g) is best summarized and referenced by Berkowitz, et al. (2), Ferguson, et al. (5), and Dunkin, et al. (7). Much of this early data is not only widely scattered but also conflicting.

The value chosen for the electron affinity of NO_2(g) is 2.38 ± 0.06 eV, based on the work of Dunkin et al. (7). This leads to $\Delta Hf^\circ_{298}(NO_2^-, g)$ = −48.45 ± 1.38 kcal/mol, using JANAF auxiliary data.

Heat Capacity and Entropy

The infrared spectrum of the NO_2^- ion isolated in an argon matrix was studied by Milligan, Jacox, and Guillory (4) and Milligan and Jacox (8). They reported that the antisymmetric stretching fundamental was ω_3 = 1244 cm^{-1}.

Hochstrasser and Marchetti (9), in combination with data from Sidman (10), reported ω_1 = 1325 cm^{-1}, ω_2 = 831 cm^{-1}, and ω_3 = 1243 cm^{-1} as the vibrational frequencies for NO_2^- in $NaNO_2$(c). Williams (11) reported ω_1 = 1320 cm^{-1}, ω_2 = 750 cm^{-1}, and ω_3 = 1220 cm^{-1} as the vibrational frequencies of the nitrite ion in solution. These frequencies are also very similar to the values reported for NO_2(g) by Herzberg (12). The ω_1 and ω_2 vibrational frequencies of NO_2^-(g) were assumed to be the same as those for nitrite ion in solution (11). The value adopted for ω_3 was that of Milligan, et al. (4, 8).

Milligan, et al (4, 8), via studies of the infrared spectrum of NO_2^- ion isolated in an argon matrix, concluded that the isotopic data were consistent with a O-N-O angle of 115°. Hochstrasser and Marchetti (9), relying on crystallographic data for $NaNO_2$(c) collected by other investigators, reported the N-O bond distance as 1.23 ± 0.04 Å and the O-N-O bond angle as 115° ± 3°. The N-O bond distance in NO_2^-(g) is assumed to be the same as that reported for $NaNO_2$(c).

The electronic states are estimated by analogy with the electronic levels of the isoelectronic molecule SO_2 (12). The enthalpy between 298 and 0 K is 2.444 kcal/mol.

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Dinitrogen Monoxide Unipositive Ion (N_2O^+)

(Ideal Gas) GFW = 44.0122

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	10.101	55.865	55.865	.000	318.690	321.498	- 235.664
300	10.118	55.927	55.865	.019	318.698	321.515	- 234.224
400	10.976	58.960	56.273	1.075	319.199	322.381	- 176.141
500	11.688	61.488	57.070	2.209	319.762	323.113	- 141.232
600	12.268	63.672	57.992	3.408	320.368	323.728	- 117.918
700	12.731	65.599	58.944	4.659	320.998	324.236	- 101.231
800	13.098	67.324	59.885	5.951	321.645	324.655	- 88.692
900	13.388	68.864	60.800	7.276	322.301	324.992	- 78.919
1000	13.619	70.307	61.681	8.626	322.961	325.256	- 71.065
1100	13.804	71.614	62.525	9.998	323.622	325.454	- 64.662
1200	13.955	72.822	63.333	11.386	324.281	325.591	- 59.298
1300	14.077	73.944	64.107	12.788	324.941	325.673	- 54.751
1400	14.179	74.991	64.847	14.201	325.597	325.705	- 50.845
1500	14.263	75.972	65.557	15.623	326.252	325.690	- 47.453
1600	14.334	76.895	66.237	17.053	326.904	325.631	- 44.479
1700	14.394	77.766	66.890	18.490	327.553	325.532	- 41.850
1800	14.445	78.590	67.517	19.932	328.199	325.394	- 39.508
1900	14.489	79.372	68.120	21.378	328.842	325.222	- 37.409
2000	14.527	80.116	68.702	22.829	329.482	325.015	- 35.516
2100	14.560	80.826	69.262	24.284	330.118	324.774	- 33.800
2200	14.589	81.504	69.804	25.741	330.750	324.505	- 32.237
2300	14.615	82.153	70.326	27.201	331.380	324.207	- 30.807
2400	14.638	82.776	70.832	28.664	332.008	323.883	- 29.494
2500	14.658	83.374	71.322	30.129	332.631	323.530	- 28.283
2600	14.676	83.949	71.797	31.596	333.251	323.154	- 27.164
2700	14.692	84.503	72.257	33.064	333.868	322.755	- 26.125
2800	14.706	85.038	72.704	34.534	334.482	322.331	- 25.159
2900	14.719	85.554	73.138	36.005	335.095	321.888	- 24.258
3000	14.731	86.053	73.561	37.478	335.703	321.423	- 23.416
3100	14.742	86.536	73.971	38.951	336.308	320.935	- 22.626
3200	14.752	87.005	74.371	40.426	336.911	320.429	- 21.884
3300	14.761	87.459	74.761	41.902	337.510	319.905	- 21.186
3400	14.769	87.899	75.141	43.378	338.108	319.364	- 20.528
3500	14.777	88.328	75.512	44.856	338.704	318.801	- 19.907
3600	14.784	88.744	75.874	46.334	339.295	318.225	- 19.319
3700	14.791	89.149	76.227	47.812	339.885	317.632	- 18.762
3800	14.798	89.544	76.572	49.292	340.473	317.024	- 18.233
3900	14.804	89.928	76.910	50.772	341.060	316.399	- 17.730
4000	14.809	90.303	77.240	52.253	341.643	315.757	- 17.252
4100	14.815	90.669	77.563	53.734	342.225	315.103	- 16.797
4200	14.820	91.026	77.879	55.216	342.805	314.435	- 16.362
4300	14.826	91.375	78.189	56.698	343.384	313.755	- 15.947
4400	14.831	91.716	78.493	58.181	343.961	313.057	- 15.550
4500	14.836	92.049	78.790	59.664	344.535	312.348	- 15.170
4600	14.841	92.375	79.082	61.148	345.109	311.630	- 14.806
4700	14.846	92.694	79.368	62.632	345.681	310.894	- 14.457
4800	14.850	93.007	79.649	64.117	346.251	310.150	- 14.122
4900	14.855	93.313	79.925	65.602	346.821	309.386	- 13.799
5000	14.860	93.613	80.196	67.088	347.389	308.619	- 13.490
5100	14.865	93.908	80.462	68.574	347.955	307.836	- 13.192
5200	14.870	94.196	80.723	70.061	348.522	307.045	- 12.905
5300	14.875	94.480	80.980	71.548	349.087	306.243	- 12.628
5400	14.880	94.758	81.232	73.036	349.651	305.427	- 12.361
5500	14.885	95.031	81.481	74.524	350.213	304.608	- 12.104
5600	14.891	95.299	81.725	76.013	350.775	303.770	- 11.855
5700	14.896	95.563	81.966	77.502	351.336	302.927	- 11.615
5800	14.901	95.822	82.202	78.992	351.896	302.076	- 11.383
5900	14.907	96.077	82.435	80.483	352.456	301.209	- 11.157
6000	14.912	96.327	82.665	81.974	353.013	300.336	- 10.940

Dec. 31, 1970

DINITROGEN MONOXIDE UNIPOSITIVE ION (N_2O^+) *(IDEAL GAS)* *GFW = 44.0122* N_2O^+

Point Group $C_{\infty v}$ ΔHf°_0 = 317.78 ± 0.15 kcal/mol

$S^\circ_{298.15}$ = 55.86 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 318.69 ± 0.15 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{3/2}$	0	2
$X^2\Pi_{1/2}$	132.4	2
$A^2\Sigma^+$	28429	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1736.6 (1)
461.2 (2)
1126.4 (1)

Bond Distance: N-N = 1.155 Å N-O = 1.185 Å

Bond Angle: N-N-O = 180° σ = 1

Rotational Constant: B_0 = 0.41159 cm^{-1}

Heat of Formation

The ionization potential of 104000 cm^{-1} (297.35 kcal) has been obtained by Tanaka et al. (1) from a Rydberg series terminating on $X^2\Pi_{3/2}$. Other Rydberg series terminating on $X^2\Pi_{1/2}$ and $A^2\Sigma^+$ were also obtained and confirm the adopted value. This value in conjunction with the heat of formation of $N_2O(g)$ (2) was used to calculate the adopted heat of formation.

Heat Capacity and Entropy

The electronic, vibrational and rotational constants are those reported by Herzberg (3) from the work of Callomon and Creutzberg (4).

References

1. Y. Tanaka, A. S. Jura and F. J. LeBlanc, J. Chem. Phys. 28, 350 (1958).
2. *JANAF Thermochemical Tables.* $N_2O(g)$ 12-31-64.
3. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Von Nostrand Co., Inc., New York, 1966.
4. J. H. Callomon and F. C. Creutzberg, Proc. Int. Conf. Spectrosc., 1st Bombay, 1, 171 (1967).

Azide (N_3)

(Ideal Gas) GFW = 42.0201

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	2.450	99.658	99.658	INFINITE
100	7.516	46.964	61.958	1.699	99.369	100.598	-219.857
200	8.595	50.445	54.956	.902	99.122	101.931	-111.385
298	9.742	54.100	54.100	.000	99.000	103.340	-75.750
300	9.761	54.160	54.100	.018	98.999	103.366	-75.302
400	10.680	57.099	54.495	1.042	98.977	104.828	-57.275
500	11.433	59.566	55.268	2.149	99.029	106.286	-46.457
600	12.047	61.706	56.167	3.324	99.136	107.729	-39.240
700	12.540	63.602	57.096	4.554	99.275	109.149	-34.078
800	12.933	65.303	58.018	5.828	99.434	110.550	-30.201
900	13.246	66.845	58.914	7.138	99.606	111.929	-27.180
1000	13.496	68.254	59.779	8.476	99.782	113.288	-24.759
1100	13.697	69.550	60.609	9.836	99.960	114.630	-22.775
1200	13.860	70.749	61.405	11.214	100.137	115.956	-21.119
1300	13.998	71.864	62.167	12.607	100.313	117.267	-19.714
1400	14.105	72.906	62.897	14.012	100.487	118.564	-18.509
1500	14.197	73.882	63.597	15.427	100.658	119.850	-17.462
1600	14.275	74.801	64.269	16.851	100.828	121.125	-16.545
1700	14.341	75.668	64.914	18.282	100.995	122.388	-15.734
1800	14.397	76.489	65.535	19.719	101.158	123.641	-15.012
1900	14.446	77.269	66.132	21.161	101.321	124.888	-14.365
2000	14.488	78.011	66.708	22.607	101.480	126.124	-13.782
2100	14.524	78.719	67.263	24.058	101.638	127.350	-13.254
2200	14.556	79.395	67.799	25.512	101.793	128.572	-12.772
2300	14.584	80.043	68.317	26.969	101.947	129.784	-12.332
2400	14.609	80.664	68.819	28.429	102.100	130.993	-11.929
2500	14.632	81.261	69.305	29.891	102.250	132.193	-11.556
2600	14.651	81.836	69.776	31.355	102.398	133.388	-11.212
2700	14.669	82.389	70.233	32.821	102.546	134.578	-10.893
2800	14.685	82.923	70.676	34.289	102.692	135.760	-10.597
2900	14.699	83.438	71.108	35.758	102.838	136.940	-10.320
3000	14.712	83.937	71.527	37.229	102.981	138.114	-10.062
3100	14.724	84.419	71.935	38.701	103.124	139.280	-9.819
3200	14.735	84.887	72.333	40.174	103.265	140.445	-9.592
3300	14.745	85.341	72.720	41.648	103.404	141.605	-9.378
3400	14.754	85.781	73.098	43.123	103.544	142.762	-9.177
3500	14.762	86.209	73.466	44.598	103.682	143.910	-8.986
3600	14.770	86.625	73.826	46.075	103.817	145.059	-8.806
3700	14.777	87.029	74.177	47.552	103.954	146.203	-8.636
3800	14.783	87.424	74.521	49.030	104.088	147.343	-8.474
3900	14.789	87.808	74.857	50.509	104.222	148.481	-8.321
4000	14.795	88.182	75.185	51.988	104.355	149.612	-8.174
4100	14.800	88.548	75.507	53.468	104.486	150.742	-8.035
4200	14.805	88.904	75.821	54.948	104.616	151.870	-7.903
4300	14.810	89.253	76.130	56.429	104.747	152.995	-7.776
4400	14.814	89.593	76.432	57.910	104.875	154.113	-7.655
4500	14.818	89.926	76.728	59.392	105.002	155.231	-7.539
4600	14.822	90.252	77.018	60.874	105.130	156.349	-7.428
4700	14.826	90.571	77.303	62.356	105.256	157.458	-7.322
4800	14.830	90.883	77.583	63.839	105.380	158.570	-7.220
4900	14.833	91.189	77.858	65.322	105.504	159.670	-7.122
5000	14.836	91.488	78.127	66.806	105.627	160.780	-7.028
5100	14.840	91.782	78.392	68.290	105.749	161.876	-6.937
5200	14.843	92.070	78.652	69.774	105.871	162.981	-6.850
5300	14.846	92.353	78.906	71.258	105.991	164.075	-6.766
5400	14.849	92.631	79.160	72.743	106.110	165.169	-6.685
5500	14.852	92.903	79.407	74.228	106.227	166.267	-6.607
5600	14.855	93.171	79.651	75.713	106.345	167.355	-6.531
5700	14.858	93.434	79.890	77.199	106.461	168.447	-6.459
5800	14.861	93.692	80.126	78.685	106.576	169.534	-6.388
5900	14.863	93.946	80.358	80.171	106.689	170.614	-6.320
6000	14.866	94.196	80.587	81.657	106.802	171.697	-6.254

Dec. 31, 1970

AZIDE (N_3) (IDEAL GAS) GFW = 42.0201 N_3

Point Group $D_{\infty h}$ ΔHf°_0 = 99.7 ± 5 kcal/mol

$S^\circ_{298.15}$ = [54.1 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 99 ± 5 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Pi_{g\ 3/2}$	0	2
$X^2\Pi_{g\ 1/2}$	71.3	2
$A^2\Sigma_u^+$	36811	2

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[1800] (1)
[500] (2)
[1200] (1)

Bond Distance: N-N = 1.1815 Å

Bond Angle: N-N-N = 180° σ = 2

Rotational Constant: B_0 = 0.43117 cm^{-1}

Heat of Formation

Okabe and Mele (1) have measured the photodissociation onset of the process

$$CN{\cdot}N_3(g) \rightarrow CN(g) + N_3(g) \qquad \Delta H^\circ_0 = 98 \pm 2.5 \text{ kcal/mol}$$

Using a value of $\Delta Hf^\circ_{298}(CN{\cdot}N_3, g)$ = 107 ± 3 kcal/mol and $\Delta Hf^\circ_{298}(CN, g)$ = 104 ± 2.5 kcal/mol (2), we derive $\Delta Hf^\circ_{298}(N_3, g)$ = 99 ± 5 kcal/mol. The heat of formation of $CN{\cdot}N_3$ is obtained from $\Delta Hf^\circ_{298}(CN{\cdot}N_3, c)$ = 92.6 ± 3 kcal/mol (3) and an estimated ΔHs°_{298} = 14.4 ± 3 kcal/mol. The heat of sublimation is similar to that for ICN(c) (2). A rough confirmation of ΔHs can be made by assuming a boiling point of 227°C (500°K), from the facts that $CN{\cdot}N_3$ sublimes in vacuo at 40°C and can be heated as a liquid to 170°C. Thus, using the Trouton rule, ΔHv = 11 kcal, in addition the heat of melting would be expected to be about 3.6 kcal for this 5 atom molecule, thus ΔHs = 14.6 kcal.

Heat Capacity and Entropy

The electronic levels and rotational constants have been reported by Douglas and Jones (4) and Thrush (5). The vibrational frequencies were estimated from the isoelectronic species NCO, NNO^+, and the related molecules NCN and NNO (2).

References

1. H. Okabe and A. Mele, J. Chem. Phys. 51, 2100 (1969).
2. JANAF Thermochemical Tables. CN(g) 6-30-69; ICN(g) 6-30-69; NCO(g) 12-31-70; NNO^+(g) 12-31-70; NCN(g) 12-31-70; N_2O(g) 12-31-64.
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. A. E. Douglas and W. J. Jones, Can. J. Phys. 43, 2216 (1965).
5. B. A. Thrush, Proc. Roy. Soc. (London) 235A, 143 (1956).

Phosphorus Monoxide (PO)

(Ideal Gas) GFW = 46.9732

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	= 2.245	= 3.246	= 3.246	INFINITE
100	7.717	44.778	60.038	= 1.526	= 2.965	= 5.223	11.415
200	7.697	50.174	53.913	= .748	= 2.852	= 7.542	8.241
298	7.591	53.218	53.218	.000	= 2.900	= 9.837	7.210
300	7.592	53.265	53.218	.014	= 2.901	= 9.879	7.197
400	7.727	55.464	53.517	.779	= 3.025	= 12.188	6.659
500	7.933	57.210	54.086	1.562	= 3.179	= 14.462	6.321
600	8.127	58.674	54.732	2.365	= 3.354	= 16.703	6.084
700	8.288	59.939	55.388	3.186	= 3.555	= 18.912	5.905
800	8.416	61.055	56.028	4.021	= 24.202	= 26.402	7.213
900	8.517	62.052	56.643	4.868	= 24.196	= 26.676	6.478
1000	8.598	62.954	57.229	5.724	= 24.194	= 26.952	5.890
1100	8.662	63.776	57.788	6.587	= 24.192	= 27.228	5.410
1200	8.715	64.532	58.319	7.456	= 24.190	= 27.505	5.009
1300	8.759	65.232	58.824	8.330	= 24.188	= 27.780	4.670
1400	8.796	65.882	59.305	9.208	= 24.186	= 28.057	4.380
1500	8.827	66.490	59.764	10.089	= 24.186	= 28.332	4.128
1600	8.854	67.061	60.202	10.973	= 24.189	= 28.609	3.908
1700	8.878	67.598	60.622	11.860	= 24.192	= 28.885	3.713
1800	8.899	68.106	61.024	12.749	= 24.195	= 29.161	3.541
1900	8.917	68.588	61.409	13.639	= 24.201	= 29.436	3.386
2000	8.934	69.046	61.780	14.532	= 24.208	= 29.714	3.247
2100	8.949	69.482	62.136	15.426	= 24.217	= 29.987	3.121
2200	8.963	69.899	62.479	16.322	= 24.228	= 30.262	3.006
2300	8.976	70.297	62.811	17.219	= 24.240	= 30.537	2.902
2400	8.988	70.680	63.131	18.117	= 24.255	= 30.811	2.806
2500	9.000	71.047	63.440	19.017	= 24.270	= 31.082	2.717
2600	9.010	71.400	63.739	19.917	= 24.289	= 31.355	2.636
2700	9.020	71.740	64.030	20.819	= 24.309	= 31.627	2.560
2800	9.030	72.068	64.311	21.721	= 24.331	= 31.897	2.490
2900	9.039	72.385	64.584	22.625	= 24.355	= 32.166	2.424
3000	9.048	72.692	64.849	23.529	= 24.381	= 32.435	2.363
3100	9.056	72.989	65.107	24.434	= 24.408	= 32.702	2.305
3200	9.064	73.278	65.358	25.340	= 24.436	= 32.971	2.252
3300	9.072	73.556	65.602	26.247	= 24.469	= 33.237	2.201
3400	9.080	73.826	65.840	27.155	= 24.502	= 33.502	2.153
3500	9.088	74.090	66.072	28.063	= 24.536	= 33.766	2.108
3600	9.096	74.346	66.298	28.972	= 24.572	= 34.030	2.066
3700	9.103	74.595	66.519	29.882	= 24.609	= 34.293	2.026
3800	9.111	74.838	66.735	30.793	= 24.647	= 34.552	1.987
3900	9.119	75.075	66.946	31.704	= 24.686	= 34.812	1.951
4000	9.126	75.306	67.152	32.617	= 24.727	= 35.074	1.916
4100	9.134	75.531	67.353	33.530	= 24.768	= 35.331	1.883
4200	9.142	75.752	67.551	34.444	= 24.811	= 35.586	1.852
4300	9.151	75.967	67.746	35.358	= 24.854	= 35.844	1.822
4400	9.159	76.177	67.933	36.274	= 24.898	= 36.097	1.793
4500	9.168	76.383	68.119	37.190	= 24.943	= 36.351	1.765
4600	9.177	76.585	68.301	38.107	= 24.988	= 36.606	1.739
4700	9.186	76.782	68.479	39.025	= 25.034	= 36.857	1.714
4800	9.196	76.976	68.654	39.944	= 25.080	= 37.107	1.690
4900	9.206	77.165	68.826	40.865	= 25.125	= 37.358	1.666
5000	9.217	77.352	68.994	41.786	= 25.172	= 37.607	1.644
5100	9.228	77.534	69.160	42.708	= 25.219	= 37.855	1.622
5200	9.239	77.713	69.323	43.631	= 25.265	= 38.106	1.602
5300	9.252	77.890	69.483	44.556	= 25.311	= 38.349	1.581
5400	9.265	78.063	69.640	45.482	= 25.356	= 38.597	1.562
5500	9.278	78.233	69.795	46.409	= 25.401	= 38.838	1.543
5600	9.292	78.400	69.947	47.337	= 25.446	= 39.085	1.525
5700	9.307	78.565	70.097	48.267	= 25.490	= 39.327	1.508
5800	9.322	78.727	70.244	49.199	= 25.533	= 39.570	1.491
5900	9.339	78.886	70.389	50.132	= 25.575	= 39.812	1.475
6000	9.356	79.043	70.532	51.066	= 25.617	= 40.051	1.459

Dec. 31, 1960; June 30, 1971

PHOSPHORUS MONOXIDE (PO) (IDEAL GAS) GFW = 46.9732 OP

Ground State Configuration $^2\Pi_r$

ΔHf°_0 = −3.2 ± 3.5 kcal/mol

$S^\circ_{298.15}$ = 53.218 ± 0.005 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −2.9 ± 1 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{1/2}$	0	2
$X^2\Pi_{3/2}$	224	2
$B^2\Sigma^+$	30696	2
$B'^2\Pi_i$	32884	4
$D'^2\Pi_r$	38055	4
$A^2\Sigma^+$	40485	2
$C'^2\Sigma^-$	43629	2
$C^2\Sigma^-$	47251	2
$D^2\Pi_r$	48580	4

ω_e = 1233.3 cm^{-1} $\omega_e x_e$ = 6.56 cm^{-1} σ = 1

B_e = 0.7337 cm^{-1} α_e = 0.0056 cm^{-1} r_e = 1.4757 Å

Heat of Formation

The dissociation energy of PO has been reported by various investigators to be from 5.15 eV to 7.4 eV. All of these values have been based on the spectroscopic properties of PO. Recently Drowart et al. (1) have measured the dissociation energy by a complex series of exchange reactions in a mass-spectrometer from which they calculate a dissociation energy of 142.2 ± 2.5 kcal (6.17 ev). Drowart et al. (1) also point out the agreement with the observed predissociation in the D' state. Couet et al. (2) and Verma and Dixit (3) have observed this predissociation. It was thought to occur between the 0 and 1 levels but recently Verma (4) has shown that the vibrational numbering is in error. This does not affect the predissociation, however, which we take as 49210 ± 350 cm^{-1}. If this is to ground state products the dissociation energy is 140.7 ± 1.0 kcal. The linear Birge-Sponer extrapolation (LBX) of the ground state vibrational energy levels yields D°_0 = 164 kcal, when corrected by the method of Hildenbrand (5) D°_0 = 138.1 kcal, in excellent agreement with the predissociation limit.

The much shorter extrapolation of the $B^2\Sigma^+$ levels yields D°_0 = 157.5 (3), 155.0 (6) and 152.7 (7) kcal using the LBX method, a non-linear extrapolation (8) yields 151.0 kcal. All these values assume ground state atoms as the products, which must be the case since a $^2\Sigma^+$ state exists which correlates with those products and the $B^2\Sigma^+$ state must be this state or be formed by an avoided crossing. It is possible then that these values are high due to a potential maximum in the $B^2\Sigma^+$ state.

The adopted value is D°_0 = 140.7 ± 1 kcal/mol and this yields ΔHf_{298}(PO, g) = −2.9 ± 1 kcal/mol.

Heat Capacity and Entropy

The ground-state constants are from Verma (9) and Verma and Dixit (3). The ground-state splitting is from Rao (10) who also reported the excitation energy of the A state. The energy of the B state is due to Singh (11), while that of the B' state is from Verma (9). The C state energy is due to Dressler (6) while Narisimham (12) reported the C' state energy. Verma and Dixit (3) reported the D state energy and Verma (4) the D' state energy, which is considerably different from earlier reports. The E' state reported by Santaram and Rao (13) has been shown to coincide with the D' state by Verma and Dixit (3). States above 50000 cm^{-1} were not included. Other states in the 40,000 cm^{-1} region have been proposed (14) from perturbation analyses.

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OP

Lead Monoxide, Red (PbO)

(Crystal) GFW = 223.1894

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	= 2.177	= 51.936	= 51.936	INFINITE
100	6.422	5.919	24.279	= 1.836	= 52.365	= 50.006	109.289
200	9.674	11.479	16.554	= 1.015	= 52.495	= 47.574	51.987
298	10.940	15.850	15.850	.000	= 52.440	= 45.244	33.165
300	10.962	15.918	15.850	.020	= 52.438	= 45.199	32.928
400	12.040	19.224	16.294	1.172	= 52.294	= 42.806	23.388
500	12.770	22.004	17.166	2.419	= 52.085	= 40.458	17.684
600	13.240	24.376	18.174	3.721	= 51.851	= 38.153	13.897
700	13.540	26.439	19.211	5.060	= 52.771	= 35.699	11.146
800	13.840	28.267	20.231	6.429	= 52.522	= 33.277	9.091
900	14.140	29.914	21.217	7.828	= 52.244	= 30.888	7.501
1000	14.440	31.420	22.163	9.257	= 51.935	= 28.530	6.235
1100	14.740	32.810	23.068	10.716	= 51.594	= 26.207	5.207
1200	15.040	34.106	23.935	12.205	= 51.220	= 23.914	4.355
1300	15.340	35.321	24.764	13.724	= 50.816	= 21.655	3.641
1400	15.640	36.469	25.560	15.273	= 50.384	= 19.429	3.033

Mar. 31, 1962; Dec. 31, 1971

LEAD MONOXIDE, RED (PbO) (CRYSTAL) GFW = 223.1894

ΔHf°_0 = -52.0 ± 0.2 kcal/mol

$S^\circ_{298.15}$ = 15.85 ± 0.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -52.44 ± 0.2 kcal/mol

Tt = 762 ± 1 K

ΔHt° = 0.04 ± 0.07 kcal/mol

Heat of Formation

The difference in the heats of formation of red and yellow PbO has been determined directly, using a solution calorimeter, by Knacke and Prescher (1) as 384 ± 70 cal/mol by dissolving both forms in nitric acid. This difference and ΔHf°_{298}(PbO, yellow) = -52.12 ± 0.15 kcal/mol yields ΔHf°_{298}(PbO, red) = -52.51 ± 0.2 kcal/mol. Smith and Woods (2) have measured the emf of reversible cells to obtain the free energy of the reaction PbO(red, c) + H_2(g) → Pb(c) + H_2O(ℓ) at two temperatures. From a second law analysis of this data we obtain ΔHr° = -15.91 kcal/mol which yields ΔHf°_{298}(PbO, red) = -52.41 ± 0.2 kcal/mol.

If we assume the entropy to be accurately known then the heat of formation can be calculated directly from the free energies of reaction. Smith and Woods (2) for the reaction given above found ΔGr°_{298} = -11.513 kcal/mol, in combination with ΔGf°_{298}(H_2O, ℓ) = -56.687 kcal/mol (3) yields ΔGf°_{298}(PbO, red) = -45.182 kcal/mol. This free energy with JANAF entropies (4) is equivalent to ΔHf°_{298}(PbO, red) = -52.45 kcal/mol. Spencer and Mote (5) measured the free energy of the reaction Pb(c) + HgO(c) → PbO(red, c) + Hg(ℓ) by means of a reversible cell and obtained ΔGr°_{298} = -31.265 kcal/mol. This value combined with ΔGf°_{298}(HgO, c) = -13.983 kcal/mol (4) yields ΔGf°_{298}(PbO, red) = -45.248 kcal/mol, which with JANAF entropies (4) is equivalent to $\Delta Hf^\circ_{298.15}$(PbO, red) = -52.52 kcal/mol.

It is apparent that the data for heat, free energy and entropy are all in excellent agreement, thus, we adopt ΔHf°_{298}(PbO, red) = -52.44 ± 0.2 kcal/mol. The adopted value was selected within all the uncertainties to assure the correct crossover of the red and yellow forms at 762 K.

Heat Capacity and Entropy

The heat capacity has been reported by King (6) from 53 to 296 K and the entropy was obtained by integration of this data based on S_{51} = 2.73 gibbs/mol. This extrapolated portion was obtained by use of a Debye-Einstein fit of the measured data. The value was then corrected by analogy with the 0.25 eu difference between the extrapolation for PbO(c, yellow) by King (6) and the measured amount. The justification for this procedure is the similarity of the two curves at all other temperatures. The high temperature heat capacities were obtained by fitting an orthogonal polynomial through the low temperature data of King (6) and the enthalpies of Spencer and Spicer (7).

Transition Data

The temperature of transition has been reported by Cohen and Addink (8) and Petersen (9). The enthalpy of transition is calculated from the adopted enthalpy at 298 K and the enthalpy difference $H_{762} - H_{298}$ between PbO yellow and red.

Vaporization Data

The vapor species over PbO(c, ℓ) consists of $(PbO)_x$ where x = 1-6 (10), 11), thus, a value for the heat of sublimation is not given.

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Lead Monoxide, Yellow (PbO)

(Crystal) GFW = 223.1894

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.208	- 51.647	- 51.647	INFINITE
100	6.620	6.760	25.160	- 1.840	- 52.049	- 49.774	108.782
200	9.570	12.320	17.445	- 1.025	- 52.185	- 47.432	51.832
298	10.940	16.420	16.420	.000	- 52.120	- 45.094	33.055
300	10.955	16.488	16.420	.020	- 52.118	- 45.050	32.819
400	11.598	19.734	16.858	1.150	- 51.996	- 42.712	23.337
500	12.061	22.373	17.705	2.334	- 51.851	- 40.408	17.662
600	12.453	24.608	18.674	3.560	- 51.692	- 38.133	13.890
700	12.812	26.554	19.664	4.823	- 52.686	- 35.696	11.145
800	13.152	28.246	20.635	6.122	- 52.509	- 33.281	9.092
900	13.482	29.856	21.574	7.453	- 52.299	- 30.889	7.501
1000	13.806	31.293	22.475	8.818	- 52.054	- 28.523	6.234
1100	14.125	32.624	23.338	10.215	- 51.775	- 26.183	5.202
1200	14.441	33.867	24.164	11.643	- 51.462	- 23.869	4.347
1300	14.756	35.035	24.956	13.103	- 51.117	- 21.584	3.629
1400	15.069	36.140	25.716	14.594	- 50.743	- 19.327	3.017
1500	15.380	37.190	26.446	16.116	- 50.340	- 17.095	2.491

Mar. 31, 1962; Dec. 31, 1971

ΔHf°_0 = -51.65 ± 0.15 kcal/mol

$S^\circ_{298.15}$ = 16.42 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -52.12 ± 0.15 kcal/mol

Tm = 1159 ± 5 K

ΔHm° = 6.1 ± 0.1 kcal/mol

Heat of Formation

Espada, Pilcher and Skinner (1) have measured calorimetrically the heat of the reaction PbO(yellow, c) + H_2(g) → Pb(c) + $H_2O(\ell)$ as ΔHr°_{298} = -16.20 ± 0.07 kcal/mol which yields the adopted heat of formation.

Spencer and Mote (2) have measured the free energy of the cell reaction Pb(c) + HgO(c) → PbO(yellow, c) + Hg(ℓ) as -31.120 kcal/mol. With JANAF auxiliary data (3) we obtain $\Delta Gf^\circ_{298.15}$(PbO, yellow) = -45.103 kcal/mol which corresponds to $\Delta Hf^\circ_{298.15}$(PbO, yellow) = -52.13 kcal/mol in excellent agreement with the adopted value.

Charette and Flengas (13) measured the free energy of formation directly in a high temperature electrolytic cell. Alcock and Belford (14) measured the free energy of the reactions (a) PbO(c) + Ni(c) → NiO(c) + Pb(ℓ) and (b) Cu_2O(c) + Pb(ℓ) → PbO(c) + 2Cu(c) in high temperature electrolytic cells. Second- and third-law analyses of these data are summarized below.

Reference	Temp. Range °K	ΔHr°, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(PbO, c) kcal/mol
13	770-1160	-52.3	-52.93±0.26	-0.6±0.2	-52.93±0.26
14a	780-1070	- 3.9	2.27±1.8	6.6±0.2	-54.0 ±0.7
14b	710-1050	-12.1	-12.61±0.25	-0.6±0.2	-52.28±0.7

These values indicate that the overall consistency between heats of formation, enthalpies, entropy and free energies is generally within the experimental error.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 12.5 K to 302.7 K by Kostryukov and Morozova (4) and from 54.1 K to 296.1 K by King (5). The two sets of data are in reasonable agreement with differences of up to 0.5%. A line fitted through both data sets yields an entropy within the stated uncertainty of the Russian set, whose results we adopt.

The high temperature heat capacity was derived from the enthalpy measurements of Rodigina, Gomel'skii and Luginina (6) by curve fitting with orthogonal polynomials. The curve was constrained to join smoothly with the low temperature heat capacities. The adopted values are in good agreement with enthalpies reported by Regnault (7), Magnus (8) and Kopp (9). The enthalpies reported by Spencer and Spicer (10) lie about 3% higher than the adopted values and are admitted to be not too accurate. The values reported by Knacke and Prescher (11) lie 5 to 8% higher than the adopted values.

Melting Data

The melting point was selected by Schneider (12) in his review of metal oxide melting points. The heat of melting was calculated from the enthalpy equations derived from the work of Rodigina et al. (6) for crystal and liquid. Knacke and Prescher (11) report a heat of melting of 6.57 kcal/mol from their enthalpy measurements.

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Lead Monoxide (PbO)

(Liquid) GFW = 223.1894

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	15.535	17.537	17.537	.000	-48.335	-41.642	30.524
300	15.535	17.633	17.537	.029	-48.325	-41.600	30.306
400	15.535	22.102	18.187	1.582	-47.779	-39.442	21.550
500	15.535	25.569	19.297	3.136	-47.264	-37.419	16.356
600	15.535	28.401	20.586	4.689	-46.778	-35.495	12.929
700	15.535	30.796	21.878	6.243	-47.483	-33.460	10.447
800	15.535	32.871	23.125	7.796	-47.050	-31.487	8.602
900	15.535	34.701	24.312	9.350	-46.617	-29.568	7.180
1000	15.535	36.337	25.434	10.904	-46.183	-27.696	6.053
1100	15.535	37.818	26.493	12.457	-45.788	-25.869	5.140
1200	15.535	39.170	27.494	14.011	-45.309	-24.080	4.386
1300	15.535	40.413	28.441	15.564	-44.870	-22.329	3.754
1400	15.535	41.565	29.338	17.118	-44.434	-20.613	3.218
1500	15.535	42.636	30.189	18.671	-44.000	-18.925	2.757
1600	15.535	43.639	30.999	20.225	-43.572	-17.268	2.359
1700	15.535	44.581	31.770	21.778	-43.148	-15.636	2.010
1800	15.535	45.469	32.507	23.332	-42.733	-14.031	1.704
1900	15.535	46.309	33.211	24.885	-42.325	-12.448	1.432
2000	15.535	47.106	33.886	26.439	-41.925	-10.886	1.190
2100	15.535	47.864	34.534	27.992	-83.982	-7.791	.811
2200	15.535	48.586	35.156	29.546	-83.504	-4.175	.415
2300	15.535	49.277	35.755	31.100	-83.049	-.579	.055
2400	15.535	49.938	36.333	32.653	-82.619	2.999	-.273
2500	15.535	50.572	36.890	34.207	-82.214	6.555	-.573

Mar. 31, 1962; Dec. 31, 1971

LEAD MONOXIDE (PbO) (LIQUID) GFW = 223.1894 0Pb

$S^\circ_{298.15}$ = 17.537 ± 0.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -48.335 ± 0.3 kcal/mol

Tm = 1159 ± 5 K

ΔHm° = 6.1 ± 0.1 kcal/mol

Heat of Formation

The heat of formation was obtained from that of PbO (yellow, c) by adding ΔHm° and the difference between $H_{1159} - H_{298}$ for (yellow, c) and (ℓ). Direct measurements of the free energy change in the reaction PbO(ℓ) + C(c) → Pb(ℓ) + CO(g) have been reported by Kvyatkovskii, Esin and Abdeev (1). Charette and Flengas (2) and Delimarskii and Andreeva (3) have also determined the free energy of formation of the liquid directly in a high temperature cell. Second- and third-law analysis of these data are summarized below.

Reference	Temp. Range K	ΔHr°, kcal/mol 2nd law	ΔHr°, kcal/mol 3rd law	Drift eu	ΔHf°_{298}(PbO,ℓ) kcal/mol
1	1173 - 1423	34.5 ± 6.5	22.81 ± 2.49	-8.6 ± 4.9	-48.20 ± 2.5
2	1160 - 1371	-49.9 ± 0.2	-49.24 ± 0.13	0.5 ± 0.1	-49.24 ± 0.13
3	1173 - 1253	-46.9 ± 5.6	-48.51 ± 0.39	-1.5 ± 4.6	-48.51 ± 0.39

Heat Capacity and Entropy

The heat capacity was obtained from the enthalpy determinations of Rodigina et al. (4) and Knacke and Prescher (5). The absolute enthalpy values differ by 2-3% but the constant heat capacities derived from each set agree very well. The entropy at 298 K is derived from that of the yellow crystal by adding the entropy of melting and difference $S_{1159} - S_{298}$ for crystal and liquid.

Melting Data

See PbO(yellow, c) for details.

Vaporization Data

See PbO(red, c) for details.

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Lead Monoxide (PbO)

(Ideal Gas) GFW = 223.1894

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	−2.142	17.340	17.340	INFINITE
100	6.964	49.452	63.915	−1.446	17.265	15.270	−33.373
200	7.271	54.345	58.038	−.739	17.022	13.369	−14.609
298	7.770	57.343	57.343	.000	16.800	11.625	−8.521
300	7.778	57.392	57.344	.014	16.796	11.593	−8.445
400	8.155	59.685	57.654	.812	16.586	9.690	−5.404
500	8.401	61.533	58.251	1.641	16.377	8.240	−3.602
600	8.562	63.080	58.930	2.490	16.158	6.634	−2.416
700	8.671	64.408	59.620	3.352	14.761	5.255	−1.641
800	8.750	65.571	60.293	4.223	14.512	3.914	−1.069
900	8.808	66.605	60.938	5.101	14.269	2.604	−.632
1000	8.853	67.536	61.552	5.984	14.033	1.321	−.289
1100	8.889	68.381	62.135	6.871	13.801	.060	−.012
1200	8.918	69.156	62.688	7.762	13.577	−1.178	.215
1300	8.943	69.871	63.213	8.655	13.355	−2.399	.403
1400	8.965	70.534	63.713	9.550	13.134	−3.603	.562
1500	8.984	71.154	64.189	10.448	12.912	−4.789	.698
1600	9.001	71.734	64.642	11.347	12.685	−5.963	.814
1700	9.017	72.280	65.076	12.248	12.456	−7.120	.915
1800	9.031	72.796	65.490	13.150	12.220	−8.266	1.004
1900	9.045	73.285	65.888	14.054	11.979	−9.399	1.081
2000	9.058	73.749	66.269	14.959	11.731	−10.517	1.149
2100	9.070	74.191	66.636	15.866	−30.973	−10.070	1.048
2200	9.083	74.613	66.989	16.773	−31.142	−9.072	.901
2300	9.095	75.017	67.330	17.682	−31.332	−8.065	.766
2400	9.108	75.405	67.658	18.592	−31.545	−7.047	.642
2500	9.121	75.777	67.975	19.504	−31.782	−6.024	.527
2600	9.136	76.135	68.282	20.417	−32.041	−4.988	.419
2700	9.151	76.480	68.580	21.331	−32.322	−3.942	.319
2800	9.169	76.813	68.868	22.247	−32.626	−2.885	.225
2900	9.188	77.135	69.147	23.165	−32.948	−1.817	.137
3000	9.210	77.447	69.419	24.085	−33.288	−.737	.054
3100	9.235	77.749	69.683	25.007	−33.645	.353	−.025
3200	9.264	78.043	69.939	25.932	−34.017	1.455	−.099
3300	9.296	78.329	70.189	26.860	−34.400	2.570	−.170
3400	9.332	78.607	70.433	27.791	−34.794	3.697	−.238
3500	9.374	78.878	70.670	28.726	−35.196	4.833	−.302
3600	9.420	79.142	70.902	29.666	−35.603	5.985	−.363
3700	9.472	79.401	71.128	30.611	−36.014	7.145	−.422
3800	9.529	79.655	71.349	31.560	−36.426	8.319	−.478
3900	9.592	79.903	71.565	32.516	−36.838	9.500	−.532
4000	9.662	80.147	71.777	33.479	−37.247	10.690	−.584
4100	9.738	80.386	71.984	34.449	−37.653	11.895	−.634
4200	9.820	80.622	72.187	35.427	−38.052	13.110	−.682
4300	9.909	80.854	72.386	36.413	−38.443	14.332	−.728
4400	10.005	81.083	72.581	37.409	−38.825	15.565	−.773
4500	10.107	81.309	72.772	38.415	−39.196	16.804	−.816
4600	10.216	81.532	72.960	39.431	−39.555	18.055	−.858
4700	10.332	81.753	73.145	40.458	−39.901	19.308	−.898
4800	10.453	81.972	73.326	41.497	−40.232	20.576	−.937
4900	10.581	82.189	73.505	42.549	−40.548	21.841	−.974
5000	10.714	82.404	73.681	43.614	−40.848	23.116	−1.010
5100	10.853	82.617	73.854	44.692	−41.131	24.400	−1.046
5200	10.997	82.829	74.025	45.784	−41.396	25.688	−1.080
5300	11.146	83.040	74.193	46.892	−41.642	26.984	−1.113
5400	11.298	83.250	74.359	48.014	−41.870	28.279	−1.144
5500	11.455	83.459	74.522	49.151	−42.079	29.579	−1.175
5600	11.615	83.667	74.684	50.305	−42.269	30.884	−1.205
5700	11.777	83.874	74.843	51.474	−42.439	32.188	−1.234
5800	11.942	84.080	75.000	52.660	−42.590	33.505	−1.262
5900	12.108	84.285	75.156	53.863	−42.721	34.815	−1.290
6000	12.276	84.490	75.310	55.082	−42.832	36.129	−1.316

Mar. 31, 1962; Dec. 31, 1971

Symmetry number = 1

ΔHf_0° = 17.3 ± 1.7 kcal/mol

$S^\circ_{298.15}$ = 57.343 ± 0.005 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 16.8 ± 1.7 kcal/mol

Electronic and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
X 0+	0	1	1.922	0.3074	0.00212	721.8	3.70
A 0+	20088	1	2.095	0.2587	0.00138	451.7	3.33
B 1	22531	2	2.071	0.2646	0.0026	493.5	2.26
C 0+	24108	1	2.11	0.254	0.002	[534]	[3.9]
C'1	25720	2	2.14	0.248	0.0018	[475]	[2.7]
D 1	30464	2	2.046	0.2711	0.0031	530.5	2.92
E 0+	34680	1	[2.183]	[0.2382]	[0.0014]	[440]	[2.6]

Heat of Formation

A value for the dissociation energy can be calculated by applying the Hildenbrand formula (1) to the linear Birge-Sponer extrapolation of the ground state vibrational levels. This procedure yields a D_0° = 91.4 kcal/mol, which corresponds to ΔHf_0° = 14.5 kcal/mol.

Recently Singh and Nair (3) have calculated D_0° = 99.2 kcal/mol from a special potential energy curve which takes into account the electronegativity of the atoms.

The heat of sublimation of PbO(yellow, c) to monomeric PbO has been measured mass-spectrometrically by Drowart et al. (2). Our analysis of their vapor pressure data yields ΔHs°_{298} = 68.9 ± 1.5 kcal/mol, which yields ΔHf°_{298}(PbO, g) = 16.8 ± 1.7 kcal/mol. This value is adopted and corresponds to a dissociation energy at 0 K of 88.6 kcal/mol.

Heat Capacity and Entropy

The tabulated molecular and electronic constants are taken from Barrow et al. (4). The state designations are those used by Barrow et al. who interpret the spectra in terms of type c coupling, when the state designations Σ, Π, etc. no longer have meaning. The estimated values for $\omega_e x_e$ for the C' and E states were obtained from the B_e values by averaging the $\omega_e x_e/B_e$ ratio for the known states. The functions were calculated from the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$, the values for Q_r^i and Q_v^i were calculated with first-order anharmonic corrections.

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Sulfur Monoxide (SO)

(Ideal Gas) GFW = 48.0634

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	-2.087	1.170	1.170	INFINITE
100	6.956	45.364	59.287	-1.392	1.354	.816	1.784
200	6.995	50.192	53.670	-.696	1.309	2.983	3.259
298	7.211	53.019	53.019	.000	1.167	5.060	3.709
300	7.217	53.064	53.019	.013	1.164	5.099	3.715
400	7.543	55.184	53.306	.751	.447	7.139	3.900
500	7.845	56.900	53.858	1.521	-.087	8.972	3.922
600	8.087	58.353	54.489	2.318	-.524	10.707	3.900
700	8.272	59.614	55.133	3.137	-.895	12.350	3.856
800	8.414	60.729	55.765	3.971	-1.284	13.232	4.161
900	8.525	61.726	56.373	4.818	-1.282	15.350	3.728
1000	8.616	62.629	56.958	5.674	-1.279	15.469	3.381
1100	8.694	63.454	57.508	6.541	-1.276	15.589	3.097
1200	8.764	64.214	58.035	7.414	-1.271	15.708	2.861
1300	8.829	64.918	58.538	8.294	-1.265	15.827	2.661
1400	8.891	65.574	59.017	9.180	-1.258	15.948	2.490
1500	8.953	66.190	59.475	10.072	-1.249	16.070	2.341
1600	9.014	66.770	59.913	10.970	-1.238	16.191	2.212
1700	9.074	67.318	60.333	11.875	-1.223	16.313	2.097
1800	9.133	67.838	60.735	12.785	-1.207	16.437	1.996
1900	9.192	68.334	61.122	13.701	-1.189	16.560	1.905
2000	9.250	68.807	61.495	14.623	-1.167	16.687	1.823
2100	9.306	69.259	61.854	15.551	-1.144	16.814	1.750
2200	9.360	69.693	62.200	16.484	-1.119	16.940	1.683
2300	9.413	70.111	62.535	17.423	-1.091	17.070	1.622
2400	9.463	70.512	62.859	18.367	-1.061	17.199	1.566
2500	9.511	70.900	63.173	19.316	-1.030	17.331	1.515
2600	9.557	71.274	63.478	20.269	-0.996	17.463	1.468
2700	9.600	71.635	63.773	21.227	-0.961	17.598	1.424
2800	9.640	71.985	64.060	22.189	-0.926	17.735	1.384
2900	9.678	72.324	64.339	23.155	-0.889	17.870	1.347
3000	9.713	72.653	64.611	24.125	-0.852	18.007	1.312
3100	9.746	72.972	64.876	25.098	-0.812	18.146	1.279
3200	9.776	73.282	65.134	26.074	-0.774	18.288	1.249
3300	9.804	73.583	65.385	27.053	-0.734	18.431	1.221
3400	9.830	73.876	65.630	28.035	-0.695	18.572	1.194
3500	9.853	74.161	65.870	29.019	-0.656	18.719	1.169
3600	9.874	74.439	66.104	30.005	-0.615	18.862	1.145
3700	9.893	74.710	66.333	30.993	-0.577	19.008	1.123
3800	9.911	74.974	66.557	31.984	-0.537	19.155	1.102
3900	9.927	75.232	66.776	32.976	-0.498	19.306	1.082
4000	9.941	75.483	66.991	33.969	-0.460	19.452	1.063
4100	9.953	75.729	67.201	34.964	-0.422	19.603	1.045
4200	9.965	75.969	67.407	35.960	-0.384	19.754	1.028
4300	9.975	76.203	67.609	36.957	-0.347	19.906	1.012
4400	9.983	76.433	67.807	37.954	-0.312	20.060	.996
4500	9.991	76.657	68.001	38.953	-0.277	20.212	.982
4600	9.998	76.877	68.191	39.953	-0.242	20.366	.968
4700	10.004	77.092	68.379	40.953	-0.207	20.523	.954
4800	10.010	77.303	68.562	41.954	-0.174	20.679	.942
4900	10.014	77.509	68.743	42.955	-0.142	20.835	.929
5000	10.019	77.711	68.920	43.956	-0.110	20.995	.918
5100	10.022	77.910	69.094	44.958	-0.080	21.150	.906
5200	10.026	78.105	69.266	45.961	-0.049	21.309	.896
5300	10.029	78.296	69.434	46.964	-0.019	21.467	.885
5400	10.031	78.483	69.600	47.967	-0.991	21.628	.875
5500	10.034	78.667	69.763	48.970	-0.962	21.787	.866
5600	10.036	78.848	69.924	49.973	-0.935	21.948	.857
5700	10.039	79.026	70.082	50.977	-0.909	22.111	.848
5800	10.041	79.200	70.238	51.981	-0.882	22.270	.839
5900	10.044	79.372	70.391	52.985	-0.856	22.436	.831
6000	10.046	79.541	70.542	53.990	-0.831	22.594	.823

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965; June 30, 1971

SULFUR MONOXIDE (SO) (IDEAL GAS) GFW = 48.0634 OS

Ground State Configuration $^3\Sigma^-$

ΔHf°_0 = 1.17 ± 0.03 kcal/mol

$S^\circ_{298.15}$ = 53.02 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 1.17 ± 0.03 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^3\Sigma^-$	0	3
$a^1\Delta$	[6350]	2
$b^1\Sigma^+$	10509.97	1
$A^3\Pi$	38292.5	2
	38455.2	2
	38616.5	2
$B^3\Sigma^-$	41628.7	3

ω_e = 1148.19 cm^{-1} $\omega_e x_e$ = 6.116 cm^{-1} σ = 1

B_e = 0.72082 cm^{-1} α_e = 0.00562 cm^{-1} r_e = 1.48108 Å

Heat of Formation

Martin (1) found spectroscopically a sharp predissociation of SO(g) and established a definite dissociation limit (5.053 eV). Norrish and Oldershaw (2) redetermined the absorption spectra of SO by flash photolysis and corrected Martin's original vibrational numbering, and then recalculated Martin's dissociation energy as D°_0(SO) = 43219 cm^{-1} (123.57 kcal/mol) assuming normal dissociation products $S(^3P) + O(^3P)$. However this limit could also lead to excited products $S(^1D) + O(^3P)$ which were favored by Herzberg (3) and yielded a lower value D°_0(SO) = 97.1 kcal/mol. The higher value, D°_0(SO) = 123.57 kcal/mol, is further confirmed by mass spectroscopic (4) and ultraviolet spectroscopic (5) studies and is adopted in the table to calculate ΔHf°_0(SO, g) = 1.17 kcal/mol, using JANAF ΔHf°_0(O, g) = 58.989 kcal/mol and ΔHf°_0(S, g) = 65.75 kcal/mol (6).

Collin et al. (4) studied mass spectrometrically the vaporization of CaS, SrS and BaS and derived D°_0(SO) = 123.5 ± 5 kcal/mol which is in good agreement with the value adopted. McGarvey and McGrath (5) investigated the absorption spectra of SO(g) in the ultraviolet region and found a convergence limit lying at 53677 cm^{-1} which corresponded to a dissociation energy D°_0(SO) = 127.1 kcal/mol. Gaydon et al. (7) repeated McGarvey's extrapolation and favored a lower limit equivalent to D°_0(SO) = 124 ± 1 kcal/mol which is in excellent agreement with the adopted value.

Equilibrium data (8, 9) also support the higher value of D°_0(SO) = 123.58 kcal/mol, although the reliability of this data is questionable. Pierre and Chipman (8) reported a tentative value, ΔHr°_0 = -18.7 ± 2 kcal/mol for $0.5\ S_2(g) + 0.5\ O_2(g) \rightarrow SO(g)$ in the equilibrium study of lime-iron oxide slags with SO_2 or SO_2-CO mixture. This leads to ΔHf°_0(SO, g) = -3.3 kcal/mol, using $\Delta Hf^\circ_0(S_2, g)$ = 30.80 kcal/mol. The value of ΔHr°_0 is questionable since it depends upon many assumptions and subsidiary data. Dewing and Richardson (9) measured equilibrium constants for reaction (a) $S_2(g) + 2\ SO_2(g) \rightarrow 4\ SO(g)$ at 1250°C and (b) $SO_2(g) \rightarrow SO(g) + 0.5\ O_2(g)$ at 1500°C. JANAF third law analysis gives ΔHf°_{298}(SO, g) = +0.13 kcal/mol from reaction (a) and -0.17 kcal/mol from reaction (b). The average of these two values is ΔHf°_{298}(SO, g) = 0 kcal/mol which is in good agreement with the value selected; however Meschi (10) and Blukis (11) found in the microwave spectroscopic studies that the S_2O species was one of the important products in the Sulfur-SO_2 equilibrium which was considered as unimportant by Dewing and Richardson.

Heat Capacity and Entropy

The molecular constants ω_e, $\omega_e x_e$ and α_e are obtained from Norrish and Oldershaw (2) and the values of B_e and α_e are obtained from precise microwave spectroscopic studies of Amano et al. (12) and Powell and Lide (13). The electronic levels and quantum weights are taken from Collin (14) who listed all known electronic states based on his own spectroscopic studies and literature data.

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Lead Dioxide (PbO_2)

(Crystal) GFW = 239.1888

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	= 2.621	= 64.502	= 64.502	INFINITE
100	7.141	5.254	28.191	= 2.294	= 65.292	= 60.797	132.872
200	11.940	11.838	18.418	= 1.316	= 65.613	= 56.183	61.350
298	14.620	17.160	17.160	.000	= 65.600	= 51.489	37.743
300	14.655	17.251	17.160	.027	= 65.598	= 51.402	37.486
400	16.160	21.691	17.755	1.574	= 65.414	= 46.694	25.513
500	17.136	25.410	18.925	3.243	= 65.149	= 42.044	18.378
600	17.810	28.597	20.277	4.992	= 64.845	= 37.450	13.641
700	18.215	31.374	21.669	6.794	= 65.691	= 32.719	10.215
800	18.540	33.828	23.038	8.632	= 65.372	= 28.031	7.658
900	18.786	36.027	24.361	10.499	= 65.033	= 23.383	5.678
1000	18.953	38.015	25.629	12.387	= 64.678	= 18.774	4.103
1100	19.041	39.827	26.838	14.287	= 64.316	= 14.202	2.822
1200	19.050	41.484	27.991	16.192	= 63.950	= 9.661	1.760

Mar. 31, 1962; Dec. 31, 1971

LEAD DIOXIDE (PbO_2) (CRYSTAL) GFW = 239.1888 O_2Pb

ΔHf°_0 = -64.5 ± 0.7 kcal/mol

$S^\circ_{298.15}$ = 17.16 ± 0.10 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -65.6 ± 0.7 kcal/mol

Heat of Formation

Espada, Pilcher and Skinner (1) have calorimetrically determined the heat of the reaction $PbO_2(c) + 2H_2(g) \rightarrow Pb(c) + 2H_2O(\ell)$ as -71.02 ± 0.16 kcal/mol from which they derive $\Delta Hf^\circ_{298}(PbO_2, c)$ = -65.61 ± 0.32 kcal/mol. This value assumes that the PbO_2 was 100% pure, in fact it is virtually impossible (2) to prepare a sample free of water and fully oxidized. Thus, Espada et al. (1) have increased their uncertainty to ± 0.7 kcal/mol, to cover the likely spread of values assuming typical compositions.

Millar (3) has recalculated the data of Glasstone for the free energy of the cell reaction $PbO_2(c) + H_2(g) \rightarrow PbO(red) + H_2O(\ell)$ as ΔGf°_{298} = -49.600 kcal/mol. With auxiliary free energy data (4, 5) we calculate $\Delta Gf^\circ_{298}(PbO_2, c)$ = -52.33 kcal/mol which corresponds to $\Delta Hf^\circ_{298}(PbO_2, c)$ = -65.45 kcal/mol in reasonable agreement with the value reported by Espada et al. (1).

We adopt the value $\Delta Hf^\circ_{298}(PbO_2, c)$ = -65.6 ± 0.7 kcal/mol.

Heat Capacity and Entropy

Duisman and Giauque (2) have reported the heat capacity of PbO_2 from 15 to 318 K and have calculated the entropy at 298 K based on S_{15} = 0.079 gibbs/mol. They had considerable difficulty in preparing a suitable sample of PbO_2 and finally used a sample containing PbO and H_2O, as impurities, for which significant corrections were made to the measured data. Millar (3) also has measured the heat capacity from 70 to 298 K but is 7% higher than the adopted values.

High temperature enthalpy data have been reported by Palmaer (6) and Bousquet et al. (7) but these data suffer from unknown amounts of impurity, for which the correction is probably substantial, and decomposition to intermediate oxides. Thus, the heat capacity above room temperature was estimated by a graphical extrapolation of the low temperature heat capacity.

Decomposition

Numerous investigators have reported the decomposition of PbO_2 at elevated temperatures, however, the exact processes are still not well defined. Otto (8) indicates a three step process to Pb_3O_4, but the intermediate compositions are not established. The temperature at which the decomposition pressure of oxygen reaches 0.2 atm was reported as 260°C by Otto while White and Roy (9) indicate 293°C. The enthalpies and entropies reported are in serious disagreement with adopted values and indicate failure to attain equilibrium.

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Lead Orthoplumbate (Pb_3O_4)

(Crystal) GFW = 685.5676

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	− 7.215	− 169.903	− 169.903	INFINITE
100	20.840	19.087	79.227	− 6.014	− 171.359	− 162.348	354.811
200	31.100	37.070	53.870	− 3.360	− 171.906	− 153.050	167.245
298	37.030	50.660	50.660	.000	− 171.770	− 143.804	105.411
300	37.128	50.859	50.661	.069	− 171.763	− 143.630	104.835
400	41.350	62.188	52.172	4.006	− 171.204	− 134.327	73.393
500	44.000	71.720	55.154	8.283	− 170.408	− 125.199	54.724
600	45.600	79.893	58.613	12.768	− 169.503	− 116.239	42.340
700	46.600	86.997	62.172	17.378	− 172.059	− 106.863	33.364
800	47.600	93.285	65.675	22.088	− 171.108	− 97.615	26.667
900	48.600	98.949	69.063	26.898	− 170.068	− 88.490	21.488
1000	49.600	104.122	72.314	31.808	− 168.930	− 79.484	17.371
1100	50.600	108.896	75.425	36.816	− 167.695	− 70.600	14.027
1200	51.600	113.342	78.402	41.928	− 166.354	− 61.829	11.261
1300	52.600	117.511	81.251	47.138	− 164.916	− 53.176	8.940
1400	53.600	121.446	83.983	52.448	− 163.389	− 44.641	6.969
1500	54.600	125.178	86.606	57.858	− 161.773	− 36.210	5.276

Mar. 31, 1962; Dec. 31, 1971

LEAD ORTHOPLUMBATE (Pb_3O_4) (CRYSTAL) GFW = 685.5676 O_4Pb_3

ΔHf°_0 = 169.9 ± 1.5 kcal/mol

$S^\circ_{298.15}$ = 50.66 ± 1.6 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 171.77 ± 1.5 kcal/mol

Heat of Formation

Espada, Pilcher and Skinner (1) have measured the heat of the reduction reaction $PbO_{1.3}(c) + 1.3H_2(g) \rightarrow Pb(c) + 1.3H_2O(\ell)$ as −32.07 kcal/mol. They assumed that the sample consisted of 80.1% mol percent $PbO_{1.333}$ and 9.9 mol PbO and corrected the observed heat of reaction to −33.82 ± 0.25 kcal/mol for the reaction $PbO_{1.333}(c) + 1.333\ H_2(g) \rightarrow Pb(c) + 1.333\ H_2O(\ell)$. This leads to $\Delta Hf(Pb_3O_4, c)$ = −171.77 ± 1.5 kcal/mol which is adopted.

Andrews and Brown (2) used reversible cells to obtain ΔGr_{298} = −6940 cal. for the reaction $Hg(\ell) + Pb_3O_4(c) \rightarrow HgO(c) + 3PbO(red, c)$, with JANAF auxiliary data (3) this yields $\Delta Gf^\circ_{298}(Pb_3O_4, c)$ = −142.76 ± 0.6 kcal/mol which is equivalent to $\Delta Hf^\circ_{298}(Pb_3O_4, c)$ = −170.73 ± 1.1 kcal/mol. This value is in agreement with the adopted value within the combined uncertainties.

Reinders and Hamburger (4) and Otto (5) studied the decomposition pressure of the reaction $Pb_3O_4(c) \rightarrow 3PbO(c) + 0.5\ O_2(g)$ a second- and third-law analysis of their data is given below.

Reference	Points	Range	ΔHr_{298} kcal/mol 2nd Law	3rd Law	Drift eu	*$\Delta Hf_{298}(Pb_3O_4, c)$ kcal/mol
4	16	718-880 K	20.19±0.14	19.08±0.17	-1.4±0.2	-175.44
5	19	757-911 K	20.84±0.10	18.98±0.22	-2.2±0.1	-175.34

*Derived from 3rd law ΔHr_{298}.

Although these two sets of data are in good agreement they are outside the adopted heat of formation uncertainty limits, and realistic adjustments of the entropy or heat capacity fail to eliminate this discrepancy.

In addition there have been cell measurements linking PbO_2 and Pb_3O_4, which serve to indicate the overall consistency of the lead-oxygen system. The absolute uncertainty in the heat of formation and the difficulty of preparing pure PbO_2 make it a poor choice on which to base the heat of formation of Pb_3O_4. Andrews and Brown (2) obtained ΔGr°_{298} = −18.12 kcal for the reaction $2Hg(\ell) + 3PbO_2(c) \rightarrow Pb_3O_4(c) + 2HgO(c)$. This yields $\Delta Gf^\circ_{298}(Pb_3O_4, c)$ = −144.62 ± 2.1 kcal/mol with JANAF auxiliary data (3), which corresponds to $\Delta Hf^\circ_{298}(Pb_3O_4, c)$ = −172.59 ± 2.6 kcal/mol. Millar (6) has recalculated the data of Glasstone for the reaction $3PbO_2(c) + 2H_2(g) \rightarrow Pb_3O_4 + 2H_2O(\ell)$ as ΔGr°_{298} = −104.36 kcal which with auxiliary data (3, 7) yields $\Delta Gf^\circ_{298}(Pb_3O_4, c)$ = −145.45 ± 2.1 kcal/mol which corresponds to $\Delta Hf^\circ_{298}(Pb_3O_4, c)$ = −173.42 ± 2.6 kcal/mol.

Heat Capacity and Entropy

The low temperature heat capacity from 71.5 K to 292.6 K has been reported by Millar (6). These values were used to calculate S_{298} based on $S_{70.8}$ = 12.67 gibbs/mol (7). Enthalpies in the range 365 to 781 K have been reported by Bousquet et al. (8). These data encompass the range where the dissociation pressure is significant (76mm) and we have not used the data above 600 K. The mean heat capacities were plotted at the mean temperatures for the five points used and a smooth curve was drawn graphically through them and the low temperature data set. The four highest points of Millar (6) were not used since at least two were reported as bad points and they did not fit onto the smooth curve.

Decomposition

The decomposition pressure reaches 1 atm. at 869.7 according to Reinders and Hamburger (4) and at 867.2 K according to Otto (5). This table indicates a temperature of 680 K for the decomposition pressure to reach 1 atm. The significant difference is due to the fact that heat and entropy derived from the dissociation cannot be simultaneously satisfied by any realistic variation of the entropy and heat capacity of Pb_3O_4.

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Sulfur, Monatomic (S)

(Ideal Gas) GFW = 32.064

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	1.591	65.750	65.750	INFINITE
100	5.104	34.126	45.045	1.092	66.085	62.969	137.619
200	5.590	37.830	40.603	.555	66.229	59.788	65.333
298	5.658	40.085	40.085	.000	66.288	56.612	41.498
300	5.657	40.120	40.085	.010	66.288	56.552	41.198
400	5.553	41.735	40.306	.571	65.750	53.326	29.136
500	5.435	42.961	40.720	1.121	65.362	50.265	21.971
600	5.339	43.943	41.178	1.659	65.043	47.277	17.221
700	5.266	44.760	41.633	2.189	64.773	44.362	13.850
800	5.210	45.460	42.068	2.713	51.472	40.195	10.981
900	5.168	46.071	42.480	3.232	51.553	38.780	9.417
1000	5.136	46.613	42.867	3.747	51.627	37.357	8.164
1100	5.111	47.102	43.230	4.259	51.696	35.926	7.138
1200	5.092	47.546	43.571	4.769	51.762	34.490	6.281
1300	5.079	47.953	43.893	5.278	51.826	33.049	5.556
1400	5.069	48.329	44.196	5.785	51.886	31.602	4.933
1500	5.063	48.678	44.484	6.292	51.945	30.150	4.393
1600	5.062	49.005	44.756	6.798	52.003	28.696	3.920
1700	5.063	49.312	45.015	7.304	52.060	27.237	3.502
1800	5.068	49.601	45.262	7.811	52.117	25.775	3.130
1900	5.075	49.875	45.498	8.318	52.174	24.311	2.796
2000	5.085	50.136	45.723	8.826	52.231	22.843	2.496
2100	5.097	50.384	45.939	9.335	52.288	21.371	2.224
2200	5.111	50.622	46.147	9.845	52.346	19.899	1.977
2300	5.127	50.849	46.346	10.357	52.405	18.422	1.750
2400	5.144	51.068	46.538	10.871	52.466	16.943	1.543
2500	5.162	51.278	46.724	11.386	52.528	15.462	1.352
2600	5.181	51.481	46.903	11.903	52.591	13.978	1.175
2700	5.200	51.677	47.076	12.422	52.656	12.491	1.011
2800	5.219	51.866	47.244	12.943	52.722	11.001	.859
2900	5.239	52.050	47.406	13.466	52.790	9.511	.717
3000	5.258	52.228	47.564	13.991	52.859	8.018	.584
3100	5.277	52.401	47.717	14.518	52.931	6.522	.460
3200	5.295	52.568	47.866	15.046	53.002	5.023	.343
3300	5.313	52.732	48.011	15.577	53.077	3.522	.233
3400	5.330	52.891	48.153	16.109	53.152	2.021	.130
3500	5.347	53.045	48.290	16.643	53.228	.513	.032
3600	5.363	53.196	48.424	17.178	53.306	−.993	.060
3700	5.378	53.343	48.555	17.715	53.384	−2.501	.148
3800	5.392	53.487	48.683	18.254	53.465	−4.013	.231
3900	5.406	53.627	48.808	18.794	53.546	−5.528	.310
4000	5.418	53.764	48.930	19.335	53.628	−7.041	.385
4100	5.430	53.898	49.050	19.877	53.711	−8.560	.456
4200	5.441	54.029	49.167	20.421	53.795	−10.079	.524
4300	5.451	54.157	49.281	20.965	53.879	−11.602	.590
4400	5.461	54.283	49.394	21.511	53.964	−13.125	.652
4500	5.469	54.405	49.504	22.058	54.050	−14.649	.711
4600	5.477	54.526	49.612	22.605	54.136	−16.178	.769
4700	5.484	54.644	49.717	23.153	54.223	−17.709	.823
4800	5.491	54.759	49.821	23.702	54.310	−19.241	.876
4900	5.497	54.872	49.923	24.251	54.397	−20.771	.926
5000	5.502	54.984	50.023	24.801	54.484	−22.308	.975
5100	5.507	55.093	50.122	25.351	54.571	−23.844	1.022
5200	5.511	55.200	50.218	25.902	54.659	−25.382	1.067
5300	5.515	55.305	50.313	26.454	54.748	−26.923	1.110
5400	5.518	55.408	50.407	27.005	54.835	−28.463	1.152
5500	5.520	55.509	50.498	27.557	54.923	−30.007	1.192
5600	5.523	55.608	50.589	28.109	55.010	−31.551	1.231
5700	5.525	55.706	50.678	28.662	55.098	−33.099	1.269
5800	5.526	55.802	50.765	29.214	55.185	−34.646	1.306
5900	5.527	55.897	50.851	29.767	55.273	−36.199	1.341
6000	5.528	55.990	50.936	30.320	55.360	−37.746	1.375

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965; June 30, 1971

SULFUR, MONATOMIC (S) (IDEAL GAS) GFW = 32.064 S

Ground State Configuration $^3P_2$ ΔHf°_0 = 65.75 ± 0.01 kcal/mol

$S^\circ_{298.15}$ = 40.09 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 66.29 ± 0.01 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.0	5	67878.03	9	73921.14	7
396.09	3	67890.45	7	74269.2	5
573.65	1	67888.25	5	74270.28	3
9238.58	5	67885.97	3	74272.32	1
22179.99	1	67884.67	1	75342.02	40
52623.88	5	69238.7	5	76706.70	73
55331.15	3	70165.9	3	77986.31	39
63446.36	3	70166.8	5	78338.35	54
63457.33	5	70170.7	7	79014.3	83
63475.26	7	[70706.0]	5	79782.1	52
64891.71	1	71352.5	3	80158.61	24
64889.23	3	72025.5	5	80634.0	89
64892.89	5	72382.5	3	81089.9	29
67816.87	3	72572.4	1	81405.23	84
67825.72	5	73911.53	3	81864.6	101
67843.38	7	73915.16	5	82353.3	25

Heat of Formation

The adopted value, $\Delta Hf^\circ_0(S, g)$ = 65.75 kcal/mol is calculated from $\Delta Hf^\circ_0(S_2, g)$ = 30.80 kcal/mol (1) and $D^\circ_0(S_2)$ = 100.69 ± 0.01 kcal/mol. The dissociation energy of $S_2(g)$ has been studied by many investigators, using a variety of techniques. Since the earlier measurements have been reviewed by Herzberg (2), Gaydon (3), Brewer (4) and Drowart and Goldfinger (5), only those of recent determinations are listed below.

Investigation	Date	Method	$D^\circ_0(S_2)$ kcal/mol
Ricks and Barrow (6)	1969	Spectroscopic	100.69 ± 0.01
Berkowitz and Chupka (7)	1969	Photoionization	101.0 ± 0.2
Dibeler and Liston (8)	1968	Photoionization	≤101.0 ± 0.8
			99.2 ± 1.2
Budininkas et al. (9)	1967	Knudsen-torsion Effusion	101.7 ± 2.9
Drowart and Goldfinger (5)	1967	Thermochemical Cycles of FeS, SnS and PbS	101.0 ± 2.5
Colin et al. (10)	1964	Mass-spectrometric	97 ± 5

Historically, there were three conflicting values for $D^\circ_0(S_2)$, i.e. 101.5, 83.0 and 76.1 kcal/mol, which were due to the ambiguity of defining the excitation state of the atomic products resulting from predissociation in the spectroscopic measurements. However the recent determinations using different techniques as shown in the table are in good agreement, and all indicate that the high value is the most probable one. The selected value, $D^\circ_0(S_2)$ = 100.69 ± 0.01 kcal/mol, is obtained from the most recent and precise spectroscopic measurements (6) and is further supported by those determined by thermochemical cycles (5), photoionization (7, 8) and mass spectrometry (9).

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights are obtained from Moore (11), except the four lowest excited levels (396.09 - 22179.99 cm^{-1}) which were redetermined by Kaufman and Radziemski (12). These values are in good agreement with McConkey et al. (13), Toresson (14) and Moore (11).

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S

Silicon Monosulfide (SiS)

(Ideal Gas) GFW = 60.152

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	= 2.137	25.010	25.010	INFINITE
100	6.962	45.594	60.007	= 1.441	25.478	21.306	= 46.565
200	7.282	50.479	54.154	= .735	25.510	17.096	= 18.682
298	7.728	53.462	53.462	.000	25.325	13.001	= 9.530
300	7.736	53.510	53.462	.014	25.320	12.925	= 9.416
400	8.115	55.791	53.771	.808	24.508	8.854	= 4.838
500	8.364	57.631	54.365	1.633	23.851	5.018	= 2.193
600	8.528	59.171	55.041	2.478	23.271	1.307	= .476
700	8.639	60.495	55.728	3.337	22.745	= 2.288	.714
800	8.718	61.654	56.398	4.205	9.188	= 7.098	1.939
900	8.777	62.684	57.040	5.080	9.013	= 9.122	2.215
1000	8.821	63.611	57.651	5.960	8.828	= 11.127	2.432
1100	8.856	64.454	58.232	6.844	8.634	= 13.115	2.606
1200	8.884	65.225	58.783	7.731	8.432	= 15.083	2.747
1300	8.908	65.938	59.306	8.620	8.221	= 17.033	2.864
1400	8.928	66.598	59.804	9.512	8.001	= 18.968	2.961
1500	8.945	67.215	60.278	10.406	7.772	= 20.887	3.043
1600	8.960	67.793	60.730	11.301	7.534	= 22.789	3.113
1700	8.974	68.336	61.161	12.198	= 4.706	= 24.571	3.159
1800	8.986	68.850	61.574	13.096	= 4.908	= 25.734	3.124
1900	8.998	69.336	61.970	13.995	= 5.109	= 26.885	3.092
2000	9.008	69.798	62.350	14.895	= 5.310	= 28.025	3.062
2100	9.018	70.238	62.715	15.797	= 5.510	= 29.157	3.034
2200	9.028	70.657	63.067	16.699	= 5.710	= 30.278	3.008
2300	9.037	71.059	63.406	17.602	= 5.910	= 31.391	2.983
2400	9.046	71.444	63.732	18.506	= 6.109	= 32.493	2.959
2500	9.055	71.813	64.048	19.411	= 6.307	= 33.589	2.936
2600	9.063	72.168	64.354	20.317	= 6.505	= 34.676	2.915
2700	9.072	72.511	64.650	21.224	= 6.702	= 35.758	2.894
2800	9.082	72.841	64.936	22.132	= 6.899	= 36.830	2.875
2900	9.092	73.159	65.214	23.041	= 7.095	= 37.895	2.856
3000	9.102	73.468	65.484	23.950	= 7.292	= 38.953	2.838
3100	9.114	73.767	65.747	24.861	= 7.486	= 40.007	2.820
3200	9.126	74.056	66.002	25.773	= 7.681	= 41.051	2.804
3300	9.140	74.337	66.250	26.686	= 7.874	= 42.092	2.788
3400	9.156	74.610	66.492	27.601	= 8.066	= 43.124	2.772
3500	9.173	74.876	66.728	28.517	= 8.258	= 44.156	2.757
3600	* 9.192	75.135	66.958	29.436	= 100.407	= 42.921	2.606
3700	9.213	75.387	67.182	30.356	= 100.497	= 41.321	2.441
3800	9.237	75.633	67.401	31.278	= 100.584	= 39.721	2.284
3900	9.263	75.873	67.616	32.203	= 100.670	= 38.121	2.136
4000	9.292	76.108	67.825	33.131	= 100.753	= 36.512	1.995
4100	9.324	76.338	68.030	34.062	= 100.834	= 34.909	1.861
4200	9.359	76.563	68.230	34.996	= 100.912	= 33.299	1.733
4300	9.397	76.783	68.427	35.934	= 100.986	= 31.689	1.611
4400	9.439	77.000	68.619	36.876	= 101.058	= 30.077	1.494
4500	9.484	77.213	68.808	37.822	= 101.125	= 28.457	1.382
4600	9.532	77.422	68.993	38.773	= 101.187	= 26.844	1.275
4700	9.584	77.627	69.174	39.729	= 101.245	= 25.220	1.173
4800	9.640	77.829	69.352	40.690	= 101.298	= 23.612	1.075
4900	9.699	78.029	69.527	41.657	= 101.345	= 21.989	.981
5000	9.762	78.225	69.699	42.630	= 101.387	= 20.374	.891
5100	9.828	78.419	69.869	43.609	= 101.423	= 18.748	.803
5200	9.898	78.611	70.035	44.595	= 101.452	= 17.128	.720
5300	9.972	78.800	70.198	45.589	= 101.472	= 15.507	.639
5400	10.049	78.987	70.359	46.590	= 101.487	= 13.884	.562
5500	10.129	79.172	70.518	47.599	= 101.494	= 12.264	.487
5600	10.213	79.356	70.674	48.616	= 101.494	= 10.637	.415
5700	10.299	79.537	70.828	49.641	= 101.486	= 9.015	.346
5800	10.389	79.717	70.980	50.676	= 101.469	= 7.393	.279
5900	10.481	79.895	71.129	51.719	= 101.444	= 5.777	.214
6000	10.576	80.072	71.277	52.772	= 101.410	= 4.152	.151

Dec. 31, 1960; Dec. 31, 1971

SILICON SULFIDE (SiS) (IDEAL GAS) GFW = 60.152 SSi

Ground State Configuration $^1\Sigma^+$

ΔHf°_0 = 25.01 ± 3.00 kcal/mol

$S^\circ_{298.15}$ = 53.46 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 25.32 ± 3.00 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
[$a^3\Pi$]	[24700]	6
$D^1\Pi$	35029	2
[$e^3\Sigma^-$]	[35140]	3
F	37114	2
$I^1\Sigma^-$	[37290]	1
$E^1\Sigma^+$	41924	1

ω_e = 740.34 cm^{-1} $\omega_e x_e$ = 2.544 cm^{-1} σ = 1

B_e = 0.29930 cm^{-1} α = 0.00145 cm^{-1} r_e = 1.92932 Å

Heat of Formation

Herzberg (2) suggests a dissociation energy for SiS(g) of 6.6 eV. This result was derived from a spectroscopic analysis of the D-X and E-X band systems by Barrow and Jevons (4), Vago and Barrow (5), and Barrow (6). Robinson and Barrow (8) extended the work of Vago and Barrow (5) and arrived at a value of 147.4 ± 3.0 kcal/mol (6.39 eV). In this latter work a graphical Birge-Sponer extrapolation was made using 28 vibrational levels of the E state. The highest level is quite near the convergence limit and thus only a short extrapolation is necessary. The extrapolation graphically indicates the absolute minimum and maximum to be 6.28 eV and 6.57 eV, respectively. This amounts to a range of maximum uncertainty of approximately 7 kcal. The products of the dissociation must be Si(^{3}p) and S(^{3}p) but it is not certain as to which of the sublevels of the ^{3}p states are involved. This leads to an uncertainty of ± 1.2 kcal/mol (8). The result is in agreement with a rotational analysis of the $D^1\Pi$-$X^1\Sigma^+$ system by Lagerqvist, Nilheden, and Barrow (7) which led to a value of 6.47 eV (149.2 kcal/mol).

The value of the dissociation energy chosen is 147.4 ± 3.0 kcal/mol, based on the work by Robinson and Barrow (8). Gaydon (1) and Vedeneyev et al. (3) suggest a similar value, based on the work by Robinson and Barrow (8) and others. This value is also consistent with the tabulated dissociation energies of Gaydon (1) as far as trends which might be expected in the oxides, sulfides, and selenides of C, Si, Ge, Sn, and Pb. The resulting heat of formation is ΔHf°_0 = 25.01 ± 3.00 kcal/mol.

Rosenqvist and Tungesvik (13) studied two reaction systems by a transportation method. By combining these two systems, the standard free energy of the reaction 2Si(s) + S_2(g) = 2SiS(g) was calculated. Using JANAF values (14) for Si(s) and S_2(g), ΔGf° values for SiS(g) at 0°K and 300°K are 27.652 kcal/mol and 15.933 kcal/mol, respectively. These values are within the error range of the values in this tabulation.

Heat Capacity and Entropy

The spectroscopic constants, corrected for the natural abundances of Si and S, are from Hoeft (9), and Lagerqvist, Nilheden, and Barrow (7).

Herzberg (2) tabulates the $X^1\Sigma^+$, $D^1\Pi$, and E states and comments on unresolved bands at 16000-29000 cm^{-1}. The $a^3\Pi$ state is predicted by an interpolation of similar $a^3\Pi$-$X^1\Sigma^+$ splittings in the sulfides and oxides of C, Ge, Sn, (10, 11). The remaining states are deduced by a rotational analysis of the E-X system of SiS (7, 12). It is not known conclusively whether the F state is $^1\Pi$ or $^1\Delta$. The energy of the e and I states are upper bound estimates.

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SSi

Silicon Disulfide (SiS_2)

(Crystal) GFW = 92.214

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.520	19.200	19.200	.000	- 51.000	- 50.833	37.262
300	18.525	19.315	19.200	.034	- 50.995	- 50.832	37.031
400	18.790	24.680	19.930	1.900	- 51.834	- 50.774	27.741
500	19.070	28.899	21.317	3.791	- 52.363	- 50.446	22.050
600	19.530	32.423	22.882	5.725	- 52.711	- 50.027	18.222
700	19.600	35.436	24.465	7.679	- 52.942	- 49.512	15.458
800	19.870	38.071	26.005	9.653	- 79.218	- 51.548	14.082
900	20.140	40.427	27.479	11.653	- 78.706	- 48.118	11.685
1000	20.410	42.563	28.882	13.681	- 78.184	- 44.747	9.779
1100	20.682	44.521	30.216	15.736	- 77.650	- 41.432	8.232
1200	20.952	46.332	31.484	17.817	- 77.102	- 38.162	6.950
1300	21.222	48.020	32.692	19.926	- 76.538	- 34.938	5.874
1400	21.492	49.602	33.844	22.062	- 75.961	- 31.760	4.958
1500	21.760	51.094	34.945	24.224	- 75.370	- 28.626	4.171
1600	22.025	52.507	35.999	26.414	- 74.761	- 25.526	3.487
1700	22.292	53.850	37.010	28.629	- 86.132	- 22.364	2.875
1800	22.560	55.132	37.981	30.872	- 85.439	- 18.632	2.262
1900	22.829	56.359	38.916	33.141	- 84.720	- 14.938	1.718
2000	23.100	57.537	39.818	35.438	- 83.975	- 11.285	1.233

Dec. 31, 1960; June 30, 1972

SILICON DISULFIDE (SiS_2) (CRYSTAL) GFW = 92.214 S_2Si

$S°_{298.15}$ = [19.2 ± 1.0] gibbs/mol

Tm = 1363 K

$\Delta Hf°_0$ = unknown

$\Delta Hf°_{298.15}$ = -51.0 ± 5.0 kcal/mol

$\Delta Hm°$ = [2.0 ± 1.0] kcal/mol

Heat of Formation

Rocquet and Ancey-Maret (1) determined the heat of reaction for the following:

$SiS_2(c) + 6HF(20\%) \rightarrow H_2SiF_6(<20\%HF) + 2H_2S(g)$, ΔHr_{298} = -72.8 ± 2.2 kcal/mol.

A related system was examined by Kilday and Prosen (2):

$SiO_2(\alpha\text{-quartz}) + 6HF(20.0\%) \rightarrow H_2SiF_6(<20.0\%HF) + 2H_2O(\ell)$, ΔHr_{298} = -32.65 ± 0.02 kcal/mol.

Combining these two systems mathematically yields approximately the following:

$SiO_2(\alpha\text{-quartz}) + 2H_2S(g) \rightarrow SiS_2(c) + 2H_2O(\ell)$, ΔHr_{298} = 40.2 ± 3.0 kcal/mol.

Using JANAF (4) and NBS (5) auxiliary data, $\Delta Hf°_{298}(SiS_2, c)$ is equal to -51.1 ± 3.0 kcal/mol. In addition to the normal experimental error in each study, another source of error arises from the saturated solution of H_2S in the former work but not the latter.

Emmons and Theisen (3) measured the equilibrium vapor pressures for the system 1/2 $SiS_2(c)$ + 1/2 Si(c) + SiS(g) and presented graphically log p_{SiS} vs 1/T data. Using these data, a Third Law analysis yields ΔHr_{298} = 55.27 kcal/mol with a drift of 5.1 ± 1.2 gibbs/mol. A Second Law analysis yields ΔHr_{298} = 50.09 kcal/mol. These results lead, respectively, to $\Delta Hf_{298}(SiS_2, c)$ = -59.84 kcal/mol and $\Delta Hf°_{298}(SiS_2, c)$ = -49.53 kcal/mol, with JANAF (4) auxiliary data.

Fruehan and Turkdogan (5) studied the same reaction by means of a silica Knudsen cell-mass spectrometer combination. A Second Law analysis of their graphical data for two different orifice sizes yields values of ΔHr_{298} = 53.74 kcal/mol and 46.49 kcal/mol. Again, using JANAF auxiliary data (4), $\Delta Hf°_{298}(SiS_2, c)$ = -56.83 kcal/mol and -42.33 kcal/mol respectively, or an average value of -49.58 kcal/mol.

The value chosen for the heat of formation is $\Delta Hf°_{298}(SiS_2, c)$ = -51.0 ± 5.0 kcal/mol. This value is a rounded value of the work of Rocquet and Ancey-Maret (1). Berezknoi (7) references five reported values for the heat of formation (through 1954) and recommends the work of Rocquet and Ancey-Maret (1) as the most accurate. Kubaschewski, Evans, and Alcock (8) in their compilation of heats of formation (through 1965) also rely on the data from Rocquet and Ancey-Maret (1).

Heat Capacity and Entropy

The heat capacity is assumed to be given by the relation Cp = 17.72 + 2.96 x 10^{-3}T for 298 ≤ T ≤ 1363 K. This relation was suggested by Rasch (9) following procedures described by Kubaschewski et al (8). This equation was linearly extrapolated to yield values of Cp up to 2000 K. Kubaschewski, et al (8) suggest $S°_{298.15}$ = 19.2 gibbs/mol.

Melting Data

The melting point of $SiS_2(c)$ was determined to be Tm = 1363 K by Tiede and Thimann (10). ΔHm was estimated, based on the entropy of melting for SiO_2 (quartz and cristobolite).

References

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Silicon Disulfide (SiS_2)

(Liquid) GFW = 92.214

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.520	20.241	20.241	- .000	- 49.456	- 49.599	36.357
300	18.525	20.355	20.241	.034	- 49.451	- 49.600	36.134
400	18.790	25.721	20.971	1.900	- 50.290	- 49.646	27.125
500	19.070	29.940	22.357	3.791	- 50.819	- 49.422	21.602
600	19.530	33.464	23.922	5.725	- 51.167	- 49.107	17.887
700	19.600	36.477	25.506	7.679	- 51.398	- 48.697	15.204
800	19.870	39.112	27.045	9.653	- 77.674	- 50.836	13.888
900	21.750	41.468	28.519	11.653	- 77.162	- 47.511	11.537
1000	21.750	43.759	29.931	13.828	- 76.493	- 44.252	9.671
1100	21.750	45.832	31.284	16.003	- 75.839	- 41.062	8.158
1200	21.750	47.725	32.576	18.178	- 75.197	- 37.928	6.908
1300	21.750	49.466	33.809	20.353	- 74.567	- 34.846	5.858
1400	21.750	51.077	34.986	22.528	- 73.951	- 31.814	4.966
1500	21.750	52.578	36.109	24.703	- 73.347	- 28.828	4.200
1600	21.750	53.982	37.183	26.878	- 72.753	- 25.877	3.535
1700	21.750	55.300	38.210	29.053	- 84.164	- 22.861	2.939
1800	21.750	56.544	39.194	31.228	- 83.539	- 19.272	2.340
1900	21.750	57.720	40.139	33.403	- 82.914	- 15.717	1.808
2000	21.750	58.835	41.046	35.578	- 82.291	- 12.197	1.333

Dec. 31, 1960; June 30, 1972

SILICON DISULFIDE (SiS_2) (LIQUID) GFW = 92.214 S_2Si

$S°_{298.15}$ = [20.241] gibbs/mol $\Delta Hf°_{298.15}$ = [-49.456] kcal/mol

Tm = 1363 K $\Delta Hm°$ = [2.0 ± 1.0] kcal/mol

Heat of Formation

The $\Delta Hf°_{298}(\ell)$ is calculated from $\Delta Hf°_{298}(c)$ by adding $\Delta Hm°$ and the difference between $H°_{1363.} - H°_{298}$ for $SiS_2(c)$ and $SiS_2(\ell)$.

Heat Capacity and Entropy

Using methods suggested by Kubaschewski, Evans, and Alcock (1), the heat capacity of the liquid is assumed to be a constant 21.75 gibbs/mol from 1363 K to 1403 K. The entropy, $S°_{298}$, was calculated in a manner similar to the heat of formation. A hypothetical glass transition is assumed at 900 K.

Melting Data

Refer to $SiS_2(c)$ table.

References

1. O. Kubaschewski, E. L. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, 1967.

Silicon U ive Ion (Si^+)

(Ideal Gas) GFW = 28.0855

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.817	39.033	39.033	.000	297.100	285.316	- 209.142
300	5.809	39.069	39.033	.011	297.111	285.283	- 207.799
400	5.483	40.691	39.256	.574	297.664	281.201	- 153.641
500	5.306	41.093	39.664	1.112	298.155	277.029	- 121.089
600	5.204	42.851	40.122	1.637	298.609	272.760	- 99.353
700	5.141	43.648	40.570	2.154	299.037	268.417	- 83.803
800	5.100	44.332	40.999	2.666	299.446	264.014	- 72.125
900	5.071	44.931	41.401	3.175	299.840	259.562	- 63.030
1000	5.051	45.464	41.783	3.681	300.219	255.066	- 55.745
1100	5.036	45.944	42.140	4.185	300.585	250.533	- 49.776
1200	5.025	46.382	42.475	4.688	300.939	245.967	- 44.797
1300	5.016	46.784	42.791	5.190	301.283	241.371	- 40.578
1400	5.010	47.156	43.090	5.692	301.617	236.751	- 36.958
1500	5.004	47.501	43.373	6.192	301.939	232.107	- 33.818
1600	5.000	47.824	43.641	6.692	302.250	227.440	- 31.067
1700	4.996	48.127	43.896	7.192	290.559	222.861	- 28.651
1800	4.993	48.412	44.139	7.692	290.906	218.870	- 26.574
1900	4.990	48.682	44.371	8.191	291.252	214.858	- 24.714
2000	4.988	48.938	44.593	8.690	291.598	210.830	- 23.038
2100	4.986	49.181	44.806	9.188	291.942	206.782	- 21.520
2200	4.984	49.413	45.010	9.687	292.288	202.718	- 20.138
2300	4.983	49.635	45.206	10.185	292.633	198.639	- 18.875
2400	4.982	49.847	45.395	10.683	292.978	194.546	- 17.716
2500	4.981	50.050	45.577	11.182	293.324	190.437	- 16.648
2600	4.980	50.245	45.753	11.680	293.668	186.314	- 15.661
2700	4.979	50.433	45.923	12.177	294.012	182.178	- 14.746
2800	4.978	50.614	46.087	12.675	294.357	178.031	- 13.896
2900	4.977	50.789	46.247	13.173	294.702	173.871	- 13.103
3000	4.977	50.958	46.401	13.671	295.047	169.697	- 12.362
3100	4.976	51.121	46.550	14.168	295.390	165.512	- 11.669
3200	4.976	51.279	46.696	14.666	295.735	161.319	- 11.018
3300	4.975	51.432	46.837	15.163	296.079	157.114	- 10.405
3400	4.975	51.581	46.974	15.661	296.424	152.897	- 9.828
3500	4.974	51.725	47.106	16.158	296.768	148.670	- 9.283
3600	4.974	51.865	47.238	16.656	205.151	146.691	- 8.905
3700	4.974	52.001	47.365	17.153	205.594	145.061	- 8.568
3800	4.973	52.134	47.489	17.651	206.038	143.419	- 8.248
3900	4.973	52.263	47.610	18.148	206.480	141.764	- 7.944
4000	4.973	52.389	47.728	18.645	206.921	140.099	- 7.655
4100	4.973	52.512	47.843	19.143	207.363	138.422	- 7.379
4200	4.973	52.632	47.955	19.640	207.805	136.735	- 7.115
4300	4.973	52.749	48.065	20.137	208.247	135.038	- 6.863
4400	4.973	52.863	48.173	20.634	208.688	133.330	- 6.623
4500	4.973	52.975	48.279	21.132	209.130	131.616	- 6.392
4600	4.973	53.084	48.382	21.629	209.572	129.887	- 6.171
4700	4.973	53.191	48.483	22.126	210.013	128.151	- 5.959
4800	4.973	53.296	48.582	22.623	210.455	126.404	- 5.755
4900	4.973	53.398	48.680	23.121	210.898	124.649	- 5.560
5000	4.974	53.499	48.775	23.618	211.339	122.881	- 5.371
5100	4.974	53.597	48.868	24.115	211.781	121.111	- 5.190
5200	4.975	53.694	48.960	24.613	212.224	119.328	- 5.015
5300	4.976	53.788	49.051	25.110	212.667	117.538	- 4.847
5400	4.977	53.881	49.139	25.608	213.110	115.738	- 4.684
5500	4.978	53.973	49.226	26.106	213.552	113.929	- 4.527
5600	4.979	54.062	49.312	26.604	213.995	112.117	- 4.376
5700	4.980	54.151	49.396	27.102	214.438	110.295	- 4.229
5800	4.982	54.237	49.479	27.600	214.880	108.463	- 4.087
5900	4.984	54.322	49.560	28.098	215.322	106.622	- 3.950
6000	4.986	54.406	49.640	28.596	215.763	104.775	- 3.816

Dec. 31, 1971

SILICON UNIPOSITIVE ION (Si^+) (IDEAL GAS) GFW = 28.0855 Si^+

Ground State Configuration $^2P_{1/2}$ ΔHf°_0 = 294.63 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 39.033 ± 0.001 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 297.1 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	55309.61	4	79355.28	5
287.32	4	55325.44	6	81191.60	2
42824.35	2	65500.73	2	81251.58	4
42932.68	4	76665.61	2	83802.21	2
43107.97	6	79338.76	4	84004.52	4

Heat of Formation

The ionization potential of Si(g) has been reported by Moore (1) to be 8.151 eV (187.962 ± 0.002 kcal). This value in conjunction with the equation $Si(g)-e^- \rightarrow Si^+(g)$ and the value $\Delta Hf^\circ_0(Si, g)$ = 106.664 ± 1 kcal/mol (2) yields $\Delta Hf^\circ_0(Si^+, g)$ = 294.626 ± 1 kcal/mol.

Heat Capacity and Entropy

The electronic levels have been tabulated by Moore (3). Levels above 90000 cm^{-1} are not used here since they do not contribute to the thermodynamic functions.

References

1. C. E. Moore, NSRDS-NBS-34, Washington, 1970.
2. JANAF Thermochemical Tables. Si(g) 3-31-67.
3. C. E. Moore, NSRDS-NBS-3, Section 1, Washington, 1970.

0	to	828°K	Crystal alpha
828	to	1041°K	Crystal gamma
1041	to	1654.13°K	Liquid
1654.13	to	6000°K	Ideal Monatomic Gas

Strontium (Sr)

(Reference State) GFW = 87.62

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	- 1.520	.000	.000	.000
100	5.300	6.000	18.000	- 1.200	.000	.000	.000
200	6.100	10.000	13.050	- .610	.000	.000	.000
298	6.393	12.500	12.500	.000	.000	.000	.000
300	6.400	12.540	12.500	.012	.000	.000	.000
400	6.790	14.434	12.756	.671	.000	.000	.000
500	7.200	15.992	13.251	1.370	.000	.000	.000
600	7.650	17.343	13.823	2.112	.000	.000	.000
700	8.180	18.561	14.414	2.903	.000	.000	.000
800	8.800	19.692	15.004	3.751	.000	.000	.000
900	9.000	20.966	15.602	4.828	.000	.000	.000
1000	9.000	21.915	16.187	5.728	.000	.000	.000
1100	8.400	24.622	16.847	8.552	.000	.000	.000
1200	8.400	25.353	17.526	9.392	.000	.000	.000
1300	8.400	26.025	18.154	10.232	.000	.000	.000
1400	8.400	26.648	18.739	11.072	.000	.000	.000
1500	8.400	27.227	19.286	11.912	.000	.000	.000
1600	8.400	27.770	19.799	12.752	.000	.000	.000
1700	4.981	47.972	20.816	46.166	.000	.000	.000
1800	4.991	48.257	22.333	46.664	.000	.000	.000
1900	5.007	48.528	23.704	47.164	.000	.000	.000
2000	5.031	48.785	24.952	47.666	.000	.000	.000
2100	5.065	49.031	26.093	48.171	.000	.000	.000
2200	5.111	49.268	27.141	48.680	.000	.000	.000
2300	5.173	49.496	28.108	49.194	.000	.000	.000
2400	5.251	49.718	29.004	49.715	.000	.000	.000
2500	5.349	49.934	29.836	50.245	.000	.000	.000
2600	5.466	50.146	30.614	50.785	.000	.000	.000
2700	5.611	50.355	31.341	51.339	.000	.000	.000
2800	5.779	50.562	32.024	51.908	.000	.000	.000
2900	5.973	50.768	32.666	52.496	.000	.000	.000
3000	6.193	50.975	33.273	53.104	.000	.000	.000
3100	6.441	51.182	33.848	53.735	.000	.000	.000
3200	6.715	51.390	34.393	54.393	.000	.000	.000
3300	7.015	51.602	34.911	55.079	.000	.000	.000
3400	7.339	51.816	35.405	55.797	.000	.000	.000
3500	7.687	52.033	35.877	56.548	.000	.000	.000
3600	8.055	52.255	36.329	57.335	.000	.000	.000
3700	8.441	52.481	36.762	58.159	.000	.000	.000
3800	8.843	52.711	37.179	59.023	.000	.000	.000
3900	9.258	52.946	37.580	59.928	.000	.000	.000
4000	9.678	53.186	37.967	60.875	.000	.000	.000
4100	10.106	53.430	38.341	61.864	.000	.000	.000
4200	10.535	53.679	38.704	62.896	.000	.000	.000
4300	10.962	53.932	39.055	63.971	.000	.000	.000
4400	11.383	54.189	39.396	65.088	.000	.000	.000
4500	11.796	54.449	39.728	66.247	.000	.000	.000
4600	12.196	54.713	40.050	67.447	.000	.000	.000
4700	12.582	54.979	40.365	68.686	.000	.000	.000
4800	12.952	55.248	40.672	69.963	.000	.000	.000
4900	13.302	55.519	40.973	71.276	.000	.000	.000
5000	13.631	55.791	41.266	72.622	.000	.000	.000
5100	13.937	56.064	41.554	74.001	.000	.000	.000
5200	14.221	56.337	41.835	75.409	.000	.000	.000
5300	14.480	56.611	42.112	76.844	.000	.000	.000
5400	14.716	56.884	42.383	78.304	.000	.000	.000
5500	14.927	57.156	42.649	79.787	.000	.000	.000
5600	15.114	57.426	42.910	81.289	.000	.000	.000
5700	15.278	57.695	43.167	82.809	.000	.000	.000
5800	15.420	57.962	43.420	84.344	.000	.000	.000
5900	15.539	58.227	43.669	85.892	.000	.000	.000
6000	15.638	58.489	43.914	87.451	.000	.000	.000

Dec. 31, 1970

Strontium, Alpha-Gamma (Sr)

(Crystal) GFW = 87.62

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	1.520	.000	.000	INFINITE
100	5.300	6.000	18.000	1.200	.000	.000	.000
200	6.100	10.000	13.050	.610	.000	.000	.000
298	6.393	12.500	12.500	.000	.000	.000	.000
300	6.400	12.540	12.500	.012	.000	.000	.000
400	6.790	14.434	12.756	.671	.000	.000	.000
500	7.200	15.992	13.251	1.370	.000	.000	.000
600	7.650	17.343	13.823	2.112	.000	.000	.000
700	8.180	18.561	14.414	2.903	.000	.000	.000
800	8.800	19.692	15.004	3.751	.000	.000	.000
900	9.000	20.966	15.602	4.828	.000	.000	.000
1000	9.000	21.915	16.187	5.728	.000	.000	.000
1100	9.000	22.772	16.747	6.628 − 1.924		.111	− .022
1200	9.000	23.556	17.282	7.528 − 1.864		.293	− .053
1300	9.000	24.276	17.793	8.428 − 1.804		.470	− .079
1400	9.000	24.943	18.280	9.328 − 1.744		.643	− .100
1500	9.000	25.564	18.745	10.228 − 1.684		.811	− .118

Dec. 31, 1970

$S^\circ_{298.15}$ = [12.5 ± 0.5] gibbs/mol

Tt = 828 ± 15°K (α→γ)

Tm = 1041 ± 3°K

ΔHf°_0 = 0 kcal/mol

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

ΔHt° = 0.18 ± 0.08 kcal/mol

ΔHm° = [1.96] kcal/mol

$\Delta Hs^\circ_{298.15}$ = 39.2 ± 0.4 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Roberts (1) measured Cp° in the range 1.5 to 20°K and Glascock (2) obtained values of 6.0 to 6.8 gibbs/mol (average 6.5) from seven measurements at room temperature. We estimate the heat capacity and enthalpy up to 298°K by comparing Roberts' lattice and electronic contributions for Ca, Sr and Ba with the observed data for Ca and Ba.

We adopt the estimated entropy of 12.5 ± 0.5 gibbs/mol from Kelley (3). Our estimated Cp° values would be more consistent with an entropy of about 12.6, but the uncertainties in this estimate are too large to warrant the change. Gurvich et al. (4) estimated 12.7 ± 0.3 gibbs/mol.

Cp° of the α-phase above 298°K is estimated by comparison with Mg (5), Ca (6, 7) and Ba (7). Cp° of the γ-phase is assumed to be 9.0 gibbs/mol based on the high-temperature forms of Ca and Ba.

Transition Data

King and coworkers (8-12) reported three allotropic forms -- α(fcc), β(hcp) and γ(bcc) -- with β-phase being stable from about 230 to 620°C. Peterson and Colburn (13) found α→β at about 240°C in a sample containing 3.27 mole % SrH_2, but they found no evidence of transition up to 285°C in a sample containing only 0.4 mole % SrH_2. The latter sample transformed, presumably to γ-Sr, at 557°C on heating and reverted at about 540°C on cooling. Peterson and Colburn concluded that the α-β transition is not well established and additional study on very pure Sr is needed.

We assume that β-Sr is stablized by impurities, by analogy with Ca, and adopt 555°C for α→γ in pure Sr (13). An approximate value of ΔHt° = 0.18 kcal/mol is calculated from ΔV = −0.09 cm^3/mol and dT/dP = −10°C/kbar based on dilatometry (14) and high pressure data (15, 15).

Melting Data

See Sr(ℓ) for details.

Sublimation Data

See Sr(g) for details.

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Strontium (Sr)

(Liquid) GFW = 87.62

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	8.400	13.656	13.656	.000	1.817	1.472	− 1.079
300	8.400	13.708	13.656	.016	1.820	1.470	− 1.071
400	8.400	16.125	13.986	.856	2.001	1.325	− .724
500	8.400	17.999	14.608	1.696	2.142	1.139	− .498
600	8.400	19.531	15.305	2.536	2.240	.928	− .338
700	8.400	20.826	16.003	3.376	2.289	.704	− .220
800	8.400	21.947	16.678	4.216	2.281	.478	− .130
900	8.400	22.937	17.319	5.056	2.044	.271	− .066
1000	8.400	23.822	17.926	5.896	1.984	.077	− .017
1100	8.400	24.622	18.499	6.736	.000	.000	.000
1200	8.400	25.353	19.040	7.576	.000	.000	.000
1300	8.400	26.025	19.552	8.416	.000	.000	.000
1400	8.400	26.648	20.037	9.256	.000	.000	.000
1500	8.400	27.227	20.497	10.096	.000	.000	.000
1600	8.400	27.770	20.935	10.936	.000	.000	.000
1700	8.400	28.279	21.352	11.776	− 32.574	.905	− .116
1800	8.400	28.759	21.750	12.616	− 32.232	2.865	− .348
1900	8.400	29.213	22.131	13.456	− 31.892	4.806	− .553
2000	8.400	29.644	22.496	14.296	− 31.554	6.728	− .735
2100	8.400	30.054	22.846	15.136	− 31.219	8.634	− .899
2200	8.400	30.445	23.183	15.976	− 30.888	10.523	− 1.045
2300	8.400	30.816	23.507	16.816	− 30.562	12.399	− 1.178
2400	8.400	31.176	23.819	17.656	− 30.243	14.259	− 1.298
2500	8.400	31.518	24.120	18.496	− 29.933	16.107	− 1.408
2600	8.400	31.848	24.411	19.336	− 29.633	17.943	− 1.508
2700	8.400	32.165	24.692	20.176	− 29.347	19.768	− 1.600
2800	8.400	32.470	24.965	21.016	− 29.076	21.582	− 1.685
2900	8.400	32.765	25.229	21.856	− 28.824	23.386	− 1.762
3000	8.400	33.050	25.485	22.696	− 28.592	25.183	− 1.835

Dec. 31, 1970

STRONTIUM (Sr) (LIQUID) GFW = 87.62 Sr

$S^\circ_{298.15}$ = [13.656] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [1.817] kcal/mol

Tm = 1041 ± 3°K

ΔHm° = [1.96 ± 0.3] kcal/mol

Tb = [1654.13]°K

ΔHv° = [32.730] kcal/mol

Heat of Formation

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

Heat Capacity and Entropy

Cp° of the liquid is assumed to be 8.4 gibbs/mol by comparison with Mg (1) and Ba (2). S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point was determined as 1041 (3, 4), 1042 ± 1 (5-7), 1043 (8) and 1047°K (9-11). We adopt 1041 ± 3°K based on Peterson and Colburn (3). Their study of the Sr-SrH_2 system emphasized that H impurity raises Tm, so that the highest observed melting point is not the most likely when H is a likely impurity. The adopted value is confirmed by the recent result of Dworkin et al. (5). ΔHm° is estimated by comparison with those of Mg (1), Ca (2) and Ba (2). Discrepancies in the data for Ba (2) suggest that the estimate for Sr may be too low by about 0.2 kcal/mol.

Vaporization Data

Tb is calculated as the temperature at which $\Delta Gr^\circ = 0$ for $Sr(\ell) \rightarrow Sr(g)$. ΔHv° is the difference between $\Delta Hf^\circ(g)$ and $\Delta Hf^\circ(\ell)$ at Tb. Bohdansky and Schins (12) reported Tb = 1649°K, which becomes 1651°K on the IPTS-68 scale.

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Strontium (Sr)

(Ideal Gas) GFW = 87.62

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	- 1.481	39.239	39.239	INFINITE
100	4.968	33.896	43.740	- .984	39.416	36.626	- 80.046
200	4.968	37.340	39.778	- .488	39.322	33.854	- 36.994
298	4.968	39.323	39.323	.000	39.200	31.203	- 22.872
300	4.968	39.354	39.323	.009	39.197	31.153	- 22.695
400	4.968	40.783	39.518	.506	39.035	28.495	- 15.569
500	4.968	41.892	39.886	1.003	38.833	25.883	- 11.313
600	4.968	42.797	40.298	1.500	38.588	23.315	- 8.493
700	4.968	43.563	40.711	1.996	38.293	20.792	- 6.492
800	4.968	44.227	41.110	2.493	37.942	18.315	- 5.003
900	4.968	44.812	41.490	2.990	37.362	15.901	- 3.861
1000	4.968	45.335	41.848	3.487	36.959	13.538	- 2.959
1100	4.968	45.809	42.187	3.984	34.632	11.326	- 2.250
1200	4.968	46.241	42.507	4.480	34.288	9.223	- 1.680
1300	4.968	46.639	42.810	4.977	33.945	7.148	- 1.202
1400	4.969	47.007	43.097	5.474	33.602	5.100	- .796
1500	4.971	47.350	43.369	5.971	33.259	3.076	- .446
1600	4.974	47.671	43.628	6.468	32.916	1.075	- .147
1700	4.981	47.972	43.875	6.966	.000	.000	.000
1800	4.991	48.257	44.110	7.464	.000	.000	.000
1900	5.007	48.528	44.336	7.964	.000	.000	.000
2000	5.031	48.785	44.552	8.466	.000	.000	.000
2100	5.065	49.031	44.759	8.971	.000	.000	.000
2200	5.111	49.268	44.959	9.480	.000	.000	.000
2300	5.173	49.496	45.151	9.994	.000	.000	.000
2400	5.251	49.718	45.337	10.515	.000	.000	.000
2500	5.349	49.934	45.518	11.045	.000	.000	.000
2600	5.468	50.146	45.690	11.585	.000	.000	.000
2700	5.611	50.355	45.859	12.139	.000	.000	.000
2800	5.779	50.562	46.024	12.708	.000	.000	.000
2900	5.973	50.768	46.184	13.296	.000	.000	.000
3000	6.193	50.975	46.340	13.904	.000	.000	.000
3100	6.441	51.182	46.493	14.535	.000	.000	.000
3200	6.715	51.390	46.643	15.193	.000	.000	.000
3300	7.015	51.602	46.790	15.879	.000	.000	.000
3400	7.339	51.816	46.934	16.597	.000	.000	.000
3500	7.687	52.033	47.077	17.348	.000	.000	.000
3600	8.055	52.255	47.218	18.135	.000	.000	.000
3700	8.441	52.481	47.357	18.959	.000	.000	.000
3800	8.843	52.711	47.495	19.823	.000	.000	.000
3900	9.256	52.946	47.631	20.728	.000	.000	.000
4000	9.676	53.186	47.767	21.675	.000	.000	.000
4100	10.106	53.430	47.902	22.664	.000	.000	.000
4200	10.535	53.679	48.037	23.696	.000	.000	.000
4300	10.962	53.932	48.171	24.771	.000	.000	.000
4400	11.383	54.189	48.305	25.888	.000	.000	.000
4500	11.796	54.449	48.439	27.047	.000	.000	.000
4600	12.196	54.713	48.572	28.247	.000	.000	.000
4700	12.582	54.979	48.706	29.486	.000	.000	.000
4800	12.952	55.248	48.839	30.763	.000	.000	.000
4900	13.302	55.519	48.973	32.076	.000	.000	.000
5000	13.631	55.791	49.106	33.422	.000	.000	.000
5100	13.937	56.064	49.240	34.801	.000	.000	.000
5200	14.221	56.337	49.374	36.209	.000	.000	.000
5300	14.480	56.611	49.508	37.644	.000	.000	.000
5400	14.716	56.884	49.642	39.104	.000	.000	.000
5500	14.927	57.156	49.776	40.587	.000	.000	.000
5600	15.114	57.426	49.910	42.089	.000	.000	.000
5700	15.278	57.695	50.044	43.609	.000	.000	.000
5800	15.420	57.962	50.179	45.144	.000	.000	.000
5900	15.539	58.227	50.313	46.692	.000	.000	.000
6000	15.638	58.489	50.447	48.251	.000	.000	.000

Dec. 31, 1970

STRONTIUM (Sr) (IDEAL GAS) GFW = 87.62 Sr

Ground State Configuration ^1S

ΔHf°_0 = 39.24 ± 0.4 kcal/mol

$S^\circ_{298.15}$ = 39.323 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 39.2 ± 0.4 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	21698	3	36994	6	41172	3	56170	3	[49000]	20
14317.5	1	29039	3	37346	12	41404	28	49569	21	[54000]	20
14504.3	3	30592	1	38008	7	51090	3	[54000]	48	[40000]	21
14898.6	5	33687	26	38444	1	55223	3	[53000]	93	[50000]	100
18159	3	33968	12	38753	21	49547	9	[56000]	93	[55000]	100
18219	5	34954	20	39308	12	54729	9	[50000]	12		
18319	7	35530	9	39662	27	49411	15	[25000]	20		
20150	5	36441	15	40834	4	53548	3	[41000]	20		

Heat of Formation

The heat of formation is the heat of sublimation, 39.2 ± 0.4 kcal/mol, selected from third-law analyses of pressure data tabulated below. The adopted value comes mainly from the recent boiling-point study of Bohdansky and Schins (1). It is confirmed by the early data of Hartmann and Schneider (2) and by the Knudsen-effusion-mass-spectrometric study of Boerboom et al. (4). Data of Ruff and Hartmann (3) are readily dismissed due to the large entropy discrepancy.

Source	Method	Range[a] T, °K	ΔHf°_{298}, kcal/mol 2nd Law	3rd Law	Entropy Test[b] δS, gibbs/mol
(1) Bohdansky (1967)	Boiling Point	1218-1982	40.1±0.4	39.16±0.46	0.6±0.3
(2) Hartmann (1929)	Boiling Point	1200-1380	40.0±0.6	39.46±0.14	0.4±0.4
(3) Ruff (1924)	Boiling Point	1218-1412	77 ±4	38.0 ±5	29 ±3
(4) Boerboom (1964)	Effusion-Mass Spec.	772-923	36.4	39.04±0.39	-3.1
(5) Priselkov (1954)	Effusion	673-873	35.7±0.5	38.65±0.57	-3.8±0.6

[a]Temperatures are adjusted to IPTS-68 by assuming published values to be IPTS-48.

[b]$\delta S = \Delta Sr^\circ_{298}$(2nd law) − ΔSr°(3rd law).

Heat Capacity and Entropy

Observed energy levels and quantum weights are from Moore (6) as modified by Garton et al. (7, 8). Energies of unobserved but predicted terms (6) are estimated by comparison of Ca I, Sr I, Ba I and their isoelectronic ions. The most important energies are for terms of the 4d5s' configuration which are estimated at 25000 ± 10000 cm^{-1}. We adopt an energy-level cutoff which is about kTmax (Tmax = 6000°K) below each series limit. For Sr I this corresponds to omitting levels above 8s, 7p, 6d and 5f. Levels above 30000 cm^{-1} are averaged. The adopted functions are essentially identical with earlier tables up to 3000°K; however, the entropies at 6000°K differ as follows: Hilsenrath et al. (9), 57.99; JANAF, 58.49; Gurvich et al. (10), 58.80 gibbs/mol. These differences arise from different methods of cutoff and different degrees of accounting for the unobserved terms.

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Zirconium Unipositive Ion (Zr^+)

(Ideal Gas) GFW = 91.21945

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	6.760	43.864	43.864	.000	307.604	295.816	= 216.838
300	6.761	43.906	43.864	.013	307.615	295.742	= 215.447
400	6.759	45.854	44.130	.690	308.166	291.702	= 159.378
500	6.669	47.353	44.630	1.361	308.683	287.525	= 125.676
600	6.576	48.561	45.188	2.023	309.164	283.247	= 103.172
700	6.517	49.569	45.748	2.678	309.609	278.891	= 87.073
800	6.498	50.438	46.278	3.328	310.023	274.475	= 74.983
900	6.508	51.204	46.783	3.978	310.408	270.008	= 65.567
1000	6.535	51.891	47.260	4.630	310.768	265.500	= 58.025
1100	6.568	52.515	47.710	5.285	311.103	260.957	= 51.847
1200	6.601	53.088	48.135	5.944	310.562	256.435	= 46.703
1300	6.630	53.617	48.536	6.605	311.026	251.906	= 42.349
1400	6.652	54.110	48.917	7.270	311.483	247.341	= 38.612
1500	6.666	54.569	49.279	7.936	311.930	242.745	= 35.368
1600	6.674	55.000	49.623	8.603	312.365	238.117	= 32.525
1700	6.676	55.404	49.951	9.270	312.791	233.464	= 30.014
1800	6.673	55.786	50.265	9.938	313.206	228.785	= 27.778
1900	6.665	56.146	50.565	10.605	313.609	224.084	= 25.775
2000	6.655	56.488	50.853	11.271	314.000	219.362	= 23.971
2100	6.642	56.812	51.129	11.935	314.377	214.620	= 22.336
2200	6.628	57.121	51.394	12.599	309.741	210.038	= 20.865
2300	6.614	57.415	51.650	13.261	310.100	205.499	= 19.527
2400	6.599	57.697	51.896	13.922	310.458	200.943	= 18.298
2500	6.585	57.966	52.133	14.581	310.814	196.373	= 17.167
2600	6.571	58.224	52.363	15.239	311.168	191.788	= 16.121
2700	6.558	58.471	52.584	15.895	311.521	187.190	= 15.152
2800	6.546	58.710	52.799	16.550	311.873	182.579	= 14.251
2900	6.536	58.939	53.007	17.204	312.224	177.955	= 13.411
3000	6.526	59.161	53.208	17.856	312.575	173.319	= 12.626
3100	6.517	59.374	53.404	18.510	312.923	168.671	= 11.891
3200	6.509	59.581	53.593	19.161	313.271	164.012	= 11.201
3300	6.502	59.781	53.778	19.811	313.618	159.343	= 10.553
3400	6.496	59.975	53.957	20.461	313.965	154.663	= 9.942
3500	6.490	60.164	54.132	21.111	314.312	149.972	= 9.365
3600	6.486	60.346	54.302	21.759	314.656	145.272	= 8.819
3700	6.482	60.524	54.468	22.408	315.002	140.561	= 8.303
3800	6.479	60.697	54.629	23.056	315.347	135.843	= 7.813
3900	6.476	60.865	54.787	23.704	315.692	131.115	= 7.347
4000	6.474	61.029	54.941	24.351	316.035	126.376	= 6.905
4100	6.472	61.189	55.092	24.998	316.379	121.631	= 6.484
4200	6.471	61.345	55.239	25.646	316.724	116.878	= 6.082
4300	6.471	61.497	55.382	26.293	317.068	112.115	= 5.698
4400	6.470	61.646	55.523	26.940	317.412	107.345	= 5.332
4500	6.471	61.791	55.661	27.587	317.755	102.566	= 4.981
4600	6.471	61.933	55.796	28.234	318.099	97.780	= 4.646
4700	6.472	62.073	55.928	28.881	318.443	92.988	= 4.324
4800	6.474	62.209	56.057	29.528	177.630	88.870	= 4.046
4900	6.476	62.342	56.184	30.176	177.871	87.019	= 3.881
5000	6.478	62.473	56.309	30.823	178.104	85.162	= 3.722
5100	6.481	62.602	56.431	31.471	178.334	83.300	= 3.570
5200	6.484	62.727	56.551	32.120	178.561	81.435	= 3.423
5300	6.488	62.851	56.668	32.768	178.783	79.565	= 3.281
5400	6.492	62.972	56.784	33.417	179.002	77.691	= 3.144
5500	6.496	63.091	56.898	34.066	179.216	75.812	= 3.012
5600	6.501	63.209	57.009	34.716	179.430	73.931	= 2.885
5700	6.506	63.324	57.119	35.367	178.641	72.045	= 2.762
5800	6.512	63.437	57.227	36.018	179.850	70.156	= 2.644
5900	6.518	63.548	57.333	36.669	180.057	68.263	= 2.529
6000	6.524	63.658	57.438	37.321	180.261	66.365	= 2.417

Dec. 31, 1967; Dec. 31, 1970

ZIRCONIUM UNIPOSITIVE ION (Zr^+) (IDEAL GAS) GFW = 91.21945 Zr^+

Ground State Configuration $^4F_{3/2}$ ΔHf°_0 = 305.7 ± 4 kcal/mol

$S^\circ_{298.15}$ = 43.864 ± 0.01 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 307.6 ± 4 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	4	7736.02	4	30405.28	54
314.67	6	8058.16	4	31981.00	40
763.44	8	9968.65	6	34607.33	36
1322.91	10	11984.46	10	37180.17	38
2572.21	4	12359.66	12	38077.59	40
2895.05	6	13428.50	4	40045.81	26
3299.64	8	14162.90	6	41556.75	50
3757.66	10	14059.76	8	43469.45	36
4248.30	4	14190.45	10	49607.74	30
4505.50	6	14298.64	4	58906.84	30
5724.38	2	14733.37	6	65207.02	42
6111.70	4	17614.00	4	71059.87	42
5752.92	6	18396.54	6	76599.79	60
6467.61	8	19486.38	16	78870.98	56
7512.67	2	20080.30	4	85380.55	58
		27931.81	26		

Heat of Formation

The heat of formation is calculated from the reaction $Zr(g) - e^-(g) = Zr^+(g)$ with the JANAF auxiliary value for Zr(g) and an ionization potential = 6.84 eV, or 157.666 kcal/mol, obtained from Moore (1).

Heat Capacity and Entropy

The electronic levels and quantum weights are taken 2). The electronic levels above 19000 cm^{-1} are averaged. The $H^\circ - H^\circ_{298}$ value at 0°K is −1.786 kcal/mol.

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