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PB 168 370-1

# JANAF THERMOCHEMICAL TABLES ADDENDUM

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# JANAF THERMOCHEMICAL TABLES

FIRST ADDENDUM PB 168 370-1

Prepared Under

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Technically Assisted by

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Thermochemical Working Group

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## FOREWORD

This first addendum to PB 168 370 represents the additions and revisions made by the Dow Thermal Research Laboratory during the period June 1965 to June 1966. These tables were prepared under contract for the U. S. Air-Force and issued as quarterly supplements numbered 18, 19, 20 and 21 to the JANAF Thermochemical Tables. These four supplements have been merged to form this first addendum to PB 168 370, at the suggestion of the JANAF Thermochemical Panel. Future addenda will be announced at a later time.

This addendum represents a changeover to the  $C_{12}$  atomic weight scale and also the physical constants recommended by the National Academy of Science - National Research Council, and the National Bureau of Standards. A new element: Copper, and some of its compounds have been added to the collection.

We want these tables to be as accurate as possible, and will appreciate having any errors called to our attention. The users of these tables can make a valuable contribution to the quality of the revised tables by supplying the compiler promptly with their own measured data.

These tables have been prepared by the following personnel: J. Chao, A. T. Hu, G. C. Karris, E. W. Phillips, H. Prophet, A. N. Syverud, D. R. Stull, G. C. Sinke, and S. K. Wollert. The latter two named participated for only a short time.

We are indebted to Viola Harrington for her services in the preparation of the tables for publication, and to Isabel Carr for her help with the literature retrieval.

Midland, Michigan  
July 1966

Daniel R. Stull

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C O N S T A N T S   U S E D   ( P A G E   1 )

The fundamental constants are those recommended by the National Academy of Sciences - National Research Council and adopted by the U. S. National Bureau of Standards, October 1963. The other constants are taken from E. R. Cohen, K. M. Crowe, and J. W. M. DuMond, "The Fundamental Constants of Physics," Interscience Publishers, New York, 1957. The physical scale based on the atomic mass of  $^{12}\text{C} = 12$  reported by A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962) is employed.

Fundamental Constants

<u>Name</u>	<u>Symbol</u>	<u>Value</u>	<u>Units</u>	<u>3 x Standard Deviation Limit</u>
Velocity of Light	c	$2.997925 \times 10^{10}$	cm s <sup>-1</sup>	$\pm 0.000003 \times 10^{10}$
Planck Constant	h	$6.6256 \times 10^{-27}$	erg s	$\pm 0.0005 \times 10^{-27}$
Avogadro Constant	N	$6.02252 \times 10^{23}$	mol <sup>-1</sup>	$\pm 0.00028 \times 10^{23}$
Faraday Constant		96,487.0	C mol <sup>-1</sup>	$\pm 1.6$
Absolute temperature of the "ice point", O°C	T <sub>0</sub> °C	273.1500	°K	$\pm 0.0002$
Molar volume of ideal gas (1 atm)	V <sub>0</sub> °C (1 atm)	22,413.6	cm <sup>3</sup> mol <sup>-1</sup>	$\pm 0.9$
Pressure-Volume product for a mole of gas at O°C and zero pressure	(PV) <sup>P=0</sup> T <sub>0</sub> °C	2271.05	J mol <sup>-1</sup>	$\pm 0.04$
Electronic Charge	e	$1.60210 \times 10^{-19}$	C	$\pm 0.00007 \times 10^{-19}$
Gas constant	R	8.3143 1.98716	J deg <sup>-1</sup> mol <sup>-1</sup> cal deg <sup>-1</sup> mol <sup>-1</sup>	$\pm 0.0012$ $\pm 0.00028$
Boltzmann Constant	k	$1.38054 \times 10^{-16}$	erg deg <sup>-1</sup> molecule <sup>-1</sup>	$\pm 0.00018 \times 10^{-16}$
Second radiation constant	c <sub>2</sub>	1.43879	cm deg	$\pm 0.00019$
Constant relating wave number and energy per mole E, in the relation $(\Delta E) = Nhc(\Delta) = Z(\Delta)$	Z	11.96256	J cm mol <sup>-1</sup>	$\pm 0.00006$
Constant relating energy, E, and mass m in the Einstein relation, $(\Delta E) = c^2(\Delta m) = Y(\Delta m)$	Y	$8.987554 \times 10^{13}$	J g <sup>-1</sup>	$\pm 0.000009 \times 10^{-13}$

Defined Constants

<u>Name</u>	<u>Symbol</u>	<u>Value</u>	<u>Units</u>
Standard gravity	g	980.665	cm s <sup>-2</sup>
Standard atmosphere	atm	1,013,250	dyn cm <sup>-2</sup>
Standard millimeter of mercury pressure	mm Hg	1/760	atm
Thermochemical calorie	cal	4.1840	J

The presentation of Mayer and Mayer "Statistical Mechanics", John Wiley & Sons, Inc., New York, (1940) forms the basis for the expressions given below for the ideal gas state. The calculations have been carried out by a Burroughs B5500 electronic computer.

I. Ideal Monatomic gas

(a) Translation

$$\begin{aligned} (H^\circ - H_0^\circ)/T &= C_p^\circ = 4.967913 \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ -(F^\circ - H_0^\circ)/T &= 6.863426 \log M + 11.439043 \log T - 7.282868 \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ S^\circ &= 6.863426 \log M + 11.439043 \log T - 2.314954 \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \end{aligned}$$

(b) Electronic

$$\begin{aligned} C_p^\circ &= \frac{4.113664}{T^2} \left[ \frac{\sum \epsilon_i^2 g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} - \left( \frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} \right)^2 \right] \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ (H^\circ - H_0^\circ)/T &= \frac{2.859114}{T} \frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} \text{ cal. deg.}^{-1} \text{ mole}^{-1} \\ -(F^\circ - H_0^\circ)/T &= 4.575617 \log \sum g_i e^{-\frac{1.438790 \epsilon_i}{T}} \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ S^\circ &= \frac{2.859114}{T} \frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} + 4.575617 \log \sum g_i e^{-\frac{1.438790 \epsilon_i}{T}} \end{aligned}$$

II. Ideal Diatomic Gas

(a) Translation and Rotation

$$\begin{aligned} C_p^\circ &= 6.955079 + 0.0914148 (B/T)^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ (H^\circ - H_0^\circ)/T &= 6.955079 - 0.953038 (B/T) - 0.0914148 (B/T)^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ -(F^\circ - H_0^\circ)/T &= 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) + 0.953038 (B/T) \\ &\quad + 0.0457074 (B/T)^2 - 8.005804 \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ S^\circ &= 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) - 0.0457074 (B/T)^2 - 1.050725 \\ &\quad \text{cal. deg.}^{-1} \text{ mole}^{-1}. \end{aligned}$$

where  $B_0 = (B_e - \alpha_e/2)$  when spectroscopic constants are available.  
 $B = \frac{2.799076 \times 10^{-39}}{T}$  when calculated from a molecular model.

(b) Vibration

$$\begin{aligned} C_p^\circ &= 1.987165 u^2 e^{-u} / (1 - e^{-u})^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ (H^\circ - H_0^\circ)/T &= 1.987165 u e^{-u} / (1 - e^{-u}) \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ + (F^\circ - H_0^\circ)/T &= 4.575617 \log (1 - e^{-u}) \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \\ S^\circ &= 1.987165 u e^{-u} / (1 - e^{-u}) - 4.575617 \log (1 - e^{-u}) \text{ cal. deg.}^{-1} \text{ mole}^{-1}. \end{aligned}$$

where  $u = (1.438790/T) \cdot (\omega_e - 2x_e \omega_e)$  when spectroscopic constants are available.  
 $u = (1.438790/T)\omega$  where  $\omega$  is the fundamental wave number of an harmonic oscillator.

(c) Electronic, same as I (b).

## (d) Anharmonicity Corrections

$$C_p^\circ = 1.987165 \left[ \frac{16\gamma}{u} - \frac{\delta u^2 e^u}{(e^u - 1)^2} + \frac{u^2 e^u (2\delta e^u - 4Xu - 8X)}{(e^u - 1)^3} + \frac{12Xu^3 e^{2u}}{(e^u - 1)^4} \right] \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

$$(H^\circ - H_0^\circ)/T = 1.987165 \left[ \frac{8\gamma}{u} + \frac{u(\delta e^u - 2X)}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3} \right] \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

$$-(F^\circ - H_0^\circ)/T = 1.987165 \left[ \frac{8\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{2Xu}{(e^u - 1)^2} \right] \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

$$S^\circ = 1.987165 \left[ \frac{16\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{\delta u e^u}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3} \right] \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

where  $u$  is the same as that used in the vibrational contribution (b)

$$X = (\omega_e x_e)/\omega_e; \quad \delta = \alpha_e/B_e = 6\gamma^{1/2}X^{1/2} - \gamma^{1/2}; \quad \gamma = 1/2 \left( \frac{D_e}{B_e} \right)^{1/2} \approx B_e \omega_e.$$

## III. Linear Polyatomic Molecule

- (a) Translation and rotation same as for II (a).
- (b) Vibration same as II (b) for each degree of freedom.
- (c) Electronic same as I (b) where levels and quantum weight are known.
- (d) Anharmonic corrections neglected.

## IV. Nonlinear Polyatomic Molecule (Rigid Rotator, Harmonic Oscillator).

## (a) Translation and Rotation

$$C_p^\circ = 7.948662 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$(H^\circ - H_0^\circ)/T = 7.948662 \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

$$-(F^\circ - H_0^\circ)/T = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} \\ - 10.297926 \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

$$S^\circ = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} \\ - 2.349265 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

- (b) Vibration same as II (b) for each degree of freedom.
- (c) Electronic same as I (b) where levels and quantum weight are known.
- (d) Anharmonic corrections neglected.

## V. Condensed States

Thermodynamic evaluation of condensed states rests upon either measured or estimated information. Heat capacity data are plotted, smoothed, and data for calculations read back at regular temperature intervals. Integration of this heat capacity data is carried out from the relations

$$H_T^\circ - H_{298.15}^\circ = \int_{298.15}^T C_p^\circ dT \quad S_T^\circ = \int_0^T \frac{C_p^\circ}{T} dT$$

by machine, three points at a time. The computer calculates the constants for a parabolic equation through the three points, and employs the constants to integrate the first temperature interval. The lowest point is discarded; the next higher point is combined with the two retained points; and a new set of parabolic constants calculated and used for integrating the next higher temperature interval. This recurrent procedure is well suited to this type of calculation. At the appropriate temperatures, transitional heats are added to the enthalpy total, while the quotient of the transitional heat divided by the absolute temperature is added to the entropy total.

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(REFERENCE STATE)

ALUMINUM (Al)

0 to 935°K. Crystal  
 933 to 2766.8°K. Liquid  
 2766.8 to 6000°K. Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub>	ΔF <sub>f</sub>	Log K <sub>p</sub>
0	.000	INFINITE	1.094	.000	.000	.000
100	3.116	1.650	.988	.000	.000	.000
200	5.158	4.302	.546	.000	.000	.000
298	5.806	6.769	.000	.000	.000	.000
300	5.814	6.805	.011	.000	.000	.000
400	6.163	8.528	.610	.000	.000	.000
500	6.450	9.934	1.241	.000	.000	.000
600	6.717	11.134	1.900	.000	.000	.000
700	6.999	12.190	2.585	.000	.000	.000
800	7.370	13.147	3.302	.000	.000	.000
900	7.801	14.044	4.064	.000	.000	.000
1000	7.588	17.603	10.205	.000	.000	.000
1100	7.588	18.326	10.911	.000	.000	.000
1200	7.588	18.986	11.557	.000	.000	.000
1300	7.588	19.593	12.152	.000	.000	.000
1400	7.588	20.156	12.704	.000	.000	.000
1500	7.588	20.679	13.218	.000	.000	.000
1600	7.588	21.169	13.700	.000	.000	.000
1700	7.588	21.629	14.153	.000	.000	.000
1800	7.588	22.063	14.581	.000	.000	.000
1900	7.588	22.473	14.985	.000	.000	.000
2000	7.588	22.862	15.370	.000	.000	.000
2100	7.588	23.232	15.735	.000	.000	.000
2200	7.588	23.585	16.084	.000	.000	.000
2300	7.588	23.923	16.418	.000	.000	.000
2400	7.588	24.246	16.737	.000	.000	.000
2500	7.588	24.555	17.044	.000	.000	.000
2600	7.588	24.853	17.338	.000	.000	.000
2700	7.588	25.130	17.622	.000	.000	.000
2800	4.970	50.501	18.892	.000	.000	.000
2900	4.971	50.675	19.109	.000	.000	.000
3000	4.971	50.844	20.257	.000	.000	.000
3100	4.971	51.007	21.343	.000	.000	.000
3200	4.972	51.165	22.373	.000	.000	.000
3300	4.973	51.318	23.351	.000	.000	.000
3400	4.975	51.466	23.981	.000	.000	.000
3500	4.977	51.610	24.769	.000	.000	.000
3600	4.979	51.751	25.516	.000	.000	.000
3700	4.982	51.887	26.227	.000	.000	.000
3800	4.986	52.020	26.904	.000	.000	.000
3900	4.991	52.150	27.550	.000	.000	.000
4000	4.996	52.276	28.166	.000	.000	.000
4100	5.002	52.399	28.756	.000	.000	.000
4200	5.010	52.520	29.320	.000	.000	.000
4300	5.019	52.638	29.861	.000	.000	.000
4400	5.029	52.754	30.380	.000	.000	.000
4500	5.041	52.867	30.879	.000	.000	.000
4600	5.055	52.978	31.358	.000	.000	.000
4700	5.071	53.086	31.819	.000	.000	.000
4800	5.088	53.193	32.263	.000	.000	.000
4900	5.108	53.299	32.691	.000	.000	.000
5000	5.130	53.402	33.105	.000	.000	.000
5100	5.154	53.504	33.503	.000	.000	.000
5200	5.181	53.604	33.889	.000	.000	.000
5300	5.211	53.703	34.262	.000	.000	.000
5400	5.244	53.801	34.623	.000	.000	.000
5500	5.280	53.897	34.972	.000	.000	.000
5600	5.319	53.993	35.311	.000	.000	.000
5700	5.361	54.087	35.640	.000	.000	.000
5800	5.406	54.181	35.959	.000	.000	.000
5900	5.456	54.274	36.268	.000	.000	.000
6000	5.508	54.366	36.569	.000	.000	.000

AT. WT. = 26.9815

(CRYSTAL)

ALUMINUM (Al)

$$\Delta H_f^0 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 2.56 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298.15} = 76.0 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 6.769 \pm 0.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m^0 = 933^\circ\text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature heat capacity curve is based on the work of N. E. Phillips, Phys. Rev. 114, 676 (1959) in the range 0.1 to 4°K; J. A. Kok and W. H. Keesom, Physica 4, 835 (1937) from 1-20°K. and W. G. Glaue and P. F. Mesds, J. Am. Chem. Soc. 53, 1897 (1941). The high temperature enthalpy adopted here is that of R. A. McDonald, private communication, Dow Thermal Research Laboratory, Oct. 1965. This data is in general agreement with the measurements of J. H. Ambery and E. Griffiths, Proc. Phys. Soc. (London) 38, 378 (1926); E. D. Eastman, A. M. Williams and T. F. Young, J. Am. Chem. Soc. 46, 1178 (1924); W. B. Kendall and R. Hultgren, private communication to D. R. Stull from R. L. Orr Mar. 29, 1960; S. Satoh, Sci. Papers, Inst. Phys. Chem. Res. (Tokyo) 29, 19 (1956); P. Wust, A. Meuthen and R. Durrer, Forsch. Arb. Ver. deut. Ing. No. 204 (1918). Other investigations have been discussed by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley "Selected Value of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York, (1963). These other determinations generally lay below the adopted values.

Melting Data.

The heat of melting was reported by McDonald, loc. cit.. It is in good agreement with the selected value of Hultgren et al., loc. cit. The chosen value also has eliminated uncertainty due to reaction of the liquid aluminum and its vessel by use of BN and TiP<sub>2</sub> containers. The melting point of 933°K. was chosen at the limit of the "well established" 932 ± 1°K., as more likely representing pure aluminum. This choice was based mainly on the work of W. F. Roeser and H. T. Wensel, J. Res. Natl. Bur. Std. 14, 247 (1935).

Sublimation Data.

See Al(ε) for details.

T, °K.	C <sub>p</sub>	S°	-(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0	0.00	0.00	INFINITE	1.094	0.00	0.00	INFINITE
100	3.116	1.650	11.530	.988	0.00	0.00	0.00
200	5.158	4.572	7.302	.546	0.00	0.00	0.00
298	5.806	6.769	6.769	.000	0.00	0.00	0.00
300	5.814	6.805	6.769	.011	0.00	0.00	0.00
400	6.163	8.528	7.002	.610	0.00	0.00	0.00
500	6.450	9.534	7.452	1.241	0.00	0.00	0.00
600	6.717	11.134	7.968	1.900	0.00	0.00	0.00
700	6.959	12.190	8.497	2.585	0.00	0.00	0.00
800	7.370	13.147	9.015	3.302	0.00	0.00	0.00
900	7.801	14.044	9.528	4.054	0.00	0.00	0.00
1000	8.430	14.907	10.073	4.883	2.514	.182	0.40
1100	8.800	15.728	10.505	5.746	2.410	.447	0.89
1200	9.080	16.505	10.973	6.640	2.275	.701	1.28
1300	9.350	17.243	11.427	7.561	2.112	.943	1.59
1400	9.600	17.945	11.868	8.509	1.923	1.172	1.83
1500	9.850	18.616	12.295	9.481	1.710	1.385	2.02

T. °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
100							
200							
300	7.598	8.420	8.420	0.000	2.072	1.580	-1.158
400	7.588	8.467	8.420	0.14	2.075	1.576	-1.148
500	7.588	10.650	8.718	0.773	2.235	1.386	-0.757
600	7.588	12.343	9.280	1.532	2.363	1.158	-0.506
700	7.588	13.727	9.909	2.290	2.462	0.907	-0.330
800	7.588	14.896	10.540	3.049	2.536	0.642	-0.200
900	7.588	15.904	11.149	3.808	2.578	0.368	-0.101
1000	7.588	16.803	11.729	4.567	2.575	0.092	-0.022
1050	7.588	17.503	12.277	5.326	2.500	0.000	0.000
1100	7.588	18.326	12.795	6.084	0.000	0.000	0.000
1200	7.588	18.986	13.283	6.843	0.000	0.000	0.000
1300	7.588	19.594	13.746	7.602	0.000	0.000	0.000
1400	7.588	20.156	14.184	8.361	0.000	0.000	0.000
1500	7.588	20.679	14.600	9.120	0.000	0.000	0.000
1600	7.588	21.169	14.995	9.878	0.000	0.000	0.000
1700	7.588	21.629	15.372	10.637	0.000	0.000	0.000
1800	7.588	22.063	15.732	11.396	0.000	0.000	0.000
1900	7.588	22.473	16.076	12.155	0.000	0.000	0.000
2000	7.588	22.862	16.405	12.914	0.000	0.000	0.000
2100	7.588	23.233	16.722	13.672	0.000	0.000	0.000
2200	7.588	23.585	17.026	14.431	0.000	0.000	0.000
2300	7.588	23.923	17.318	15.190	0.000	0.000	0.000
2400	7.588	24.246	17.600	15.949	0.000	0.000	0.000
2500	7.588	24.555	17.872	16.708	0.000	0.000	0.000
2600	7.588	24.853	18.135	17.466	0.000	0.000	0.000
2700	7.588	25.139	18.389	18.225	0.000	0.000	0.000
2800	7.588	25.415	18.632	18.984	0.000	0.000	0.000
2900	7.588	25.682	18.872	19.743	66.448	6.032	-4.655
3000	7.588	25.939	19.105	20.502	66.187	8.528	-6.621
3100	7.588	26.188	19.330	21.260	65.926	11.013	-7.776
3200	7.588	26.429	19.548	22.019	65.664	13.491	-9.21
3300	7.588	26.662	19.760	22.778	65.402	15.963	-1.057
3400	7.588	26.889	19.966	23.537	65.141	18.421	-1.184
3500	7.588	27.109	20.167	24.296	64.879	20.874	-1.303
3600	7.588	27.322	20.363	25.054	64.619	23.326	-1.416
3700	7.588	27.530	20.554	25.813	64.358	25.763	-1.522
3800	7.588	27.733	20.740	26.572	64.097	28.194	-1.621
3900	7.588	27.930	20.922	27.331	63.837	30.621	-1.716
4000	7.588	28.122	21.099	28.090	63.578	33.038	-1.805

ΔH<sub>f</sub><sup>o</sup> 298.15 = 2.072 kcal. mole<sup>-1</sup>

ΔH<sub>m</sub><sup>o</sup> = 2.56 ± 0.05 kcal. mole<sup>-1</sup>

ΔH<sub>v</sub><sup>o</sup> = 68.497 kcal. mole<sup>-1</sup>

S<sub>298.15</sub> = 8.42 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub><sup>o</sup> = 933°K.

T<sub>b</sub><sup>o</sup> = 2766.8°K.

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding the heat of melting and the difference between H<sub>333</sub><sup>o</sup>-H<sub>298</sub><sup>o</sup> for (c) and (1).

Heat Capacity and Entropy.

The heat capacity was adopted from the enthalpy measurements of R. A. McDonald, private communication, Dow Thermal Research Laboratory, Oct. 1965. The liquid enthalpies were determined in crucibles of BN and TiP<sub>2</sub> sealed in a platinum-rhodium capsule. The liquid enthalpies are in agreement with the determination of J. H. Awherry and E. Griffiths, Proc. Phys. Soc. (London) 58, 378 (1926) and higher, by as much as 12%, than those of F. Wust, A. Meuthen and R. Dorrer, Forsch. Arb. Ver. deut. Ing. No. 204 (1918) and S. Umano, Sci. Repts. Tohoku. Imp. Univ. Ser. 1, 15, 597 (1926). The enthalpy data was adequately represented by a constant heat capacity. The entropy was calculated from that of the crystal in a manner analogous to the heat of formation.

Melting Data.

See Al(c) for details.

Vaporization Data.

The temperature of boiling and the heat of vaporization were derived from the adopted functions and the heat of sublimation in order to maintain thermodynamic consistency.

Ground State Configuration  $2P_{1/2}^2$   
 $S_{298.15}^\circ = 39.304 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^\circ 0 = 77.44 \pm 0.9 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^\circ 298.15 = 76.0 \pm 0.9 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$E_i$ , cm <sup>-1</sup>	$g_i$	$E_i$ , cm <sup>-1</sup>	$g_i$
0	2	32700	16
112	4	37689	2
25348	2	36930	10
29100	12	40275	6
		41319	14
		43600	20
		46130	84

Heat of Formation.

The heat of sublimation of aluminum has been derived from a second and third law analysis of the vapor pressure data of several investigators; the results are tabulated below.

Ref.	Range °K.	Method	Points	$\Delta H_{298}^\circ$ subl. kcal. mole <sup>-1</sup>	3rd law	Drift
1	1273-1473	Knudsen	10*	76.3 ± 2.3	75.32 ± 0.7	-0.8 ± 1.7
2	1734-2237	Boiling	4	83.1 ± 0.3	74.58 ± 1.8	-4.3 ± 0.2
3	1385-1468	Knudsen	10	89.8 ± 32.9	77.29 ± 3.7	-9.0 ± 23.3
4	1410-1468	Knudsen	6	71.9 ± 19.2	78.4 ± 1.3	4.5 ± 13.2
5	1511-1723	Mass Spec	11	77.2 ± 2		
6	2473	Boiling	1		70.5	
7	1476	Knudsen	1		77.35	
8	1400-1611	Torsion	104	80.3 ± 1.2	79.5 ± 0.3	-0.3 ± 0.8

\*1 point rejected due to failure of statistical test.

References:

1. Yu. A. Priselkov, Yu. A. Sapozhnikov and A. V. Tseplyaeva, *Izv. Akad. Nauk. SSR, Otd. Tech. Nauk. No. 1*, 106 (1959)
2. E. Baur and R. Brunner, *Helv. Chim. Acta*, **17**, 958 (1934).
3. L. Brewer and A. W. Searcy, *J. Am. Chem. Soc.* **73**, 5308 (1951).
4. Ref. 3 omitting data from TAC cells.
5. R. P. Porter, P. Schisael and M. G. Ingraham, *J. Chem Phys.* **23**, 339 (1955).
6. H. von Warrenberg, *Z. Elektrochem.* **19**, 482 (1913).
7. L. Parkas, *Z. Physik*, **7**, 735 (1931).
8. N. D. Potter, Philco Corporation, Newport Beach, California. Private communication Jan. 11, 1966.

It is apparent that there is little real agreement in the data; in Ref. 3 some of this is due to diffusion of liquid Al through the TAC crucibles, while Ref. 8 reports surface oxidation of the sample. The data for Ref. 5 have been reworked since they corrected their data using  $\Delta C_p$  between (l) and (g) of -2 cal. deg<sup>-1</sup> mole<sup>-1</sup>, where our tables give a value of -2.62 cal. deg<sup>-1</sup> mole<sup>-1</sup>. Ref. 8 has obtained by far the largest number of data points all of which are in good agreement, show no trend and little scatter. Ref. 1 has gone to a great deal of trouble to ensure uniform heating, total collection of effluents and good Knudsen conditions and also has no trend. It is difficult to imagine why these two series differ by a factor of 3 in the pressure. An intermediate value of the heat of sublimation has been adopted at 78 ± 2 kcal. mole<sup>-1</sup>. This choice is also indicated by the decomposition of AlN(c) to Al(g) and 1/2 N<sub>2</sub>(g), which has been well established as 153.7 ± 0.8 kcal. mole<sup>-1</sup>, combined with the heat of formation of AlN(c) = -76 ± 0.3 kcal. mole<sup>-1</sup>, to yield  $\Delta H_{sub}^\circ \text{Al} = 77.7 \pm 0.9 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

The electronic ground state configuration and the higher electronic levels are taken from C. E. Moore, *Natl. Bur. Stds. Circular* 467, "Atomic Energy Levels" Washington 1949.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	$\Delta H_f^\circ$	$\Delta F_f^\circ$	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.020	33.345	43.998	1.065	77.440	74.753	163.365
200	5.290	37.231	39.775	0.500	78.037	71.505	78.134
298	5.112	39.304	39.304	∞	78.000	68.300	50.083
300	5.111	39.335	39.304	∞	77.998	68.239	49.710
400	5.047	40.795	39.503	1.517	77.907	65.000	35.513
500	5.018	41.918	39.878	1.020	77.779	61.787	27.006
600	5.002	42.832	40.297	1.521	77.621	58.602	21.345
700	4.993	43.602	40.715	2.021	77.436	55.547	17.311
800	4.987	44.268	41.119	2.520	77.218	52.521	14.253
900	4.983	44.855	41.502	3.018	76.954	49.523	11.253
1000	4.980	45.380	41.864	3.516	76.619	46.542	8.318
1100	4.978	45.855	42.206	4.014	76.285	43.576	5.457
1200	4.976	46.288	42.535	4.512	75.959	40.635	2.673
1300	4.974	46.679	42.851	5.010	75.641	37.721	0.000
1400	4.974	47.025	43.151	5.507	75.337	34.836	-2.673
1500	4.973	47.338	43.435	6.004	75.045	31.977	-5.346
1600	4.973	47.619	43.695	6.502	74.762	29.143	-8.019
1700	4.972	47.870	43.933	6.999	74.488	26.334	-10.692
1800	4.972	48.100	44.140	7.496	74.229	23.551	-13.365
1900	4.971	48.316	44.326	7.993	73.977	20.797	-16.038
2000	4.971	48.528	44.493	8.490	73.735	18.073	-18.711
2100	4.971	48.731	44.641	8.988	73.502	15.377	-21.384
2200	4.971	48.925	44.771	9.485	73.276	12.711	-24.057
2300	4.970	49.110	44.885	9.982	73.057	10.075	-26.730
2400	4.970	49.285	44.993	10.479	72.845	7.473	-29.403
2500	4.970	49.452	45.097	10.976	72.639	4.900	-32.076
2600	4.970	49.612	45.197	11.473	72.439	2.367	-34.749
2700	4.970	49.767	45.293	11.970	72.244	-0.164	-37.422
2800	4.970	49.917	45.385	12.467	72.054	-2.697	-40.095
2900	4.971	50.062	45.473	12.964	71.869	-5.230	-42.768
3000	4.971	50.202	45.557	13.461	71.689	-7.763	-45.441
3100	4.971	50.337	45.637	13.958	71.514	-10.296	-48.114
3200	4.972	50.467	45.713	14.455	71.344	-12.829	-50.787
3300	4.973	50.592	45.785	14.952	71.179	-15.362	-53.460
3400	4.975	50.712	45.853	15.449	71.019	-17.895	-56.133
3500	4.977	50.827	45.919	15.946	70.864	-20.428	-58.806
3600	4.979	50.938	45.981	16.443	70.714	-22.961	-61.479
3700	4.982	51.044	46.039	16.940	70.569	-25.494	-64.152
3800	4.986	51.146	46.093	17.437	70.429	-28.027	-66.825
3900	4.991	51.244	46.143	17.934	70.294	-30.560	-69.498
4000	4.996	51.338	46.189	18.431	70.164	-33.093	-72.171
4100	5.002	51.429	46.231	18.928	70.039	-35.626	-74.844
4200	5.010	51.516	46.270	19.425	69.919	-38.159	-77.517
4300	5.019	51.600	46.306	19.922	69.804	-40.692	-80.190
4400	5.029	51.680	46.339	20.419	69.694	-43.225	-82.863
4500	5.041	51.757	46.369	20.916	69.589	-45.758	-85.536
4600	5.055	51.832	46.396	21.413	69.489	-48.291	-88.209
4700	5.071	51.904	46.420	21.910	69.394	-50.824	-90.882
4800	5.088	51.973	46.441	22.407	69.304	-53.357	-93.555
4900	5.108	52.039	46.459	22.904	69.219	-55.890	-96.228
5000	5.130	52.102	46.474	23.401	69.139	-58.423	-98.901
5100	5.154	52.162	46.487	23.898	69.064	-60.956	-101.574
5200	5.181	52.219	46.498	24.395	69.000	-63.489	-104.247
5300	5.211	52.273	46.507	24.892	68.947	-66.022	-106.920
5400	5.244	52.324	46.513	25.389	68.904	-68.555	-109.593
5500	5.280	52.372	46.517	25.886	68.871	-71.088	-112.266
5600	5.319	52.417	46.519	26.383	68.848	-73.621	-114.939
5700	5.361	52.459	46.519	26.880	68.834	-76.154	-117.612
5800	5.406	52.498	46.517	27.377	68.829	-78.687	-120.285
5900	5.456	52.534	46.513	27.874	68.834	-81.220	-122.958
6000	5.508	52.567	46.507	28.371	68.848	-83.753	-125.631

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965



Ground State Configuration <sup>1</sup>S<sub>0</sub> ΔH<sub>f</sub><sup>0</sup> = 215.4 ± .5 kcal/mole  
 S<sub>298.15</sub><sup>0</sup> = 35.813 cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>0</sup> 298.15 = 217.3 ± .5 kcal/mole

Electronic Levels and Quantum Weight

E <sub>1</sub> , cm. <sup>-1</sup>	g <sub>1</sub>	E <sub>1</sub> , cm. <sup>-1</sup>	g <sub>1</sub>
0.0	1	94084.5	1
37392.0	1	94146.8	3
37453.8	3	94267.7	5
37579.3	5	95348.2	1
59849.7	3	95546.8	7
85479.0	5	95547.9	5
91271.2	3	95548.8	3

Heat of Formation.

The heat of formation was calculated from the equation: Al(g) - e<sup>-</sup> → Al<sup>+</sup>(g) with the JANAF auxiliary value for Al(g); using an I.P. = 4.827916 X 10<sup>4</sup> cm<sup>-1</sup> (136.047 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above 1 X 10<sup>5</sup> cm<sup>-1</sup> were omitted because their contribution is negligible below 6000°K. The H<sup>0</sup>-H<sub>298</sub><sup>0</sup> value at 0°K. is -1.461 kcal./mole.

T, °K.	C <sub>p</sub> <sup>0</sup>	S <sup>0</sup> - (F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K P
0						
100	4.968	35.813	0.000	217.300	207.153	- 151.840
200	4.968	35.844	0.009	217.307	207.090	- 150.858
300	4.968	35.873	0.036	217.304	203.624	- 111.250
400	4.968	36.008	0.506	218.071	200.061	- 87.442
500	4.968	36.376	1.403	218.409	186.426	- 71.545
600	4.968	36.748	1.506	218.714	162.737	- 60.172
700	4.968	37.201	2.403	218.992	149.007	- 51.632
800	4.968	37.600	2.490	219.239	135.245	- 44.982
900	4.968	37.980	3.447	216.961	141.641	- 39.696
1000	4.968	38.339	3.984	217.255	178.095	- 35.382
1100	4.968	38.677	4.481	217.549	174.523	- 31.793
1200	4.968	38.998	4.977	217.841	170.923	- 28.793
1300	4.968	39.300	5.474	218.135	167.304	- 26.116
1400	4.968	39.587	5.971	218.429	163.662	- 23.844
1500	4.968	39.859	6.468	218.723	160.001	- 21.854
1600	4.968	40.118	6.965	219.017	156.322	- 20.096
1700	4.968	40.365	7.461	219.309	152.625	- 18.550
1800	4.968	40.600	7.958	219.603	148.916	- 17.128
1900	4.968	40.822	8.455	219.897	145.187	- 15.865
2000	4.968	41.042	8.952	220.191	141.441	- 14.719
2100	4.968	41.249	9.449	220.485	137.685	- 13.677
2200	4.968	41.448	9.945	220.777	133.913	- 12.724
2300	4.968	41.639	10.442	221.071	130.133	- 11.850
2400	4.968	41.824	10.939	221.365	126.338	- 11.044
2500	4.968	42.002	11.436	221.659	122.529	- 10.299
2600	4.968	42.174	11.933	221.953	118.713	- 9.609
2700	4.968	42.341	12.430	222.247	114.896	- 8.973
2800	4.968	42.502	12.926	222.541	111.079	- 8.387
2900	4.968	42.658	13.423	222.835	107.262	- 7.850
3000	4.968	42.809	13.920	223.129	103.445	- 7.360
3100	4.968	42.956	14.417	223.423	99.628	- 6.916
3200	4.968	43.099	14.914	223.717	95.811	- 6.518
3300	4.968	43.238	15.411	224.011	92.000	- 6.164
3400	4.968	43.373	15.908	224.305	88.194	- 5.854
3500	4.968	43.504	16.404	224.600	84.393	- 5.587
3600	4.968	43.633	16.901	224.894	80.597	- 5.362
3700	4.970	43.758	17.398	225.188	76.806	- 5.177
3800	4.971	43.878	17.895	225.482	73.020	- 5.030
3900	4.971	43.993	18.392	225.776	69.239	- 4.920
4000	4.971	44.104	18.889	226.070	65.463	- 4.841
4100	4.974	44.211	19.386	226.364	61.692	- 4.791
4200	4.976	44.316	19.883	226.658	57.926	- 4.767
4300	4.978	44.419	20.380	226.952	54.165	- 4.767
4400	4.981	44.519	20.877	227.246	50.409	- 4.791
4500	4.984	44.616	21.374	227.540	46.658	- 4.839
4600	4.988	44.711	21.871	227.834	42.912	- 4.911
4700	4.992	44.804	22.368	228.128	39.170	- 5.006
4800	4.996	44.896	22.865	228.422	35.433	- 5.124
4900	5.004	44.986	23.362	228.716	31.699	- 5.266
5000	5.011	45.074	23.859	229.010	27.970	- 5.434
5100	5.019	45.161	24.356	229.304	24.245	- 5.630
5200	5.028	45.246	24.853	229.598	20.525	- 5.854
5300	5.038	45.329	25.350	229.892	16.809	- 6.106
5400	5.049	45.411	25.847	230.186	13.097	- 6.384
5500	5.062	45.492	26.344	230.480	9.389	- 6.688
5600	5.077	45.573	26.841	230.774	5.685	- 7.018
5700	5.092	45.654	27.338	231.068	1.985	- 7.374
5800	5.109	45.734	27.835	231.362	- 1.719	- 7.756
5900	5.128	45.814	28.332	231.656	- 5.467	- 8.164
6000	5.148	45.894	28.829	231.950	- 9.221	- 8.598

ALUMINUM TRIFLUORIDE (AlF<sub>3</sub>) (CRYSTAL)

MOL. WT. = 83.9767

$$\Delta H_f^0 = -359.3 \pm 1.7 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -360.8 \pm 1.7 \text{ kcal. mole}^{-1}$$

$$\Delta H_c^{\circ} = 0.16 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^{\circ} 298.15 = 71.2 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$S^{\circ} 298.15 = 15.881 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_c = 718^{\circ}\text{K.}$$

$$T_g = 1545^{\circ}\text{K.}$$

## Heat of Formation.

By fluorine bomb calorimetry, the enthalpy of formation ( $\Delta H_f^{\circ}$  298.15) for AlF<sub>3</sub>(c) was determined to be -360.4 ± 1.6 and -361.1 ± 0.6 kcal. mole<sup>-1</sup> by E. S. Domalski and G. T. Armstrong, J. Res. Natl. Bur. Std. 69A, 137 (1965) and G. Rudzitis, E. Van Deventer, H. M. Feder and W. N. Hubbard, private communication, August 19, 1965, respectively. The value of  $\Delta H_f^{\circ}$  298.15 (AlF<sub>3</sub>, c) adopted is the average of these two.

The chemical equilibria of the reaction 2/3 AlF<sub>3</sub>(c) + H<sub>2</sub>O(g) = 1/3 Al<sub>2</sub>O<sub>3</sub>(c) + 2HF(g) were studied by V. P. Mashovets and B. F. Yudin, Izv. Vysishkh Uchebn. Zavedeni, Tsvein. Met. 5, (4) 95 (1962). Using the equilibrium constants reported, the enthalpy change ( $\Delta H_r^{\circ}$  298.15) of the reaction was evaluated by the second and third law methods to be 30.79 and 33.04 kcal. mole<sup>-1</sup>, respectively. Based on the third law value of  $\Delta H_f^{\circ}$  298.15, the enthalpy of formation ( $\Delta H_f^{\circ}$  298.15) for AlF<sub>3</sub>(c) was derived as -357.5 kcal. mole<sup>-1</sup>.

## Heat Capacity and Entropy.

The low temperature (51-298°K) heat capacities were measured by E. G. King, J. Am. Chem. Soc. 79, 2056 (1956). The high temperature (400-1400°K.) heat capacities were determined by C. J. O'Brien and K. K. Kelley, J. Am. Chem. Soc. 79, 5616 (1957) and later corrected by W. B. Frank, J. Phys. Chem. 65, 2081 (1961). These two sets of  $C_p$  data were plotted and joined smoothly at 298.15°K. The  $C_p$  values above 1400°K. were obtained by graphical extrapolation.  $S^{\circ} 298.15$  was derived from heat capacities, using  $S_{51}^{\circ}$ (extrap.) = 0.56 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

## Transition Data.

$T_c$  and  $\Delta H_c^{\circ}$  were obtained from W. B. Frank, loc. cit.

## Sublimation Data.

The enthalpy of sublimation ( $\Delta H_g^{\circ}$  298.15) was selected by analyses of fifteen sets of vapor pressure data reported by nine investigators. An assumption was made that the partial pressure due to the presence of (AlF<sub>3</sub>)<sub>2</sub>(g) in AlF<sub>3</sub>(g) is negligible. See the AlF<sub>3</sub>(g) table for details.  $T_g$  is calculated as the temperature at which the free energy change ( $\Delta G_r^{\circ}$ ) of the reaction AlF<sub>3</sub>(c) → AlF<sub>3</sub>(g) approaches zero.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>f</sub>
0	-0.00	-0.00	INFINITE	-2.778	-359.319	-359.319	INFINITE
100	5.959	2.882	28.642	-2.276	-360.265	-354.284	774.251
200	13.594	9.298	17.403	-1.569	-360.751	-348.085	380.351
298	17.951	13.881	11.881	-0.000	-360.800	-341.850	250.571
300	18.035	15.992	15.981	+0.933	-360.799	-341.733	248.940
400	20.987	21.586	18.027	1.195	-360.599	-335.401	183.246
500	22.316	26.402	18.112	4.145	-360.277	-329.140	143.860
600	23.744	30.598	19.851	6.448	-359.877	-322.948	117.628
700	25.077	34.359	21.659	8.890	-359.390	-316.829	98.231
800	26.180	37.784	23.427	11.447	-358.810	-310.807	84.901
900	27.156	40.810	25.225	13.846	-358.139	-304.874	74.214
1000	27.982	43.412	26.894	16.278	-357.387	-299.073	65.272
1100	28.608	45.520	28.482	18.742	-356.560	-293.492	58.110
1200	29.034	47.093	29.993	21.240	-355.688	-288.130	52.149
1300	29.400	48.171	31.433	23.769	-354.783	-283.027	47.112
1400	29.786	51.616	32.808	26.332	-353.831	-278.183	42.800
1500	26.111	53.406	34.122	28.926	-352.833	-268.153	39.068
1600	26.436	55.102	35.381	31.554	-351.748	-262.163	35.808
1700	26.761	56.714	36.589	34.214	-350.576	-256.205	32.936
1800	27.085	58.253	37.750	36.906	-349.326	-250.287	30.388
1900	27.409	59.726	38.868	39.631	-347.997	-244.398	28.111
2000	27.732	61.140	39.946	42.388	-346.591	-238.544	26.066
2100	28.055	62.501	40.988	45.177	-345.117	-232.729	24.219
2200	28.377	63.814	41.996	47.999	-343.584	-226.945	22.544
2300	28.698	65.082	42.972	50.852	-341.993	-221.192	21.017
2400	29.018	66.310	43.919	53.738	-340.344	-215.474	19.621
2500	29.337	67.501	44.839	56.656	-338.549	-209.789	18.339

ALUMINUM TRIFLUORIDE (AlF<sub>3</sub>) (IDEAL GAS) MOL. WT. = 85.9787

Point Group D<sub>3h</sub>  
 $\Delta H_f^0 = -288.7 \pm 1.8 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -289.6 \pm 1.8 \text{ kcal. mole}^{-1}$   
 $S_{298.15}^0 = 66.17 \text{ cal. deg}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\nu$ , cm <sup>-1</sup>	$\nu$ , cm <sup>-1</sup>
297 (1)	935 (2)
297 (1)	263 (2)

Bond Distances: Al-F = 1.63 ± 0.03 Å  
 Bond Angle: F-Al-F = 120°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 3.97553 X 10<sup>-114</sup> g<sup>3</sup> cm<sup>6</sup>

Heat of Formation

The heat of formation ( $\Delta H_f^{298.15}$ ) for AlF<sub>3</sub>(g) was calculated from the heats of sublimation and formation for AlF<sub>3</sub>(c). The value of heat of sublimation ( $\Delta H_{sub}^{298.15}$ ) was selected based on the second and third law analyses of the vapor pressure data for the reaction AlF<sub>3</sub>(c) = AlF<sub>3</sub>(g), reported by many investigators. The results obtained are presented as follows.

Investigator

Investigator	Temperature, °K.	Second Law Value	Third Law Value
Olbrych (1)	1371.0	76.32 ± 1.69	72.23
Huff and Boucher (2)	1106.2	84.56 ± 17.08	72.36
Witt and Barrow (4)	955.0	72.94	72.07
Vetnikov and Blushstein (5)	885.2	86.38 ± 5.87	72.82
Sveevy (6)	885.0	72.60 ± 1.01	71.61
Blackburn (6)	885.0	72.60 ± 1.01	72.74
Hildenbrand (6)	867.8	66.88 ± 0.79	71.21
Graphite Cell No. 7	866.9	89.02 ± 0.60	71.19
" " " " " " " "	866.9	70.03 ± 0.40	71.11
" " " " " " " "	866.9	91.62 ± 0.95	71.26
" " " " " " " "	866.9	88.56 ± 0.49	71.05
Platinum Cell No. 19	863.1	105.11 ± 0.18	71.09
" " " " " " " "	863.1	87.65 ± 0.18	71.09

(1) M. Olbrych, *Chem. Zvesten*, **10**, 100 (1936).  
 (2) L. I. Huff and L. L. Boucher, *J. Res. Nat. Bur. Stand.*, **67**, 219 (1953).  
 (3) I. O. Ryzhenkin, *Zh. Fiz. Khim.*, **33**, 526 (1959).  
 (4) M. P. Witt and R. F. Barrow, *Trans. Faraday Soc.*, **55**, 750 (1959).  
 (5) M. M. Vetnikov, M. L. Blushstein and V. P. Fodymov, *Izv. Vsesoyuz. Inst. Tsvetnykh Met.*, **2**, 126 (1959).  
 (6) R. M. Sveevy, G. V. Foznarovaya, A. M. Nemesyanov and Y. I. Gerasimov, *Zh. Neorg. Khim.*, **5**, 2196 (1959).  
 (7) R. P. Kraus, Jr., A. C. Victor and T. B. Douglas, *National Bureau of Standards Report* 7796, Jan. 1, 1963.  
 (8) P. E. Blackburn, "Thermodynamics of Condensed and Vapor Phases in the Binary and Ternary Systems of Be-O, Al-B-O, Si-O, Al-Be-O and Al-B-P," Final Report, May 31, 1965, Arthur D. Little, Inc. In the report, the quantity  $1/T \times 10^3$ , °K<sup>-1</sup> was given as  $T$ , °K, due to a typographical error.  
 (9) D. L. Hildenbrand, Aeronutronic Division, Ford Motor Company, private communication, July 30, 1963.

The value of  $\Delta H_f^{298.15}$  (AlF<sub>3</sub>, c) is selected to be 71.2 ± 0.5 kcal. mole<sup>-1</sup>, yielding  $\Delta H_f^{298.15}$  (AlF<sub>3</sub>, g) = -289.6 ± 1.8 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy  
 The molecular structure, bond distance and angle were taken from P. A. Klichin, N. G. Rambidi and E. Z. Zaslavino, *Kristallografiya*, **5**, 186 (1959). The vibrational frequencies were obtained from A. Büchner, loc. cit., Progress Report No. 2, Apr. 1 to June 30, 1962, except  $\nu_2$  which was estimated by comparison with other related data. The vibrational frequencies were also reported by M. J. Linevsky, Second Quarterly Report, Contract No. AF33(615)-1150; A. Shelton, Report No. ITRM-C-6013-6, 1964; and L. J. McCarty, R. C. Faule and J. L. Margrave, *J. Phys. Chem.*, **67**, 1066 (1963). The three principle moments of inertia are: I<sub>A</sub> = I<sub>B</sub> = 1.2571 X 10<sup>-38</sup> and I<sub>C</sub> = 2.5142 X 10<sup>-38</sup> g<sup>2</sup> cm<sup>2</sup>.

T, °K.	C <sub>v</sub>	S°	-(F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	0.000	INFINITE	INFINITE	3.371	-288.712	-288.712	INFINITE
100	9.841	52.729	78.015	2.529	-289.018	-288.022	629.441
200	12.946	60.876	66.876	1.375	-289.357	-286.899	313.494
298	14.966	66.167	60.167	0.000	-289.600	-285.643	209.372
300	14.998	66.260	60.168	0.28	-289.604	-285.619	208.063
400	16.820	70.783	66.775	1.603	-289.781	-284.261	125.305
500	17.365	74.556	67.964	3.296	-289.926	-282.865	123.634
600	17.996	77.781	69.338	5.066	-290.060	-281.440	102.510
700	18.426	80.590	70.749	6.888	-290.201	-279.993	87.413
800	18.729	83.071	72.137	8.747	-290.357	-278.525	76.086
900	18.949	85.290	73.478	10.631	-290.534	-277.034	67.270
1000	19.112	87.296	74.761	12.535	-290.730	-275.540	60.173
1100	19.236	89.123	75.985	14.453	-290.950	-273.945	54.346
1200	19.333	90.801	77.150	16.381	-291.200	-271.738	49.488
1300	19.409	92.352	78.261	18.318	-291.584	-269.023	45.376
1400	19.471	93.793	79.319	20.263	-292.000	-266.099	41.850
1500	19.521	95.138	80.330	22.212	-292.517	-262.965	38.793
1600	19.562	96.399	81.295	24.166	-293.096	-259.442	36.117
1700	19.597	97.586	82.124	26.124	-293.725	-255.576	33.755
1800	19.626	98.707	83.104	28.086	-294.417	-251.324	31.655
1900	19.651	99.769	83.953	30.050	-295.168	-246.681	29.774
2000	19.672	100.777	84.769	32.016	-295.990	-241.642	28.081
2100	19.690	101.738	85.555	33.984	-296.900	-236.100	26.549
2200	19.706	102.654	86.311	35.954	-297.895	-230.156	25.156
2300	19.720	103.530	87.041	37.925	-298.975	-223.813	23.883
2400	19.732	104.370	87.746	39.898	-299.945	-217.074	22.715
2500	19.743	105.175	88.427	41.871	-300.803	-210.042	21.642
2600	19.753	105.950	89.086	43.846	-301.552	-202.716	20.648
2700	19.762	106.696	89.725	45.822	-302.292	-195.100	20.729
2800	19.770	107.414	90.344	47.799	-303.022	-187.200	19.876
2900	19.778	108.108	90.944	49.776	-303.742	-179.124	19.084
3000	19.785	108.779	91.528	51.754	-304.452	-170.872	18.344
3100	19.788	109.428	92.095	53.732	-305.152	-162.448	17.652
3200	19.793	110.056	92.646	55.711	-305.842	-153.852	17.008
3300	19.798	110.665	93.183	57.691	-306.522	-145.096	16.412
3400	19.802	111.256	93.706	59.672	-307.192	-136.180	15.864
3500	19.806	111.830	94.216	61.651	-307.852	-127.112	15.364
3600	19.810	112.388	94.713	63.632	-308.502	-117.904	14.908
3700	19.813	112.931	95.198	65.613	-309.142	-108.564	14.492
3800	19.816	113.461	95.671	67.595	-309.772	-99.092	14.112
3900	19.819	113.974	96.134	69.577	-310.392	-89.496	13.764
4000	19.822	114.476	96.586	71.559	-311.002	-79.776	13.448
4100	19.824	114.966	97.029	73.541	-311.602	-69.932	13.164
4200	19.826	115.443	97.462	75.524	-312.192	-59.972	12.908
4300	19.829	115.910	97.885	77.506	-312.772	-49.904	12.676
4400	19.831	116.366	98.299	79.489	-313.342	-39.728	12.464
4500	19.832	116.811	98.706	81.472	-313.902	-29.448	12.272
4600	19.834	117.247	99.105	83.456	-314.452	-19.064	12.104
4700	19.836	117.674	99.495	85.439	-315.002	-8.576	11.956
4800	19.837	118.092	99.878	87.423	-315.542	1.916	11.828
4900	19.839	118.501	100.254	89.407	-316.072	12.164	11.716
5000	19.840	118.901	100.623	91.391	-316.602	22.312	11.616
5100	19.841	119.294	100.986	93.375	-317.122	32.372	11.524
5200	19.842	119.680	101.341	95.359	-317.632	42.344	11.436
5300	19.844	120.058	101.697	97.343	-318.132	52.228	11.352
5400	19.845	120.435	102.035	99.328	-318.622	62.024	11.272
5500	19.846	120.793	102.372	101.312	-319.102	71.732	11.196
5600	19.847	121.150	102.704	103.287	-319.572	81.352	11.124
5700	19.847	121.501	103.028	105.261	-320.032	90.884	11.056
5800	19.848	121.847	103.353	107.236	-320.482	100.328	10.992
5900	19.849	122.186	103.669	109.211	-320.922	109.684	10.932
6000	19.850	122.520	103.980	111.236	-321.352	118.948	10.876

(CRYSTAL)

CRYOLITE (Na<sub>3</sub>AlF<sub>6</sub>)

$\Delta H_f^0 = -787.0 \pm 2.0$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -790.0 \pm 2.0$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = 2.22$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^0 = 26.71$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 57.0 \pm 0.4$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_m = 833.5^\circ\text{K}$ .  
 $T_m = 1279^\circ\text{K}$ .

Heat of Formation.

The value of  $\Delta H_f^0$  298.15 (Na<sub>3</sub>AlF<sub>6</sub>, c) adopted is a weighted average of four independent  $\Delta H_f^0$  298.15 values. They were evaluated from four different chemical reactions as follows.

Chemical Reaction

- 2AlF<sub>3</sub>(c) + 6NaF(c) = 2Na<sub>3</sub>AlF<sub>6</sub>(c)  $\Delta H_f^0$  298.15 kcal. mole<sup>-1</sup> -40.7
- Al(c) + 2.96 NaCl(c) + 5.96 (H<sub>2</sub>O)(sol) + 3.617 H<sub>2</sub>O(l)  $\Delta H_f^0$  298.15 kcal. mole<sup>-1</sup> -788.8 ± 0.7  
 = Na<sub>2</sub>.96AlF<sub>5</sub>.96(c) + 2.96 (HCl.12.731 H<sub>2</sub>O)(sol) + 3/2 H<sub>2</sub>O(l) -153.22 ± 0.14
- 3/2 PbF<sub>2</sub>(c) + Al(c) + 3NaF(c) = 3/2 Pb(c) + Na<sub>3</sub>AlF<sub>6</sub>(c)  $\Delta H_f^0$  298.15 kcal. mole<sup>-1</sup> -138.3 ± 0.1
- 2/3 Na<sub>3</sub>AlF<sub>6</sub>(c) + H<sub>2</sub>O(g) = 1/3 Al<sub>2</sub>O<sub>3</sub>(c) + 2HF(g) + 2NaF(c)  $\Delta H_f^0$  298.15 kcal. mole<sup>-1</sup> 46.32 ± 0.2\*  
 -788.7 ± 0.3

\*This is the third law value. The second law value is 48.34 ± 0.75 kcal. mole<sup>-1</sup>.

1. E. Baud, Ann. Chim. Phys. 1, 8 (1904).

2. J. P. Coughlin, J. Am. Chem. Soc. 80, 1802 (1958). The listed  $\Delta H_f^0$  298.15 value was recalculated from the reported value, -784.8 kcal. mole<sup>-1</sup>, by using recent values of  $\Delta H_f^0$  298.15 for HF(sol.) and HCl(sol.) obtained from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, National Bureau of Standards Technical Note 270-1, October 1, 1965, Washington, D.C.

3. P. Gross, C. Hayman and D. L. Levi "Physical Chemistry of Process Metallurgy", Part II, Interscience Publishers, Inc., New York, 1961, using  $\Delta H_f^0$  298.15 (PbF<sub>2</sub>, c) = -161.8 ± 1.2 kcal. mole<sup>-1</sup>.

4. V. P. Mashovets and B. F. Udin, Izv. Vysshikh Uchebn. Zavedeni, Tsvetn. Met. 5, 95 (1962).

The value of  $\Delta H_f^0$  298.15 for Na<sub>3</sub>AlF<sub>6</sub>(c) is selected as -790.0 ± 2.0 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The low temperature heat capacities, 51-298°K., were measured by E. G. King, J. Am. Chem. Soc. 79, 2056 (1957). The high temperature enthalpies were measured by C. J. O'Brien and K. K. Kelley, J. Am. Chem. Soc. 79, 5616 (1957) and later corrected by W. B. Frank, J. Phys. Chem. 65, 2081 (1961). The corrected values were used. These two sets of data were plotted and joined smoothly at 298°K.  $S_{298.15}^0$  was reported by E. G. King, loc. cit., using  $S_{51}^0$  (extrap.) = 4.12 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Transition Data.

$T_m$  and  $\Delta H_m^0$  were obtained from W. B. Frank, loc. cit., which were derived from the related data reported by C. J. O'Brien and K. K. Kelley, loc. cit. The transition temperatures measured by other investigators were also reviewed by W. B. Frank, loc. cit.

Melting Data.

$T_m$  and  $\Delta H_m^0$  were reported by W. B. Frank, loc. cit. This phase transformation at 1279°K. does not represent true melting of solid to pure liquid cryolite, but a transformation from β-cryolite to a liquid solution of cryolite and its dissociation products. The melting temperatures determined by other investigators were also reviewed by W. B. Frank, loc. cit.

T, °K.	C <sub>p</sub>	S°	-(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	40.0	INFINITE	94.106	-787.059	-787.059		INFINITE
100	24.873	14.898	96.216	-784.236	-776.645		1697.276
200	42.860	35.590	61.470	-4.676	-790.083		834.411
298	51.650	57.000	57.000	0.000	-790.000		550.210
300	51.740	57.320	57.001	0.096	-789.993		546.638
400	56.550	72.591	59.096	5.538	-791.492		402.716
500	61.250	86.117	63.215	-1.451	-795.854		316.260
600	64.800	97.601	68.009	17.755	-789.868		258.681
700	67.850	107.826	72.880	44.392	-788.587		217.612
800	70.480	117.596	77.024	71.333	-787.046		186.866
900	72.720	127.048	82.032	97.335	-785.504		163.060
1000	74.680	135.611	87.780	122.423	-784.666		143.991
1100	76.415	143.410	92.390	146.473	-782.967		128.419
1200	77.920	150.852	96.757	169.591	-782.637		113.222
1300	79.240	158.152	100.977	191.763	-782.655		98.352
1400	80.420	165.488	105.083	213.083	-784.356		83.166
1500	81.470	172.866	109.006	233.676	-784.876		68.397
1600	82.400	179.289	112.810	253.521	-783.776		54.178
1700	83.220	184.868	116.498	272.729	-782.505		40.522
1800	83.950	190.607	120.086	291.307	-781.149		27.412
1900	84.590	196.500	123.581	309.266	-779.709		14.847
2000	85.150	202.643	126.994	326.637	-778.198		2.894
2100	85.630	209.143	130.330	343.438	-776.644		0.560
2200	86.030	215.996	133.596	359.684	-775.000		
2300	86.350	223.209	136.799	375.497	-773.391		
2400	86.600	230.783	139.943	390.876	-771.824		
2500	86.780	238.624	143.032	405.826	-770.241		

$\Delta H_f^0 = 21.6 \pm 5 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 52.170 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Quantum Weight

$\epsilon$ , cm. <sup>-1</sup>	$g_i$
0	2
20699.2	2
33151.0	[1]

$\omega_e x_e = 6.97 \text{ cm.}^{-1}$

$\alpha_e = 0.00579 \text{ cm.}^{-1}$

$r_e = 1.6176 \text{ \AA}$

Heat of Formation

The pressures of the dissociation  $\text{AlO(g)} = \text{Al(g)} + \text{O(g)}$  in the temperature range from 2000° to 2500°K have been measured by mass spectrometry by J. Drowart, G. DeMaris, R. P. Burns and M. G. Ingram, J. Chem. Phys., 32, 1366 (1960). Using the reported pressures the heat of dissociation of  $\text{AlO(g)}$  has been calculated by both the second law method  $D_{298}^0 \text{AlO(g)} = 115 \pm 5 \text{ kcal. mole}^{-1}$  and the third law method  $D_{298}^0 \text{AlO(g)} = 116 \text{ kcal. mole}^{-1}$ . The third law value has been adopted to derive the standard enthalpy of formation of  $\text{AlO(g)}$  at 298°K.

Other values of the dissociation energy of  $\text{AlO(g)}$  given in the literature are:

(1)  $D_0 = 127 \text{ kcal. mole}^{-1}$  based on the vapor pressure measurement of  $\text{Al}$  and  $\text{Al}_2\text{O}_3$  by the Knudsen method by L. Brewer and A. W. Search, J. Am. Chem. Soc., 73, 5306(1951).

(2)  $D_0 = 137 \text{ kcal. mole}^{-1}$ , based on the study of dissociation equilibrium in gases by L. V. Gurvich and I. V. Veits, Izvest, Akad. Nauk, S.S.R. Ser. Fiz. 22, 673 (1958).

(3)  $D_0 = 5.04 \text{ e.v. (116.2 kcal. mole}^{-1})$ , based on the Morse potential extrapolation from the spectra of  $\text{AlO(g)}$  by M. Becart and P. Declerck, Comptes Rendus 251, 2153 (1960).

The last one is in good agreement with the result obtained by Drowart and co-workers.

Heat Capacity and Entropy

The rotational and vibrational constants were obtained from ultraviolet spectrum measurement by A. Lagerqvist, N. E. L. Nilsson and R. P. Barron, Arkiv Fysik 12, 543 (1957). The  $T_e$  values of the electronic levels and their quantum weights were taken from O. Herzberg "Spectra of Diatomic Molecules" 2nd Ed., D. Van Nostrand Company, New York.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	6.097	44.660	2.101	21.631	21.631	INFINITE
200	7.052	49.298	1.605	19.659	19.659	- 12.062
298	7.391	52.170	.000	21.780	17.458	- 19.076
				15.330	13.369	- 11.265
300	7.389	52.170	.014	21.596	15.330	- 11.167
400	7.765	54.394	.772	21.402	13.271	- 7.251
500	8.066	56.161	1.564	21.202	11.261	- 4.922
600	8.288	57.652	2.392	20.986	9.293	- 3.385
700	8.448	58.943	3.220	20.748	7.362	- 2.298
800	8.567	60.079	4.071	20.484	5.467	- 1.494
900	8.657	61.093	4.932	20.191	3.609	- .876
1000	8.727	62.009	5.801	17.375	1.968	- .430
1100	8.783	62.844	6.677	17.131	.438	- .087
1200	8.828	63.610	7.568	16.888	- 1.059	.195
1300	8.866	64.318	8.442	16.644	- 2.555	.430
1400	8.898	64.976	9.331	16.400	- 4.022	.628
1500	8.926	65.591	10.222	16.156	- 5.473	.797
1600	8.950	66.168	11.116	15.911	- 6.907	.943
1700	8.972	66.711	12.012	15.666	- 8.325	1.070
1800	8.991	67.225	12.910	15.420	- 9.731	1.181
1900	9.009	67.711	13.810	15.172	- 11.119	1.279
2000	9.026	68.174	14.712	14.924	- 12.498	1.366
2100	9.042	68.615	15.615	14.675	- 13.864	1.443
2200	9.057	69.036	16.520	14.426	- 15.217	1.511
2300	9.070	69.438	17.426	14.172	- 16.557	1.573
2400	9.084	69.825	18.334	13.919	- 17.888	1.629
2500	9.097	70.196	19.243	13.668	- 19.209	1.679
2600	9.110	70.553	20.153	13.408	- 20.519	1.725
2700	9.123	70.897	21.063	13.151	- 21.819	1.766
2800	9.135	71.229	21.978	12.892	- 23.104	1.803
2900	9.148	71.550	22.892	12.632	- 24.377	1.836
3000	9.161	71.860	23.807	12.377	- 25.641	1.865
3100	9.174	72.161	24.724	12.124	- 26.896	1.890
3200	9.186	72.452	25.642	11.872	- 28.142	1.911
3300	9.197	72.735	26.562	11.620	- 29.379	1.928
3400	9.206	73.010	27.483	11.368	- 30.606	1.942
3500	9.213	73.277	28.405	11.116	- 31.824	1.953
3600	9.219	73.537	29.329	10.864	- 33.033	1.961
3700	9.224	73.791	30.254	10.612	- 34.233	1.966
3800	9.229	74.038	31.181	10.360	- 35.424	1.969
3900	9.232	74.280	32.110	10.108	- 36.606	1.971
4000	9.234	74.515	33.040	9.856	- 37.779	1.972
4100	9.236	74.745	33.973	9.604	- 38.943	1.973
4200	9.237	74.970	34.907	9.352	- 40.098	1.974
4300	9.238	75.191	35.843	9.100	- 41.244	1.974
4400	9.239	75.406	36.781	8.848	- 42.381	1.974
4500	9.240	75.618	37.721	8.596	- 43.509	1.974
4600	9.241	75.825	38.664	8.344	- 44.628	1.974
4700	9.242	76.029	39.608	8.092	- 45.738	1.974
4800	9.243	76.227	40.555	7.840	- 46.839	1.974
4900	9.244	76.421	41.504	7.588	- 47.931	1.974
5000	9.245	76.611	42.455	7.336	- 49.014	1.974
5100	9.246	76.804	43.409	7.084	- 50.088	1.974
5200	9.247	77.000	44.365	6.832	- 51.153	1.974
5300	9.248	77.192	45.324	6.580	- 52.209	1.974
5400	9.249	77.381	46.284	6.328	- 53.256	1.974
5500	9.250	77.567	47.248	6.076	- 54.294	1.974
5600	9.251	77.750	48.215	5.824	- 55.323	1.974
5700	9.252	77.931	49.184	5.572	- 56.343	1.974
5800	9.253	78.109	50.155	5.320	- 57.354	1.974
5900	9.254	78.284	51.130	5.068	- 58.356	1.974
6000	9.255	78.456	52.106	4.816	- 59.349	1.974

$\Delta H_f^0 = -31.0 \pm 7 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -31.4 \pm 7 \text{ kcal. mole}^{-1}$

Point Group  $C_{2v}$   
 $S_{298.15} = 82.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_j, \text{ cm.}^{-1}$
715 (1)
984 (1)

Bond Distance: Al-O = 1.66 Å  
 Bond Angle: Al-O-Al = 145°

Product of the Moments of Inertia:  $I_A I_B I_C = 263.2477 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

$C_p = 2$

Heat of Formation

The value of  $\Delta H_f^{298}$  = -31.4 ± 7 kcal. mole<sup>-1</sup> for Al<sub>2</sub>O(g) was calculated from  $\Delta H_f^{298}$  = 247 ± 7 kcal. mole<sup>-1</sup> for the reaction Al<sub>2</sub>O(g) = 2Al(g) + O(g) and  $\Delta H_f^{298}$  = 131 ± 7 kcal. mole<sup>-1</sup> for the reaction Al<sub>2</sub>O(g) = AlO(g) + Al(g). The values of  $\Delta H_f^{298}$  were obtained by the third law method, using the partial pressure data reported by J. Brewster, G. DeMaris, R. Burns and M. Ingraham, *J. Chem. Phys.*, **32**, 1366 (1960). (The second law values which are in poor agreement with the third law values, are  $\Delta H_f^{298}$  = 271 ± 10 kcal. mole<sup>-1</sup> and  $\Delta H_f^{298}$  = 154 ± 10 kcal. mole<sup>-1</sup>, respectively.) L. Brewer and A. Seary, *J. Am. Chem. Soc.*, **73**, 5308 (1951), reported that under reducing conditions, Al<sub>2</sub>O<sub>3</sub> vaporizes mostly to Al<sub>2</sub>O(g), but under neutral condition AlO(g) and O(g) are the major products. Brewer and Seary also measured the vapor pressures of the Al-Al<sub>2</sub>O<sub>3</sub> system by Knudsen effusion method, and obtained the heat of formation of Al<sub>2</sub>O(g) from gaseous atoms as  $\Delta H_f^{298}$  = -248 kcal. mole<sup>-1</sup>. This value leads the heat of formation of Al<sub>2</sub>O(g),  $\Delta H_f^{298}$  = -32.4 ± 7, which agrees with the value selected.

Other references appearing in the recent literature were:

1. Leo Brewer, AEC Report UCRL-8356 (1958).
2. G. DeMaris, J. Drowart, M. Ingraham, *J. Chem. Phys.*, **30**, 318 (1959).
3. R. Porter, P. Shisael and M. Ingraham, *J. Chem. Phys.*, **23**, 339 (1955).
4. R. J. Ackerman and R. J. Thorn, *J. Am. Chem. Soc.*, **78**, 4183 (1956).
5. C. N. Cochrane, *J. Am. Chem. Soc.*, **77**, 2190 (1955).
6. M. Cook, A. Piller, R. Keyes, W. Partridge and W. Ursebach, *J. Phys. Chem.*, **61**, 189 (1957)

Heat Capacity and Entropy

The matrix isolation of high temperature vapors for the investigation of the infrared spectrum of Al<sub>2</sub>O has been used to determine the bond distance, angle and vibrational frequencies by M. Linevsky, D. White and D. Mann, *J. Chem. Phys.*, **41**, 542 (1964). These reported data have been adopted in this table. The symmetric structure Al-O-Al instead of Al-Al-O for Al<sub>2</sub>O(g) was chosen for two reasons: (1) The dissociation energy of Al<sub>2</sub>O(g),  $D_{298} = 247 \pm 7 \text{ kcal/mole}$ , is approximately twice the dissociation energy of AlO(g),  $D_{298} = 115 \pm 5 \text{ kcal. mole}^{-1}$ , which implies that the symmetric structure is more reasonable. (2) The dissociation energy of Al<sub>2</sub>O(g) has been estimated to be only 39 kcal. mole<sup>-1</sup> by J. Drowart and R. Honig, *J. Phys. Chem.*, **61**, 980 (1957). This implies that the Al-O bond energy in "Al-Al-O" structure would be as large as 208 kcal. mole<sup>-1</sup> if Al-Al = 39 kcal. mole<sup>-1</sup>. Therefore Al<sub>2</sub>O(g) must have a symmetric structure. Linevsky et al., loc. cit., have also concluded the bent symmetric structure (instead of a linear one) and the calculated  $\omega_2$  from the observed infrared spectra and the re-analysis of the ultraviolet spectra. The three principal moments of inertia are  $I_A = 0.5105 \times 10^{-35} \text{ g. cm.}^2$ ,  $I_B = 22.4539 \times 10^{-35} \text{ g. cm.}^2$  and  $I_C = 22.9844 \times 10^{-35} \text{ g. cm.}^2$

Drowart, et al. (loc. cit.), also postulated a bent symmetric molecule for Al<sub>2</sub>O(g), and estimated the bond distance Al-O = [1.6176] Å and angle Al-O-Al = [110]° and the vibrational frequencies as [1079] cm<sup>-1</sup>, [351] cm<sup>-1</sup> and [921] cm<sup>-1</sup>.

The National Bureau of Standards Report No. 6644 "Preliminary Report on the Thermodynamic Properties of Li, Be, Mg, Al and Their Compounds with Hydrogen, Oxygen, Nitrogen, Fluorine and Chlorine" July, 1959, has proposed a trigonal structure for Al<sub>2</sub>O(g) with bond distance Al-O = [1.87] Å, and Al-Al = [2.0] Å. Its vibration frequencies were estimated as [450] cm<sup>-1</sup>, [1000] cm<sup>-1</sup> and [1000] cm<sup>-1</sup>.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	8.767	51.379	70.943	-2.777	30.951	30.951	INFINITE
200	9.965	57.818	67.832	-1.959	30.702	33.433	73.065
298	10.916	61.966	61.966	-1.023	30.990	36.101	39.448
				0.000	31.400	38.534	28.244
300	10.934	62.433	61.940	0.200	31.408	38.578	28.103
400	11.749	65.297	62.405	1.157	31.821	40.904	22.348
500	12.321	67.984	63.240	2.362	32.236	43.128	18.850
600	12.711	70.224	64.262	3.615	32.672	45.266	16.487
700	12.982	72.028	65.248	4.900	33.150	47.329	14.776
800	13.174	73.594	66.234	6.208	33.673	49.319	13.473
900	13.314	75.555	67.184	7.533	34.249	51.240	12.442
1000	13.418	76.963	68.093	8.870	34.870	52.725	11.522
1100	13.498	78.246	68.959	10.216	40.343	53.988	10.726
1200	13.561	79.423	69.782	11.569	40.814	55.207	10.054
1300	13.610	80.511	70.566	12.928	41.284	56.389	9.479
1400	13.650	81.521	71.313	14.291	41.753	57.533	8.981
1500	13.682	82.464	72.025	15.657	42.222	58.644	8.544
1600	13.709	83.347	72.706	17.027	42.691	59.721	8.157
1700	13.731	84.179	73.356	18.399	43.159	60.772	7.812
1800	13.750	84.965	73.980	19.773	43.630	61.796	7.503
1900	13.766	85.709	74.578	21.149	44.102	62.791	7.222
2000	13.780	86.415	75.152	22.526	44.574	63.762	6.967
2100	13.792	87.088	75.704	23.905	45.048	64.712	6.734
2200	13.807	87.730	76.236	25.285	45.524	65.637	6.520
2300	13.812	88.343	76.750	26.665	46.002	66.539	6.322
2400	13.820	88.931	77.245	28.047	46.481	67.421	6.139
2500	13.827	89.496	77.724	29.429	46.963	68.285	5.969
2600	13.833	90.038	78.187	30.812	47.446	69.130	5.811
2700	13.838	90.560	78.632	32.196	47.931	69.952	5.662
2800	13.843	91.063	79.071	33.580	48.417	70.752	5.525
2900	13.848	91.549	79.495	34.965	48.904	71.528	5.395
3000	13.852	92.019	79.902	36.350	49.392	72.281	5.270
3100	13.856	92.473	80.301	37.735	49.881	73.012	5.150
3200	13.859	92.913	80.688	39.120	50.372	73.724	5.034
3300	13.862	93.340	81.065	40.507	50.864	74.417	4.921
3400	13.865	93.754	81.432	41.893	51.358	75.092	4.811
3500	13.868	94.155	81.790	43.280	51.851	75.749	4.704
3600	13.870	94.546	82.139	44.667	52.345	76.387	4.600
3700	13.872	94.926	82.479	46.054	52.840	77.007	4.500
3800	13.874	95.299	82.812	47.441	53.336	77.609	4.404
3900	13.876	95.657	83.136	48.829	53.833	78.194	4.311
4000	13.878	96.008	83.454	50.216	54.331	78.764	4.220
4100	13.879	96.351	83.764	51.604	54.830	79.317	4.131
4200	13.881	96.688	84.068	52.992	55.330	79.854	4.044
4300	13.882	97.012	84.365	54.380	55.830	80.374	3.959
4400	13.883	97.331	84.656	55.768	56.330	80.878	3.875
4500	13.885	97.643	84.941	57.157	56.830	81.366	3.792
4600	13.886	97.948	85.221	58.546	57.330	81.837	3.710
4700	13.887	98.247	85.495	59.934	57.830	82.292	3.629
4800	13.888	98.539	85.764	61.323	58.330	82.727	3.549
4900	13.889	98.825	86.027	62.712	58.830	83.146	3.470
5000	13.890	99.106	86.286	64.100	59.330	83.549	3.392
5100	13.890	99.381	86.540	65.489	59.830	83.937	3.316
5200	13.891	99.651	86.790	66.879	60.330	84.311	3.241
5300	13.891	99.915	87.035	68.268	60.830	84.671	3.167
5400	13.893	100.175	87.276	69.657	61.330	85.018	3.093
5500	13.893	100.430	87.513	71.046	61.830	85.352	3.020
5600	13.894	100.680	87.745	72.436	62.330	85.673	2.947
5700	13.894	100.926	87.975	73.825	62.830	85.981	2.874
5800	13.895	101.168	88.200	75.214	63.330	86.276	2.801
5900	13.896	101.405	88.422	76.604	63.830	86.559	2.728
6000	13.896	101.639	88.640	77.994	64.330	86.829	2.655

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

T, K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	9.017	52.453	2.100	95.666	95.666	INFINITE
200	10.510	63.695	4.000	96.525	97.344	210.945
298	12.496	69.136	6.372	97.000	97.344	106.106
300	12.534	69.136	6.372	97.012	97.346	71.351
400	14.394	76.643	8.210	97.567	97.370	70.913
500	15.780	81.118	9.812	98.039	97.266	53.198
600	16.758	83.062	10.856	98.476	97.070	42.513
700	17.447	83.695	11.451	98.816	96.802	35.356
800	17.941	84.023	11.798	99.076	96.468	30.221
900	18.304	84.118	12.017	99.276	96.074	26.353
1000	18.576	84.062	12.149	99.426	95.674	23.329
1100	18.785	84.862	13.525	99.529	95.255	20.817
1200	18.948	85.484	15.412	99.579	94.821	18.719
1300	19.078	85.968	17.313	99.585	94.375	16.965
1400	19.182	86.324	19.226	99.559	93.920	15.476
1500	19.268	86.561	21.149	99.509	93.455	14.196
1600	19.339	86.696	23.080	99.439	92.980	13.082
1700	19.398	86.741	25.016	99.349	92.495	12.104
1800	19.448	86.696	26.959	99.239	91.999	11.259
1900	19.490	86.561	28.906	99.109	91.494	10.498
2000	19.527	86.334	30.857	98.959	90.979	9.775
2100	19.558	86.016	32.811	98.789	90.454	9.150
2200	19.585	85.609	34.768	98.599	89.919	8.582
2300	19.609	85.124	36.728	98.389	89.374	8.064
2400	19.631	84.569	38.693	98.159	88.819	7.590
2500	19.649	84.044	40.654	97.909	88.254	7.154
2600	19.666	83.549	42.620	97.639	87.679	6.751
2700	19.681	83.084	44.587	97.349	87.094	6.379
2800	19.694	82.649	46.556	97.039	86.509	6.032
2900	19.706	82.244	48.526	96.709	85.914	5.714
3000	19.717	81.869	50.497	96.359	85.319	5.426
3100	19.727	81.524	52.469	96.009	84.724	5.166
3200	19.736	81.209	54.442	95.649	84.129	4.934
3300	19.744	80.924	56.416	95.279	83.534	4.726
3400	19.751	80.669	58.391	94.909	82.939	4.544
3500	19.758	80.444	60.366	94.539	82.344	4.386
3600	19.764	80.249	62.343	94.169	81.749	4.254
3700	19.770	80.084	64.319	93.799	81.154	4.146
3800	19.775	80.009	66.296	93.429	80.559	4.058
3900	19.780	80.009	68.274	93.059	79.964	3.986
4000	19.785	80.009	70.252	92.689	79.369	3.926
4100	19.789	80.009	72.231	92.319	78.774	3.876
4200	19.793	80.009	74.210	91.949	78.179	3.836
4300	19.796	80.009	76.189	91.579	77.584	3.806
4400	19.800	80.009	78.168	91.209	76.989	3.786
4500	19.803	80.009	80.147	90.839	76.394	3.776
4600	19.806	80.009	82.126	90.469	75.799	3.776
4700	19.809	80.009	84.105	90.109	75.204	3.786
4800	19.812	80.009	86.084	89.739	74.609	3.806
4900	19.814	80.009	88.063	89.369	74.014	3.836
5000	19.816	80.009	90.042	89.009	73.419	3.876
5100	19.818	80.009	92.021	88.639	72.824	3.926
5200	19.820	80.009	94.000	88.269	72.229	3.986
5300	19.822	80.009	95.979	87.909	71.634	4.056
5400	19.824	80.009	97.958	87.539	71.039	4.136
5500	19.826	80.009	99.937	87.169	70.444	4.226
5600	19.828	80.009	101.916	86.809	69.849	4.326
5700	19.829	80.009	103.895	86.439	69.254	4.436
5800	19.831	80.009	105.874	86.069	68.659	4.556
5900	19.832	80.009	107.853	85.709	68.064	4.686
6000	19.833	80.009	109.832	85.339	67.469	4.826

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

ALUMINUM MONOXIDE, DIMERIC ((AlO)<sub>2</sub>) (IDEAL GAS)

MOL. WT. = 85.9618

Point Group [V<sub>h</sub>] ΔH<sub>f</sub><sup>0</sup> = -95.7 ± 7 kcal. mole<sup>-1</sup>  
 S<sup>0</sup><sub>298.15</sub> = [63.7] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 ΔH<sub>f</sub><sup>0</sup> 298.15 = -97.0 ± 7 kcal. mole<sup>-1</sup>

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

(ω) <sub>v</sub> , cm. <sup>-1</sup>	(ω) <sub>v</sub> , cm. <sup>-1</sup>
[200] [1]	[930] [1]
[600] [1]	[1000] [1]
[930] [1]	[1000] [1]

Bond Distance: Al-O = [1.60] Å

Bond Angle: Al-O-Al = [90]°, O-Al-O = [90]°

Products of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [1.4246 X 10<sup>-114</sup>] g.<sup>3</sup> cm.<sup>6</sup>

σ = [4]

Heat of Formation.

The value of ΔH<sub>f</sub><sup>0</sup> 298 = -97 ± 7 kcal. mole<sup>-1</sup> for Al<sub>2</sub>O<sub>2</sub>(g) was calculated from ΔH<sub>f</sub><sup>0</sup> 298 = 372 ± 7 kcal. mole<sup>-1</sup> for the reaction Al<sub>2</sub>O<sub>2</sub>(g) = 2Al(g) + O<sub>2</sub>(g). The value of ΔH<sub>f</sub><sup>0</sup> 298 was obtained by the third law method, using the partial pressure data reported by J. Drowart, G. deMaris, R. Burns and M. Inghram, J. Chem. Phys. 32, 1366 (1960). (The second law value for ΔH<sub>f</sub><sup>0</sup>, which is in poor agreement with the third law value, is 451 ± 25 kcal. mole<sup>-1</sup>.)

Heat Capacity and Entropy.

The molecular structure (plane cyclic model) and vibrational frequencies of Al<sub>2</sub>O<sub>2</sub>(g) were obtained from Drowart, et al., J. Chem. Phys., 32, 1366 (1960). The bond distance Al-O in Al<sub>2</sub>O<sub>2</sub> was assumed to be the same as that in AlO (g). The three principal moments of inertia are I<sub>A</sub> = 6.8005 X 10<sup>-59</sup>, I<sub>B</sub> = 11.4674 X 10<sup>-59</sup> and I<sub>C</sub> = 18.2679 X 10<sup>-59</sup> g. cm.<sup>2</sup>

The configuration was proposed by Drowart, et al., instead of the alternate linear structure OAl-AlO for the reason discussed below. The OB-BO bond  $\nu_2$  compares to the B<sub>2</sub> dissociation energy  $\nu_4$  in the same way as the NC-CN bond compares to the C-C single bond. However, for Al<sub>2</sub>O<sub>2</sub>(g), the relationship between OAl-AlO and Al<sub>2</sub> would be quite different.

- References (1) M. Inghram, R. Porter and W. Chupka, J. Chem. Phys., 25, 498 (1956).  
 (2) D. White, P. Walsh and D. Mann, J. Chem. Phys., 28, 508 (1958).  
 (3) T. L. Cottrell, "The Strength of Chemical Bonds", Butterworths Scientific Publications, London (1958).  
 (4) G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., (1950).

T, °K.	C <sub>p</sub>	S°	-(F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0							
100	10.833	12.550	174.550	0.000	-396.000	-373.790	273.982
200	10.548	12.560	124.560	0.037	-396.037	-373.652	272.193
300	10.315	12.573	134.573	2.264	-396.052	-369.184	260.164
400	10.112	12.585	144.585	4.799	-396.066	-366.736	156.796
500	9.933	12.596	154.596	7.545	-396.070	-365.337	127.968
600	9.777	12.606	164.606	10.428	-396.074	-364.981	107.394
700	9.633	12.615	174.615	13.407	-396.076	-364.766	91.977
800	9.500	12.623	184.623	16.458	-396.076	-364.670	79.996
900	9.377	12.630	194.630	19.565	-396.074	-364.683	70.338
1000	9.263	12.635	204.635	22.711	-396.070	-364.722	62.407
1100	9.158	12.639	214.639	25.991	-396.061	-364.783	55.805
1200	9.061	12.642	224.642	29.413	-396.048	-364.864	50.223
1300	8.971	12.644	234.644	32.878	-396.032	-364.964	45.444
1400	8.887	12.645	244.645	36.381	-396.014	-365.081	41.308
1500	8.809	12.645	254.645	39.916	-396.000	-365.212	37.693
1600	8.736	12.644	264.644	43.484	-396.000	-365.356	34.507
1700	8.668	12.642	274.642	47.081	-396.000	-365.512	31.679
1800	8.604	12.639	284.639	50.706	-396.000	-365.678	29.152
1900	8.544	12.635	294.635	54.356	-396.000	-365.854	26.882
2000	8.487	12.630	304.630	58.031	-396.000	-366.040	24.830
2100	8.433	12.624	314.624	61.728	-396.000	-366.236	22.968
2200	8.381	12.617	324.617	65.446	-396.000	-366.442	21.271
2300	8.330	12.609	334.609	69.184	-396.000	-366.658	19.717
2400	8.280	12.600	344.600	72.941	-396.000	-366.884	18.291
2500	8.231	12.590	354.590	76.716	-396.000	-367.120	16.976
2600	8.183	12.579	364.579	80.506	-396.000	-367.366	15.761
2700	8.136	12.567	374.567	84.311	-396.000	-367.622	14.595
2800	8.090	12.554	384.554	88.131	-396.000	-367.888	13.485
2900	8.045	12.540	394.540	91.966	-396.000	-368.164	12.425
3000	8.001	12.525	404.525	95.816	-396.000	-368.450	11.413

ΔH<sub>f</sub><sup>o</sup> = Unknown

ΔH<sub>f</sub><sup>o</sup> 298.15 = [-396.0 ± 0.5] kcal. mole<sup>-1</sup>

ΔH<sub>m</sub><sup>o</sup> = [20.9] kcal. mole<sup>-1</sup>

S<sub>298.15</sub><sup>o</sup> = [12.55] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = 2323°K.

Heat of Formation.

The enthalpy change (ΔH<sub>f</sub><sup>o</sup>) for the transition Al<sub>2</sub>O<sub>3</sub>(γ, c) → Al<sub>2</sub>O<sub>3</sub>(α, c) has been determined by (1) V. Kostomarov and M. Rey, *Silicates Ind.* 29, 9 (1963); and (2) T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.* 68, 3246 (1964). The results obtained are presented in the table. The enthalpies of solution for Al<sub>2</sub>O<sub>3</sub>(γ, c) and Al(c) in 2N KOH(aq.) have been measured by (3) K. K. Kelley, C. H. Shomate, F. E. Young, B. F. Naylor, A. E. Salo and E. H. Huffman, *U. S. Bur. Mines Tech. Rept.* 688 (1946). Based on their reported values, -16.13 ± 1.0 and -196.02 ± 0.25 kcal. mole<sup>-1</sup>, respectively, the heat of formation (ΔH<sub>f</sub><sup>o</sup> 298.15) for Al<sub>2</sub>O<sub>3</sub>(γ, c) was evaluated to be -384.84 ± 1.1 kcal. mole<sup>-1</sup>. Hence, the enthalpy of transition (γ → α) was calculated as -15.6 ± 1.1 kcal. mole<sup>-1</sup>, using ΔH<sub>f</sub><sup>o</sup> 298.15 (Al<sub>2</sub>O<sub>3</sub>, α, c) = -400.4 kcal. mole<sup>-1</sup>.

Source	Method	Temperature, °K.	ΔH <sub>f</sub> <sup>o</sup> , kcal. mole <sup>-1</sup>	ΔH <sub>f</sub> <sup>o</sup> 298.15, kcal. mole <sup>-1</sup>
(2)	solution calorimetry	978	-5.3	-4.4
(1)	differential thermal analysis	1473	-11.0	-9.4
(3)	solution calorimetry	298.15	-15.6	-15.6

The heat of formation for Al<sub>2</sub>O<sub>3</sub>(γ, c) was calculated from that for Al<sub>2</sub>O<sub>3</sub>(α, c) and the ΔH<sub>f</sub><sup>o</sup> value reported by Yokokawa and Kleppa, loc. cit., which was arbitrarily selected.

Heat Capacity and Entropy.

The heat capacities were assumed to be larger than those for Al<sub>2</sub>O<sub>3</sub>(α, c) by 5% at each temperature. The value of S<sub>298.15</sub> was estimated such that at T<sub>m</sub>, ΔH<sub>f</sub><sup>o</sup> (Al<sub>2</sub>O<sub>3</sub>, γ, c) > ΔH<sub>f</sub><sup>o</sup> (Al<sub>2</sub>O<sub>3</sub>, α, c).

Melting Data.

T<sub>m</sub> was reported by M. Plummer, *J. Appl. Chem.* 8, 35 (1958). The difference between ΔH<sub>f</sub><sup>o</sup> for Al<sub>2</sub>O<sub>3</sub>(γ, c) and Al<sub>2</sub>O<sub>3</sub>(l) at T<sub>m</sub> is ΔH<sub>m</sub><sup>o</sup>.



T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	9.325	68.192	3.017	20.854	20.854	20.854	INFINITE
200	10.922	70.885	2.170	24.249	24.249	24.249	53.249
298	12.726	73.817	1.162	21.605	21.605	21.605	30.027
		69.817	∞	25.000	25.000	25.000	21.915
300	12.757	69.896	∞	25.021	25.021	25.021	21.802
400	14.209	73.776	1.376	32.578	32.578	32.578	16.403
500	15.247	77.065	2.852	32.747	32.747	32.747	12.835
600	16.006	79.915	4.416	32.896	32.896	32.896	10.444
700	16.589	82.428	6.047	33.025	33.025	33.025	8.729
800	17.054	84.675	7.501	33.136	33.136	33.136	7.438
900	17.434	86.706	8.855	33.231	33.231	33.231	6.431
1000	17.748	88.560	11.214	33.316	33.316	33.316	5.623
1100	18.011	90.264	13.003	33.396	33.396	33.396	4.960
1200	18.231	91.841	14.815	33.473	33.473	33.473	4.407
1300	18.418	93.308	16.648	33.551	33.551	33.551	3.937
1400	18.577	94.678	18.498	33.631	33.631	33.631	3.533
1500	18.713	95.965	20.363	33.718	33.718	33.718	3.183
1600	18.830	97.176	22.240	33.812	33.812	33.812	2.876
1700	18.931	98.321	24.128	33.912	33.912	33.912	2.604
1800	19.018	99.406	26.026	34.019	34.019	34.019	2.361
1900	19.095	100.436	27.931	34.132	34.132	34.132	2.143
2000	19.162	101.417	29.844	34.249	34.249	34.249	1.947
2100	19.221	102.354	31.763	34.371	34.371	34.371	1.768
2200	19.273	103.249	33.688	34.498	34.498	34.498	1.605
2300	19.319	104.107	35.618	34.630	34.630	34.630	1.456
2400	19.361	104.930	37.552	34.768	34.768	34.768	1.319
2500	19.398	105.721	39.490	40.297	40.297	40.297	1.182
2600	19.431	106.482	41.431	40.336	40.336	40.336	1.046
2700	19.460	107.216	42.576	40.378	40.378	40.378	0.923
2800	19.486	107.924	43.733	40.423	40.423	40.423	0.803
2900	19.512	108.609	44.903	40.470	40.470	40.470	0.693
3000	19.534	109.271	46.082	41.003	41.003	41.003	0.590
3100	19.555	109.911	47.269	41.149	41.149	41.149	0.494
3200	19.573	110.533	48.467	41.296	41.296	41.296	0.403
3300	19.589	111.135	49.676	41.445	41.445	41.445	0.317
3400	19.606	111.720	50.895	41.595	41.595	41.595	0.236
3500	19.620	112.289	52.127	41.748	41.748	41.748	0.162
3600	19.633	112.842	53.372	41.903	41.903	41.903	0.087
3700	19.646	113.380	54.627	42.059	42.059	42.059	0.019
3800	19.657	113.904	55.893	42.218	42.218	42.218	0.047
3900	19.668	114.415	57.167	42.380	42.380	42.380	0.109
4000	19.677	114.913	58.441	42.544	42.544	42.544	0.186
4100	19.686	115.399	59.716	42.710	42.710	42.710	0.266
4200	19.695	115.873	60.991	42.877	42.877	42.877	0.350
4300	19.703	116.337	62.266	43.045	43.045	43.045	0.438
4400	19.710	116.790	63.539	43.214	43.214	43.214	0.530
4500	19.717	117.233	64.816	43.384	43.384	43.384	0.626
4600	19.724	117.666	66.094	43.555	43.555	43.555	0.726
4700	19.730	118.090	67.372	43.727	43.727	43.727	0.830
4800	19.735	118.506	68.650	43.900	43.900	43.900	0.938
4900	19.741	118.913	69.928	44.074	44.074	44.074	1.050
5000	19.746	119.312	71.206	44.249	44.249	44.249	1.166
5100	19.751	119.703	72.484	44.425	44.425	44.425	1.286
5200	19.755	120.086	73.762	44.602	44.602	44.602	1.410
5300	19.759	120.463	75.040	44.779	44.779	44.779	1.538
5400	19.763	120.832	76.318	44.957	44.957	44.957	1.670
5500	19.767	121.195	77.596	45.135	45.135	45.135	1.806
5600	19.771	121.551	78.874	45.314	45.314	45.314	1.946
5700	19.774	121.901	80.152	45.493	45.493	45.493	2.090
5800	19.778	122.245	81.430	45.672	45.672	45.672	2.238
5900	19.781	122.583	82.708	45.852	45.852	45.852	2.390
6000	19.784	122.915	83.986	46.032	46.032	46.032	2.546

Mar. 31, 1966

MOL. WT. = 171.63697

(IDEAL GAS)

BORON DIBROMIDE HYDRIDE (BBr<sub>2</sub>H)

Point Group C<sub>2v</sub>

S<sub>298.15</sub> = [69.82] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm. <sup>-1</sup>	ω, cm. <sup>-1</sup>
2600 (1)	1044 (1)
[532](1)	775 (1)
[158](1)	783 (1)

Bond Distance : B-H = 1.20 Å B-Br = [1.87] Å

Bond Angle: Br-B-Br = 119.3 ± 2° Br-B-H = 120.3 ± 1°

σ = 2

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 1.08645 X 10<sup>-113</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The value of ΔH<sub>f</sub>° 298.15 (BBr<sub>2</sub>H, g) was derived by assuming the B-H bond strength to be 92 kcal. mole<sup>-1</sup>, the same as that in BCl<sub>2</sub>H(g).

Heat Capacity and Entropy.

The molecular structure, B-H bond distance and bond angle were obtained from L. Lynds and C. D. Bass, J. Chem. Phys. 41, 3165 (1964). The B-Br bond distance was taken from that in BBr<sub>2</sub>(g) molecule. The vibrational frequencies adopted and corrected to the average isotopic species were assigned by O. Brieux de Mandirola and J. F. Westerkamp, Spectrochim. Acta, 21, 1101 (1965), from infrared spectrum. The values in brackets are calculated by the Wilson's FG-method. Infrared spectrum of BBr<sub>2</sub>H(g) was also reported by S. K. Watson and R. P. Porter, J. Phys. Chem. 59, 2461 (1965), and three frequencies, ν<sub>1</sub>, ν<sub>4</sub> and ν<sub>5</sub>, were assigned. The three principal moments of inertia are: I<sub>A</sub> = 6.87842 X 10<sup>-38</sup>, I<sub>B</sub> = 2.2244 X 10<sup>-39</sup> and I<sub>C</sub> = 7.10086 X 10<sup>-38</sup> g. cm.<sup>2</sup>

BBr<sub>2</sub>H

BORON DICHLORIDE HYDRIDE (BCl<sub>2</sub>H) (IDEAL GAS)

Point Group C<sub>2v</sub>  
 $\Delta H_f^\circ 0 = -58.6 \pm 1$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^\circ 298.15 = -59.3 \pm 1$  kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

( $\omega$ ), cm. <sup>-1</sup>	( $\omega$ ), cm. <sup>-1</sup>
[2810](1)	1091 (1)
744 (1)	[894](1)
[287](1)	786 (1)

Bond Distance: B-H =  $1.13 \pm 0.2$  Å B-Cl =  $[1.75]$  Å  
 Bond Angle: Cl-B-Cl =  $119.7 \pm 3^\circ$  Cl-B-H =  $120.15 \pm 1.5^\circ$   
 Product of the Moments of Inertia:  $I_A I_B I_C = 1.39215 \times 10^{-114}$  g.<sup>3</sup> cm.<sup>6</sup>

$\sigma = 2$

Heat of Formation.

The chemical equilibria for the following two reactions: (A) BCl<sub>3</sub>(g) + H<sub>2</sub>(g) = BHC1<sub>2</sub>(g) + HCl(g), and (B) 6BHC1<sub>2</sub>(g) = B<sub>2</sub>H<sub>6</sub>(g) + 4BCl<sub>3</sub>(l, g) were investigated by (1) J. H. Murib, D. Horvitz, and C. A. Bonecutter, Ind. Eng. Chem. Prod. Res. Develop. **4**, 273 (1965); (2) F. H. Mook, G. R. Seller, and E. R. Watson, "Process Development, Preplant and Pilot Plant Investigations - High Energy Boron Fuels," ASDTR 62-7-558 A, Vol. IV, March 1962; and (3) L. Lynds and C. D. Bass, Inorg. Chem. **3**, 1147 (1964). Using the reported equilibrium constants, the corresponding enthalpy changes and the respective  $\Delta H_f^\circ 298.15$  values were evaluated. The results obtained are presented as follows.

Reaction	Temperature, °K.	$\Delta H_f^\circ 298.15^\circ$ , kcal. mole <sup>-1</sup>		Reference
		Third Law Value	Second Law Value	
A	873 - 973	16.19	$15.57 \pm 0.8$	(1)
A	1073 - 1273	13.91	$13.50 \pm 3.0$	(2)
B	273	-17.85	---	(1)
B	298	-19.09	---	(3)

\*Based on the third law value of  $\Delta H_f^\circ 298.15^\circ$ .

The value of  $\Delta H_f^\circ 298.15$  for BHC1<sub>2</sub>(g) is selected as  $-59.3 \pm 1$  kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The molecular structure, B-H bond distance and Cl-B-Cl bond angle were obtained from L. Lynds and C. D. Bass, J. Chem. Phys. **40**, 1590 (1964). The B-Cl bond distance was assumed to be the same as that in BCl<sub>3</sub>(g). The vibrational frequencies adopted were reported by C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeJames, J. Chem. Phys. **40**, 3611 (1964), and corrected to the average isotopic species. It has been pointed out that the complete assignment of the infrared spectra of BHC1<sub>2</sub>(g) is quite difficult due to the unavoidable presence of BCl<sub>3</sub>(g). The adopted frequencies were obtained using the Green's function and partitioning techniques, taking HBC1<sub>2</sub> as an "isotopic" species of BCl<sub>3</sub>. An excellent agreement between the calculated and observed spectra reported by L. Lynds and C. D. Bass, loc. cit. was claimed. Spectra of the mixture of BCl<sub>3</sub>, HBC1<sub>2</sub> and BCl<sub>2</sub> are quite complex and have been observed by L. Lynds and D. R. Stern, J. Am. Chem. Soc. **81**, 5006 (1959), H. G. Nadeau and D. M. Oaks, Jr., Anal. Chem. **32**, 1481 (1961), and H. W. Mayers and R. F. Putnam, Inorg. Chem. **2**, 655 (1963) and only three bands were correlated with HBC1<sub>2</sub>. Analysis of infrared data from previous works, according to the conventional Wilson's method of symmetry coordinates, has been undertaken by O. B. de Mandirola and J. F. Westerkamp, Spectrochim. Acta, **20**, 1653 (1964). Based on four observed frequencies, a set of six frequencies was derived and assigned. The three principal moments of inertia are:  $I_A = 2.6960 \times 10^{-36}$ ,  $I_B = 1.7957 \times 10^{-39}$  and  $I_C = 2.87557 \times 10^{-38}$  gm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S°	-(F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	$\Delta H_f^\circ$	$\Delta F_f^\circ$	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	8.521	53.399	2.407	58.609	58.609	58.609	INFINITE
200	10.635	59.744	1.709	58.887	58.887	58.887	127.809
298	11.865	64.092	1.075	59.066	59.066	59.066	63.394
300	11.898	64.165	1.022	59.305	57.439	57.439	42.112
400	13.499	67.818	0.595	59.530	56.783	56.783	41.844
500	14.686	70.964	0.208	59.733	56.071	56.071	24.509
600	15.564	73.723	0.086	59.913	55.321	55.321	20.151
700	16.236	76.175	0.047	60.066	54.544	54.544	17.029
800	16.768	78.374	0.028	60.199	53.747	53.747	14.683
900	17.198	80.380	0.016	60.312	52.933	52.933	12.854
1000	17.551	82.210	0.009	60.412	52.107	52.107	11.388
1100	17.843	83.847	0.005	60.506	51.273	51.273	10.187
1200	18.088	85.461	0.003	60.595	50.429	50.429	9.184
1300	18.294	86.917	0.002	60.684	49.579	49.579	8.335
1400	18.469	88.276	0.001	60.773	48.720	48.720	7.606
1500	18.617	89.559	0.001	60.869	47.858	47.858	6.973
1600	18.745	90.764	0.001	60.971	46.986	46.986	6.418
1700	18.855	91.904	0.001	61.078	46.107	46.107	5.927
1800	18.953	92.984	0.001	61.172	45.224	45.224	5.486
1900	19.041	94.016	0.001	61.264	44.332	44.332	5.099
2000	19.116	95.000	0.001	61.353	43.437	43.437	4.747
2100	19.170	95.924	0.000	61.440	42.533	42.533	4.426
2200	19.216	96.816	0.000	61.526	41.624	41.624	4.135
2300	19.257	97.672	0.000	61.613	40.718	40.718	3.868
2400	19.291	98.494	0.000	61.701	39.816	39.816	3.623
2500	19.316	99.284	0.000	61.790	38.919	38.919	3.388
2600	19.347	100.043	0.000	61.880	38.027	38.027	3.160
2700	19.374	100.776	0.000	61.971	37.140	37.140	2.949
2800	19.400	101.483	0.000	62.064	36.257	36.257	2.753
2900	19.425	102.166	0.000	62.159	35.379	35.379	2.570
3000	19.451	102.827	0.000	62.256	34.506	34.506	2.399
3100	19.478	103.467	0.000	62.355	33.639	33.639	2.238
3200	19.501	104.088	0.000	62.456	32.778	32.778	2.087
3300	19.521	104.690	0.000	62.559	31.923	31.923	1.945
3400	19.536	105.274	0.000	62.664	31.075	31.075	1.811
3500	19.551	105.842	0.000	62.771	30.234	30.234	1.684
3600	19.566	106.394	0.000	62.880	29.400	29.400	1.564
3700	19.581	106.932	0.000	62.991	28.573	28.573	1.450
3800	19.594	107.456	0.000	63.104	27.753	27.753	1.342
3900	19.607	107.966	0.000	63.219	26.940	26.940	1.239
4000	19.623	108.464	0.000	63.336	26.134	26.134	1.142
4100	19.633	108.949	0.000	63.455	25.335	25.335	1.051
4200	19.642	109.424	0.000	63.576	24.542	24.542	0.969
4300	19.650	109.887	0.000	63.699	23.756	23.756	0.894
4400	19.658	110.340	0.000	63.824	22.976	22.976	0.824
4500	19.670	110.782	0.000	63.951	22.201	22.201	0.764
4600	19.673	111.215	0.000	64.080	21.431	21.431	0.709
4700	19.679	111.639	0.000	64.211	20.666	20.666	0.659
4800	19.685	112.055	0.000	64.344	19.915	19.915	0.613
4900	19.691	112.464	0.000	64.479	19.178	19.178	0.571
5000	19.697	112.866	0.000	64.616	18.454	18.454	0.532
5100	19.702	113.251	0.000	64.755	17.743	17.743	0.496
5200	19.707	113.631	0.000	64.896	17.044	17.044	0.464
5300	19.711	114.011	0.000	65.039	16.357	16.357	0.434
5400	19.715	114.380	0.000	65.184	15.682	15.682	0.406
5500	19.719	114.742	0.000	65.331	15.020	15.020	0.381
5600	19.723	115.098	0.000	65.480	14.371	14.371	0.357
5700	19.727	115.448	0.000	65.631	13.734	13.734	0.335
5800	19.731	115.792	0.000	65.784	13.109	13.109	0.314
5900	19.734	116.130	0.000	65.939	12.496	12.496	0.295
6000	19.737	116.462	0.000	66.096	11.895	11.895	0.278

Mar. 31, 1966

DIFLUOROBORANE (BHF<sub>2</sub>) (IDEAL GAS)

$\Delta H_f^0 = -174.5 \pm 0.8 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -175.4 \pm 0.8 \text{ kcal. mole}^{-1}$

Point Group C<sub>2v</sub>  
 $S_{298.15} = 58.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\nu$ , cm. <sup>-1</sup>	$\nu$ , cm. <sup>-1</sup>
2640 (1)	1411 (1)
1174 (1)	[1158](1)
544 (1)	928 (1)

Bond Distance: B-H = 1.15 Å B-F = 1.30 ± 0.15 Å  
 Bond Angle: F-B-F = 120 ± 5° F-B-H = 120 ± 2.5°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 7.5168 X 10<sup>-116</sup> g.<sup>3</sup> cm.<sup>6</sup>

$\sigma = 2$

Heat of Formation.

The equilibrium pressures at 296 and 360°K. for the reaction 1/6 B<sub>2</sub>H<sub>6</sub>(g) + 2/3 BF<sub>3</sub>(g) = HBF<sub>2</sub>(g) were determined by R. F. Porter and S. K. Mason, J. Phys. Chem. 59, 2208 (1965). By the third law method, the enthalpy change was evaluated to be 3.06 ± 0.33 kcal. mole<sup>-1</sup>. Based on the values of  $\Delta H_f^0$  for B<sub>2</sub>H<sub>6</sub>(g) and BF<sub>3</sub>(g) as 9.8 and -270.1 kcal. mole<sup>-1</sup>, respectively, the heat of formation for HBF<sub>2</sub>(g) was derived to be -175.4 ± 0.8 kcal. mole<sup>-1</sup>. The drift in the third law heat of reaction is 3.6 e.u.

Heat Capacity and Entropy.

The infrared spectrum of BHF<sub>2</sub>(g) has been observed by the following investigators:  
 T. D. Coyle, J. J. Ritter and T. C. Farrar, Proc. Chem. Soc. 25 (1964).  
 M. Percic and L. N. Becker, J. Chem. Phys. 43, 721 (1965).  
 L. Lynds, J. Chem. Phys. 42, 1124 (1965).  
 R. F. Porter and S. K. Mason, J. Phys. Chem. 69, 2208 (1965).

The vibrational frequencies, except  $\nu_5$ , were obtained from Porter and Mason, and corrected to the average isotopic species. The value of  $\nu_5$  was estimated by comparison with the same value reported by other investigators. The molecular structure, bond distances and angle were obtained from Percic and Becker, loc. cit. The three principal moments of inertia are: I<sub>A</sub> = 7.9959 X 10<sup>-39</sup>, I<sub>B</sub> = 1.0404 X 10<sup>-39</sup> and I<sub>C</sub> = 9.0362 X 10<sup>-39</sup> g. cm.<sup>2</sup>  
 The vibrational-rotational spectrum of BHF<sub>2</sub>(g) has been studied by L. Lynds and C. D. Bass, J. Chem. Phys. 43, 4357 (1965). The values of  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_6$  were assigned as 1164.2, 2620.8, 541.5 and 923.5 cm.<sup>-1</sup>, respectively, which are in fair agreement with the adopted values reported by Porter and Mason, loc. cit.

T, °K.	C <sub>p</sub>	S°	(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	6.000	INF INITE	-	2.550	-174.536	-174.536	INF INITE
100	7.998	48.830	66.379	1.155	-174.821	-174.821	381.149
200	8.765	54.360	59.179	0.724	-175.072	-175.072	190.026
298	10.124	58.300	58.300	0.000	-175.400	-175.400	127.002
300	10.152	58.363	58.300	0.19	-175.607	-173.254	126.210
400	11.677	61.494	58.717	1.111	-175.754	-172.483	94.236
500	13.027	64.244	59.553	2.348	-176.086	-171.628	75.015
600	14.134	66.726	60.566	3.708	-176.583	-170.708	62.177
700	15.026	68.974	61.852	5.168	-176.740	-169.740	52.993
800	15.746	71.029	62.665	6.708	-176.865	-168.739	46.095
900	16.332	72.939	63.668	8.313	-177.058	-167.712	40.724
1000	16.812	74.665	64.665	9.970	-177.230	-166.664	36.423
1100	17.208	76.287	65.667	11.672	-177.387	-165.600	32.900
1200	17.537	77.799	66.624	13.410	-177.532	-164.521	29.962
1300	17.813	79.214	67.538	15.178	-177.673	-163.432	27.474
1400	18.046	80.543	68.420	16.971	-177.811	-162.330	25.340
1500	18.243	81.794	69.271	18.786	-177.951	-161.215	23.488
1600	18.411	82.977	70.091	20.619	-178.095	-160.099	21.868
1700	18.556	84.098	70.882	22.467	-178.243	-158.970	20.436
1800	18.681	85.162	71.646	24.329	-178.397	-157.834	19.163
1900	18.790	86.175	72.384	26.203	-178.553	-156.686	18.022
2000	18.885	87.141	73.098	28.087	-178.713	-155.529	16.995
2100	18.968	88.065	73.789	29.979	-178.877	-154.368	16.065
2200	19.042	88.949	74.458	31.880	-179.046	-153.218	15.218
2300	19.107	89.797	75.107	33.787	-179.218	-152.081	14.444
2400	19.165	90.611	75.736	35.701	-179.395	-150.959	13.734
2500	19.216	91.395	76.347	37.620	-179.566	-149.850	13.071
2600	19.263	92.149	76.940	39.544	-179.745	-148.757	12.449
2700	19.305	92.877	77.517	41.473	-179.930	-147.677	11.872
2800	19.342	93.580	78.078	43.405	-180.120	-146.616	11.336
2900	19.376	94.259	78.624	45.341	-180.313	-145.579	10.836
3000	19.407	94.917	79.157	47.280	-180.510	-144.558	10.370
3100	19.435	95.551	79.675	49.222	-180.710	-143.550	9.933
3200	19.461	96.171	80.181	51.167	-180.913	-142.564	9.523
3300	19.485	96.770	80.675	53.114	-181.119	-141.599	9.137
3400	19.506	97.352	81.157	55.064	-181.328	-140.654	8.774
3500	19.526	97.918	81.628	57.016	-181.539	-139.727	8.431
3600	19.544	98.468	82.088	58.964	-181.752	-138.816	8.107
3700	19.562	99.004	82.538	60.924	-181.967	-137.920	7.800
3800	19.577	99.526	82.978	62.881	-182.184	-137.039	7.508
3900	19.592	100.035	83.409	64.840	-182.403	-136.172	7.232
4000	19.605	100.531	83.831	66.800	-182.624	-135.319	6.972
4100	19.618	101.015	84.244	68.761	-182.847	-134.479	6.726
4200	19.629	101.488	84.649	70.723	-183.072	-133.652	6.494
4300	19.640	101.950	85.046	72.687	-183.299	-132.838	6.274
4400	19.651	102.402	85.435	74.651	-183.528	-132.036	6.067
4500	19.660	102.845	85.817	76.617	-183.759	-131.245	5.872
4600	19.669	103.275	86.192	78.584	-183.992	-130.465	5.690
4700	19.677	103.699	86.560	80.551	-184.227	-129.696	5.520
4800	19.685	104.113	86.921	82.519	-184.464	-128.938	5.361
4900	19.693	104.519	87.276	84.488	-184.703	-128.191	5.213
5000	19.700	104.917	87.625	86.457	-184.944	-127.455	5.076
5100	19.706	105.307	87.965	88.428	-185.187	-126.729	4.949
5200	19.713	105.690	88.305	90.399	-185.432	-126.013	4.832
5300	19.718	106.065	88.637	92.370	-185.679	-125.306	4.724
5400	19.724	106.434	88.963	94.342	-185.928	-124.608	4.622
5500	19.729	106.796	89.284	96.315	-186.179	-123.919	4.526
5600	19.734	107.151	89.600	98.288	-186.432	-123.238	4.435
5700	19.739	107.501	89.911	100.262	-186.687	-122.564	4.348
5800	19.744	107.844	90.217	102.236	-186.944	-121.897	4.265
5900	19.748	108.182	90.519	104.210	-187.203	-121.237	4.186
6000	19.752	108.513	90.816	106.185	-187.464	-120.583	4.111

$\Delta H_f^\circ = [-249 \pm 25] \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ = [-250 \pm 25] \text{ kcal. mole}^{-1}$

Point Group C<sub>2v</sub>

S<sub>298.15</sub> = [64] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
875 (1)	[136S] (1)
856 (1)	491 (1)
1377 (1)	481 (1)

Bond Distance: B-F = [1.3] Å

B-O = [1.2] Å

Bond Angle: F-B-O = [120]°

P-B-F = [120]°

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [7.38944 x 10<sup>-115</sup>] g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The molecule BF<sub>2</sub>O(g) is similar to BO<sub>2</sub>(g) in that both have an extra electron. In BO<sub>2</sub>(g) there is definite probability of resonance stabilization. Since the B-O bond in BOF(g) appears to be much stronger than that in BO(g) or BO<sub>2</sub>(g), it seems reasonable to expect the B-O bond in BF<sub>2</sub>O(g) to be also stronger than that in BO(g) or BO<sub>2</sub>(g). Using the average bond energy in BO<sub>2</sub>(g) as the B-O bond energy in BF<sub>2</sub>O(g), i.e.  $\Delta H_f^\circ = 162 \text{ kcal. mole}^{-1}$  for the reaction  $\text{BF}_2\text{O}(g) \rightarrow \text{BF}_2(g) + \text{O}(g)$ ,  $\Delta H_f^\circ = -233 \text{ kcal. mole}^{-1}$  for BF<sub>2</sub>O(g) was obtained. However, for reasons discussed above, this value is probably too positive. Using B-F bond energy in BF<sub>3</sub>(g), i.e.  $\Delta H_f^\circ = 159 \text{ kcal. mole}^{-1}$  for the reaction  $\text{BF}_2\text{O}(g) \rightarrow \text{BFO}(g) + \text{F}(g)$ , the value of  $\Delta H_f^\circ$  for BF<sub>2</sub>O(g) is calculated to be -283 kcal. mole<sup>-1</sup> which is probably a limiting negative value. Therefore a medium value of -250 ± 25 kcal. mole<sup>-1</sup> is adopted.

Heat Capacity and Entropy.

The vibrational frequencies (except  $\nu_4$ ) were obtained from C. W. Mathews and K. K. Innes, J. Mol. Spectry. 15, 199 (1965) and corrected to the average isotopic species. The frequency  $\nu_4$  was estimated by comparison with the corresponding value for BF<sub>3</sub>(g). The B - F and B - O bond distances were assumed to be the same as those in BF<sub>3</sub>(g) and BO(g) molecules, respectively. The ground state quantum weight was taken as 2. The three principal moments of inertia are: I<sub>A</sub> = 7.9984 x 10<sup>-39</sup>, I<sub>B</sub> = 6.4131 x 10<sup>-39</sup>, and I<sub>C</sub> = 1.44095 x 10<sup>-36</sup> g. cm.<sup>2</sup>

T. °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	8.131	72.832	2.752	249.313	249.313	INFINITE
200	9.841	63.708	1.065	249.573	248.748	543.611
298	11.843	63.688	∞	249.803	247.830	270.803
300	11.878	63.688	∞	250.000	246.821	180.916
400	15.632	67.428	0.022	250.004	246.801	17.786
500	15.608	70.624	1.301	250.172	245.772	134.242
600	16.243	73.457	4.291	250.323	244.573	106.898
700	16.814	75.991	7.935	250.452	243.411	88.658
800	17.392	78.275	11.410	250.564	242.288	75.623
900	17.829	80.350	14.906	250.662	241.211	65.843
1000	18.166	82.247	18.410	250.749	240.182	58.234
1100	18.429	83.991	21.925	250.832	239.203	52.144
1200	18.638	85.604	25.454	250.917	238.277	47.160
1300	18.805	87.103	28.994	251.003	237.401	43.205
1400	18.942	88.501	32.544	251.096	236.577	39.488
1500	19.054	89.812	36.100	251.195	235.802	36.042
1600	19.148	91.045	39.664	251.297	235.077	33.858
1700	19.226	92.208	43.234	251.401	234.401	31.599
1800	19.289	93.300	46.804	251.506	233.777	29.548
1900	19.338	94.334	50.374	251.612	233.202	27.752
2000	19.379	95.348	53.944	251.719	232.677	26.183
2100	19.412	96.295	57.514	251.827	232.202	24.694
2200	19.439	97.208	61.084	251.936	231.777	23.383
2300	19.461	98.081	64.654	252.046	231.401	22.190
2400	19.478	98.914	68.224	252.156	231.077	21.100
2500	19.491	99.696	71.794	252.266	230.802	20.100
2600	19.500	100.427	75.364	252.376	230.577	19.170
2700	19.506	101.104	78.934	252.486	230.401	18.302
2800	19.509	101.727	82.504	252.596	230.277	17.488
2900	19.511	102.297	86.074	252.706	230.202	16.724
3000	19.512	102.814	89.644	252.816	230.177	16.002
3100	19.513	103.277	93.214	252.926	230.202	15.402
3200	19.514	103.690	96.784	253.036	230.277	14.902
3300	19.515	104.053	100.354	253.146	230.401	14.498
3400	19.516	104.366	103.924	253.256	230.577	14.183
3500	19.517	104.629	107.494	253.366	230.802	13.948
3600	19.518	104.842	111.064	253.476	231.077	13.783
3700	19.519	105.005	114.634	253.586	231.401	13.678
3800	19.520	105.118	118.204	253.696	231.777	13.623
3900	19.521	105.181	121.774	253.806	232.202	13.618
4000	19.522	105.204	125.344	253.916	232.677	13.663
4100	19.523	105.187	128.914	254.026	233.202	13.758
4200	19.524	105.130	132.484	254.136	233.777	13.903
4300	19.525	105.033	136.054	254.246	234.401	14.108
4400	19.526	104.896	139.624	254.356	235.077	14.373
4500	19.527	104.719	143.194	254.466	235.802	14.708
4600	19.528	104.502	146.764	254.576	236.577	15.113
4700	19.529	104.245	150.334	254.686	237.401	15.588
4800	19.530	103.948	153.904	254.796	238.277	16.133
4900	19.531	103.611	157.474	254.906	239.202	16.748
5000	19.532	103.234	161.044	255.016	240.177	17.433
5100	19.533	102.817	164.614	255.126	241.202	18.188
5200	19.534	102.360	168.184	255.236	242.277	19.013
5300	19.535	101.863	171.754	255.346	243.401	19.908
5400	19.536	101.326	175.324	255.456	244.577	20.873
5500	19.537	100.749	178.894	255.566	245.802	21.918
5600	19.538	100.132	182.464	255.676	247.077	23.043
5700	19.539	99.475	186.034	255.786	248.401	24.248
5800	19.540	98.778	189.604	255.896	249.777	25.533
5900	19.541	98.041	193.174	256.006	251.202	26.898
6000	19.542	97.264	196.744	256.116	252.677	28.343

Point Group D<sub>3h</sub>  
 $\Delta H_f^0 = -270.98 \pm 0.22 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -271.65 \pm 0.22 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

$\nu$ , cm. <sup>-1</sup>	$\nu$ , cm. <sup>-1</sup>
888 (1)	1463.2 (g)
696.5 (1)	480.7 (2)

Bond Distance: B-F = 1.295 ± 0.01 Å  
 Bond Angle: F-B-F = 120°

Product of Moments of Inertia:  $I_A I_B I_C = 998.9 \times 10^{-11} \text{ g.}^3 \text{ cm.}^6$   
 $\sigma = 6$

Heat of Formation

The energy change ( $\Delta E_c$ ) of burning B(c) in F<sub>2</sub>(g) to form BF<sub>3</sub>(g) was determined in the fluorine bomb calorimeter to be -25,113.5 ± 18.3 cal./g. of B(c), by G. K. Johnson, H. M. Feder and W. N. Hubbard, private communication, Aug. 18, 1965, in which -29.0 + 5.5 cal./g. of B(c) was due to the correction for the impurities in the B(c) sample. They also measured the B<sup>10</sup>/B<sup>11</sup> ratio of the sample and thus calculated the values,  $\Delta E_c^{298.15} = -271.35 \pm 0.22$  and  $\Delta H_f^{298.15} = -271.65 \pm 0.22 \text{ kcal. mole}^{-1}$ , for BF<sub>3</sub>(g), based on the isotopic masses of the C<sub>12</sub> scale. However, this calculation performed on any other scale still gives the same value within ± 40 cal. for the heat of combustion of a gram formula weight of boron on that scale. The slight differences, due to internal consistency changes from scale to scale are considered negligible within the experimental uncertainty. Therefore the reported  $\Delta H_f^{298.15}$  value is adopted here.

This  $\Delta H_f^{298.15}$  (BF<sub>3</sub>, g) value is more negative than the one,  $\Delta H_f^{298.15} = -270.1 \text{ kcal. mole}^{-1}$ , determined by S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, J. Phys. Chem. 65, 2157 (1961) using a similar method in the same laboratory. Reanalysis of the boron sample used in the previous work uncovered additional impurities which account for the difference.

Similar measurements by P. Gross, C. Hayman, D. L. Levi, and M. C. Stuart, Fulmer Research Institute Report R-146/4/25, November, 1960, gave values of -270.8 kcal. mole<sup>-1</sup> for a sample of zone-refined boron and -271.6 kcal. mole<sup>-1</sup> for a sample prepared by thermal decomposition of diborane. Impurity effects are unknown for oxygen, nitrogen, carbon, and hydrogen in the zone-refined boron and for oxygen and nitrogen in the sample from diborane. The sample obtained from decomposition of diborane may be the amorphous form. Using  $\Delta H_f^{298.15} = 0.4 \text{ kcal. mole}^{-1}$  for the transition B(c) → B(amorph.), the latter  $\Delta H_f^{298.15}$  (BF<sub>3</sub>, g) value was recalculated as -271.2 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy

The fundamental frequencies were selected from the measurements of Lindeman and Wilson, J. Chem. Phys. 24, 242 (1956), D. C. McKean, ibid., 1002 (1956), A. H. Nielsen, ibid., 22, 659 (1954), Anderson, Lassette and Yost, ibid., 4, 703 (1936) and Yost, DeVault, Anderson and Lassette, ibid., 5 424 (1936). Other measurements include those of Oge and Barker, J. Chem. Phys. 7, 455 (1939), Bailey, Hale and Thompson, Proc. Roy. Soc. 161, 107 (1937) and Suz and Wuhmann, Helv. Chim. Acta 40, 722 (1957). The structural constants determined by A. H. Nielsen, loc. cit., are consistent with the electron diffraction studies of Levy and Brockway, J. Am. Chem. Soc. 59, 2085 (1937). The three principal moments of inertia are:  $I_A = I_B = 7.9549 \times 10^{-39}$ , and  $I_C = 1.5867 \times 10^{-38} \text{ g. cm.}^2$

T, K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> )/T	H° - H <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞
100	8.148	50.161	2.784	-270.977	-270.977	INFINITE
200	10.050	56.319	1.986	-271.228	-270.131	590.343
298	12.058	60.713	1.087	-271.458	-268.941	293.871
300	12.082	60.713	1.087	-271.458	-268.941	186.195
400	13.753	64.503	0.722	-271.654	-267.643	194.968
500	15.045	67.717	0.516	-271.835	-266.276	145.880
600	16.031	70.552	0.357	-272.013	-264.867	115.768
700	16.778	73.081	0.259	-272.183	-263.421	95.946
800	17.345	75.361	0.190	-272.333	-261.947	81.780
900	17.780	77.430	0.136	-272.470	-260.457	71.150
1000	18.118	79.321	0.092	-272.593	-258.947	62.878
1100	18.384	81.061	0.062	-272.709	-257.424	56.257
1200	18.595	82.670	0.042	-272.826	-255.891	50.838
1300	18.766	84.165	0.029	-272.941	-254.345	46.320
1400	18.906	85.561	0.020	-273.061	-252.790	42.496
1500	19.022	86.870	0.015	-273.185	-251.225	39.216
1600	19.118	88.101	0.011	-273.316	-249.653	36.373
1700	19.199	89.262	0.008	-273.454	-248.072	33.883
1800	19.268	90.362	0.006	-273.600	-246.479	31.686
1900	19.327	91.405	0.005	-273.755	-244.883	29.731
2000	19.378	92.398	0.004	-273.914	-243.273	27.981
2100	19.423	93.344	0.003	-274.078	-241.655	26.406
2200	19.461	94.249	0.003	-274.248	-240.030	24.979
2300	19.495	95.115	0.002	-274.423	-238.398	23.682
2400	19.525	95.945	0.002	-274.603	-236.756	22.496
2500	19.551	96.743	0.002	-274.789	-235.106	21.408
2600	19.575	97.510	0.001	-274.982	-233.341	20.398
2700	19.596	98.249	0.001	-275.185	-231.566	19.455
2800	19.615	98.962	0.001	-275.394	-229.660	18.581
2900	19.632	99.651	0.001	-275.617	-227.634	17.769
3000	19.648	100.317	0.001	-275.852	-225.488	17.012
3100	19.662	100.961	0.001	-276.100	-223.222	16.307
3200	19.674	101.585	0.001	-276.361	-220.828	15.645
3300	19.684	102.189	0.001	-276.634	-218.309	15.025
3400	19.692	102.773	0.001	-276.919	-215.661	14.441
3500	19.700	103.350	0.001	-277.215	-212.884	13.894
3600	19.716	103.905	0.001	-277.522	-210.000	13.374
3700	19.724	104.444	0.001	-277.842	-207.016	12.884
3800	19.731	104.972	0.001	-278.176	-203.931	12.420
3900	19.738	105.484	0.001	-278.524	-200.746	11.980
4000	19.745	105.984	0.001	-278.887	-197.461	11.563
4100	19.751	106.472	0.001	-279.264	-194.076	11.169
4200	19.757	106.948	0.001	-279.654	-190.591	10.800
4300	19.762	107.413	0.001	-279.958	-187.006	10.450
4400	19.767	107.867	0.001	-280.276	-183.321	10.120
4500	19.772	108.311	0.001	-280.608	-179.536	9.810
4600	19.776	108.746	0.001	-280.954	-175.651	9.520
4700	19.780	109.171	0.001	-281.314	-171.666	9.250
4800	19.784	109.588	0.001	-281.688	-167.581	9.000
4900	19.787	109.996	0.001	-282.076	-163.396	8.770
5000	19.791	110.396	0.001	-282.478	-159.111	8.560
5100	19.794	110.787	0.001	-282.894	-154.726	8.370
5200	19.797	111.172	0.001	-283.324	-150.241	8.200
5300	19.800	111.549	0.001	-283.768	-145.656	8.050
5400	19.802	111.919	0.001	-284.226	-140.971	7.910
5500	19.805	112.283	0.001	-284.699	-136.186	7.780
5600	19.807	112.639	0.001	-285.187	-131.291	7.660
5700	19.809	112.990	0.001	-285.690	-126.286	7.550
5800	19.812	113.335	0.001	-286.208	-121.171	7.450
5900	19.814	113.673	0.001	-286.741	-115.946	7.360
6000	19.816	114.006	0.001	-287.289	-110.601	7.280

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>F</sub> <sup>o</sup>	ΔF <sub>F</sub> <sup>o</sup>	Log K <sub>F</sub>
0							
100	7.097	8.300	8.300	0.000	-38.300	-38.171	27.079
200							
298							
300	7.150	8.344	8.300	0.013	-38.303	-38.170	27.806
400	7.640	10.771	8.614	0.863	-38.395	-38.109	20.821
500	10.926	17.071	9.279	1.896	-38.424	-38.033	16.624
600	11.608	15.128	10.086	3.025	-38.443	-37.953	13.824
700	11.980	10.939	4.206	38.472	-37.870	-37.823	11.823
800	12.168	11.793	5.414	38.510	-37.781	-37.781	10.321
900	12.306	20.002	6.638	38.586	-37.685	-37.685	9.151
1000	12.408	21.304	7.874	38.675	-37.580	-37.580	8.213
1100	12.474	22.490	9.118	38.789	-37.466	-37.466	7.444
1200	12.506	24.937	10.367	38.875	-37.350	-37.350	6.793
1300	12.538	24.579	15.641	40.034	-37.082	-37.082	6.334
1400	12.570	25.509	16.313	40.216	-36.882	-36.882	5.933
1500	12.602	26.378	16.955	40.418	-36.682	-36.682	5.573
1600	12.634	27.192	17.570	40.641	-36.481	-36.481	5.243
1700	12.666	27.959	18.159	40.882	-36.274	-36.274	4.936
1800	12.698	28.684	18.724	41.139	-36.064	-36.064	4.643
1900	12.730	28.371	19.266	41.412	-35.847	-35.847	4.369
2000	12.762	30.025	19.788	41.700	-35.623	-35.623	4.113
2100	12.794	30.649	20.290	42.000	-35.393	-35.393	3.870
2200	12.826	31.244	20.775	42.313	-35.158	-35.158	3.637
2300	12.858	31.811	21.242	42.640	-34.918	-34.918	3.413
2400	12.890	32.350	21.694	42.980	-34.673	-34.673	3.197
2500	12.922	32.860	22.132	43.333	-34.423	-34.423	2.987
2600	12.954	33.347	22.555	43.699	-34.168	-34.168	2.781
2700	12.986	33.811	22.964	44.078	-33.908	-33.908	2.579
2800	13.018	34.250	23.365	44.469	-33.643	-33.643	2.381
2900	13.050	34.675	23.752	44.870	-33.373	-33.373	2.187
3000	13.082	35.086	24.128	45.283	-33.098	-33.098	2.000
3100	13.114	35.483	24.494	45.706	-32.818	-32.818	1.817
3200	13.146	35.866	24.850	46.139	-32.533	-32.533	1.638
3300	13.178	36.235	25.198	46.581	-32.243	-32.243	1.463
3400	13.210	36.590	25.536	47.031	-31.948	-31.948	1.291
3500	13.242	36.931	25.867	47.488	-31.648	-31.648	1.122
3600	13.274	37.259	26.191	47.951	-31.343	-31.343	0.957
3700	13.306	37.575	26.504	48.419	-31.033	-31.033	0.796
3800	13.338	37.879	26.812	48.891	-30.718	-30.718	0.639
3900	13.370	38.171	27.113	49.368	-30.400	-30.400	0.487
4000	13.402	38.452	27.408	49.849	-30.078	-30.078	0.340

ΔH<sub>F</sub><sup>o</sup> = UnknownΔH<sub>F</sub><sup>o</sup> 298.15 = [8.3 ± 1.5] cal. deg.<sup>-1</sup> mole<sup>-1</sup>S<sub>298.15</sub> = [8.3 ± 1.5] cal. deg.<sup>-1</sup> mole<sup>-1</sup>T<sub>d</sub> = [2500]\*K.Heat of Formation.

P. O. Schissee and O. C. Trulson, *J. Phys. Chem.*, **66**, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system and obtained ΔF<sub>2340</sub><sup>o</sup> = -118.54 kcal. mole<sup>-1</sup> for the reaction TiB(c) = Ti(g) + B(g). This corresponds to ΔF<sub>2340</sub><sup>o</sup>(TiB(c)) = -33.266 ± 9 kcal. mole<sup>-1</sup>, where 4 kcal. mole<sup>-1</sup> of the uncertainty is due to the heat of sublimation of boron. When this is reduced to 298°K. one obtains ΔF<sub>298</sub><sup>o</sup>(TiB(c)) = -38.3 ± 9 kcal. mole<sup>-1</sup>. This value implies a high stability for TiB. This is also indicated by the phase studies of H. Nowotny, F. Benesovsky, C. Brukl and O. Schob, Monatshefte für Chemie **92**, 403 (1961).

Heat Capacity and Entropy.

The heat capacities from 298 to 1200°K. were estimated from that of TiB<sub>2</sub> by assuming the difference to be the same as that between CrB and CrB<sub>2</sub> as determined by R. Mezaki, E. W. Tilleux, D. W. Barnes and J. L. Margrave (Paper presented at the International Symposium on Nuclear Materials, Vienna, May 1962). A linear extrapolation was assumed above 1200°K.

The heat capacities above 298°K. were also estimated from the relationship C<sub>p</sub>(Ti) + C<sub>p</sub>(2B) - C<sub>p</sub>(TiB<sub>2</sub>) = 2/3 [C<sub>p</sub>(Ti) + C<sub>p</sub>(B) - C<sub>p</sub>(TiB)]. This estimation agreed with the above to 4% over the temperature range 400 to 1000°K.

S<sub>298</sub>(TiB, c) = 8.3 cal. mole<sup>-1</sup> deg.<sup>-1</sup> was calculated by the method of W. M. Latimer, *J. Am. Chem. Soc.*, **73**, 1480 (1951). Using JANAF S<sub>298</sub><sup>o</sup>(TiB<sub>2</sub>, c) = 6.8 cal. mole<sup>-1</sup> deg.<sup>-1</sup> and Latimer's value of 9.8 e.u. for the entropy contribution of Ti, an entropy contribution of -1.5 e.u. per Boron atom was calculated.

Decomposition Data.

The phase diagram given in, "The Metallurgy of the Rarer Metals - No. 4 Titanium", by A. D. McQuillan and M. K. McQuillan, Academic Press, New York (1956) was used to estimate the decomposition temperature. This diagram shows the decomposition products are TiB<sub>2</sub> and Ti<sub>2</sub>B. However, Nowotny et al. (loc. cit.) have shown Ti<sub>2</sub>B to be nonexistent and so the decomposition products are not defined, probably a eutectic of TiB and TiB<sub>2</sub> is involved.

$\Delta H_f^0 = -322 \pm 10$  kcal. mole<sup>-1</sup>

$\Delta H_f^0 = [78.079]$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Point Group [C<sub>2h</sub>]

S<sub>298.15</sub> = [78.079] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies

$\nu$ , cm. <sup>-1</sup>	$\nu$ , cm. <sup>-1</sup>	$\nu$ , cm. <sup>-1</sup>
[2000] (1)	[1050] (1)	[400] (1)
[1600] (1)	[650] (1)	[350] (1)
[1200] (1)	[650] (1)	[200] (1)
[1200] (1)	[600] (1)	[150] (1)
[1050] (1)	[500] (1)	[120] (1)

Bond Distance: Be-O = [1.63] Å O-B = [1.34] Å B-O = [1.20] Å

Bond Angle: O-B-O = [180°] O-Be-O = [180°] B-O-Be = [95°]

Product of Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 5.3801 X 10<sup>-113</sup> g.<sup>3</sup> cm.<sup>6</sup>

$\sigma = 2$

Heat of Formation.

The heat of formation was obtained from mass spectrometric studies; the following reactions at 1500°K. were reported by P. E. Blackburn and A. Büchler, Interim Technical Report No. 1, March 1965:

1. P<sub>2</sub>O<sub>3</sub>(l) → P<sub>2</sub>O<sub>3</sub>(g) ΔH<sub>1</sub> = 92.226 kcal/mole
2. 1/3 Be<sub>3</sub>B<sub>2</sub>O<sub>6</sub>(c) + 2/3 B<sub>2</sub>O<sub>3</sub>(l) → Be(BO<sub>2</sub>)<sub>2</sub>(g) ΔH<sub>2</sub> = 118 ± 2 kcal/mole
3. Be<sub>3</sub>B<sub>2</sub>O<sub>6</sub>(c) → 3BeO(c) + B<sub>2</sub>O<sub>3</sub>(g) ΔH<sub>3</sub> = 112 ± 1 kcal/mole
4. Be<sub>3</sub>B<sub>2</sub>O<sub>6</sub>(c) → 2BeO(c) + Be(BO<sub>2</sub>)<sub>2</sub>(g) ΔH<sub>4</sub> = 137 ± 3 kcal/mole
5. 3BeO(c) + B<sub>2</sub>O<sub>3</sub>(l) → Be<sub>3</sub>B<sub>2</sub>O<sub>6</sub>(c) ΔH<sub>5</sub> = -23 kcal/mole
6. BeO(c) + B<sub>2</sub>O<sub>3</sub>(g) → Be(BO<sub>2</sub>)<sub>2</sub>(g) ΔH<sub>6</sub> = 22 kcal/mole

The value of ΔH<sub>1</sub> was obtained from JANAF values for P<sub>2</sub>O<sub>3</sub>(l) and B<sub>2</sub>O<sub>3</sub>(g). The values for ΔH<sub>2</sub>, ΔH<sub>3</sub> and ΔH<sub>4</sub> were obtained from P. E. Blackburn and A. Büchler loc. cit. The value for ΔH<sub>5</sub> was obtained by taking the average of ΔH<sub>5</sub> = -20 kcal/mole in a weight loss experiment, ΔH<sub>5</sub> = ΔH<sub>1</sub> - ΔH<sub>3</sub> = -19.774 kcal/mole, and ΔH<sub>5</sub> = 3/2 (ΔH<sub>2</sub> - ΔH<sub>4</sub>) = -28.5 kcal/mole. The ΔH<sub>6</sub> value was obtained by taking the average of ΔH<sub>6</sub> = ΔH<sub>4</sub> - ΔH<sub>3</sub> = 25 kcal/mole and ΔH<sub>6</sub> = ΔH<sub>2</sub> - ΔH<sub>1</sub> + 1/3 ΔH<sub>5</sub> = 18.107 kcal/mole. The ΔH<sub>f</sub> 298.15 of BeB<sub>2</sub>O<sub>4</sub> was calculated from reaction 6 with auxiliary JANAF values.

Heat Capacity and Entropy.

The vibrational frequencies estimated by comparison with P<sub>2</sub>O<sub>3</sub>, were adjusted to obtain an S<sub>298.15</sub> = 127 obtained in a manner analogous with ΔH<sub>f</sub> from the report of P. E. Blackburn and A. Büchler loc. cit. The frequencies listed are not in point group order. All other molecular constants were estimated by comparison with related boron oxide molecules. The individual moments of inertia are I<sub>A</sub> = 8.5561 X 10<sup>-39</sup> g. cm.<sup>2</sup>, I<sub>B</sub> = 75.1345 X 10<sup>-39</sup> g. cm.<sup>2</sup> and I<sub>C</sub> = 83.6909 X 10<sup>-39</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	12.591	59.799	4.455	322.253	-322.253	-322.253	INFINITE
200	17.793	70.171	3.484	322.730	-320.376	-320.376	700.148
298	21.932	78.079	2.412	323.000	-317.965	-317.965	347.440
300	22.001	78.215	2.412	323.002	-315.496	-315.496	229.828
400	25.697	83.016	1.605	323.136	-312.974	-312.974	170.993
500	27.839	86.946	1.075	323.265	-310.417	-310.417	135.677
600	29.782	90.292	0.760	323.382	-307.836	-307.836	112.124
700	31.266	92.400	0.556	323.486	-305.236	-305.236	93.295
800	32.407	93.716	0.415	323.578	-302.626	-302.626	82.670
900	33.294	94.400	0.321	323.659	-300.000	-300.000	72.846
1000	33.989	94.577	0.262	323.720	-297.362	-297.362	64.985
1100	34.543	94.844	0.222	323.802	-294.718	-294.718	58.582
1200	34.988	95.109	0.192	323.878	-292.058	-292.058	53.182
1300	35.330	95.372	0.168	323.948	-289.387	-289.387	48.582
1400	35.647	95.625	0.148	324.012	-286.699	-286.699	44.582
1500	35.935	95.868	0.130	324.068	-284.000	-284.000	41.377
1600	36.192	96.101	0.115	324.115	-281.198	-281.198	38.408
1700	36.427	96.325	0.103	324.155	-278.285	-278.285	35.774
1800	36.647	96.540	0.093	324.188	-275.161	-275.161	33.432
1900	36.855	96.745	0.085	324.215	-272.421	-272.421	31.334
2000	37.046	96.940	0.078	324.235	-269.470	-269.470	29.445
2100	37.223	97.125	0.072	324.250	-266.500	-266.500	27.734
2200	37.387	97.299	0.067	324.260	-263.522	-263.522	26.175
2300	37.540	97.462	0.063	324.265	-260.527	-260.527	24.755
2400	37.682	97.615	0.059	324.268	-257.514	-257.514	23.449
2500	37.815	97.758	0.056	324.268	-254.279	-254.279	22.228
2600	37.938	97.891	0.053	324.265	-250.800	-250.800	21.081
2700	38.052	98.015	0.051	324.258	-247.306	-247.306	20.017
2800	38.157	98.130	0.049	324.248	-242.698	-242.698	18.942
2900	38.254	98.235	0.047	324.235	-236.598	-236.598	17.830
3000	38.343	98.330	0.045	324.218	-230.508	-230.508	16.792
3100	38.425	98.415	0.043	324.198	-224.411	-224.411	15.820
3200	38.500	98.490	0.042	324.175	-218.303	-218.303	14.909
3300	38.568	98.555	0.041	324.150	-212.193	-212.193	14.052
3400	38.629	98.610	0.040	324.125	-206.077	-206.077	13.246
3500	38.683	98.655	0.039	324.100	-199.967	-199.967	12.486
3600	38.731	98.690	0.038	324.075	-193.831	-193.831	11.767
3700	38.773	98.715	0.038	324.050	-187.701	-187.701	11.087
3800	38.810	98.730	0.037	324.025	-181.562	-181.562	10.442
3900	38.842	98.735	0.037	324.000	-175.424	-175.424	9.830
4000	38.869	98.730	0.037	323.975	-169.286	-169.286	9.244
4100	38.891	98.715	0.037	323.950	-163.149	-163.149	8.688
4200	38.908	98.690	0.037	323.925	-157.012	-157.012	8.158
4300	38.920	98.655	0.037	323.900	-150.875	-150.875	7.652
4400	38.927	98.610	0.037	323.875	-144.738	-144.738	7.168
4500	38.930	98.555	0.037	323.850	-138.601	-138.601	6.704
4600	38.929	98.490	0.037	323.825	-132.464	-132.464	6.258
4700	38.924	98.415	0.037	323.800	-126.327	-126.327	5.832
4800	38.915	98.330	0.037	323.775	-120.190	-120.190	5.422
4900	38.902	98.235	0.037	323.750	-114.053	-114.053	5.032
5000	38.885	98.130	0.037	323.725	-107.916	-107.916	4.668
5100	38.864	98.015	0.037	323.700	-101.779	-101.779	4.328
5200	38.839	97.890	0.037	323.675	-95.642	-95.642	4.008
5300	38.810	97.755	0.037	323.650	-89.505	-89.505	3.704
5400	38.777	97.610	0.037	323.625	-83.368	-83.368	3.414
5500	38.740	97.455	0.037	323.600	-77.231	-77.231	3.134
5600	38.699	97.290	0.037	323.575	-71.094	-71.094	2.864
5700	38.654	97.115	0.037	323.550	-64.957	-64.957	2.612
5800	38.605	96.930	0.037	323.525	-58.820	-58.820	2.374
5900	38.552	96.735	0.037	323.500	-52.683	-52.683	2.148
6000	38.495	96.530	0.037	323.475	-46.546	-46.546	1.934

BORON DIBOROXIDE, DIMERIC (B<sub>2</sub>(OH)<sub>4</sub>) (CRYSTAL)

MOL. WT. = 89.65148

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298°)/T</sub>	H° - H <sub>298°</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub>	Log K <sub>p</sub>
0						
100	27.770	30.000	0.000	- 337.100	- 297.377	217.983
200	27.916	30.172	0.052	- 337.110	- 297.132	216.460
300	34.210	39.097	3.169	- 337.447	- 283.744	155.031
400	39.140	47.272	6.842	- 337.460	- 270.311	118.153
500	43.430	54.797	10.976	- 337.186	- 256.902	93.577
600	47.090	61.774	15.505	- 336.649	- 243.559	76.043
700	50.290	68.276	20.379	- 335.873	- 230.315	62.919
800	52.930	74.354	25.542	- 334.894	- 217.175	52.737
900	55.290	80.056	30.956	- 333.740	- 204.154	44.618
1000	57.360	85.425	36.591	- 332.443	- 191.259	38.000
1100	59.140	90.494	42.418	- 331.018	- 178.484	32.508
1200	60.660	95.299	48.410	- 329.496	- 165.835	27.879
1300	61.900	99.832	54.741	- 327.895	- 153.304	23.932
1400	62.860	104.137	60.781	- 326.251	- 140.892	20.528

ΔH<sub>f</sub>° = Unknown

ΔH<sub>f</sub> 298.15 = -337.1 ± 2.0 kcal. mole<sup>-1</sup>

ΔH<sub>m</sub>° = Unknown

ΔH<sub>g</sub>° 298.15 = [30.1] kcal. mole<sup>-1</sup>

S<sub>298.15</sub>° = [30 ± 1] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = Unknown

Heat of Formation.

The enthalpy change, ΔH<sub>f</sub>° 298.15 = -91.3 ± 1.0 kcal. mole<sup>-1</sup>, for the reaction B<sub>2</sub>(OH)<sub>4</sub>(c) + (m + 2)·AgNO<sub>3</sub>(aq.) + (n + 2)·H<sub>2</sub>O(l) = 2Ag(c) + [2H<sub>3</sub>BO<sub>3</sub> + 2HNO<sub>3</sub> + mAgNO<sub>3</sub>·nH<sub>2</sub>O(aq.)] was determined calorimetrically by A. Finch, P. J. Gardner and I. J. Hyams, Trans. Faraday Soc. 61, 649 (1965). The heat of formation of B<sub>2</sub>(OH)<sub>4</sub>(c) was reported to be -335.1 kcal. mole<sup>-1</sup>. This value was corrected to be -337.1 ± 2 kcal. mole<sup>-1</sup> by use of more recent data on the ΔH<sub>f</sub>° 298.15 values used for calculation.

Heat Capacity and Entropy.

The heat capacity for B<sub>2</sub>(OH)<sub>4</sub>(c) was estimated by comparison with those for B(OH)<sub>3</sub>(c). The value of S<sub>298.15</sub> was calculated based on 3 cal. deg.<sup>-1</sup> mole<sup>-1</sup> per atom for B<sub>2</sub>(OH)<sub>4</sub>(c), which was obtained from the corresponding values for HBO<sub>2</sub>(c) and B(OH)<sub>3</sub>(c).

Heat of Sublimation.

The value, ΔH<sub>g</sub>° 298.15, was calculated as the difference between ΔH<sub>f</sub>° 298.15 for B<sub>2</sub>(OH)<sub>4</sub>(g) and B<sub>2</sub>(OH)<sub>4</sub>(c).



Point Group [C<sub>2</sub>]  
 $\Delta H_f^0 =$  Unknown  
 $\Delta H_f^0 298.15 = [-307 \pm 5]$  kcal. mole<sup>-1</sup>  
 $S_{298.15}^0 = [85.57]$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies  
 $\omega_e$ , cm.<sup>-1</sup>       $\omega_e$ , cm.<sup>-1</sup>       $\omega_e$ , cm.<sup>-1</sup>

[1380](1)	[1386](1)	[824](2)
[630](1)	[657](1)	[209](2)
[304](1)	[325](1)	[3200](4)
Rotation (1)	[1378](1)	[1200](2)
[1155](1)	[662](1)	[660](2)
[542](1)	[325](1)	

Bond Distance: B-B = [1.67] Å      B-O = [1.36] Å      B-H = [0.96] Å  
 Bond Angle: H-O-B = [114]°      O-B-O = [120]°      O-B-B = [120]°  
 Product of the Moments of Inertia:  $I_A I_B I_C = [2.2995 \times 10^{-113}]$  g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The heat of formation ( $\Delta H_f^0 298.15$ ) for B<sub>2</sub>(OH)<sub>4</sub>(g) was calculated, using bond energies, D(B-OH) = 132 and D(B-B) = 78 kcal. mole<sup>-1</sup>. The bond energy D(B-OH) was taken from that in B(OH)<sub>3</sub>(g) and D(B-B) was estimated by comparison with that in B<sub>2</sub>F<sub>4</sub>(g).

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that for B<sub>2</sub>F<sub>4</sub>(g), i.e. the two B(OH)<sub>2</sub> units have staggered configuration, and free rotation about B-B bond. The B-B bond distance was taken as that in B<sub>2</sub>F<sub>4</sub> molecule. Those for B-O and B-H bond and bond angles were adopted from H<sub>2</sub>BO<sub>3</sub> molecule. Eleven vibrational frequencies were assumed to be the same as those for B<sub>2</sub>F<sub>4</sub>(g). In addition to these were added four OH torsion frequencies, 824(2) and 209(2), four OH stretching, 3200(4), and four B-O-H bending frequencies, 1200(2) and 880(2). The thermodynamic functions were evaluated based on a molecular model having free internal rotation of two B(OH)<sub>2</sub> groups about B-B bond. The reduced moment of inertia for the rotation is calculated as 4.10146 X 10<sup>-39</sup> g. cm.<sup>2</sup>. The three principal moments of inertia are:  $I_A = 1.64037 \times 10^{-38}$  and  $I_B = I_C = 3.7441 \times 10^{-39}$  g. cm.<sup>2</sup>.

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (F <sup>o</sup> - H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> - H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100	12.326	64.168	101.205	- 3.704	- 304.878	- 298.096
200	18.820	74.732	85.444	- 2.142	- 306.042	- 290.852
300	24.824	83.369	83.369	.000	- 307.000	- 283.189
400	29.857	91.380	84.407	.046	- 307.016	- 283.043
500	33.765	98.482	86.523	2.789	- 307.727	- 274.837
600	36.761	104.915	89.061	5.912	- 308.450	- 266.679
700	39.115	110.732	91.750	9.310	- 308.744	- 258.337
800	41.023	116.117	94.467	17.320	- 308.832	- 249.949
900	42.614	121.043	97.149	21.504	- 308.832	- 241.546
1000	43.963	125.605	99.770	25.835	- 308.761	- 233.134
1100	45.120	129.850	102.314	30.291	- 308.643	- 224.724
1200	46.119	133.820	104.775	34.854	- 308.482	- 216.327
1300	46.986	137.547	107.154	39.510	- 308.296	- 207.939
1400	47.741	141.057	109.452	44.247	- 308.089	- 199.570
1500	48.400	144.374	111.671	49.055	- 307.877	- 191.213
1600	48.977	147.516	113.814	53.924	- 307.664	- 182.873
1700	49.484	150.501	115.885	58.848	- 307.448	- 174.547
1800	49.931	153.342	117.887	63.819	- 307.239	- 166.231
1900	50.326	156.053	119.823	68.832	- 307.034	- 157.932
2000	50.678	158.643	121.702	73.883	- 306.831	- 149.643
2100	50.988	161.123	123.520	78.966	- 306.636	- 141.365
2200	51.267	163.502	125.284	84.079	- 306.451	- 133.094
2300	51.516	165.786	126.996	89.219	- 306.271	- 124.836
2400	51.740	167.984	128.658	94.382	- 306.106	- 116.586
2500	51.942	170.100	130.274	99.566	- 316.730	- 108.337
2600	52.124	172.141	131.845	104.769	- 316.571	- 99.890
2700	52.289	174.111	133.374	109.990	- 316.420	- 91.216
2800	52.439	176.016	134.863	115.227	- 316.275	- 82.549
2900	52.575	177.858	136.314	120.477	- 316.137	- 73.896
3000	52.700	179.643	137.729	125.741	- 316.007	- 65.258
3100	52.814	181.373	139.109	131.017	- 315.881	- 56.588
3200	52.918	183.051	140.456	136.304	- 315.766	- 47.945
3300	53.014	184.681	141.772	141.600	- 315.660	- 39.302
3400	53.103	186.265	143.057	146.906	- 315.562	- 30.662
3500	53.184	187.805	144.314	152.221	- 315.473	- 22.030
3600	53.260	189.305	145.543	157.543	- 315.393	- 13.399
3700	53.329	190.765	146.745	162.872	- 315.326	- 4.767
3800	53.394	192.188	147.923	168.209	- 315.263	- 3.862
3900	53.454	193.576	149.075	173.551	- 315.213	- 2.28
4000	53.510	194.930	150.205	178.899	- 315.173	- .719
4100	53.563	196.252	151.312	184.253	- 315.141	1.183
4200	53.611	197.543	152.397	189.612	- 315.115	2.601
4300	53.657	198.805	153.462	194.975	- 315.095	4.009
4400	53.700	200.039	154.507	200.343	- 315.079	5.402
4500	53.740	201.246	155.532	205.715	- 315.066	6.776
4600	53.777	202.428	156.539	211.091	- 315.056	8.122
4700	53.813	203.585	157.527	216.470	- 315.049	9.445
4800	53.846	204.718	158.499	221.853	- 315.044	10.748
4900	53.877	205.829	159.453	227.239	- 315.041	12.031
5000	53.907	206.917	160.392	232.629	- 315.039	13.296
5100	53.935	207.985	161.314	238.021	- 315.038	14.543
5200	53.961	209.033	162.222	243.415	- 315.038	15.773
5300	53.986	210.051	163.115	248.813	- 315.039	16.987
5400	54.009	211.070	163.994	254.213	- 315.041	18.187
5500	54.032	212.091	164.859	259.613	- 315.044	19.373
5600	54.053	213.035	165.710	265.019	- 315.048	20.545
5700	54.073	213.992	166.546	270.432	- 315.053	21.700
5800	54.092	214.933	167.375	275.843	- 315.059	22.840
5900	54.111	215.857	168.187	281.244	- 315.066	23.965
6000	54.128	216.767	168.991	286.656	- 315.073	25.076

$\Delta H_f^0 = -66.4 \pm 4.0$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -66.8 \pm 4.0$  kcal. mole<sup>-1</sup>  
 $\Delta H_m = [24]$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 6.808 \pm 0.1$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\eta_m = 3193^{\circ}\text{K}$ .

Heat of Formation.

G. M. Kibler, T. F. Lyon, M. J. Linevsky, and V. J. Desantis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1964) studied the vapor pressure of the reaction TiB<sub>2</sub>(c) + 1/2 C(c) = Ti(g) + 1/2 B<sub>2</sub>(c) by comparing the absorption intensity of the 3371.45Å Ti resonance line of the above reaction at temperature T<sub>1</sub> to Ti(g) over pure titanium metal at temperature T<sub>2</sub>. Using JANAF auxiliary data  $\Delta F_{298}^0 = 81.612$  kcal. mole<sup>-1</sup> for the above reaction and  $\Delta H_f^{298}(\text{TiB}_2(c)) = -66.9$  kcal. mole<sup>-1</sup> were calculated.

W. S. Williams, J. Phys. Chem. 65, 2213 (1961) found 2150 ± 25°K. to be the temperature at which TiB<sub>2</sub>(c) was formed from a mixture of TiN(c) and BN(c). If  $\Delta F_{2150}^0 = 0$  is assumed for the reaction TiN(c) + 2BN(c) = TiB<sub>2</sub>(c) + 3/2 N<sub>2</sub>(g) then  $\Delta H_f^{298}(\text{TiB}_2(c)) = -70.7$  kcal. mole<sup>-1</sup>. If, however, N<sub>2</sub>(g) is 1/2 atm. then  $\Delta F_{2150}^0 = 4.4$  kcal. mole<sup>-1</sup> and  $\Delta H_f^{298}(\text{TiB}_2(c)) = -66.3$  kcal. mole<sup>-1</sup>. He has also shown by stability comparisons that  $\Delta F$  and  $\Delta H > 0$  for the reaction TiB<sub>2</sub> + 3/2 C = TiC + 1/2 B<sub>2</sub>. Thus  $\Delta H_f^{298}(\text{TiB}_2) < -51$  kcal. mole<sup>-1</sup>.

P. O. Schissel and O. C. Trulsson, J. Phys. Chem. 66, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system. Only the set of measurements without excess boron or titanium was used. The value  $\Delta F_{2261}^0 = 194.9$  kcal. mole<sup>-1</sup> for the reaction TiB<sub>2</sub>(c) = Ti(g) + 2B(g) was obtained. This corresponds to  $\Delta H_f^{298}(\text{TiB}_2(c)) = -62.9$  kcal. mole<sup>-1</sup> using JANAF auxiliary data.

V. A. Epel'baum and M. I. Starostina, Bor Trudy Konf. Khim. Bora i Ego Soedineni 97 (1955-pub.1958) report  $\Delta H_f^{298}(\text{TiB}_2(c)) = -66.85 \pm 2.7$  kcal. mole<sup>-1</sup> from combustion calorimetry.

C. E. Lowell and W. S. Williams, Rev. Sci. Inst. 32, 1120 (1961) used high temperature calorimetry to obtain the heat of formation of TiB<sub>2</sub>(c). From their data and JANAF auxiliary data  $\Delta H_f^{298}(\text{TiB}_2(c)) = -48.2 \pm 5$  kcal. mole<sup>-1</sup> was calculated. We question the adiabaticity of the experiment and believe their value is an upper limit.  $\Delta H_f^{298}(\text{TiB}_2(c)) = -66.8 \pm 4$  kcal. mole<sup>-1</sup> was chosen as representative of the first four investigations.

Heat Capacity and Entropy.

The heat capacity of TiB<sub>2</sub>(c) has been determined by the following investigators:

Investigator	Method	Temperature Range
Westrum <sup>1</sup>	Adiabatic calorimetry	5-350°K.
Walker et al. <sup>2</sup>	Drop calorimeter	373-977°K.
Southern Research Institute <sup>3</sup>	Drop type ice calorimeter	586-2689°K.
Mezaki <sup>4</sup>	Copper-block drop calorimeter	420-1180°K.
Prophet <sup>5</sup>	Arc-imaging furnace	1300-2150°K.
Barrault et al. <sup>6</sup>	Pulse-method	1733-2417°K.

<sup>1</sup>L. Kaufman and E. V. Clougherty, Technical Documentary Report No. RFD-TDR-63-4096 Part 1 p. 239 (Dec. 1963).

<sup>2</sup>B. E. Walker, C. T. Ewing, and R. R. Miller, J. Phys. Chem. 61, 1822 (1957).

<sup>3</sup>Southern Research Institute, Technical Documentary Report No. ASD-TDR-62-675 p. 253 (Jan. 1963).

<sup>4</sup>R. Mezaki, M. S. Thesis, University of Wisconsin (1961).

<sup>5</sup>H. Prophet, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)7554.

<sup>6</sup>R. J. Barrault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TR-61-260, Part I, Vol. 1, (May 1962).

The low temperature data of Westrum<sup>1</sup> and the medium range data of Walker et al.<sup>2</sup> were used to obtain the C<sub>p</sub>'s of this tabulation. Their data were fitted to a Shomate plot and extrapolated to 4000°K.

$S_{298.15}^0 = 6.808$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> was determined by Westrum<sup>1</sup>.

Melting Data.

The melting point has been reported as 3063°, 3193°, and 3203°K. by F. W. Glaser, Trans. AIME 194, 391 (1952), B. Post, F. W. Glaser, and D. Moskowitz, Acta. Met. 2, 20 (1954), and by G. V. Samsonov and G. V. Petrash, Metalloved. Obrabotka Metalov No. 4, 19 (1955) respectively. The heat of melting is derived from an estimated  $\Delta S_m = 2.5$  cal. deg.<sup>-1</sup> g. atom<sup>-1</sup> at 3193°K. It should be pointed out that an error of 0.5 cal. deg.<sup>-1</sup> g. atom<sup>-1</sup> in the estimation of  $\Delta S_m$  is 5 kcal. mole<sup>-1</sup> in  $\Delta H_m$ .

T, °K.	C <sub>p</sub>	S°	-(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> °	cal. mole <sup>-1</sup> deg. <sup>-1</sup>	kcal. mole <sup>-1</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	.000	INFINITE	-	1.333	-	66.399	-	INFINITE
100	1.798	.602	13.472	1.287	66.499	66.347	144.095	
200	6.722	3.557	6.662	.861	66.691	66.116	72.245	
298	10.583	6.808	6.808	.000	66.808	65.802	48.236	
300	10.641	6.874	6.808	.020	66.801	65.802	47.934	
400	13.119	10.310	7.260	1.270	66.865	65.459	35.763	
500	14.739	13.422	8.187	2.618	66.942	65.099	28.453	
600	15.814	16.298	9.296	4.147	67.036	64.721	23.573	
700	16.610	18.708	10.465	5.770	67.139	64.328	20.083	
800	17.225	20.966	11.639	7.467	67.247	63.919	17.461	
900	17.814	23.029	13.017	9.214	67.352	63.496	15.418	
1000	18.377	24.836	14.612	11.024	67.452	63.062	13.782	
1100	18.914	26.413	16.429	12.889	67.549	62.620	12.441	
1200	19.427	27.800	18.466	14.806	67.642	62.175	11.315	
1300	19.914	29.055	20.617	16.773	67.731	61.729	10.354	
1400	20.375	31.448	18.028	18.788	67.816	61.284	9.528	
1500	20.810	33.868	18.870	20.848	67.896	60.841	8.813	
1600	21.219	36.225	19.881	22.944	67.972	60.401	8.186	
1700	21.602	38.523	20.764	25.090	68.045	59.963	7.633	
1800	21.959	40.768	21.612	27.269	68.116	59.526	7.053	
1900	22.290	42.964	22.447	29.481	68.184	59.091	6.470	
2000	22.595	45.115	23.252	31.726	68.249	58.657	5.893	
2100	22.874	47.224	24.034	34.000	68.311	58.224	5.321	
2200	23.127	49.294	24.794	36.300	68.370	57.791	4.754	
2300	23.354	51.327	25.534	38.624	68.426	57.358	4.191	
2400	23.555	53.326	26.254	40.974	68.479	56.926	3.633	
2500	23.735	55.291	26.957	43.355	68.529	56.495	3.080	
2600	23.895	57.227	27.642	45.720	68.576	56.064	2.532	
2700	24.135	59.134	28.310	48.124	68.620	55.633	1.989	
2800	24.355	61.017	28.963	50.551	68.661	55.202	1.451	
2900	24.555	62.875	29.600	52.997	68.700	54.771	0.918	
3000	24.735	64.711	30.223	55.462	68.736	54.340	0.391	
3100	24.885	66.524	30.833	57.948	68.769	53.909	-0.140	
3200	25.015	68.315	31.429	60.453	68.799	53.478	-0.663	
3300	25.135	70.088	32.014	62.976	68.826	53.047	-1.186	
3400	25.245	71.843	32.584	65.524	68.851	52.616	-1.709	
3500	25.345	73.580	33.148	68.090	68.874	52.185	-2.232	
3600	25.435	75.300	33.698	70.675	68.895	51.754	-2.755	
3700	25.515	77.004	34.248	73.281	68.913	51.323	-3.278	
3800	25.585	78.694	34.786	75.906	68.929	50.892	-3.801	
3900	25.645	80.370	35.316	78.552	68.943	50.461	-4.324	
4000	25.695	82.036	35.840	81.217	68.955	50.030	-4.847	

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100						
200						
298	10.583	13.455	0.000	44.993	45.983	33.705
300						
300	10.641	13.521	0.070	44.994	45.989	33.501
300	10.657	13.605	1.020	45.058	46.311	28.500
400	14.739	20.069	2.618	45.138	46.615	20.375
600	15.814	22.855	4.147	45.203	47.000	17.083
700	16.610	25.355	5.770	45.232	47.174	14.728
800	17.225	27.613	7.462	45.240	47.429	12.956
900	17.614	29.676	9.214	45.245	47.671	11.576
1000	18.377	31.583	11.024	45.245	47.902	10.468
1100	18.914	33.360	12.889	45.242	48.125	9.561
1200	19.427	35.027	14.806	46.779	48.298	8.796
1300	19.914	36.602	16.773	46.858	48.423	8.140
1400	20.375	38.095	18.788	46.927	48.540	7.577
1500	20.810	39.515	20.848	46.989	48.654	7.089
1600	21.219	40.872	22.949	47.045	48.762	6.660
1700	21.602	42.170	25.090	47.095	48.869	6.282
1800	21.959	43.415	27.269	47.137	48.973	5.946
1900	22.290	44.611	29.084	47.172	49.074	5.644
2000	22.595	45.762	29.899	47.206	49.172	5.363
2100	26.000	46.871	30.681	47.238	49.267	5.098
2200	26.000	48.081	31.445	47.269	49.358	4.858
2300	26.000	49.237	32.193	47.298	49.444	4.641
2400	26.000	50.343	32.927	47.325	49.525	4.443
2500	26.000	51.405	33.645	47.350	49.602	4.244
2600	26.000	52.424	34.347	47.373	49.675	4.042
2700	26.000	53.406	35.035	47.394	49.745	3.856
2800	26.000	54.351	35.708	47.413	49.811	3.684
2900	26.000	55.263	36.367	47.430	49.873	3.525
3000	26.000	56.145	37.012	47.445	49.931	3.378
3100	26.000	56.997	37.653	47.458	49.985	3.241
3200	26.000	57.823	38.283	47.469	50.035	3.113
3300	26.000	58.623	38.903	47.478	50.081	2.993
3400	26.000	59.398	39.513	47.485	50.123	2.882
3500	26.000	60.153	40.113	47.490	50.161	2.778
3600	26.000	60.885	40.708	47.494	50.195	2.680
3700	26.000	61.598	41.291	47.496	50.225	2.591
3800	26.000	62.291	41.862	47.497	50.251	2.504
3900	26.000	62.964	42.429	47.497	50.273	2.424
4000	26.000	63.625	42.992	47.496	50.291	2.346
4100	26.000	64.267	43.549	47.494	50.305	2.271
4200	26.000	64.893	44.102	47.491	50.316	2.200
4300	26.000	65.505	44.651	47.487	50.324	2.132
4400	26.000	66.103	45.196	47.482	50.329	2.068
4500	26.000	66.687	45.735	47.476	50.331	2.009
4600	26.000	67.258	46.269	47.469	50.330	1.954
4700	26.000	67.818	46.800	47.461	50.326	1.901
4800	26.000	68.365	47.328	47.451	50.319	1.851
4900	26.000	68.901	47.852	47.440	50.309	1.801
5000	26.000	69.426	48.372	47.428	50.296	1.751
5100	26.000	69.941	48.888	47.415	50.280	1.701
5200	26.000	70.446	49.400	47.401	50.261	1.651
5300	26.000	70.941	49.908	47.386	50.239	1.601
5400	26.000	71.427	50.412	47.370	50.214	1.551
5500	26.000	71.904	50.912	47.353	50.186	1.501
5600	26.000	72.373	51.408	47.335	50.155	1.451
5700	26.000	72.833	51.900	47.316	50.121	1.401
5800	26.000	73.283	52.388	47.296	50.084	1.351
5900	26.000	73.730	52.872	47.274	50.044	1.301
6000	26.000	74.167	53.352	47.251	50.000	1.251

$S_{298.15}^o = [13.455] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^o [298.15] = [-44.99] \text{ kcal. mole}^{-1}$

$T_m = 3193^\circ\text{K.}$

$T_d = [4250]^\circ\text{K.}$

Heat of Formation.

$\Delta H_f^o [298.15(1)]$  was calculated from  $\Delta H_f^o [298.15(c)]$  by adding  $\Delta H_{Tm}^o$  and the difference between  $\Delta H_{Tm}^o - H_{298.15}^o$  for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at  $2100^\circ\text{K.}$   $C_p(1)$  at and below  $2100^\circ\text{K.}$  were assumed to be equal to those of  $TiB_2(c)$ . Above  $2100^\circ\text{K.}$  the heat capacities were estimated to be constant.  $S_{298.15}^o(1)$  is calculated based on  $S_{298.15}^o(c)$  and an estimated  $\Delta S_m^o = 2.5 \text{ cal. deg.}^{-1} \text{ gm. atom}^{-1}$ .

Melting Data.

See  $TiB_2(c)$  table for details.

Decomposition Data.

$T_d$  estimated from  $\Delta H_{Td}^o = 0$  for the reaction  $TiB_2(1) = Ti(l) + 2B(g)$ .

$\Delta H_f^0 = -76.8 \pm 1.6 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0(298.15) = -77.1 \pm 1.6 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^0 = [25] \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 8.55 \pm 0.01 \text{ cal. deg}^{-1} \text{ mole}^{-1}$   
 $T_m = 3325^\circ\text{K.}$

Heat of Formation.

G. K. Johnson, Argonne National Laboratory, private communication, Ma, 1965, reported  $\Delta H_f^0(298.15) = -78.7 \pm 1.5 \text{ kcal. mole}^{-1}$ . Their value was obtained by fluorine bomb calorimetry and was based on their recently redetermined value of  $\Delta H_f^0(298.15)(\text{BF}_3) = -271.90 \pm 0.20 \text{ kcal. mole}^{-1}$ .  
 G. M. Kibler, T. P. Lyon, M. J. Linevsky, and V. J. De Santis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1962) studied the vaporization of ZrB<sub>2</sub> by the Knudsen effusion method. Over the range 2860 to 2500°K,  $\log K_p = 22.048 - \frac{10,152}{T} + \frac{1.10}{T^2}$  for the reaction  $\text{ZrB}_2(\text{s}) \rightleftharpoons (\text{g}) + 2\text{B}(\text{g})$ .  
 J. H. Van Wazer, JAMP auxiliary data were used to calculate  $\Delta H_f^0(298.15) = -76.5 \pm 1.5 \text{ kcal. mole}^{-1}$  by the 3rd law method and  $\Delta H_f^0(298.15) = -76.7 \pm 3.2 \text{ kcal. mole}^{-1}$ .  
 O. C. Truison and H. W. Goldstein, Union Carbide Res. Inst., report No. C-25 (October 1964), investigated the decomposition vapor pressure of the reaction  $\text{ZrB}_2(\text{s}) \rightleftharpoons (\text{g}) + 2\text{B}(\text{g})$  and reported  $\Delta H_f^0(298.15) = -76.1 \pm 5 \text{ kcal. mole}^{-1}$ . They also reported  $\Delta H_f^0(298.15) = -289.7 \text{ kcal. mole}^{-1}$  for the reaction  $\text{ZrB}_2(\text{s}) + \text{C}(\text{s}) \rightleftharpoons \text{ZrC}(\text{s}) + 2\text{B}(\text{g})$ . Using the JANAP  $\Delta H_f^0(298.15) = -47.0 \pm 3 \text{ kcal. mole}^{-1}$ ,  $\Delta H_f^0(298.15) = -76.1 \pm 5 \text{ kcal. mole}^{-1}$  was calculated. JANAP values for  $\Delta H_f^0(298.15)$  of Zr and B were not used since their independent determinations serve to cancel instrumental constants.  
 From oxygen bomb calorimetry, E. J. Huber, Jr., E. L. Heed, and C. E. Holley, Jr., J. Phys. Chem. **69**, 3040 (1964) reported  $\Delta H_f^0(298.15) = -77.2 \pm 1.2 \text{ kcal. mole}^{-1}$ .  
 $\Delta H_f^0(298.15) = -77.1 \pm 1.6$  was chosen as a value representative of the above.

Heat Capacity and Entropy.

The heat capacity of ZrB<sub>2</sub>(s) has been determined by the following investigators:  
 Westrum and Peick<sup>1</sup> Adiabatic calorimetry  
 Valentine et al.<sup>2</sup> Copper-block drop calorimeter  
 Mezaki<sup>3</sup> Arc-heating furnace  
 Barrault et al.<sup>5</sup> Pulse-method  
 Southern Research Institute<sup>6</sup> Drop type ice calorimeter  
 1. E. P. Westrum, Jr. and G. Peick, J. Chem. Eng. Data **5**(2), 153 (1963).  
 2. R. H. Valentine, T. P. Jambois, and J. L. Margrave, J. Chem. Eng. Data **5**(2), 182 (1964).  
 3. R. Mezaki, M. S. Thesis, University of Wisconsin (1961).  
 4. H. Proppe, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)775-1.  
 5. R. J. Barrault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TR-61-260, Part I, Vol. 1, (May 1962).  
 6. D. Need, C. Pears, and C. Oglesby, Southern Research Institute, report ASD-TRD-62-675 (August 1962).

Westrum and Peick's  $C_p$  values were adopted to 350°K. The disparities in heat capacities above room temperatures seem too great to be errors in measurement and are probably due to sample differences. Since the samples used by Westrum and Peick<sup>1</sup> and by Valentine et al.<sup>2</sup> were from the same batch, Valentine's data were used above 350°K. The two sets of data were fitted to a Shomate plot which was extrapolated to 4000°K. However, in consideration of the results of Mezaki<sup>3</sup>, Proppe<sup>4</sup>, and Southern Research Institute<sup>6</sup>, the  $C_p$  extrapolation ran somewhat higher than a direct extrapolation of Valentine's data would yield.  
 $S_{298.15}^0(\text{ZrB}_2) = 8.59 \text{ cal. mole}^{-1} \text{ deg}^{-1} \text{ K}^{-1}$  was determined by Westrum<sup>1</sup>.

Melting Data.

The melting point has been reported as 3313°, 3325°, and 3265°K. by P. Glaeser and B. Post, J. of Metals, **5**, 1117 (1953), B. Post, P. Glaeser, and D. W. Moskowitz, Acta. Met. **2**, 70 (1954) and H. Greenwood, Engineer **187**, 349 (1949) respectively. The heat of melting is derived from an estimated  $\Delta S_m = 2.5 \text{ cal. deg}^{-1} \text{ g. atom}^{-1}$  at 3325°K. It should be pointed out that an error of 0.5 cal. deg<sup>-1</sup> g. atom<sup>-1</sup> in the estimation of  $\Delta S_m$  is 5 kcal. mole<sup>-1</sup> in  $\Delta H_m^0$ .

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	0.000	INFINITE	1.590	76.789	76.789	INFINITE
100	2.870	1.177	1.503	76.926	75.690	167.599
200	7.840	4.716	0.964	77.070	76.388	83.469
298	11.530	8.500	0.000	77.100	76.049	55.743
300	11.589	8.562	0.021	77.100	76.042	55.194
400	13.744	9.076	1.301	77.090	75.691	41.354
500	14.970	10.054	2.742	77.155	75.334	32.027
600	15.729	11.207	4.279	77.272	74.959	27.302
700	16.259	12.405	5.870	77.429	74.561	23.278
800	16.661	13.505	7.526	77.610	74.140	20.000
900	16.991	14.472	9.209	77.804	73.695	17.495
1000	17.245	15.267	10.921	78.016	73.225	16.003
1100	17.489	16.036	12.657	78.254	72.737	14.451
1200	17.733	16.789	14.419	78.522	72.234	12.846
1300	17.977	17.524	16.204	78.828	71.717	11.190
1400	18.221	18.242	18.014	79.164	71.187	9.493
1500	18.465	18.946	19.849	80.527	70.643	7.758
1600	18.709	19.633	21.707	80.553	69.504	6.863
1700	18.953	20.305	23.590	80.843	68.290	6.458
1800	19.197	20.963	25.499	81.134	68.178	6.081
1900	19.441	21.607	27.429	81.425	67.450	5.734
2000	19.685	22.237	29.386	81.710	66.708	5.405
2100	19.929	22.852	31.366	81.990	65.950	5.084
2200	20.173	23.453	33.372	82.264	65.015	4.755
2300	20.417	24.040	35.401	82.535	64.003	4.429
2400	20.661	24.613	37.455	82.791	62.976	4.201
2500	20.905	25.172	39.533	83.035	61.722	3.951
2600	21.149	25.716	41.636	83.266	60.242	3.718
2700	21.393	26.246	43.763	83.488	58.749	3.498
2800	21.637	26.762	45.915	83.699	57.253	3.292
2900	21.881	27.266	48.090	83.899	55.745	3.107
3000	22.125	27.757	50.291	84.087	54.242	2.915
3100	22.369	28.235	52.515	84.263	52.735	2.742
3200	22.613	28.700	54.765	84.428	51.221	2.578
3300	22.857	29.152	57.038	84.582	49.680	2.423
3400	23.101	29.591	59.336	84.726	48.189	2.277
3500	23.345	30.018	61.658	84.860	46.679	2.130
3600	23.589	30.433	64.005	84.983	45.164	1.993
3700	23.833	30.837	66.376	85.096	43.649	1.863
3800	24.077	31.231	68.772	85.199	42.135	1.738
3900	24.321	31.615	71.191	85.292	40.620	1.618
4000	24.565	31.989	73.636	85.376	39.105	1.503

T, °K.	C <sub>p</sub>	S°	-(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0							
100							
200							
298	11.530	15.448	15.448	0.000	54.194	55.187	40.452
300	11.589	15.520	15.448	0.021	54.194	55.194	40.207
400	13.744	19.186	15.634	1.301	54.193	55.528	30.338
500	14.976	22.196	16.012	2.742	54.249	55.857	24.414
600	15.729	25.196	16.065	4.279	54.366	56.168	20.458
700	16.229	27.663	16.263	5.879	54.523	56.456	17.625
800	16.601	29.860	16.453	7.526	54.704	56.720	15.495
900	16.851	31.852	16.610	9.206	54.898	56.961	13.831
1000	17.075	33.646	16.775	10.921	55.110	57.177	12.495
1100	17.289	35.301	16.904	12.657	55.352	57.374	11.399
1200	17.473	36.833	17.000	14.413	55.625	57.548	10.471
1300	17.627	38.262	17.077	16.204	55.923	57.697	9.677
1400	17.751	39.597	17.137	18.034	56.240	57.823	8.993
1500	17.845	40.866	17.183	19.904	56.585	57.928	8.398
1600	17.909	42.068	17.216	21.707	56.957	58.013	7.874
1700	17.953	43.210	17.238	23.500	57.357	58.079	7.410
1800	17.977	44.300	17.251	25.288	57.782	58.126	6.995
1900	17.981	45.344	17.256	27.079	58.231	58.156	6.622
2000	17.965	46.348	17.255	28.866	58.704	58.168	6.285
2100	17.929	47.314	17.247	30.651	59.208	58.162	5.978
2200	17.873	48.247	17.232	32.437	59.742	58.138	5.682
2300	17.800	49.149	17.211	34.224	60.305	58.095	5.404
2400	17.713	50.028	17.176	36.012	60.897	58.035	5.150
2500	17.613	50.885	17.128	37.801	61.518	57.958	4.916
2600	17.500	51.720	17.068	39.591	62.169	57.865	4.696
2700	17.373	52.529	16.997	41.382	62.850	57.757	4.484
2800	17.242	53.316	16.916	43.174	63.561	57.635	4.277
2900	17.107	54.082	16.825	44.967	64.302	57.499	4.080
3000	16.968	54.827	16.725	46.761	65.073	57.350	3.892
3100	16.825	55.552	16.616	48.556	65.874	57.188	3.712
3200	16.678	56.257	16.500	50.351	66.705	57.014	3.546
3300	16.527	56.942	16.375	52.146	67.566	56.828	3.394
3400	16.373	57.607	16.250	53.941	68.457	56.630	3.254
3500	16.216	58.252	16.125	55.736	69.378	56.419	3.124
3600	16.057	58.877	16.000	57.531	70.329	56.196	2.999
3700	15.896	59.482	15.875	59.326	71.310	55.961	2.879
3800	15.733	60.067	15.750	61.121	72.321	55.706	2.764
3900	15.568	60.632	15.625	62.932	73.362	55.431	2.654
4000	15.401	61.177	15.500	64.743	74.433	55.136	2.549
4100	15.232	61.702	15.375	66.554	75.534	54.821	2.449
4200	15.061	62.207	15.250	68.365	76.665	54.486	2.354
4300	14.888	62.692	15.125	70.176	77.826	54.131	2.264
4400	14.713	63.157	15.000	71.987	79.007	53.756	2.179
4500	14.536	63.602	14.875	73.798	80.208	53.361	2.099
4600	14.357	64.027	14.750	75.609	81.429	52.946	2.024
4700	14.176	64.432	14.625	77.420	82.670	52.511	1.954
4800	14.000	64.817	14.500	79.231	83.931	52.056	1.889
4900	13.821	65.182	14.375	81.042	85.212	51.581	1.829
5000	13.640	65.527	14.250	82.853	86.513	51.086	1.774
5100	13.457	65.852	14.125	84.664	87.834	50.571	1.724
5200	13.272	66.157	14.000	86.475	89.175	50.036	1.679
5300	13.085	66.442	13.875	88.286	90.536	49.481	1.639
5400	12.896	66.707	13.750	90.097	91.917	48.906	1.604
5500	12.705	66.952	13.625	91.908	93.318	48.311	1.574
5600	12.512	67.177	13.500	93.719	94.739	47.696	1.549
5700	12.317	67.382	13.375	95.530	96.180	47.061	1.529
5800	12.120	67.567	13.250	97.341	97.641	46.406	1.514
5900	11.921	67.732	13.125	99.152	99.122	45.731	1.504
6000	11.720	67.877	13.000	100.963	100.623	45.036	1.504

ΔH<sub>f</sub><sup>o</sup> 298.15 = [15.448] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 ΔH<sub>f</sub><sup>o</sup> = [25] kcal. mole<sup>-1</sup>  
 T<sub>m</sub> = 3323°K.  
 T<sub>d</sub> = [4466]°K.

Heat of Formation.

ΔH<sub>f</sub><sup>o</sup> 298.15(1) was calculated from ΔH<sub>f</sub><sup>o</sup> 298.15(c) by adding ΔH<sub>Tm</sub><sup>o</sup> and the difference between ΔH<sub>Tm</sub><sup>o</sup> and ΔH<sub>Tm</sub><sup>o</sup> 298.15 for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2200°K. C<sub>p</sub>(1) at and below 2200°K. were assumed to be equal to those of ZrB<sub>2</sub>(c). Above 2200°K. the heat capacities were estimated to be constant. S<sub>298.15</sub><sup>o</sup>(c) and an estimated ΔS<sub>m</sub><sup>o</sup> = 2.5 cal. deg.<sup>-1</sup> gm. atom<sup>-1</sup>.

Melting Data.

See ZrB<sub>2</sub>(c) table for details.

Decomposition Data.

T<sub>d</sub> estimated from ΔF<sub>fd</sub><sup>o</sup> = 0 for the reaction ZrB<sub>2</sub>(l) = Zr(g) + 2B(g).

Point Group [C<sub>2v</sub>]

ΔH<sub>f</sub>° = -379 ± 6 kcal. mole<sup>-1</sup>

ΔH<sub>f</sub>° = [75.225] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

ΔH<sub>f</sub>° 298.15 = -392 ± 6 kcal. mole<sup>-1</sup>

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. <sup>-1</sup>	ω, cm. <sup>-1</sup>	ω, cm. <sup>-1</sup>
[2100] (1)	[880] (1)	[350] (1)
[870] (1)	[1460] (1)	[225] (1)
[670] (1)	[520] (1)	[800] (1)
[2200] (1)	[2230] (1)	[225] (1)
[1390] (1)	[1390] (1)	[840] (1)
[1200] (1)	[1200] (1)	[800] (1)
[680] (1)	[350] (1)	[260] (1)

Bond Distances: B-O = [1.36] Å B-H = [1.18] Å B-F = [1.41] Å

Bond Angle: B-O-B = [120°] O-B-H = [120°] O-B-F = [120°]

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [2.1654] X 10<sup>-113</sup> g.<sup>3</sup> cm.<sup>6</sup>

σ = [2]

Heat of Formation.

The equilibrium constants (K), 1246-1326°K, for the two reactions 2B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H(g) = B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H<sub>2</sub>(g) + E<sub>3</sub>O<sub>3</sub>F<sub>3</sub>(g) and 2B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H<sub>2</sub>(g) = B<sub>3</sub>O<sub>3</sub>H<sub>3</sub>(g) + B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H(g) were reported by P. R. Porter and W. P. Sholette, J. Chem. Phys. 37, 198 (1962). The ΔH<sub>f</sub>° 298.15 for B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H(g) adopted was evaluated by use of K values slightly outside the ranges given by Porter and Sholette. See the table for B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H(g) for details.

Heat Capacity and Entropy.

The structure was assumed to be a planar six membered ring structure of C<sub>2v</sub> symmetry, which has 21 vibrations of the type 8A<sub>1</sub>, 7B<sub>1</sub>, 2A<sub>2</sub>, and 4B<sub>2</sub>. These frequencies were estimated from the values for boroxin and trifluoroboroxin, the symmetry being reduced from D<sub>3h</sub> as follows: 3A<sub>1</sub> → 3A<sub>1</sub>, 2A<sub>2</sub> → 2B<sub>1</sub>, 5E<sub>1</sub> → 5A<sub>1</sub> + 5B<sub>1</sub>, 2A<sub>2</sub> → 2B<sub>2</sub> and 2E<sub>2</sub> → 2A<sub>2</sub> + 2B<sub>2</sub>.

The B-F distance was taken as approximately equal to that in (CH<sub>3</sub>)<sub>2</sub>O·BF<sub>3</sub> reported by S. H. Bauer, G. R. Findlay and A. W. Laubengayer, J. Am. Chem. Soc. 57, 339 (1945). The other bond lengths and angles were taken equal to those in boroxin. The individual moments of inertia were calculated to be I<sub>A</sub> = 32.995 X 10<sup>-39</sup>, I<sub>B</sub> = 13.975 X 10<sup>-39</sup>, and I<sub>C</sub> = 46.968 X 10<sup>-39</sup> g. cm.<sup>2</sup>

T, K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	-379.205	-379.205	INFINITE
100	11.152	57.652	91.583	4.273	-379.205	-379.205	820.744
200	17.734	67.208	77.332	1.967	-380.520	-375.559	404.609
298	22.764	75.225	75.225	4.000	-381.306	-370.285	267.342
300	22.863	75.326	75.226	4.042	-382.012	-364.731	265.616
400	27.749	82.635	76.184	2.580	-382.586	-358.738	195.996
500	31.713	89.259	78.147	5.561	-383.043	-352.721	154.167
600	34.866	95.341	80.514	8.896	-383.381	-346.622	126.251
700	37.367	101.911	83.031	12.512	-383.608	-340.475	106.296
800	39.354	108.035	85.595	16.352	-383.739	-334.307	91.324
900	40.941	113.766	88.132	20.370	-383.790	-328.125	78.676
1000	42.218	119.148	90.617	24.530	-383.786	-321.936	70.356
1100	43.240	124.222	93.035	28.806	-383.753	-315.755	62.732
1200	44.100	129.023	95.377	33.175	-383.695	-309.573	55.378
1300	44.799	133.581	97.662	37.621	-383.632	-303.400	48.304
1400	45.386	137.923	99.830	42.131	-383.567	-297.229	41.397
1500	45.867	142.071	101.942	46.694	-383.515	-291.067	34.406
1600	46.279	146.045	103.981	51.301	-383.477	-284.904	27.414
1700	46.630	149.861	105.951	55.947	-383.455	-278.742	20.422
1800	46.930	153.535	107.854	60.626	-383.451	-272.586	13.430
1900	47.190	157.080	109.694	65.332	-383.466	-266.426	6.438
2000	47.415	160.506	111.475	70.063	-383.491	-260.264	28.439
2100	47.612	163.824	113.189	74.814	-383.531	-254.100	26.443
2200	47.785	167.043	114.869	79.584	-383.584	-247.936	24.451
2300	47.937	170.171	116.488	84.370	-383.657	-241.771	22.459
2400	48.072	173.219	118.059	89.171	-383.746	-235.605	20.467
2500	48.192	176.188	119.585	93.984	-400.013	-229.439	18.475
2600	48.299	179.071	121.068	98.804	-400.108	-223.273	16.483
2700	48.396	181.896	122.509	103.644	-400.159	-217.107	14.491
2800	48.482	184.657	123.912	108.488	-400.216	-210.941	12.500
2900	48.561	187.360	125.277	113.340	-400.279	-204.775	10.508
3000	48.632	190.008	126.608	118.200	-400.349	-198.609	8.516
3100	48.696	192.603	127.909	123.066	-400.426	-192.443	6.524
3200	48.753	195.150	129.169	127.939	-400.509	-186.277	4.532
3300	48.805	197.651	130.404	132.819	-400.596	-180.111	2.540
3400	48.852	200.109	131.609	137.700	-401.092	-173.945	0.548
3500	48.903	202.526	132.787	142.588	-401.246	-167.779	0.024
3600	48.945	204.904	133.937	147.481	-401.406	-161.613	9.327
3700	48.983	207.246	135.063	152.377	-401.576	-155.447	8.669
3800	49.019	209.553	136.164	157.277	-401.750	-149.281	8.044
3900	49.052	211.826	137.242	162.181	-401.933	-143.115	7.452
4000	49.082	214.069	138.297	167.088	-402.126	-136.949	6.897
4100	49.110	216.281	139.330	171.997	-402.334	-130.783	6.377
4200	49.137	218.465	140.339	176.910	-402.546	-124.617	5.886
4300	49.162	220.621	141.337	181.825	-402.762	-118.451	5.424
4400	49.184	222.752	142.310	186.742	-402.981	-112.285	4.991
4500	49.206	224.856	143.266	191.661	-403.204	-106.119	4.586
4600	49.226	226.939	144.204	196.583	-403.431	-100.000	4.209
4700	49.245	228.998	145.128	201.507	-403.661	-93.881	3.859
4800	49.263	231.035	146.048	206.432	-403.894	-87.762	3.534
4900	49.280	233.051	146.956	211.359	-404.130	-81.643	3.232
5000	49.295	235.047	147.859	216.288	-404.369	-75.524	2.951
5100	49.310	237.023	148.747	221.218	-404.611	-69.405	2.690
5200	49.324	238.981	149.620	226.150	-404.856	-63.286	2.448
5300	49.337	240.920	150.479	231.083	-405.104	-57.167	2.224
5400	49.350	242.843	151.326	236.017	-405.354	-51.048	2.016
5500	49.362	244.752	152.159	240.953	-405.606	-44.929	1.822
5600	49.373	246.638	152.979	245.880	-405.860	-38.810	1.642
5700	49.383	248.501	153.787	250.827	-406.116	-32.691	1.475
5800	49.394	250.343	154.584	255.766	-406.374	-26.572	1.320
5900	49.403	252.166	155.374	260.706	-406.634	-20.453	1.176
6000	49.412	253.974	156.151	265.647	-406.895	-14.334	1.042

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	+0.00	INFINITE	-	4.571	-472.461	-472.461	INFINITE
100	11.771	59.043	56.365	3.672	-473.724	-468.147	1023.084
200	18.724	69.975	80.684	2.842	-474.455	-482.266	505.117
298	24.744	78.608	78.608	+0.000	-475.000	-456.169	334.365
300	24.847	78.761	78.608	+0.466	-475.009	-456.054	332.219
400	29.837	86.619	79.666	2.989	-475.415	-449.669	245.676
500	33.785	93.719	81.762	5.979	-475.718	-443.396	193.712
600	36.857	100.157	84.301	9.517	-475.919	-436.670	159.049
700	39.230	106.030	86.982	13.327	-476.026	-430.116	134.283
800	41.066	111.394	89.712	17.345	-476.059	-423.561	113.706
900	42.495	116.316	92.398	21.526	-476.029	-417.000	101.258
1000	43.4518	120.894	95.050	25.934	-475.960	-410.441	89.698
1100	44.4512	125.095	97.562	30.242	-475.878	-403.896	80.243
1200	45.4230	128.890	100.038	34.731	-475.782	-397.354	72.565
1300	46.4614	132.017	102.389	39.284	-475.682	-390.823	65.700
1400	46.8274	134.607	104.665	43.800	-475.607	-384.296	59.988
1500	47.4692	136.825	106.805	48.540	-475.540	-377.779	55.040
1600	47.6026	142.250	108.983	53.226	-475.492	-371.263	50.710
1700	47.5368	147.109	111.025	57.943	-475.465	-364.747	46.889
1800	47.3548	147.820	112.994	62.686	-475.461	-358.238	43.494
1900	47.1753	150.397	114.896	67.452	-475.474	-351.726	40.456
2000	47.933	152.481	116.733	72.236	-475.501	-345.211	37.721
2100	48.088	155.143	118.509	77.038	-475.544	-338.693	35.247
2200	48.423	157.434	120.228	81.853	-475.605	-332.177	32.997
2300	48.4342	159.580	121.892	86.682	-475.680	-325.657	30.943
2400	48.448	161.640	123.506	91.521	-475.775	-319.128	29.059
2500	48.4541	163.619	125.071	96.371	-475.892	-312.257	27.298
2600	48.4625	165.525	126.590	101.229	-482.152	-305.083	25.643
2700	48.4699	167.361	128.067	106.095	-492.261	-297.880	24.111
2800	48.4766	169.134	129.502	110.969	-492.376	-290.686	22.688
2900	48.4827	170.846	130.898	115.848	-492.497	-283.468	21.362
3000	48.4882	172.502	132.257	120.734	-492.626	-276.266	20.125
3100	48.4931	174.106	133.582	125.625	-492.759	-269.055	18.967
3200	48.4976	175.660	134.872	130.520	-492.900	-261.835	17.882
3300	49.018	177.168	136.131	135.420	-493.048	-254.610	16.861
3400	49.4204	185.373	143.093	140.323	-493.204	-247.382	15.901
3500	49.6590	180.054	138.560	145.231	-493.366	-240.153	14.995
3600	49.122	181.437	139.732	150.141	-493.534	-232.908	14.139
3700	49.151	182.784	140.877	155.055	-493.710	-225.669	13.329
3800	49.178	184.095	141.997	159.972	-493.892	-218.415	12.561
3900	49.204	185.373	143.093	164.891	-494.082	-211.178	11.834
4000	49.227	186.619	144.166	169.812	-494.281	-203.964	11.152
4100	49.248	187.834	145.216	174.736	-494.487	-196.767	10.517
4200	49.269	189.021	146.262	179.662	-494.699	-189.586	9.922
4300	49.287	190.181	147.275	184.590	-494.916	-182.414	9.362
4400	49.303	191.314	148.242	189.519	-495.138	-175.244	8.831
4500	49.321	192.423	149.221	194.451	-495.365	-168.078	8.322
4600	49.337	193.507	150.162	199.384	-495.596	-160.914	7.832
4700	49.351	194.568	151.062	204.318	-495.831	-153.756	7.352
4800	49.363	195.607	151.913	209.251	-496.069	-146.601	6.882
4900	49.377	196.625	152.713	214.181	-496.311	-139.451	6.421
5000	49.389	197.623	153.477	219.129	-496.556	-132.301	5.969
5100	49.400	198.601	154.209	224.069	-496.804	-125.151	5.526
5200	49.411	199.560	154.920	229.009	-497.056	-118.001	5.091
5300	49.421	200.502	155.630	233.951	-497.311	-110.851	4.656
5400	49.431	201.425	156.339	238.893	-497.568	-103.701	4.221
5500	49.439	202.332	157.039	243.837	-497.826	-96.551	3.786
5600	49.448	203.223	157.732	248.781	-498.086	-89.401	3.351
5700	49.456	204.099	158.419	253.726	-498.348	-82.251	2.916
5800	49.464	204.959	159.102	258.672	-498.612	-75.101	2.481
5900	49.471	205.804	159.781	263.619	-498.878	-67.951	2.046
6000	49.478	206.636	161.875	268.567	-499.146	-60.801	1.611

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965; Dec. 31, 1965

DIFLUOROBOROXIN (B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>)

(IDEAL GAS)

MOL. WT. = 119.43597

Point Group [C<sub>2v</sub>]  
 $\Delta H_f^o = -472 \pm 5$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^o = -475 \pm 5$  kcal. mole<sup>-1</sup>  
 $S_{298.15}^o = [78.6] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
[1650] (1)	[660] (1)	[300] (1)
[850] (1)	[1570] (1)	[220] (1)
[610] (1)	[490] (1)	[710] (1)
[1800] (1)	[1840] (1)	[220] (1)
[1385] (1)	[1385] (1)	[780] (1)
[1080] (1)	[1080] (1)	[700] (1)
[660] (1)	[310] (1)	[230] (1)

Bond Distance: B-O = [1.36] Å    B-H = [1.18] Å    B-F = [1.41] Å  
 Bond Angle: B-O-B = [120°]    O-B-H = [120°]    O-B-F = [120°]  
 Product of the Moments of Inertia:  $I_A I_B I_C = [7.5869] \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The stabilities of gaseous boroxin (B<sub>3</sub>O<sub>3</sub>) and its fluoro derivatives have been studied by R. P. Porter and M. P. Shollette, J. Chem. Phys. 37, 199 (1962). From the mass spectra of the gaseous reaction products generated by reaction of an H<sub>2</sub>-BF<sub>3</sub> mixture on B<sub>2</sub>O<sub>3</sub> at 1250°K., the equilibrium constants (K) for the following proposed reactions were reported.

Reaction	Temperature, °K.	K	$\Delta H_f^o$ 298.15°, kcal. mole <sup>-1</sup>
(1) H <sub>2</sub> (g) + B <sub>3</sub> O <sub>3</sub> F <sub>2</sub> (g) = HF(g) + B <sub>3</sub> O <sub>3</sub> F <sub>2</sub> H(g)	1246 - 1326	$4.2 \times 10^{-3} - 2.3 \times 10^{-2}$	20.45 - 17.17
(2) 2B <sub>3</sub> O <sub>3</sub> F <sub>2</sub> H(g) = B <sub>3</sub> O <sub>3</sub> FH <sub>2</sub> (g) + B <sub>3</sub> O <sub>3</sub> F <sub>2</sub> (g)	1246 - 1326	0.62 - 0.46	1.28 - 2.15
(3) 2B <sub>3</sub> O <sub>3</sub> FH <sub>2</sub> (g) = B <sub>3</sub> O <sub>3</sub> H <sub>3</sub> (g) + B <sub>3</sub> O <sub>3</sub> F <sub>2</sub> H(g)	1246 - 1326	1.0 - 0.63	-2.56 - -1.51

Using these reported K values the corresponding enthalpy changes ( $\Delta H_f^o$  298.15°) were evaluated by the third law method. The results obtained are listed in the above table. Based on  $\Delta H_f^o$  298.15° = -565.3 and -64.8 kcal. mole<sup>-1</sup> for B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>(g) and HF(g), respectively, the value of  $\Delta H_f^o$  298.15° for B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H(g) was calculated from Reaction (1) as -482 kcal. mole<sup>-1</sup>. From Reaction (2), the  $\Delta H_f^o$  298.15° value for B<sub>3</sub>O<sub>3</sub>FH<sub>2</sub>(g) was calculated as -397 kcal. mole<sup>-1</sup>. However, employing  $\Delta H_f^o$  298.15°(B<sub>3</sub>O<sub>3</sub>H<sub>3</sub>, g) = -291 kcal. mole<sup>-1</sup>, the values of  $\Delta H_f^o$  298.15° for B<sub>3</sub>O<sub>3</sub>FH<sub>2</sub>(g) and B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H(g) thus obtained do not fit properly for Reaction (3). Therefore the  $\Delta H_f^o$  298.15° for B<sub>3</sub>O<sub>3</sub>FH<sub>2</sub>(g) and B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>H(g) adopted were evaluated by use of K values slightly outside the ranges given by Porter and Shollette.

Heat Capacity and Entropy.

The vibrational frequencies were obtained by comparison with B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>(g) and B<sub>3</sub>H<sub>3</sub>O<sub>3</sub>(g). The types of vibration and symmetry are identical to those given for B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>(g). The bond angles and lengths were taken equal to those for B<sub>3</sub>O<sub>3</sub>F<sub>2</sub>(g). The individual moments of inertia were calculated to be I<sub>A</sub> = 22.051 × 10<sup>-39</sup>, I<sub>B</sub> = 48.669 × 10<sup>-39</sup> and I<sub>C</sub> = 70.710 × 10<sup>-39</sup> g. cm<sup>2</sup>.

B<sub>3</sub>F<sub>2</sub>HO<sub>3</sub>

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (F <sup>o</sup> - H <sub>298<sup>o</sup>)/T</sub>	H <sup>o</sup> - H <sub>298<sup>o</sup></sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0						
100	43.750	37.200	0.000	- 803.600	- 757.734	555.408
200	43.761	37.471	0.081	- 803.607	- 757.452	551.777
300	47.239	38.043	4.616	- 804.090	- 741.998	405.390
400	52.567	41.610	9.608	- 806.144	- 726.257	317.431
500	57.625	46.446	15.174	- 806.597	- 710.231	258.689
600	61.950	50.715	21.108	- 806.800	- 694.151	216.713
700	65.586	54.384	27.489	- 806.776	- 678.063	185.229
800	68.766	57.294	34.208	- 806.552	- 661.985	160.744
900	71.803	60.465	41.234	- 806.140	- 645.937	141.163
1000	75.052	63.928	48.578	- 805.525	- 629.948	125.153
1100	78.198	67.597	56.278	- 804.663	- 614.021	111.453
1200	81.244	71.467	64.218	- 803.513	- 598.176	100.058
1300	84.490	75.401	72.509	- 802.303	- 582.417	90.915
1400	87.636	79.482	81.116	- 800.755	- 566.770	82.574
1500	90.782	83.703	90.036	- 798.958	- 551.222	75.290
1600	93.928	88.074	99.272	- 797.004	- 535.145	68.537
1700	97.074	92.593	108.822	- 794.939	- 519.581	62.354
1800	100.220	97.256	118.687	- 792.767	- 494.172	56.840
2000	107.366	104.185	128.866	- 788.215	- 474.027	51.895

ΔH<sub>f</sub><sup>o</sup> = Unknown

ΔH<sub>f</sub><sup>o</sup> 298.15 = -803.6 ± 1.5 kcal. mole<sup>-1</sup>

ΔH<sub>m</sub><sup>o</sup> = 28.8 ± 1.5 kcal. mole<sup>-1</sup>

S<sub>298.15</sub><sup>o</sup> = [37.2 ± 1.0] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = 1190 ± 2°K.

Heat of Formation.

The heat of formation was calculated from ΔH<sub>f</sub><sup>o</sup> 298 = -12.2 kcal. for the reaction Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>(c) + 2HNO<sub>3</sub>(aq.) + 5H<sub>2</sub>O(l) = 4H<sub>2</sub>BO<sub>3</sub>(aq.) + 2LiNO<sub>3</sub>(aq.). The heat of solution (ΔH<sub>f</sub><sup>o</sup>) was interpolated from the heat of solution data of L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27 (1954). Auxilliary data are from National Bureau of Standards Circular 500 (1952).

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1190°K. were smoothed graphically and used to determine C<sub>p</sub>. A linear extrapolation of C<sub>p</sub> was used from 1190 to 2000°K.

S<sub>298</sub><sup>o</sup> was estimated by three routes: (1) S<sub>298</sub><sup>o</sup> (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) = 37.3 cal. mole<sup>-1</sup> deg.<sup>-1</sup> based on JANAP S<sub>298</sub><sup>o</sup> (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) = 45.3 and ΔS<sub>298</sub><sup>o</sup> (2Na-2Li) = 8 cal. deg.<sup>-1</sup> from W. M. Latimer, J. Am. Chem. Soc. 73, 1480 (1951); (2) S<sub>298</sub><sup>o</sup> (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) = 36.7 cal. mole<sup>-1</sup> deg.<sup>-1</sup> in a similar manner based on ΔS<sub>298</sub><sup>o</sup> (2Na<sup>+</sup>-2Li<sup>+</sup>) = 8.6 cal. deg.<sup>-1</sup> from K. K. Kelley, Bureau of Mines, private communication, June 1960; and (3) S<sub>298</sub><sup>o</sup> (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) = 37.6 cal. mole<sup>-1</sup> deg.<sup>-1</sup> based on addition of the JANAP entropies for 2LiBO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. The value adopted is an average of these estimates.

Melting Data.

The value for T<sub>m</sub> is from B. S. R. Sastry and P. A. Hummel, J. Am. Chem. Soc. 42, 216 (1959). A. F. Rollet and R. Bouaziz, Compt. rend. 240, 2417 (1955) earlier reported T<sub>m</sub> = 1188°K. ΔH<sub>m</sub><sup>o</sup> = 28.8 kcal. mole<sup>-1</sup> is from G. S. Smith loc. cit.



$S_{298.15}^{\circ} = [41.564 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{\circ} 298.15 = -792.79 \pm 1.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^{\circ} = 26.3 \pm 1.5 \text{ kcal. mole}^{-1}$   
 $T_m = 1130 \pm 2^{\circ}\text{K.}$

Heat of Formation.  
 $\Delta H_f^{\circ} 298.15(1)$  was calculated from  $\Delta H_f^{\circ} 298.15(c)$  by adding  $\Delta H_m^{\circ}$  and the difference between  $H_m^{\circ} - H_{298.15}^{\circ}$  for crystal and liquid.

Heat Capacity and Entropy.  
 The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. M1c 59-2916 in the range 288 to 1373°K. were smoothed graphically and used to determine  $C_p$ . The  $C_p$  data have a discontinuity at about 756°K. A linear extrapolation of  $C_p$  was used from 1373 to 3000°K.

The entropy at 298°K. is set so that  $\Delta F$  is equal at  $T_m$  for the crystal and liquid.

Melting Data.  
 See crystal table for details.

T, °K.	$C_p^{\circ}$	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>F</sub>
0						
100						
200						
298	41.295	41.564	0.000	-792.790	-748.226	548.438
300						
400	41.832	41.565	0.080	-792.797	-747.951	544.656
500	43.050	43.335	4.703	-793.193	-732.941	400.441
600	54.701	66.644	46.863	-795.052	-717.682	313.683
700						
800	60.252	77.116	15.643	-795.268	-702.180	255.757
900	66.003	86.844	55.472	-795.137	-686.671	214.378
1000	104.165	98.205	60.033	-792.917	-671.261	183.371
1100	109.835	111.101	65.004	-788.462	-656.322	159.369
1200	110.505	122.708	70.204	-784.060	-641.870	140.274
1300	111.175	134.272	75.464	-779.704	-627.866	124.740
1400	111.845	145.874	80.691	-775.373	-614.252	111.865
1500	112.515	157.513	85.832	-771.063	-601.003	101.033
1600	113.156	169.142	90.957	-766.760	-588.080	91.799
1700	113.728	180.728	95.751	-762.475	-575.473	84.882
1800	114.315	192.264	100.508	-758.196	-563.139	76.917
1900	114.914	203.744	105.125	-754.016	-551.026	70.501
2000	115.537	215.169	109.606	-750.016	-539.126	64.603
2100	116.172	226.538	113.952	-746.272	-527.426	59.141
2200	116.822	237.853	118.170	-742.760	-516.924	54.179
2300	117.488	249.114	122.264	-739.463	-506.611	50.536
2400	118.170	260.321	126.244	-736.374	-496.584	46.737
2500	118.866	271.473	130.102	-733.494	-486.831	43.290
2600	119.581	282.571	133.845	-730.818	-477.346	40.167
2700	120.310	293.614	137.474	-728.344	-468.119	37.236
2800	121.055	304.602	141.080	-726.060	-459.149	34.528
2900	121.816	315.535	144.669	-723.957	-450.432	32.036
3000	122.592	326.414	148.245	-722.025	-441.957	29.736
3100	123.384	337.238	151.811	-720.265	-433.724	27.607
3200	124.185	348.007	155.368	-718.665	-425.733	25.634

MOL. WT. = 9.0165

(IDEAL GAS)

BERYLLIUM UNIPOSITIVE ION (Be<sup>+</sup>)

Ground State Configuration  $2s^1/2$   $\Delta H_f^0 = 292.2 \pm .5$  kcal/mole

$S_{298.15}^0 = 33.922$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  $\Delta H_f^0 298.15 = 294.7 \pm .5$  kcal/mole

Electronic Levels and Quantum Weight

$E_i$ , cm. <sup>-1</sup>	$E_i$
0.0	2
31928.8	2
31935.4	4
88231.2	2
96486.4	2
96496.2	4
98053.2	10

Heat of Formation.

The heat of formation was calculated from the equation:  $Be(g) - e^- \rightarrow Be^+(g)$  with the JANAF auxiliary value for  $Be(g)$  using an I.P. =  $7.519229 \times 10^4$  cm<sup>-1</sup> (215.001 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above  $1 \times 10^5$  cm<sup>-1</sup> were omitted because their contribution is negligible below 6000°K. The  $H^0 - H^0_{298}$  value at 0°K. is -1.481 kcal./mole.

T, °K.	$C_p^0$	$S^0 - (F^0 - H^0_{298})/T$	$H^0 - H^0_{298}$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0						
100	4.968	33.922	0.000	294.700	283.779	-208.005
200	4.968	33.922	0.000	294.711	283.779	-208.005
298	4.968	33.922	0.000	294.711	283.779	-208.005
300	4.968	33.922	0.000	294.711	283.779	-208.005
400	4.968	33.922	0.000	294.711	283.779	-208.005
500	4.968	33.922	0.000	294.711	283.779	-208.005
600	4.968	33.922	0.000	294.711	283.779	-208.005
700	4.968	33.922	0.000	294.711	283.779	-208.005
800	4.968	33.922	0.000	294.711	283.779	-208.005
900	4.968	33.922	0.000	294.711	283.779	-208.005
1000	4.968	33.922	0.000	294.711	283.779	-208.005
1100	4.968	33.922	0.000	294.711	283.779	-208.005
1200	4.968	33.922	0.000	294.711	283.779	-208.005
1300	4.968	33.922	0.000	294.711	283.779	-208.005
1400	4.968	33.922	0.000	294.711	283.779	-208.005
1500	4.968	33.922	0.000	294.711	283.779	-208.005
1600	4.968	33.922	0.000	294.711	283.779	-208.005
1700	4.968	33.922	0.000	294.711	283.779	-208.005
1800	4.968	33.922	0.000	294.711	283.779	-208.005
1900	4.968	33.922	0.000	294.711	283.779	-208.005
2000	4.968	33.922	0.000	294.711	283.779	-208.005
2100	4.968	33.922	0.000	294.711	283.779	-208.005
2200	4.968	33.922	0.000	294.711	283.779	-208.005
2300	4.968	33.922	0.000	294.711	283.779	-208.005
2400	4.968	33.922	0.000	294.711	283.779	-208.005
2500	4.968	33.922	0.000	294.711	283.779	-208.005
2600	4.968	33.922	0.000	294.711	283.779	-208.005
2700	4.968	33.922	0.000	294.711	283.779	-208.005
2800	4.968	33.922	0.000	294.711	283.779	-208.005
2900	4.968	33.922	0.000	294.711	283.779	-208.005
3000	4.968	33.922	0.000	294.711	283.779	-208.005
3100	4.969	33.920	0.000	294.700	283.764	-208.000
3200	4.969	33.920	0.000	294.700	283.764	-208.000
3300	4.969	33.920	0.000	294.700	283.764	-208.000
3400	4.970	33.918	0.000	294.694	283.758	-207.994
3500	4.970	33.918	0.000	294.694	283.758	-207.994
3600	4.971	33.916	0.000	294.688	283.752	-207.988
3700	4.972	33.914	0.000	294.682	283.746	-207.982
3800	4.973	33.912	0.000	294.676	283.740	-207.976
3900	4.974	33.910	0.000	294.670	283.734	-207.970
4000	4.976	33.908	0.000	294.664	283.728	-207.964
4100	4.978	33.906	0.000	294.658	283.722	-207.958
4200	4.981	33.904	0.000	294.652	283.716	-207.952
4300	4.984	33.902	0.000	294.646	283.710	-207.946
4400	4.987	33.900	0.000	294.640	283.704	-207.940
4500	4.991	33.898	0.000	294.634	283.698	-207.934
4600	4.995	33.896	0.000	294.628	283.692	-207.928
4700	5.001	33.894	0.000	294.622	283.686	-207.922
4800	5.006	33.892	0.000	294.616	283.680	-207.916
4900	5.013	33.890	0.000	294.610	283.674	-207.910
5000	5.020	33.888	0.000	294.604	283.668	-207.904
5100	5.027	33.886	0.000	294.598	283.662	-207.898
5200	5.036	33.884	0.000	294.592	283.656	-207.892
5300	5.045	33.882	0.000	294.586	283.650	-207.886
5400	5.055	33.880	0.000	294.580	283.644	-207.880
5500	5.066	33.878	0.000	294.574	283.638	-207.874
5600	5.078	33.876	0.000	294.568	283.632	-207.868
5700	5.090	33.874	0.000	294.562	283.626	-207.862
5800	5.104	33.872	0.000	294.556	283.620	-207.856
5900	5.118	33.870	0.000	294.550	283.614	-207.850
6000	5.133	33.868	0.000	294.544	283.608	-207.844

June 30, 1965

T, °K.	$C_p^0$	$S^0 - (F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>f</sub>
0						
100						
200						
298	16.500	25.400	0.000	- 88.400	- 84.445	61.897
300	16.542	25.502	0.071	- 88.409	- 84.420	61.497
400	18.100	30.506	1.774	- 95.345	- 81.642	44.605
500	18.850	34.630	3.674	- 94.883	- 78.270	34.210
600	19.350	38.114	5.595	- 94.401	- 74.983	27.315
700	19.656	41.120	7.495	- 93.916	- 71.796	22.415
800	19.900	43.762	9.464	- 93.428	- 68.671	18.759
900	20.063	46.115	11.462	- 92.945	- 65.604	15.930
1000	20.200	48.236	13.475	- 92.472	- 62.591	13.678
1100	20.311	50.167	15.501	- 92.012	- 59.626	11.846
1200	20.397	51.894	17.537	- 91.568	- 56.701	10.326
1300	20.467	53.423	19.580	- 91.142	- 53.811	9.046
1400	20.521	54.761	21.627	- 90.737	- 50.957	7.954
1500	20.560	55.905	23.677	- 90.355	- 48.130	7.012

BERYLLIUM DIBROMIDE (BeBr<sub>2</sub>)

(CRYSTAL)

MOL. WT. = 166.8302

$\Delta H_f^0 =$  Unknown  
 $\Delta H_f^0 298.15 = [-88.4 \pm 0] \text{ kcal. mole}^{-1}$   
 $S_{298.15}^0 = [25.4 \pm 2.0] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$   
 $T_m = 761^\circ \text{K.}$   
 $\Delta H_m^0 = [4.5] \text{ kcal. mole}^{-1}$   
 $\Delta H_s^0 298.15 = 23.8 \pm 1.5 \text{ kcal. mole}^{-1}$

Heat of Formation.

The heat of formation was estimated from the work of W. Biltz and C. Messerknecht, Z. Anorg. Chem. **148**, 157 (1925) and Biltz, Klatte and Rahlfs, Z. Anorg. Chem. **166**, 339 (1927) as reported in N. B. S. Circular 500, Washington, 1952. They measured the heat of solution of BeBr<sub>2</sub> in aq. HCl to an unknown concentration. This value was apparently adjusted and used with Be<sup>++</sup> and 2Br<sup>-</sup> to obtain  $\Delta H_f^0$  of the crystal. However Be<sup>++</sup> was estimated by N. B. S. An uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with BeCl<sub>2</sub> and BeF<sub>2</sub>. The entropy was also estimated by comparing with  $\alpha\text{-BeCl}_2$  and BeF<sub>2</sub> and using additive entropy values for the halide ions.

Melting Data.

The melting point has been reported by O. Rahlfs and W. Fischer, Z. Anorg. Chem. **211**, 351 (1933) and by Lebean, Ann. Chim. Phys. **16**, 472 (1899) as reported in N. B. S. Circular 500, Washington, 1952. The heat of melting was estimated by comparison with the sum of the heat of transition and melting for BeF<sub>2</sub> and BeCl<sub>2</sub>.

Sublimation Data.

The heat of sublimation was obtained from an analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 624-695°K. The 3rd law analysis gave  $\Delta H_{\text{sub}}^{298} = 29.78$  with a drift of  $-2.1 \pm 0.8 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ . A 2nd law analysis gave  $\Delta H_{\text{sub}}^{298} = 31.1 \pm 0.5 \text{ kcal. mole}^{-1}$ . The 2nd law result was adopted in order to yield a real liquid region, no attempt was made to eliminate the drift since this would have caused the liquid region to become unreal.

BERYLLIUM DIBROMIDE (BeBr<sub>2</sub>) (LIQUID)

$S_{298.15}^{\circ} = [28.07] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$   $\Delta H_f^{\circ} 298.15 = [-85.88 \pm 3] \text{ kcal. mole}^{-1}$   
 $T_m = 761^{\circ}\text{K.}$   $\Delta H_m^{\circ} = [4.5] \text{ kcal. mole}^{-1}$   
 $T_b = [794]^{\circ}\text{K.}$   $\Delta H_v^{\circ} = [23.9] \text{ kcal. mole}^{-1}$

Heat of Formation.

The heat of formation was obtained from that of BeBr<sub>2</sub>(c) by adding  $\Delta H_m^{\circ}$  and the difference between H<sub>298.15</sub> for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for BeCl<sub>2</sub>. A glass transition was assumed at 500°K. below which the heat capacity is that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See BeBr<sub>2</sub>(c) table for details.

Vaporization Data.

The temperature and heat of vaporization were calculated from the cross over between BeBr<sub>2</sub>(l) and (g).

T. °K.	C:	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0						
100						60.634
200						60.245
298	16.500	28.070	0.000	- 85.880	- 82.721	60.245
300	16.542	28.070	0.031	- 85.889	- 82.701	60.245
400	18.100	28.742	1.774	- 92.825	- 80.190	43.812
500	27.000	37.307	3.626	- 92.360	- 77.085	33.692
600	27.000	42.230	6.326	- 91.090	- 74.150	27.008
700	27.000	46.392	9.026	- 89.855	- 71.442	22.299
800	27.000	49.957	11.726	- 88.646	- 68.878	18.815
900	27.000	53.177	14.426	- 87.461	- 66.475	16.142
1000	27.000	56.022	17.126	- 86.301	- 64.206	14.031
1100	27.000	58.596	19.826	- 85.167	- 62.082	12.328
1200	27.000	60.910	22.526	- 84.059	- 60.000	10.927
1300	27.000	62.910	25.226	- 82.976	- 58.038	9.757
1400	27.000	64.549	27.926	- 81.918	- 56.160	8.767
1500	27.000	65.897	30.626	- 80.886	- 54.338	7.920
1600	27.000	66.912	33.326	- 82.634	- 52.542	7.177
1700	27.000	67.549	36.026	- 81.537	- 50.695	6.517
1800	27.000	67.892	38.726	- 80.446	- 48.913	5.939
1900	27.000	67.932	41.426	- 79.361	- 47.190	5.428
2000	27.000	67.737	44.126	- 78.283	- 45.527	4.975

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH°	ΔF°	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	10.302	53.468	77.372	3.200	54.173	54.173	INFINITE
200	12.217	61.357	67.565	2.389	54.039	58.088	126.946
298	13.036	66.400	66.400	2.000	54.202	62.992	67.848
300	13.048	66.481	66.481	2.024	57.316	65.620	48.061
400	13.504	70.315	66.019	1.358	64.661	66.881	36.540
500	13.955	73.300	67.016	2.737	64.669	67.536	20.475
600	14.194	75.957	69.048	4.165	64.691	67.988	24.763
700	14.358	78.158	70.136	5.573	64.728	68.535	21.397
800	14.473	80.008	71.314	7.015	64.777	69.076	18.670
900	14.556	81.792	72.385	8.467	64.840	69.609	16.902
1000	14.617	83.326	73.404	9.925	64.922	70.134	15.327
1100	14.664	84.725	74.371	11.390	65.073	70.651	14.036
1200	14.701	86.002	75.288	12.858	65.147	71.157	12.959
1300	14.730	87.180	76.158	14.330	65.292	71.651	12.045
1400	14.753	88.273	76.984	15.804	65.460	72.136	11.260
1500	14.772	89.291	77.771	17.280	65.652	72.606	10.578
1600	14.787	90.245	78.521	18.758	65.822	73.064	9.969
1700	14.800	91.142	79.238	20.237	66.074	73.522	9.417
1800	14.811	91.988	79.923	21.718	66.374	73.974	8.925
1900	14.821	92.789	80.579	23.200	66.707	74.421	8.485
2000	14.829	93.550	81.209	24.682	67.074	74.864	8.088
2100	14.836	94.274	81.814	26.165	67.469	75.303	7.728
2200	14.842	94.964	82.398	27.641	67.841	75.740	7.400
2300	14.847	95.624	82.957	29.114	68.256	76.174	7.099
2400	14.852	96.256	83.498	30.619	68.757	76.602	6.823
2500	14.856	96.862	84.070	32.104	69.254	77.025	6.569
2600	14.859	97.445	84.672	33.580	70.097	77.549	6.333
2700	14.863	98.004	85.301	35.074	70.774	78.066	6.112
2800	14.866	98.546	85.948	36.562	71.468	78.572	5.902
2900	14.868	99.068	86.614	38.044	72.184	79.068	5.700
3000	14.870	99.577	87.302	39.516	72.921	79.554	5.508
3100	14.873	100.060	87.936	41.023	73.681	80.031	5.325
3200	14.875	100.528	88.614	42.510	74.466	80.497	5.148
3300	14.877	100.980	89.337	44.008	75.281	80.954	4.976
3400	14.878	101.433	90.106	45.586	76.124	81.402	4.808
3500	14.879	101.865	90.914	47.244	77.000	81.840	4.644
3600	14.881	102.284	91.762	48.982	77.908	82.269	4.484
3700	14.882	102.692	92.648	50.800	78.848	82.689	4.328
3800	14.883	103.089	93.571	52.698	79.818	83.099	4.176
3900	14.884	103.475	94.531	54.676	80.818	83.499	4.028
4000	14.885	103.852	95.514	56.734	81.848	83.889	3.884
4100	14.886	104.220	96.518	58.872	82.908	84.269	3.744
4200	14.887	104.579	97.543	61.090	84.000	84.640	3.608
4300	14.888	104.929	98.589	63.388	85.124	84.992	3.476
4400	14.889	105.271	99.658	65.766	86.280	85.326	3.348
4500	14.889	105.606	100.750	68.234	87.468	85.648	3.224
4600	14.890	105.933	101.858	70.792	88.688	85.956	3.104
4700	14.891	106.253	102.986	73.320	89.940	86.250	2.988
4800	14.891	106.567	104.144	75.928	91.224	86.530	2.876
4900	14.892	106.874	105.324	78.616	92.540	86.796	2.768
5000	14.892	107.175	106.526	81.384	93.888	87.048	2.664
5100	14.893	107.470	107.750	84.232	95.268	87.288	2.564
5200	14.893	107.759	109.000	87.150	96.680	87.514	2.468
5300	14.894	108.042	110.264	90.140	98.124	87.726	2.376
5400	14.894	108.321	111.544	93.200	99.592	87.924	2.288
5500	14.894	108.594	112.840	96.324	101.096	88.108	2.204
5600	14.895	108.862	114.152	99.516	102.636	88.278	2.124
5700	14.895	109.126	115.480	102.772	104.212	88.434	2.048
5800	14.895	109.385	116.832	106.064	105.824	88.576	1.976
5900	14.896	109.640	118.200	109.416	107.472	88.704	1.908
6000	14.896	109.890	120.584	112.824	109.156	88.818	1.844

MOL. WT. = 168.8302

(IDEAL GAS)

BERYLLIUM DIBROMIDE (BeBr<sub>2</sub>)

ΔH°<sub>f,0</sub> = [-54.2 ± 9.5] kcal. mole<sup>-1</sup>

ΔH°<sub>f,298.15</sub> = [-57.3 ± 9.5] kcal. mole<sup>-1</sup>

Point Group D<sub>∞h</sub>

S°<sub>298.15</sub> = [66.4 ± 2] cal. mole<sup>-1</sup> deg.<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

(Δ), cm.<sup>-1</sup>  
 [205] (1)  
 [180] (2)  
 [890] (1)

Bond Distance: Be-Br = 1.90 Å

Bond Angle: Br-Be-Br = [180°]

Rotational Constant: B<sub>0</sub> = 0.02922 cm.<sup>-1</sup>

σ = 2

Heat of Formation.

The heat of formation was obtained from that of the crystal plus ΔH°<sub>S</sub> 298.15, see BeBr<sub>2</sub>(c) for details.

Heat Capacity and Entropy.

The linear structure was assumed by analogy with BeCl<sub>2</sub>. The bond length was reported by P. A. Akishin, V. P. Spirodinov and G. A. Sobolev, Dokl. Akad. Nauk. SSSR 118, 1134 (1958) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants k<sub>1</sub> for the BeF<sub>2</sub>, BeCl<sub>2</sub>, BeBr<sub>2</sub>, BeI<sub>2</sub> series and also assuming k<sub>1</sub>/k<sub>2</sub><sup>1/2</sup> = 50 as for BeF<sub>2</sub>. The principal moment of inertia is 95.7984 x 10<sup>-39</sup> g. cm.<sup>2</sup>

MOL. WT. = 65.4636

BERYLLIUM CHLORIDE FLUORIDE (BeClF) (IDEAL GAS)

Log K<sub>P</sub>

$$\Delta H_f^{\circ} = [137.2 \pm 10] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} = [58.89] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$$\frac{\omega, \text{ cm.}^{-1}}{(500)(1) [270](2) [1300](1)}$$

$$\text{Be-F} = [1.43] \text{ \AA}$$

$$\sigma = 1$$

Rotational Constant: B<sub>0</sub> = 0.12970 cm.<sup>-1</sup>

Heat of Formation.

The heat of formation was estimated by assuming ΔH<sub>f</sub> = 0 for the reaction BeF<sub>2</sub> + BeCl<sub>2</sub> → 2BeClF

Heat Capacity and Entropy.

The structure, bond lengths and frequencies were all estimated from the properties of BeCl<sub>2</sub> and BeF<sub>2</sub>. The principal moment of inertia is 21.579 x 10<sup>-39</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>P</sub>
0	∞	∞	∞	∞	∞	∞
100	6.518	67.894	2.797	-137.177	-137.177	300.781
200	10.818	58.584	2.065	-137.156	-137.156	300.781
298	14.810	58.887	∞	-137.000	-138.711	101.873
300	11.827	58.980	∞	-137.000	-138.722	101.054
400	12.572	62.471	1.244	-137.016	-139.294	61.129
500	13.106	65.337	2.529	-137.065	-139.858	61.129
600	13.495	67.343	3.860	-137.127	-140.412	51.142
700	13.782	68.865	5.225	-137.198	-141.053	44.005
800	13.996	70.170	6.614	-137.280	-141.885	38.650
900	14.157	71.379	8.022	-137.372	-142.805	34.482
1000	14.281	72.487	9.445	-137.432	-142.514	31.145
1100	14.377	73.503	10.878	-137.605	-143.012	28.412
1200	14.454	74.431	12.319	-137.751	-143.497	26.133
1300	14.515	75.277	13.768	-137.917	-143.969	24.202
1400	14.565	76.041	15.222	-138.104	-144.428	22.545
1500	14.606	76.740	16.681	-138.316	-144.872	21.107
1600	14.640	77.384	18.143	-141.302	-145.224	19.836
1700	14.669	77.981	19.608	-141.443	-145.464	18.700
1800	14.693	78.534	21.077	-141.589	-145.698	17.689
1900	14.714	79.047	22.547	-141.740	-145.921	16.784
2000	14.732	79.522	24.019	-141.897	-146.137	15.968
2100	14.747	80.000	25.493	-142.058	-146.345	15.230
2200	14.761	80.485	26.969	-142.226	-146.547	14.557
2300	14.773	80.974	28.445	-142.400	-146.736	13.942
2400	14.783	81.465	29.923	-142.579	-146.921	13.378
2500	14.793	81.957	31.402	-142.767	-147.101	12.859
2600	14.801	82.451	32.882	-142.959	-147.267	12.378
2700	14.808	82.946	34.362	-143.157	-147.430	11.933
2800	14.814	83.442	35.843	-143.362	-147.589	11.522
2900	14.821	83.939	37.325	-143.574	-147.744	11.141
3000	14.826	84.437	38.808	-143.791	-147.895	10.787
3100	14.831	84.936	40.290	-144.013	-148.042	10.458
3200	14.835	85.436	41.774	-144.240	-148.185	10.152
3300	14.839	85.936	43.258	-144.472	-148.325	9.869
3400	14.843	86.436	44.742	-144.710	-148.461	9.604
3500	14.847	86.936	46.226	-144.953	-148.593	9.351
3600	14.850	87.436	47.711	-145.201	-148.722	9.115
3700	14.853	87.936	49.196	-145.453	-148.848	8.889
3800	14.855	88.436	50.682	-145.710	-148.971	8.672
3900	14.858	88.936	52.167	-145.971	-149.091	8.464
4000	14.860	89.436	53.653	-146.236	-149.208	8.264
4100	14.862	89.936	55.139	-146.505	-149.322	8.072
4200	14.864	90.436	56.626	-146.778	-149.433	7.888
4300	14.866	90.936	58.112	-147.054	-149.541	7.711
4400	14.868	91.436	59.599	-147.333	-149.646	7.540
4500	14.869	91.936	61.086	-147.615	-149.748	7.376
4600	14.871	92.436	62.573	-147.900	-149.847	7.217
4700	14.872	92.936	64.060	-148.188	-149.943	7.064
4800	14.874	93.436	65.547	-148.479	-150.036	6.916
4900	14.875	93.936	67.034	-148.772	-150.126	6.773
5000	14.876	94.436	68.522	-149.067	-150.213	6.635
5100	14.877	94.936	70.010	-149.364	-150.297	6.502
5200	14.878	95.436	71.498	-149.663	-150.378	6.373
5300	14.879	95.936	72.986	-149.964	-150.456	6.248
5400	14.880	96.436	74.473	-150.266	-150.531	6.126
5500	14.881	96.936	75.961	-150.569	-150.603	6.006
5600	14.882	97.436	77.448	-150.878	-150.672	5.888
5700	14.883	97.936	78.936	-151.188	-150.738	5.773
5800	14.884	98.436	80.424	-151.498	-150.801	5.659
5900	14.884	98.936	81.911	-151.809	-150.861	5.546
6000	14.885	99.436	83.403	-152.121	-150.918	5.433

MOL. WT. = 79.9182

BERYLLIUM DICHLORIDE, ALPHA ( $\alpha$ -BeCl<sub>2</sub>) (CRYSTAL)

$\Delta H_f^0 = -117.5 \pm 0.8$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -117.3 \pm 0.8$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^0 = 2.07 \pm 0.06$  kcal. mole<sup>-1</sup>  
 $\Delta H_s^{298.15} = 31.3$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 19.76 \pm 0.06$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>  
 $T_m = 688^\circ\text{K}$ .

Heat of Formation.  
 W. H. Johnson and A. A. Gilliland, J. Res. Nat'l. Bur. Stand. 65A, 59 (1961) have directly reacted beryllium and chlorine and obtained  $\Delta H_f^0 = -118.03 \pm 0.56$  though the crystal form of the product was unknown. P. Gross, C. Hayman, P. D. Greene and J. T. Bingham, Fulmer Research Institute, Report R. 163/SR-1/Sept. 1964 under Contract AF61(052)-447 also by direct combustion of the elements obtain  $\Delta H_f^0 = -117.1 \pm 0.4$  kcal. mole<sup>-1</sup>. The crystal form of the sample was deduced to be  $\alpha'$  by a comparison experiment, the assumption is made here that  $\alpha$  and  $\alpha'$  are identical. C. J. Thompson, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 380 (1962) by solution calorimetry report a  $\Delta H_f^0 = -118.25 \pm 0.5$  kcal. mole<sup>-1</sup>. Initially this sample was reported to be of unknown crystal form. However, G. C. Sinke, private communication February 1965, reports that an x-ray of the sample used has been reinterpreted, in the light of more recent data, as being approximately 50%  $\alpha'$  and 50%  $\beta$ . Using the heats of transition adopted for these tables heats of formation of  $-117.3 \pm 0.8$  kcal. mole<sup>-1</sup> for  $\alpha$  and  $-118.6 \pm 0.8$  kcal. mole<sup>-1</sup> for  $\beta$  have been adopted as being the most consistent with all measurements.

Heat Capacity and Entropy.

R. A. McDonald and F. L. Oetting, J. Phys. Chem. scheduled for publication in the Nov. 1965 issue have measured the heat capacity of the  $\alpha'$  form from 13° to 304°K. and the enthalpy (relative to the  $\alpha'$  form) from 676° to 688°K. The assumption has been made that the  $\alpha$  and  $\alpha'$  forms are identical and the heat capacity curve between 304° and 676°K. has been estimated graphically. The entropy was obtained by integration of the heat capacity curve assuming  $S_{13} = 0.16$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>. The sample was identified as  $\alpha'$  by x-ray diffraction both before and after the experiments.

Melting Data.

The temperature and heat of melting were reported by McDonald and Oetting, loc. cit. Several investigations of the melting point are in disagreement mainly due to the uncertainty of the crystal form of the material and a solid state transition just below the pure  $\alpha$ -liquid melting point.

Sublimation Data.

The adopted heat of sublimation was derived from that of the  $\beta$  form and heat of the  $\alpha$ - $\beta$  transition at 298°K.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	∞	∞	∞	∞	-117.536	-117.536	INFINITE
100	8.045	6.925	31.535	2.863	-117.536	-114.006	249.147
200	12.800	14.110	21.895	1.437	-117.640	-110.229	120.446
298	15.500	18.760	16.000	∞	-117.335	-106.659	78.179
300	15.540	19.856	15.760	∞	-117.328	-106.592	77.649
400	17.390	24.598	20.304	1.682	-116.944	-103.070	56.312
500	18.530	28.612	21.647	3.482	-116.501	-99.651	43.555
600	19.140	32.049	23.101	5.369	-116.025	-96.325	35.085
700	19.445	35.024	24.597	7.260	-115.515	-93.080	29.050
800	19.660	37.635	26.067	9.255	-115.070	-89.904	24.559
900	19.843	39.862	27.464	11.230	-114.602	-86.786	21.073
1000	20.000	42.061	28.838	13.222	-114.144	-83.721	18.096
1100	20.131	43.973	30.129	15.229	-113.698	-80.699	16.033
1200	20.237	45.730	31.457	17.248	-113.268	-77.719	14.154
1300	20.317	47.353	32.725	19.276	-112.854	-74.773	12.570
1400	20.371	48.861	33.939	21.310	-112.460	-71.860	11.217
1500	20.400	50.267	34.701	23.349	-112.087	-68.972	10.049

(CRYSTAL)

BERYLLIUM DICHLORIDE, BETA ( $\beta$ -BeCl<sub>2</sub>)

$$\Delta H_f^0 = -119.7 \pm 0.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -119.6 \pm 0.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [3.65] \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_c^0 = [1.63] \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_s^0 = 32.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 18.12 \pm 0.05 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_m = [682^\circ\text{K.}]$$

$$T_c = 676^\circ\text{K. } (\beta \rightarrow \alpha)$$

Heat of Formation.See table for  $\alpha$ -BeCl<sub>2</sub> for details.Heat Capacity and Entropy.

R. A. McDonald and P. L. Oetting, J. Phys. Chem. scheduled for publication in the November 1965 issue have measured the heat capacity of the  $\beta$ -form from 13 to 304°K. and the enthalpy of the  $\beta$ -form from 298° to 676°K. The entropy was obtained by integration of the heat capacity curve based on  $S_{13} = 0.06 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ . The sample was identified as  $\beta$ -BeCl<sub>2</sub> both before and after the low temperature experiments.

Melting Data.

The temperature and heat of melting were obtained from cross over point of the tables for  $\beta$ -BeCl<sub>2</sub> and liquid BeCl<sub>2</sub>.

Transition Data.

The temperature of the  $\beta$  to  $\alpha$  transition was obtained from McDonald and Oetting, loc. cit. The heat of the transition is a function of the heat capacity curve chosen for  $\alpha$ -BeCl<sub>2</sub> between 298 and 676°K. A straight line interpolation was used by McDonald and Oetting, which gives a different result (1.49 kcal. mole<sup>-1</sup>) than the curve employed here. It should also be noted that the transitional heat is not included in this table, which is for  $\beta$ -BeCl<sub>2</sub> only.

Sublimation Data.

The heat of sublimation was determined by 2nd and 3rd law analysis of vapor pressure data as described fully on the table for BeCl<sub>2</sub> (g).

T. °K.	C <sub>p</sub> <sup>0</sup>	S <sup>0</sup> - (F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> - H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.000	INFINITE	2.729	-118.667	-118.667	INFINITE
100	7.595	30.501	2.874	-115.167	-115.167	251.686
200	12.380	19.410	1.952	-111.157	-111.157	121.460
298	14.920	18.120	.000	-118.600	-107.835	78.748
300	14.960	18.212	.028	-118.594	-107.865	78.212
400	16.420	22.729	1.601	-118.290	-103.667	56.639
500	17.400	26.506	3.295	-117.953	-100.050	43.730
600	18.120	29.744	5.073	-117.486	-96.503	35.149
700	18.680	32.583	6.915	-117.194	-93.020	29.041
800	19.110	35.106	8.805	-116.785	-89.595	24.475
900	19.450	37.377	10.734	-116.363	-86.220	20.496
1000	19.730	39.442	12.693	-115.938	-82.896	18.116
1100	19.930	41.332	14.677	-115.515	-79.611	15.817
1200	20.080	43.083	16.692	-115.103	-76.356	13.707
1300	20.190	44.714	18.734	-114.703	-73.136	11.789
1400	20.263	46.238	20.774	-114.321	-69.973	10.023
1500	20.300	47.583	22.743	-113.958	-66.818	9.733



T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298°)/T</sub>	H° - H <sub>298°</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100						
200						
298	14.920	19.065	0.000	-117.425	-106.541	78.093
300	14.960	19.065	0.028	-117.419	-106.474	77.562
400	16.420	23.671	1.601	-117.115	-102.870	56.203
500	20.020	28.432	3.766	-116.307	-99.167	43.431
600	29.020	33.724	6.668	-114.816	-96.120	35.010
700	36.020	38.156	9.570	-113.562	-93.119	28.072
800	42.071	42.071	12.472	-111.943	-90.325	24.675
900	45.489	45.489	15.374	-110.548	-87.706	21.297
1000	48.547	48.547	18.276	-109.180	-85.243	18.629
1100	51.313	51.313	21.178	-107.839	-82.914	16.473
1200	53.838	53.838	24.080	-106.526	-80.707	14.698
1300	56.161	56.161	26.982	-105.238	-78.608	13.214
1400	58.311	58.311	29.884	-103.976	-76.606	11.958
1500	60.313	60.313	32.786	-102.740	-74.695	10.882
1600	62.186	62.186	35.688	-101.525	-72.786	9.942
1700	63.946	63.946	38.590	-100.328	-70.857	9.109
1800	65.604	65.604	41.492	-99.149	-69.004	8.378
1900	67.173	67.173	44.394	-98.005	-67.222	7.732
2000	68.662	68.662	47.296	-96.892	-65.510	7.158

S<sub>298,15</sub> = 19.065 ± 1 cal. mole<sup>-1</sup> deg.<sup>-1</sup>  
 ΔH<sub>f</sub><sup>o</sup> 298.15 = -117.4 ± 1.5 kcal. mole<sup>-1</sup>  
 ΔH<sub>m</sub><sup>o</sup> = 2.07 ± 0.06 kcal. mole<sup>-1</sup>  
 T<sub>m</sub> = 688°K.  
 T<sub>b</sub> = 805°K.  
 ΔH<sub>v</sub><sup>o</sup> = 25.0 ± 2 kcal. mole<sup>-1</sup>

Heat of Formation.

The heat of formation was obtained from that of the α-BeCl<sub>2</sub> plus the difference of H<sub>688</sub>-H<sub>298</sub> for crystal and liquid.

Heat Capacity and Entropy.

R. A. McDonald and P. L. Oetting, J. Phys. Chem. scheduled for publication in the November 1965 issue have measured the enthalpy of the liquid, relative to α-BeCl<sub>2</sub>, from 688° to 713°K. The heat capacity was assumed constant above this point and also below the melting point to 460°K. where a glass transition was assumed. Below 416°K. the heat capacity was assumed to be that of β-BeCl<sub>2</sub>. The entropy was calculated in a manner analogous to the heat of formation.

Melting Data.

See the table for α-BeCl<sub>2</sub> (c) for details.

Vaporization Data.

The boiling point and heat of vaporization were obtained from the cross over point of the BeCl<sub>2</sub> (l) and (g) tables. The analysis of the liquid vapor pressure data is given on the table for BeCl<sub>2</sub> (g).

MOL. WT. = 79.9182

(IDEAL GAS)

BERYLLIUM DICHLORIDE (BeCl<sub>2</sub>)

$$\Delta H_f^{\circ} = -86.4 \pm 2.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} = -86.1 \pm 2.5 \text{ kcal. mole}^{-1}$$

Point Group D<sub>∞h</sub>

$$S_{298}^{298} = 60 \pm 1 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm <sup>-1</sup>
[375] (1)
[230] (2)
1113 (1)

Bond Distance: Be-Cl = 1.77Å

Bond Angle: Cl-Be-Cl = 180°

Rotational Constant: B<sub>0</sub> = 0.0759 cm<sup>-1</sup>

σ = 2

Heat of Formation

The vapor pressure data over the crystal was assumed to be for the β-form. The 2nd and 3rd law analyses of the data are summarized below after conversion to a common process. The data were also analyzed using gaseous free energy functions based on a bending frequency of 170 cm<sup>-1</sup> but no significant improvement of the results was noted.

Ref.	Temperature Range °C.	ΔH <sub>298</sub> sub β-BeCl <sub>2</sub> kcal. mole <sup>-1</sup>	3rd law	2nd law	Drift in 3rd law cal. mole <sup>-1</sup> deg. <sup>-1</sup>
1	680 - 740*	33.5 ± 0.6	31.38		-3.4 ± 0.7
2	680 - 740	34.3	31.22		-4.7
3	613 - 663	31.6 ± 1.6	30.91		-1.3 ± 2.6
2	638 - 668	35.6	31.07		-7.0
3	441 - 518	31.4 ± 0.8	32.45		2.5 ± 1.7
3	510 - 600*	31.8 ± 0.3	32.07		0.40 ± 0.5
4	460 - 504*	32.45 ± 0.4	32.48		0.14 ± 0.8

\*Points rejected due to failure of a statistical test.

References:

- O. Reihls and W. Fischer, Z. Anorg. Allgem. Chem. **211**, 349 (1933).
- M. Fischer, T. Petzel and S. Lauter, Z. Anorg. Allgem. Chem. **333**, 226 (1964).
- M. A. Greenbaum et al., Rocket Power, Inc., 7th quarterly Report March 31, 1963 under Contract AF 04(611)-7414.
- D. L. Hildenbrand, L. P. Theard, E. Murad and P. Ju, Ford Motor Co., Aeronutronic Div., Report U-3088 April 1952 under Contract AF (04) 611-8523.

It is obvious that there is no real agreement between the data sets, and some of this is undoubtedly due to the difficulty of keeping a single crystal form throughout a series of measurements. It is also doubtful that water-vapor was adequately excluded in some experiments. We have adopted the only piece of work which shows adequate 2nd and 3rd law agreement, and no third law trend, that is ΔH<sub>sub</sub> = 32.5 ± 1 kcal. mole<sup>-1</sup> from ref. 4. It is interesting to note that all the other data can be made much more precise and its drift removed if a constant pressure is added to all points. The addition which varied from 20-50% of the lowest pressure in each data set serves to indicate the magnitude of possible systematic errors.

Heat Capacity and Entropy

The linear structure of BeCl<sub>2</sub>(g) has been confirmed by the electric deflection experiments of A. Büchler, A. D. Little, Inc. Progress Report No. 6, 31st Dec. 1963 under contract No. DA-19-020-ORD-5584. The bond length was obtained from the electron diffraction data of P. A. Akshinin, V. P. Spiridonov and G. A. Sobolev, Dokl. Akad. Nauk SSSR **118**, 1154 (1958). A Büchler and W. Klempner, J. Chem. Phys. **29**, 121 (1956) have reported the infra-red spectrum and assigned 1113 as the asymmetric stretch ν<sub>3</sub> and 482 as the bending frequency ν<sub>2</sub>. However, A. Smeison, IIT Research Institute, Report No. IITRI-66013-4 May 1964 under contract No. DA-31-124-ARO(D)-111 using matrix isolation experiments has shown this second band to be due to beryllium chloride solid. The unobserved frequencies were estimated from a valence force field treatment by assuming that the ratio of stretching to bending force constant was 50:1 the same as for Be<sub>2</sub>(g). This gives 230 cm<sup>-1</sup> for ν<sub>2</sub> and 375 cm<sup>-1</sup> for the symmetric stretch. The principal moment of inertia is 36.884 x 10<sup>-35</sup> g. cm<sup>2</sup>.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>p</sub>
0	.000	INFINITE	2.945	86.383	86.383	INFINITE
100	8.934	48.490	2.195	86.344	86.661	189.388
200	11.297	55.536	1.465	86.173	87.046	95.115
298	12.338	60.260	.000	86.100	87.499	64.135
300	12.353	60.337	.023	86.099	87.507	63.746
400	13.055	63.888	1.694	86.097	87.978	48.067
500	13.493	66.948	2.621	86.127	88.445	38.657
600	13.822	69.430	3.988	86.171	88.905	32.382
700	14.056	71.580	5.792	86.227	89.360	27.897
800	14.226	73.477	8.051	86.291	89.811	24.521
900	14.351	75.160	10.766	86.371	90.253	21.810
1000	14.446	76.671	13.966	86.465	90.686	19.612
1100	14.519	78.058	17.654	86.578	91.072	18.093
1200	14.576	79.324	21.869	86.712	91.476	16.659
1300	14.621	80.492	26.670	86.866	91.866	15.443
1400	14.658	81.577	32.010	87.042	92.244	14.399
1500	14.689	82.589	37.844	87.240	92.609	13.492
1600	14.714	83.538	44.111	90.217	92.881	12.686
1700	14.735	84.431	50.773	90.347	93.043	11.963
1800	14.752	85.274	57.889	90.481	93.199	11.315
1900	14.768	86.072	65.506	90.620	93.345	10.737
2000	14.781	86.829	73.664	90.766	93.484	10.215
2100	14.792	87.551	82.310	90.915	93.618	9.742
2200	14.802	88.239	91.454	91.072	93.742	9.312
2300	14.810	88.897	101.100	91.233	93.857	8.918
2400	14.818	89.528	111.251	91.401	93.969	8.557
2500	14.824	90.133	121.909	91.576	94.074	8.224
2600	14.830	90.714	133.076	91.757	94.167	7.915
2700	14.836	91.274	144.753	91.943	94.257	7.629
2800	14.840	91.814	156.940	163.168	93.232	7.277
2900	14.845	92.335	169.646	163.116	96.838	6.838
3000	14.849	92.838	182.871	163.070	98.241	6.428
3100	14.852	93.325	196.627	163.027	98.750	6.045
3200	14.855	93.797	210.903	162.987	93.256	5.686
3300	14.858	94.254	225.708	162.954	80.764	5.349
3400	14.861	94.697	241.044	162.925	78.271	5.031
3500	14.863	95.128	256.919	162.901	75.786	4.732
3600	14.865	95.547	273.335	162.884	73.294	4.449
3700	14.868	95.954	290.291	162.873	70.806	4.182
3800	14.869	96.351	307.796	162.870	68.322	3.929
3900	14.871	96.737	325.850	162.872	65.839	3.689
4000	14.873	97.114	344.463	162.884	63.344	3.461
4100	14.874	97.481	363.636	162.903	60.850	3.244
4200	14.875	97.839	383.369	162.930	58.357	3.037
4300	14.877	98.189	403.662	162.966	55.874	2.840
4400	14.878	98.531	424.516	163.011	53.381	2.651
4500	14.879	98.866	445.931	163.066	50.889	2.472
4600	14.881	99.193	467.907	163.130	48.402	2.299
4700	14.882	99.513	490.444	163.204	45.906	2.135
4800	14.882	99.826	513.541	163.289	43.409	1.976
4900	14.883	100.133	537.198	163.384	40.908	1.824
5000	14.884	100.434	561.415	163.488	38.408	1.679
5100	14.885	100.728	586.192	163.604	35.909	1.538
5200	14.886	101.017	611.629	163.730	33.407	1.404
5300	14.886	101.301	637.726	163.870	30.903	1.274
5400	14.887	101.579	664.483	164.010	28.392	1.149
5500	14.888	101.852	691.900	164.180	25.866	1.028
5600	14.888	102.121	719.977	164.352	23.356	.911
5700	14.889	102.386	748.714	164.531	20.834	.799
5800	14.889	102.643	778.111	164.720	18.309	.690
5900	14.890	102.898	808.168	164.940	15.788	.585
6000	14.890	103.148	838.985	165.159	13.257	.483

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

BERYLLIUM DIIODIDE (BeI<sub>2</sub>) (CRYSTAL) MOL. WT. = 262.821

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0						
100						
200						
298	17.000	28.800	0.000	50.600	50.231	36.818
300	17.041	28.905	0.041	50.600	50.228	36.589
400	18.500	34.039	1.820	54.422	49.973	27.303
500	18.200	38.247	3.707	64.562	47.905	20.938
600	19.650	41.790	5.650	64.058	44.623	16.253
700	19.931	44.891	7.630	63.565	41.424	12.932
800	20.150	47.517	9.634	63.041	38.297	10.462
900	20.289	49.809	11.657	62.539	35.234	8.556
1000	20.400	52.042	13.691	62.050	32.226	7.043
1100	20.484	53.991	15.746	61.576	29.267	5.815
1200	20.541	55.776	17.817	61.123	26.350	4.799
1300	20.571	57.421	19.893	60.688	23.469	3.945
1400	20.574	58.946	21.901	60.278	20.622	3.219

ΔH<sub>f</sub>° = Unknown  
 ΔH<sub>f</sub>° 298.15 = [-50.6 ± 8] kcal. mole<sup>-1</sup>  
 ΔH<sub>m</sub>° = [5] kcal. mole<sup>-1</sup>  
 ΔH<sub>s</sub>° 298.15 = 30.3 ± 2.0 kcal. mole<sup>-1</sup>

S° 298.15 = [28.8 ± 2] cal. mole<sup>-1</sup> deg.<sup>-1</sup>  
 T<sub>m</sub>° = 753°K.

Heat of Formation.

The heat of formation was estimated from the work of W. Biltz and C. Messerknecht, Z. anorg. Chem. 148, 157 (1925) and Biltz, Klatte and Rahlfs, Z. anorg. Chem. 166, 339 (1927) as reported in N.B.S. Circular 500, Washington 1952. They measured the heat of solution of BeI<sub>2</sub> in aq. HCl in an unknown concentration. This value was apparently adjusted and used with Be<sup>++</sup> and 2I<sup>-</sup> to obtain ΔH<sub>f</sub>° of the crystal. However Be<sup>++</sup> was estimated by the Bureau and a total uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with BeCl<sub>2</sub> and BeF<sub>2</sub>. The entropy was also estimated by comparing with α-BeCl<sub>2</sub> and BeF<sub>2</sub> and using additive entropy values for the halide ions. K. N. Semencko and T. N. Naumova, Zhur. Strukt. Khim. 4, 67 (1963) have reported that between 563 and 643°C BeI<sub>2</sub> exists in a β<sub>1</sub> form and above 643°C a β<sub>2</sub> form and an unknown form also exist. No allowance has been made for these modifications in the present table.

Melting Data.

The melting point was reported by O. Rahlfs and W. Fischer, Z. anorg. Chem. 211, 351 (1953). The heat of melting was estimated by comparison with the heats of transition and melting for BeCl<sub>2</sub> and BeF<sub>2</sub>.

Sublimation Data.

The heat of sublimation was obtained from a third law analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 578-703°K. This gave ΔH<sub>s</sub>° 298 = 30.34 kcal. mole<sup>-1</sup> with a drift of 3.2 ± 1.1 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. A second law analysis gave ΔH<sub>s</sub>° 298 = 28.1 ± 0.7 kcal. mole<sup>-1</sup>. No attempt was made to change the functions to eliminate the drift, since a correlation with BeCl<sub>2</sub>, BeBr<sub>2</sub> and BeI<sub>2</sub> indicated that the drift was probably due to the data rather than the functions.

(LIQUID)

BERYLLIUM DIIODIDE (BeI<sub>2</sub>)

$$\Delta H_f^{298,15} = [-47.45 \pm 3] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [5] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^0 = [23] \text{ kcal. mole}^{-1}$$

$$S_{298,15}^0 = [32.4] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_m^0 = 753^\circ \text{K.}$$

$$T_b^0 = [755]^\circ \text{K.}$$

Heat of Formation.

The heat of formation was obtained from that of the crystal by adding  $\Delta H_m^0$  and the difference between  $H_{753}^0 - H_{298}^0$  for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for BeCl<sub>2</sub>. A glass transition was assumed at 500°K. below which the heat capacity was that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See BeI<sub>2</sub>(c) table for details.

Vaporization Data.

The temperature and heat of vaporization were calculated from the cross over point BeI<sub>2</sub>(i) and (g).

T, °K.	C <sub>p</sub>	S°	-(F° - H <sub>298}^0)/T</sub>	H° - H <sub>298}^0</sub>	ΔH <sub>f</sub> °	ΔF°	Log K <sub>p</sub>
0							
100							
200							
298	17.000	32.397	32.397	0.000	-47.446	-48.119	35.294
300	17.041	32.502	32.397	0.31	-47.446	-48.153	35.078
400	18.500	31.636	33.087	1.820	-51.288	-48.228	20.365
500	27.000	41.850	34.432	3.709	-61.406	-48.550	20.346
600	27.000	46.772	36.091	6.409	-60.145	-43.689	15.917
700	27.000	50.935	37.921	9.109	-59.914	-41.506	12.516
800	27.000	54.560	39.776	11.809	-57.715	-38.589	10.541
900	27.000	57.720	41.599	14.509	-54.514	-36.257	9.806
1000	27.000	60.565	43.376	17.209	-54.378	-34.077	7.447
1100	27.000	63.138	45.039	19.909	-54.240	-32.001	6.358
1200	27.000	65.487	46.644	22.609	-53.147	-30.028	5.650
1300	27.000	67.649	48.180	25.309	-52.068	-28.145	4.731
1400	27.000	69.649	49.643	28.009	-51.016	-26.344	4.112
1500	27.000	71.512	51.040	30.709	-49.989	-24.619	3.587
1600	27.000	73.255	52.374	33.409	-51.742	-22.881	3.125
1700	27.000	74.892	53.651	36.109	-50.651	-21.112	2.714
1800	27.000	76.435	54.874	38.809	-49.566	-19.405	2.356
1900	27.000	77.895	56.048	41.509	-48.488	-17.759	2.043
2000	27.000	79.280	57.175	44.209	-47.416	-16.172	1.767

MOL. WT. = 262.821

(IDEAL GAS)

BERYLLIUM DIODIDE (BeI<sub>2</sub>)

Point Group D<sub>∞h</sub>  
 $\Delta H_f^{\circ} 0 = -20 \pm 4$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{\circ} 298.15 = [-20.3 \pm 10]$  kcal. mole<sup>-1</sup>

$S_{298.15}^{\circ} = [70.44 \pm 2]$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
[140](1)
[155](2)
[770](1)

Bond Distance: Be-I = 2.12Å  
 Bond Angle: I-Be-I = [180°]  
 Rotational Constant: B<sub>0</sub> = 0.01478 cm.<sup>-1</sup>

$\sigma = 2$

Heat of Formation.

The heat of formation was obtained from that of the crystal plus  $\Delta H_s$  298, see BeI<sub>2</sub> (c) table for details.

Heat Capacity and Entropy.

The linear structure was assumed by analogy with BeCl<sub>2</sub>. The bond length was reported by P. A. Akishin, V. P. Spirodinov and G. A. Sobeliev, Dokl. Akad. Nauk SSSR, 118, 1134 (1958) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants  $k_i$  for the BeF<sub>2</sub>, BeCl<sub>2</sub>, BeBr<sub>2</sub> and BeI<sub>2</sub> series and also assuming  $k_i/k_j = 1/2 = 50$  as for BeF<sub>2</sub>. The principal moment of inertia is 189.402 x 10<sup>-39</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S°	(-F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	11.060	57.007	81.766	3.340	20.018	20.018	INFINITE
200	12.611	65.254	71.661	2.476	19.893	24.123	52.717
298	13.364	70.441	70.441	1.677	20.010	32.346	20.945
300	13.376	70.524	70.441	1.675	20.306	32.461	23.617
400	14.862	74.545	70.672	1.284	24.853	36.266	19.814
500	14.166	77.572	71.690	2.701	35.178	38.183	16.689
600	14.360	80.173	73.143	4.218	35.190	38.785	14.127
700	14.490	82.397	75.310	5.661	35.218	39.382	12.295
800	14.578	84.338	77.235	7.115	35.260	39.973	10.920
900	14.643	86.049	78.840	8.576	35.320	40.559	9.849
1000	14.690	87.605	79.562	10.043	35.398	41.137	8.990
1100	14.726	89.007	79.540	11.514	35.498	41.707	8.286
1200	14.753	90.280	79.646	12.998	35.622	42.266	7.697
1300	14.775	91.471	80.365	14.464	35.767	42.813	7.197
1400	14.792	92.566	81.176	15.942	35.937	43.348	6.767
1500	14.806	93.587	81.973	17.422	36.130	43.873	6.392
1600	14.818	94.543	82.759	18.904	36.341	44.391	6.051
1700	14.828	95.442	83.450	20.386	36.566	44.924	5.737
1800	14.836	96.290	84.140	21.869	36.800	45.456	5.456
1900	14.843	97.092	84.801	23.353	37.048	45.984	5.204
2000	14.849	97.854	85.435	24.837	37.302	46.506	4.977
2100	14.854	98.578	86.044	26.323	37.560	47.024	4.770
2200	14.858	99.269	86.628	27.808	37.822	47.538	4.581
2300	14.862	99.930	87.183	29.294	38.087	48.048	4.408
2400	14.866	100.562	87.717	30.781	38.353	48.552	4.249
2500	14.869	101.169	88.242	32.267	38.622	49.052	4.102
2600	14.871	101.753	88.770	33.754	38.892	49.548	3.966
2700	14.874	102.314	89.281	35.242	39.162	50.040	3.832
2800	14.876	102.855	89.777	36.729	39.432	50.528	3.698
2900	14.878	103.377	90.259	38.217	39.702	51.012	3.564
3000	14.879	103.881	90.746	39.705	39.972	51.492	3.433
3100	14.881	104.369	91.221	41.193	40.242	51.968	3.302
3200	14.882	104.842	91.694	42.681	40.512	52.440	3.172
3300	14.884	105.300	92.161	44.169	40.782	52.908	3.041
3400	14.885	105.744	92.621	45.657	41.052	53.372	2.910
3500	14.886	106.175	92.705	47.146	41.317	53.832	2.779
3600	14.887	106.595	93.085	48.634	41.582	54.288	2.648
3700	14.888	107.003	93.486	50.123	41.847	54.740	2.517
3800	14.889	107.400	93.818	51.612	42.112	55.188	2.386
3900	14.890	107.787	94.171	53.101	42.377	55.632	2.255
4000	14.890	108.163	94.516	54.590	42.642	56.072	2.124
4100	14.891	108.531	94.853	56.079	42.907	56.508	1.993
4200	14.892	108.890	95.183	57.568	43.172	56.940	1.862
4300	14.892	109.240	95.506	59.054	43.437	57.368	1.731
4400	14.893	109.583	95.822	60.541	43.702	57.792	1.600
4500	14.893	109.915	96.132	62.026	43.967	58.212	1.469
4600	14.894	110.245	96.435	63.511	44.232	58.628	1.338
4700	14.894	110.565	96.730	65.000	44.497	59.040	1.207
4800	14.895	110.875	97.024	66.504	44.762	59.448	1.076
4900	14.895	111.186	97.310	68.004	45.027	59.852	0.945
5000	14.895	111.487	97.590	69.503	45.292	60.252	0.814
5100	14.896	111.782	97.865	70.973	45.557	60.648	0.683
5200	14.896	112.071	98.136	72.443	45.822	61.040	0.552
5300	14.896	112.355	98.402	73.912	46.087	61.428	0.421
5400	14.897	112.633	98.662	75.379	46.352	61.812	0.290
5500	14.897	112.907	98.919	76.841	46.617	62.192	0.159
5600	14.897	113.175	99.171	78.291	46.882	62.568	0.028
5700	14.897	113.439	99.419	79.731	47.147	62.940	-0.103
5800	14.898	113.699	99.663	81.161	47.412	63.308	-0.234
5900	14.898	113.950	99.903	82.580	47.677	63.672	-0.365
6000	14.898	114.203	100.139	84.000	47.942	64.032	-0.496

Point Group [D<sub>2h</sub>] $\Delta H_f^{\circ} = [-180] \text{ kcal. mole}^{-1}$  $\Delta H_f^{\circ} = [-179] \text{ kcal. mole}^{-1}$  $S^{\circ}_{298.15} = [91.15] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ 

Ground State Quantum Weight = 1

## Vibrational Frequencies and Degeneracies

$(\omega, \text{cm.}^{-1})$	$(\omega, \text{cm.}^{-1})$	$(\omega, \text{cm.}^{-1})$
[220](1)	[185](1)	[250](1)
[180](1)	[100](1)	[400](1)
[105](1)	[300](1)	640 (1)

Bond Distance: Be-Cl = [1.7]Å

Be-Cl' (in ring) = [1.8]Å

Bond Angle: Cl'-Be-Cl' (in ring) = [98°]

Cl'-Be-Cl = [136°]

 $\sigma = 4$ Product of the Moments of Inertia:  $I_A I_B I_C = 2.62616 \times 10^{-112} \text{ g.}^3 \text{ cm.}^6$ 

## Heat of Formation

The heat of formation was estimated by assuming that the concentration of dimer in equilibrium with the monomer was ~5% at 500°K. as reported by D. L. Hildenbrand, L. P. Theard, E. Murad and P. Ju, Aeronutronic Div. of Philco Corp., Report U-3068, April 1965 under contract AF 04(611)-8523, giving an effective  $K_p = 5.5 \times 10^{-4}$  for  $2\text{BeCl}_2(\text{g}) \rightarrow \text{Be}_2\text{Cl}_4$  at 500°K.

## Heat Capacity and Entropy

The structure was assumed planar with a D<sub>2h</sub> symmetry, the bond lengths were estimated from the values for BeCl<sub>2</sub> (g), a lengthening being assumed in the ring. The frequencies were estimated using K<sub>2</sub>Cl<sub>2</sub> as a basis for the ring vibrations. Two polymeric frequencies had been observed by A. Shnelson, IIT Research Institute, Report No. IITRI-C6013-4, May 1964, under Contract No. DA-31-124-AR0(D)-111. These were observed in matrix isolated BeCl<sub>2</sub> gas and were ascribed to polymeric species on account of their warm up behavior. They are here assigned to the B<sub>3u</sub> asymmetric stretching mode and the B<sub>1u</sub> symmetric out of plane wag of the non ring chlorines. The order of the frequencies listed above is arbitrary and not related to their specie types. The individual moments of inertia are:  $I_A = 18.396 \times 10^{-39} \text{ g. cm.}^2$ ,  $I_B = 110.638 \times 10^{-39} \text{ g. cm.}^2$  and  $I_C = 129.034 \text{ g. cm.}^2$ .

T, °K.	C <sub>v</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>p</sub>
0	.000	INFINITE	-	6.048	-179.724	-179.724	INFINITE
100	18.636	65.446	113.638	4.819	-179.917	-177.998	387.684
200	24.503	80.950	93.949	2.590	-179.406	-175.297	191.297
298	27.574	91.150	61.150	.000	-179.000	-173.041	126.836
300	27.610	91.321	61.151	.051	-178.993	-173.003	126.077
400	29.654	99.461	97.784	2.891	-178.691	-171.055	93.436
500	29.890	106.062	94.379	5.842	-178.454	-169.173	73.692
600	30.405	111.551	86.797	8.859	-178.259	-167.336	60.949
700	30.773	116.571	82.751	11.917	-178.101	-165.529	51.678
800	31.073	120.956	101.642	18.004	-177.976	-163.744	44.751
900	31.336	124.734	103.953	21.110	-177.884	-162.009	39.379
1000	31.526	127.942	106.112	24.250	-177.832	-160.208	35.011
1100	31.646	130.325	108.180	27.428	-177.824	-158.443	31.478
1200	31.704	132.056	110.140	30.643	-177.864	-156.681	28.534
1300	31.741	133.572	112.001	33.902	-177.947	-154.911	26.042
1400	31.764	134.906	113.749	37.212	-178.078	-153.136	23.904
1500	31.780	136.082	115.442	40.565	-178.257	-151.350	22.051
1600	31.789	137.119	117.055	43.962	-178.478	-149.549	20.405
1700	31.794	138.034	118.587	47.402	-178.740	-147.724	18.926
1800	31.797	138.841	120.031	50.884	-179.046	-145.879	17.612
1900	31.799	139.552	121.454	54.412	-179.398	-144.016	16.435
2000	31.800	140.175	122.800	57.984	-179.797	-142.137	15.376
2100	31.800	140.720	124.093	61.602	-180.243	-140.243	14.417
2200	31.800	141.193	125.337	65.264	-180.733	-138.333	13.545
2300	31.800	141.600	126.535	68.976	-181.268	-136.552	12.748
2400	31.800	141.951	127.691	72.736	-181.850	-134.860	12.017
2500	31.800	142.254	128.808	76.542	-182.482	-133.246	11.344
2600	31.713	157.488	129.887	80.400	-183.168	-131.713	10.722
2700	31.719	158.685	130.932	84.315	-183.909	-130.249	10.146
2800	31.724	159.839	131.944	88.284	-184.706	-128.844	9.617
2900	31.729	160.952	132.922	92.304	-185.558	-127.488	9.133
3000	31.734	162.028	133.877	96.372	-186.466	-126.189	8.694
3100	31.738	163.069	134.802	100.488	-187.430	-124.944	8.298
3200	31.741	164.076	135.701	104.650	-188.450	-123.750	7.934
3300	31.744	165.053	136.576	108.858	-189.526	-122.606	7.598
3400	31.747	166.001	137.428	113.112	-190.658	-121.512	7.288
3500	31.750	166.921	138.257	117.412	-191.846	-120.466	6.999
3600	31.753	167.816	139.066	121.756	-193.090	-119.466	6.730
3700	31.755	168.686	139.855	126.144	-194.390	-118.512	6.480
3800	31.757	169.533	140.625	130.576	-195.746	-117.600	6.248
3900	31.759	170.358	141.376	135.052	-197.158	-116.730	6.032
4000	31.761	171.162	142.111	139.572	-198.626	-115.900	5.830
4100	31.763	171.944	142.829	144.136	-200.150	-115.110	5.642
4200	31.764	172.711	143.532	148.744	-201.730	-114.360	5.466
4300	31.766	173.459	144.219	153.396	-203.366	-113.640	5.302
4400	31.767	174.189	144.892	158.092	-205.058	-112.960	5.148
4500	31.768	174.903	145.551	162.832	-206.806	-112.320	5.004
4600	31.769	175.601	146.187	167.616	-208.610	-111.710	4.870
4700	31.771	176.285	146.899	172.444	-210.470	-111.130	4.746
4800	31.772	176.953	147.580	177.316	-212.386	-110.580	4.632
4900	31.773	177.609	148.239	182.232	-214.358	-110.060	4.528
5000	31.774	178.250	148.876	187.192	-216.386	-109.570	4.434
5100	31.774	178.880	149.493	192.196	-218.470	-109.110	4.350
5200	31.775	179.497	149.819	197.244	-220.610	-108.680	4.276
5300	31.776	180.102	150.384	202.336	-222.806	-108.280	4.212
5400	31.777	180.696	150.940	207.472	-225.058	-107.910	4.158
5500	31.777	181.279	151.487	212.652	-227.366	-107.560	4.114
5600	31.778	181.852	152.024	217.876	-229.730	-107.230	4.070
5700	31.778	182.414	152.552	223.144	-232.150	-106.920	4.036
5800	31.779	182.967	153.072	228.456	-234.626	-106.630	4.002
5900	31.780	183.510	153.583	233.812	-237.158	-106.360	3.978
6000	31.780	184.044	154.086	239.212	-239.746	-106.110	3.954

T, °K.	C <sub>p</sub>	S°	$-(F^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	4.492	1.785	-2.922	-503.096	-503.096	-503.096	INFINITE
200	14.444	7.946	-2.791	-504.475	-496.232	-496.232	1084.662
298	22.840	15.342	-1.845	-505.466	-487.581	-487.581	532.778
			0.000	-506.029	-478.682	-478.682	350.966
300	22.968	15.483	-0.042	-506.036	-478.512	-478.512	348.579
400	26.850	22.946	2.651	-506.235	-469.299	-469.299	256.401
500	32.730	29.819	5.738	-506.168	-460.066	-460.066	201.085
600	35.650	36.054	9.162	-505.911	-450.868	-450.868	164.221
700	37.970	41.732	12.848	-505.515	-441.725	-441.725	137.006
800	39.680	46.920	16.735	-505.016	-432.647	-432.647	118.188
900	40.810	51.662	20.763	-504.464	-423.631	-423.631	102.867
1000	41.600	56.005	24.885	-503.901	-414.679	-414.679	90.424
1100	42.150	59.996	29.074	-503.350	-405.784	-405.784	80.618
1200	42.590	63.681	33.312	-502.824	-396.938	-396.938	72.280
1300	42.934	67.106	37.588	-502.328	-388.133	-388.133	65.248
1400	43.240	70.300	41.897	-501.865	-379.369	-379.369	59.210
1500	43.472	73.291	46.233	-501.440	-370.636	-370.636	53.999
1600	43.702	76.104	50.592	-501.054	-361.769	-361.769	49.413
1700	43.930	78.760	54.973	-500.708	-352.628	-352.628	45.331
1800	44.156	81.277	59.378	-500.400	-343.293	-343.293	41.633
1900	44.380	83.671	63.804	-500.128	-333.734	-333.734	38.329
2000	44.600	85.953	68.253	-500.000	-323.988	-323.988	35.458
2100	44.812	88.134	72.724	-500.000	-313.968	-313.968	32.673
2200	45.024	90.224	77.161	-500.000	-304.365	-304.365	30.256
2300	45.236	92.250	81.579	-500.000	-294.822	-294.822	28.013
2400	45.448	94.219	86.063	-500.000	-285.474	-285.474	25.977
2500	45.660	96.019	90.618	-500.000	-276.284	-276.284	24.108
2600	45.872	97.814	95.305	-500.000	-266.298	-266.298	22.383
2700	46.084	99.540	99.993	-500.000	-256.841	-256.841	20.780
2800	46.296	101.220	104.612	-500.000	-246.937	-246.937	19.137
2900	46.508	102.857	109.252	-500.000	-236.630	-236.630	17.480
3000	46.720	104.437	113.913	-500.000	-226.114	-226.114	15.743

BERYLLIUM ORTHOSILICATE (Be<sub>2</sub>SiO<sub>4</sub>) (CRYSTAL)

MOL. WT. = 110.108

$\Delta H_f^{\circ} 0 = -503.1 \pm 7$  kcal. mole<sup>-1</sup>

$\Delta H_f^{\circ} 298.15 = [-506.0 \pm 7]$  kcal. mole<sup>-1</sup>

$S_{298.15}^{\circ} = 15.342 \pm 0.1$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

$T_m = 1833^{\circ}$  K.

Heat of Formation.

The  $\Delta H_f^{\circ} 298.15$  was estimated from the  $\Delta H_f^{\circ} 298.15$  of Mg, Ca and Ba oxides with SiO<sub>2</sub> given by K. K. Kelley in the report of Investigations 5901, U. S. Department of the Interior, Bureau of Mines 1962, and from the  $\Delta H_f^{\circ} 298.15$  of BeO(c) (Sept. 30, 1963) and SiO<sub>2</sub>(c) (Dec. 31, 1962) in JANAF tables. The  $\Delta H_f^{\circ} 298.15 = 0 \pm 7$  kcal. mole<sup>-1</sup> was estimated for the reaction  $2\text{BeO}(c) + \text{SiO}_2(c) \rightarrow \text{Be}_2\text{SiO}_4(c)$ .

Heat Capacity and Entropy.

At low temperatures  $C_p$  was used from K. K. Kelley, J. Am. Chem. Soc., 61, 1217 (1939). Above 298.15°K.  $C_p$  values were estimated by summation of the component oxides using JANAF tables, BeO (Sept. 30, 1963) and SiO<sub>2</sub>(c) (Dec. 31, 1962). The entropy was calculated at 54.7°K. using the Debye and Planck-Einstein functions  $D(\frac{422}{T}) + 2E(\frac{2527}{T})$  given by K. K. Kelley, J. Am. Chem. Soc., 61, 1217 (1939). The value of  $S_{54.7}^{\circ} = 13.59$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Data.

The incongruent melting point was taken from Kubaschewski and Evans, "Metallurgical Thermochemistry" 3rd edition, Pergamon Press., New York 1958.

$\Delta H_f^0 = 5.28 \pm 0.30 \text{ kcal. mole}^{-1}$

$\Delta H_f^{298.15} = 5.50 \pm 0.3 \text{ kcal. mole}^{-1}$

Ground State Configuration  $1\sum^+$

$S_{298.15}^0 = 57.337 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Quantum Weight

$\epsilon, \text{ cm.}^{-1} \frac{\epsilon_1}{0} 1$

$\omega_e x_e = 1.8 \text{ cm.}^{-1}$

$\omega_e = 443.1 \text{ cm.}^{-1}$

$B_e = 0.150797 \text{ cm.}^{-1}$

$\sigma^- = 1$

$r_e = 2.136 \text{ \AA}$

Heat of Formation.

The average  $\Delta H_f^{298.15} = 0.406 \text{ kcal. mole}^{-1}$  for the reaction  $\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{BrCl}(\text{g})$  and the  $\Delta H_f^{298.15} = 3.694 \text{ kcal. mole}^{-1}$  for  $1/2 \text{ Br}_2(\text{g})$  from JANAF tables were used to calculate the  $\Delta H_f^{298.15} = 3.5 \pm 0.3 \text{ kcal. mole}^{-1}$ . Other equilibrium measurements not included below have been summarized by Beeson and Yost, loc. cit.

Third Law  $\Delta H_f^{298.15}$

Source	T°K	Method	kcal. mole <sup>-1</sup>
1	301	Light absorption	.51
2	298	Light absorption	0.34
3	372-492	Total pressure Run III	0.39
5	372-492	Total pressure Run II	0.47
4	313±5	Mass spectrometric	0.32
Average			0.406

Source

- H. G. Vesper and G. K. Rollefson, J. Am. Chem. Soc. **56**, 620 (1934).
- G. Braune and E. Victor, Z. Elektrochem. **41**, 508 (1935).
- C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. **61**, 1432 (1939).
- H. C. Matraw, C. F. Pachucki and M. J. Hawkins, General Electric Co., Report No. KAPL-1016 (1953) Knolls Atomic Power Laboratory, Schenectady, New York.

Heat Capacity and Entropy.

All spectroscopic and molecular constants were obtained from W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. of Standards, **55**, 147 (1955) except  $r_e$  which was calculated from  $B_e$ . The value of  $r_e$  was reported to be 2.13 Å and 2.11 Å by C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. **61**, 1432 (1939) and L. G. Cole and G. W. Elverum Jr., J. Chem. Phys., **20**, 1543 (1952), respectively. Ground state configuration was taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

T, °K.	C <sub>p</sub>	S°	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	.000	INFINITE	-	2.247	5.279	5.279	INFINITE
100	7.101	46.926	66.421	1.550	3.503	3.503	7.218
200	7.884	54.089	58.999	.800	1.384	1.384	1.512
298	8.363	57.337	.000	.000	3.500	.000	.166
300	8.369	57.389	.015	.015	3.491	.250	.182
400	8.611	58.633	.576	.576	1.193	.741	.405
500	8.774	59.771	1.774	1.774	1.193	.478	.384
600	8.826	59.773	59.018	2.613	.192	1.015	.370
700	8.851	59.773	59.740	3.499	.192	1.153	.360
800	8.821	59.579	60.440	4.369	.193	1.290	.352
900	8.727	60.279	61.109	5.232	.194	1.427	.347
1000	8.577	61.823	61.744	6.179	.194	1.564	.342
1100	8.398	64.780	62.346	7.078	.195	1.701	.338
1200	8.216	69.563	62.915	7.978	.196	1.837	.335
1300	8.033	76.286	63.454	8.881	.197	1.974	.332
1400	7.848	84.967	63.967	9.785	.198	2.111	.330
1500	7.663	95.581	64.454	10.690	.199	2.249	.328
1600	7.476	108.166	64.918	11.597	.201	2.385	.326
1700	7.289	122.717	65.360	12.506	.202	2.521	.324
1800	7.102	139.236	65.784	13.415	.203	2.657	.323
1900	6.914	157.729	66.189	14.326	.204	2.792	.321
2000	6.726	178.197	66.578	15.238	.207	2.930	.320
2100	6.537	199.642	66.951	16.151	.208	3.065	.319
2200	6.348	223.068	67.311	17.065	.211	3.203	.318
2300	6.159	248.474	67.657	17.981	.214	3.346	.317
2400	5.970	275.865	67.991	18.897	.217	3.473	.316
2500	5.781	305.239	68.313	19.815	.221	3.608	.315
2600	5.592	336.599	68.627	20.734	.224	3.742	.315
2700	5.403	369.947	68.927	21.653	.229	3.881	.314
2800	5.214	405.281	69.219	22.574	.235	4.012	.313
2900	5.024	442.603	69.503	23.496	.241	4.149	.313
3000	4.835	481.918	69.778	24.419	.248	4.285	.312
3100	4.645	523.221	70.046	25.343	.257	4.419	.311
3200	4.455	566.514	70.306	26.268	.266	4.551	.311
3300	4.265	611.800	70.559	27.194	.276	4.685	.310
3400	4.075	659.076	70.805	28.121	.287	4.819	.310
3500	3.885	708.345	71.045	29.050	.299	4.952	.309
3600	3.695	759.607	71.280	29.979	.312	5.085	.309
3700	3.505	812.862	71.508	30.909	.325	5.218	.308
3800	3.315	868.110	71.731	31.840	.339	5.350	.308
3900	3.125	925.352	71.949	32.772	.355	5.479	.307
4000	2.935	984.589	72.162	33.706	.371	5.615	.307
4100	2.745	1045.819	72.371	34.640	.387	5.744	.306
4200	2.555	1109.045	72.574	35.575	.404	5.877	.306
4300	2.365	1184.265	72.774	36.512	.421	6.005	.305
4400	2.175	1271.481	72.969	37.449	.439	6.134	.305
4500	1.985	1370.691	73.161	38.387	.457	6.262	.304
4600	1.795	1482.909	73.349	39.327	.475	6.393	.304
4700	1.605	1608.135	73.532	40.267	.493	6.518	.303
4800	1.415	1746.369	73.713	41.208	.512	6.648	.303
4900	1.225	1898.612	73.890	42.151	.530	6.777	.302
5000	1.035	2065.873	74.064	43.094	.547	6.902	.302
5100	0.845	2248.149	74.235	44.039	.565	7.029	.301
5200	0.655	2446.431	74.404	44.984	.582	7.157	.301
5300	0.465	2660.718	74.568	45.931	.599	7.282	.300
5400	0.275	2891.009	74.727	46.878	.616	7.409	.300
5500	0.085	3137.304	74.880	47.826	.632	7.532	.299
5600		3400.603	75.026	48.776	.648	7.659	.299
5700		3680.906	75.167	49.726	.664	7.789	.299
5800		4000.213	75.303	50.678	.679	7.908	.298
5900		4369.524	75.435	51.630	.694	8.036	.298
6000		4788.839	75.563	52.584	.708	8.160	.297

Sept. 30, 1962; Sept. 30, 1965



Ground State Configuration  $1 \sum^+$   
 $\Delta H_f^0 = -12.1 \pm 0.4 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -14.0 \pm 0.4 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\epsilon, \text{ cm.}^{-1} \frac{\epsilon_1}{0}$

$\sigma^- = 1$

$r_e = 1.7555 \text{ \AA}$

$\omega_e x_e = 4 \text{ cm.}^{-1}$

$\alpha_e = 0.005206 \text{ cm.}^{-1}$

$\omega_e = 873 \text{ cm.}^{-1}$

$B_e = 0.3565319 \text{ cm.}^{-1}$

Heat of Formation.

The equilibrium constant for the reaction  $\text{Br}_2(\text{g}) + \text{BrF}_3(\text{g}) = 3\text{BrF}(\text{g})$  has been measured over the temperature range 328-380°K. by R. K. Steunenberg, R. C. Vogel and J. Fischer, J. Am. Chem. Soc. 79, 1320 (1957). Third law analysis of the data yields a  $\Delta H_f^0$  298 =  $11.785 \pm 0.2 \text{ kcal. mole}^{-1}$ , with a drift of  $-0.6 \pm 1.2 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ . Second law analysis yields  $\Delta H_f^0$  298 =  $11.98 \pm 0.45 \text{ kcal. mole}^{-1}$ , thus it is obvious that the data is thermodynamically self consistent. There is an uncertainty in the entropy of  $\text{BrF}_3(\text{g})$  of  $\pm 1 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$  but this corresponds only to  $\pm 0.35 \text{ kcal. mole}^{-1}$  in  $\Delta H_f^0$  298, thus a best value of  $\Delta H_f^0$  298 =  $11.78 \pm 0.5 \text{ kcal. mole}^{-1}$  is adopted. This yields  $\Delta H_f^0$  298  $\text{BrF} = -13.973 \pm 0.4 \text{ kcal. mole}^{-1}$ , the uncertainty in the heat of formation being a maximum value comprising the sum of the uncertainties in  $\text{Br}_2$ ,  $\text{BrF}_3$  and  $\Delta H_f^0$ .

Attempts have been made to analyse the spectra of BrF to obtain a  $D_0$  value. P. H. Broderick and J. E. Sicre, Z. Physik 141, 515 (1955) obtained two dissociation limits for BrF of 65.52 kcal. mole<sup>-1</sup> and 54.98 kcal. mole<sup>-1</sup>. The difference corresponds to the  $\text{Br}(^2P_{1/2}) - \text{Br}(^2P_{3/2})$  excitation energy, indicating that the upper state goes to  $\text{F}(^2P_{3/2})$  and  $\text{Br}(^2P_{1/2})$ . This yields a heat of formation of BrF of  $-10.23 \text{ kcal. mole}^{-1}$ . Since this value is well outside the possible uncertainty limits of the equilibrium data we must conclude that the extrapolation is in error. W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. Std. 55, 147 (1955) have also analysed the spectra and conclude that a heat of formation of  $-14.4 \text{ kcal. mole}^{-1}$  is possible. However W. H. Evans, private communication Nov. 1965, now believes that the dissociating state was too strongly perturbed for meaningful extrapolation.

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Standards 55, 147 (1955) except  $r_e$  and ground state configuration which were taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

T. °K.	C <sub>p</sub>	S°	$-(F^0 - H_{298}^0)/T$	H° - H <sub>298}^0</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0							INFINITE
100	6.570	66.743	2.456	12.144	12.144	12.144	30.872
200	7.252	81.663	7.68	12.354	16.042	16.042	17.529
298	7.877	94.700	0.000	13.973	17.656	17.656	12.927
300	7.885	94.749	0.015	13.982	17.658	17.658	12.863
400	8.295	97.072	0.23	17.679	18.125	18.125	9.903
500	8.488	98.941	1.661	17.686	18.237	18.237	7.971
600	8.640	99.503	2.518	17.689	18.347	18.347	6.682
700	8.744	99.843	3.387	17.691	18.456	18.456	5.762
800	8.820	99.915	4.266	17.694	18.565	18.565	5.071
900	8.877	99.958	5.151	17.696	18.674	18.674	4.534
1000	8.922	99.985	6.041	17.698	18.782	18.782	4.105
1100	8.960	99.998	6.935	17.701	18.891	18.891	3.753
1200	8.992	99.999	7.833	17.703	18.999	18.999	3.460
1300	9.019	99.999	8.733	17.707	19.105	19.105	3.212
1400	9.044	99.999	9.636	17.710	19.214	19.214	2.999
1500	9.067	99.999	10.542	17.714	19.321	19.321	2.815
1600	9.087	99.999	11.450	17.718	19.427	19.427	2.654
1700	9.107	99.999	12.359	17.723	19.534	19.534	2.511
1800	9.125	99.999	13.271	17.728	19.642	19.642	2.385
1900	9.143	99.999	14.184	17.732	19.751	19.751	2.271
2000	9.160	99.999	15.099	17.738	19.863	19.863	2.169
2100	9.176	99.999	16.016	17.743	19.976	19.976	2.077
2200	9.192	99.999	16.934	17.749	20.093	20.093	1.993
2300	9.207	99.999	17.852	17.755	20.210	20.210	1.916
2400	9.222	99.999	18.772	17.761	20.274	20.274	1.846
2500	9.237	99.999	19.694	17.768	20.380	20.380	1.782
2600	9.252	99.999	20.623	17.776	20.482	20.482	1.722
2700	9.266	99.999	21.549	17.783	20.588	20.588	1.666
2800	9.280	99.999	22.477	17.790	20.691	20.691	1.615
2900	9.295	99.999	23.405	17.798	20.794	20.794	1.567
3000	9.309	99.999	24.336	17.806	20.898	20.898	1.522
3100	9.322	99.999	25.267	17.815	21.002	21.002	1.481
3200	9.336	99.999	26.200	17.823	21.103	21.103	1.441
3300	9.350	99.999	27.134	17.833	21.205	21.205	1.404
3400	9.363	99.999	28.070	17.841	21.309	21.309	1.370
3500	9.377	99.999	29.007	17.851	21.407	21.407	1.337
3600	9.390	99.999	29.945	17.861	21.511	21.511	1.306
3700	9.404	99.999	30.885	17.871	21.612	21.612	1.276
3800	9.417	99.999	31.826	17.881	21.712	21.712	1.249
3900	9.430	99.999	32.769	17.892	21.814	21.814	1.222
4000	9.444	99.999	33.712	17.903	21.915	21.915	1.197
4100	9.457	99.999	34.657	17.915	22.015	22.015	1.173
4200	9.470	99.999	35.604	17.926	22.114	22.114	1.151
4300	9.483	99.999	36.551	17.938	22.212	22.212	1.129
4400	9.496	99.999	37.500	17.950	22.311	22.311	1.108
4500	9.509	99.999	38.451	17.962	22.413	22.413	1.088
4600	9.523	99.999	39.402	17.975	22.510	22.510	1.069
4700	9.536	99.999	40.355	17.988	22.608	22.608	1.051
4800	9.549	99.999	41.309	18.001	22.708	22.708	1.034
4900	9.562	99.999	42.265	18.015	22.804	22.804	1.017
5000	9.575	99.999	43.222	18.028	22.894	22.894	1.001
5100	9.588	99.999	44.180	18.043	23.002	23.002	0.986
5200	9.601	99.999	45.139	18.057	23.096	23.096	0.971
5300	9.614	99.999	46.100	18.071	23.191	23.191	0.956
5400	9.627	99.999	47.062	18.087	23.282	23.282	0.943
5500	9.640	99.999	48.025	18.101	23.387	23.387	0.929
5600	9.653	99.999	48.990	18.117	23.485	23.485	0.916
5700	9.666	99.999	49.956	18.133	23.574	23.574	0.904
5800	9.678	99.999	50.923	18.148	23.674	23.674	0.890
5900	9.691	99.999	51.891	18.164	23.747	23.747	0.880
6000	9.704	99.999	52.861	18.182	23.864	23.864	0.869

BROMINE TRIFLUORIDE (BrF<sub>3</sub>) (IDEAL GAS)

Point Group C<sub>2v</sub>  
 $\Delta H_f^0 = -58.4 \pm 0.7$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = 69.867$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -61.1 \pm 0.7$  kcal. mole<sup>-1</sup>

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
674 (1)	613 (1)
[528] (1)	[384] (1)
[300] (1)	[289] (1)

Bond Distance: Br-F<sub>1</sub> = Br-F<sub>3</sub> = 1.8061 Å Br-F<sub>2</sub> = 1.721 Å

Bond Angle: F<sub>1</sub>-Br-F<sub>2</sub> = 86° 12.6' F<sub>2</sub>-Br-F<sub>3</sub> = 86° 12.6' F<sub>3</sub>-Br-F<sub>1</sub> = 187° 34.8'

Product of the Moment of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 4.519225 X 10<sup>-11</sup>4 g. 3 cm.<sup>6</sup>

Heat of Formation.

The  $\Delta H_f^{298.15} = -61.087 \pm 0.7$  kcal. mole<sup>-1</sup> is from L. Stein, J. Phys. Chem. **66**, 288 (1962) and was derived from heats of reaction of F<sub>2</sub> with Br<sub>2</sub> which were measured in an adiabatic calorimeter. Stein's value for the  $\Delta H_f^{298.15} = -64.78$  kcal. mole<sup>-1</sup> was based upon gaseous Br<sub>2</sub>, which has been adjusted to the liquid Br<sub>2</sub> reference state at 288.15°K.

Heat Capacity and Entropy.

D. W. Magnuson, Report No. K-1179, Carbide and Carbon Chemicals Co., K-25 plant, Oak Ridge, Tennessee (December, 1954) determined the moments of inertia and quadrupole coupling coefficients of both Br<sup>79</sup>F<sub>3</sub> and Br<sup>81</sup>F<sub>3</sub> from a number of microwave transitions. From the moment of inertia the bromine trifluoride molecule was found to have a distorted "m" structure with one short, 1.721 Å, and two long, 1.810 Å Br-F bonds. The FBrF angle was found to be 86° 12.6'.

H. H. Claassen, B. Weinstock, and J. G. Malm, J. Chem. Phys. **28**, 285 (1958), observed two of the six vibrational levels in the vapor, and calculated the other four levels from a normal coordinate treatment of the molecule. They also obtained a measured entropy of BrF<sub>3</sub>(g), from low temperature data combined with vapor pressure data and an approximate correction for dimerization. This value is 71.9 e.u. at 316.27°K. compared with a value of 70.82 e.u. from this table, the difference is probably within the uncertainty of the data. The three principal moments of inertia are: I<sub>A</sub> = 7.7514 X 10<sup>-39</sup>, I<sub>B</sub> = 2.05791 X 10<sup>-38</sup> and I<sub>C</sub> = 2.83306 X 10<sup>-38</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.000	INFINITE	- 3.412	- 58.404	- 58.404	INFINITE
100	9.347	56.276	82.142	- 58.956	- 57.835	12.6393
200	19.336	64.017	71.250	- 59.451	- 56.501	61.7539
298	15.893	69.867	.000	- 61.087	- 54.827	40.187
300	15.829	69.966	.079	- 61.005	- 54.789	39.012
400	17.475	74.765	1.700	- 61.602	- 55.939	28.377
500	18.145	78.127	3.478	- 64.573	- 48.765	21.314
600	18.627	82.081	5.319	- 64.425	- 45.616	16.615
700	18.936	84.978	7.198	- 64.268	- 42.494	13.267
800	19.145	87.521	9.103	- 64.111	- 39.396	10.762
900	19.291	89.785	11.025	- 63.952	- 36.315	8.818
1000	19.398	91.823	12.960	- 63.794	- 33.253	7.267
1100	19.478	93.676	14.904	- 63.639	- 30.207	6.001
1200	19.540	95.373	16.855	- 63.485	- 27.173	4.949
1300	19.588	96.939	18.811	- 63.336	- 24.152	4.060
1400	19.627	98.392	20.772	- 63.188	- 21.144	3.301
1500	19.658	99.748	22.736	- 63.045	- 18.146	2.644
1600	19.684	101.017	24.704	- 62.904	- 15.157	2.070
1700	19.705	102.211	26.673	- 62.767	- 12.176	1.565
1800	19.723	103.338	28.644	- 62.634	- 9.207	1.118
1900	19.738	104.405	30.617	- 62.503	- 6.241	0.733
2000	19.751	105.417	32.592	- 62.376	- 3.281	.359
2100	19.762	106.381	34.568	- 62.252	- .332	.035
2200	19.772	107.301	36.544	- 62.133	- 2.613	.260
2300	19.781	108.180	38.522	- 62.017	- 5.555	.528
2400	19.788	109.022	40.500	- 61.904	- 8.490	.773
2500	19.795	109.830	42.480	- 61.796	- 11.420	.998
2600	19.800	110.606	44.459	- 61.691	- 14.349	1.206
2700	19.806	111.354	46.440	- 61.588	- 17.271	1.398
2800	19.810	112.074	48.420	- 61.490	- 20.189	1.576
2900	19.815	112.769	50.402	- 61.395	- 23.108	1.741
3000	19.818	113.441	52.383	- 61.305	- 26.015	1.895
3100	19.822	114.091	54.365	- 61.217	- 28.925	2.039
3200	19.828	114.721	56.348	- 61.133	- 31.830	2.174
3300	19.833	115.331	58.330	- 61.053	- 34.733	2.300
3400	19.837	115.923	60.313	- 60.975	- 37.635	2.419
3500	19.840	116.497	62.296	- 60.903	- 40.541	2.531
3600	19.843	117.056	64.280	- 60.833	- 43.438	2.637
3700	19.847	117.600	66.263	- 60.767	- 46.330	2.736
3800	19.850	118.129	68.247	- 60.704	- 49.226	2.831
3900	19.840	118.644	70.231	- 60.647	- 52.116	2.920
4000	19.842	119.146	72.215	- 60.591	- 55.009	3.005
4100	19.843	119.636	74.199	- 60.541	- 57.896	3.086
4200	19.845	120.115	76.184	- 60.493	- 60.782	3.163
4300	19.846	120.581	78.168	- 60.448	- 63.676	3.236
4400	19.847	121.038	80.153	- 60.408	- 66.568	3.306
4500	19.848	121.484	82.138	- 60.371	- 69.440	3.372
4600	19.849	121.920	84.123	- 60.337	- 72.327	3.436
4700	19.850	122.347	86.108	- 60.308	- 75.217	3.497
4800	19.851	122.765	88.093	- 60.282	- 78.105	3.556
4900	19.852	123.174	90.078	- 60.259	- 80.991	3.612
5000	19.853	123.575	92.063	- 60.241	- 83.882	3.665
5100	19.854	123.968	94.049	- 60.226	- 86.738	3.717
5200	19.854	124.354	96.034	- 60.214	- 89.624	3.767
5300	19.855	124.732	98.020	- 60.205	- 92.509	3.814
5400	19.856	125.103	100.005	- 60.202	- 95.382	3.860
5500	19.856	125.468	101.991	- 60.201	- 98.265	3.905
5600	19.857	125.825	103.976	- 60.205	- 101.151	3.947
5700	19.858	126.177	105.962	- 60.212	- 104.031	3.989
5800	19.858	126.522	107.948	- 60.221	- 106.915	4.028
5900	19.859	126.862	109.934	- 60.235	- 109.788	4.067
6000	19.859	127.195	111.920	- 60.252	- 112.674	4.104

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	11.313	95.297	5.184	98.846	98.846	INFINITE
200	18.311	79.417	3.710	100.843	100.843	2.07712
298	24.436	77.337	2.151	102.466	83.989	98.404
			∞	102.466	83.989	61.563
300	24.504	77.487	0.945	102.473	83.875	61.100
400	27.695	84.868	2.624	105.939	76.946	42.039
500	28.524	91.952	5.467	105.614	69.736	30.480
600	29.439	96.380	8.209	105.237	62.594	22.799
700	30.424	100.065	11.284	104.835	55.518	17.333
800	30.419	103.802	14.307	104.425	48.503	13.250
900	30.677	105.927	17.364	104.007	41.538	10.086
1000	30.873	111.847	20.444	103.590	34.619	7.566
1100	31.026	116.799	23.562	103.173	27.743	5.512
1200	31.147	121.707	26.653	102.756	20.902	3.807
1300	31.233	126.585	29.775	102.344	14.097	2.370
1400	31.293	131.434	32.904	101.935	7.325	1.143
1500	31.330	136.253	36.040	101.531	∞	∞
1600	31.439	141.041	39.182	101.131	6.1136	∞
1700	31.472	145.797	42.328	100.735	12.831	1.649
1800	31.513	150.524	45.478	100.346	19.494	2.567
1900	31.542	155.227	48.630	99.959	26.145	3.307
2000	31.566	159.906	51.786	99.578	32.773	3.881
2100	31.588	164.567	54.943	99.203	39.376	4.568
2200	31.606	169.206	58.103	98.833	45.939	5.292
2300	31.622	173.825	61.265	98.468	52.451	5.982
2400	31.636	178.424	64.427	98.109	58.914	6.636
2500	31.646	183.003	67.592	97.757	65.324	7.266
2600	31.650	187.562	70.757	97.409	71.684	7.877
2700	31.670	192.101	73.924	97.065	78.011	8.469
2800	31.678	196.620	77.091	96.727	84.312	9.043
2900	31.685	201.129	80.259	96.395	90.587	9.609
3000	31.694	205.627	83.428	96.071	96.834	10.166
3100	31.700	210.106	86.598	95.749	103.052	10.716
3200	31.706	214.565	89.768	95.430	109.241	11.261
3300	31.711	219.004	92.939	95.113	115.401	11.791
3400	31.715	223.423	96.113	94.800	121.536	12.306
3500	31.721	227.822	99.292	94.492	127.648	12.807
3600	31.725	232.201	102.465	94.189	133.728	13.294
3700	31.729	236.560	105.647	93.892	139.774	13.768
3800	31.732	240.900	108.829	93.600	145.786	14.229
3900	31.735	245.220	112.012	93.313	151.764	14.677
4000	31.738	249.529	115.197	93.031	157.718	15.113
4100	31.741	253.818	118.381	92.754	163.648	15.536
4200	31.744	258.087	121.564	92.481	169.554	15.947
4300	31.746	262.336	124.749	92.212	175.436	16.345
4400	31.748	266.565	127.934	91.947	181.294	16.730
4500	31.750	270.774	131.120	91.686	187.128	17.102
4600	31.752	274.963	134.305	91.429	192.938	17.461
4700	31.754	279.132	137.490	91.176	198.724	17.807
4800	31.756	283.281	140.676	90.927	204.486	18.140
4900	31.758	287.410	143.861	90.681	210.224	18.460
5000	31.759	291.519	147.046	90.438	215.938	18.767
5100	31.761	295.608	150.231	90.198	221.628	19.061
5200	31.762	299.677	153.416	90.118	227.294	19.342
5300	31.763	303.726	156.601	90.038	232.936	19.609
5400	31.764	307.755	159.786	89.958	238.554	19.864
5500	31.765	311.764	162.971	89.878	244.148	20.107
5600	31.766	315.753	166.156	89.798	249.718	20.338
5700	31.767	319.722	169.341	89.718	255.264	20.557
5800	31.768	323.671	172.526	89.638	260.786	20.765
5900	31.770	327.600	175.711	89.558	266.284	20.962
6000	31.770	331.509	178.896	89.478	271.758	21.147

BROMINE PENTAFLUORIDE (BrF<sub>5</sub>) (IDEAL GAS) MOL. WT. = 174.901

Point Group C<sub>4v</sub>  
 $\Delta H_f^0 = -98.8 \pm 0.5$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0$  298.15 = -102.5 ± 0.5 kcal. mole<sup>-1</sup>

Vibrational Frequencies and Degeneracies		
$\nu$ , cm. <sup>-1</sup>	$\nu$ , cm. <sup>-1</sup>	$\nu$ , cm. <sup>-1</sup>
685 (1)	585 (1)	644 (2)
587 (1)	(281)(1)	415 (2)
369 (1)	312 (1)	245 (2)

Bond Distances: Br-F(equatorial) = 1.79 Å Br-F(axial) = 1.68 Å  
 Bond Angle: F(equatorial)-Br-F(equatorial) = [90°] and F(axial)-Br-F(equatorial) = [90°] σ = 4  
 Product of the Moment of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 3.2035 X 10<sup>-113</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The ΔH<sub>f</sub><sup>0</sup> 298.15 = -102.466 ± 0.5 kcal. mole<sup>-1</sup> is from L. Stein J. Phys. Chem. 66, 288 (1962) and was derived from heats of reaction of F<sub>2</sub> with Br<sub>2</sub> which were measured in an adiabatic calorimeter. Stein's value for the ΔH<sub>f</sub><sup>0</sup> 298.15 = -106.16 kcal. mole<sup>-1</sup> was based upon gaseous Br<sub>2</sub> which has been adjusted to the liquid Br<sub>2</sub> reference state at 298.15°K.

Heat Capacity and Entropy.

G. M. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965) report the infrared (gas phase) and Raman (liquid phase) spectra and correlate the observations by means of normal coordinate calculations for the similar molecules BrF<sub>5</sub>, IP<sub>5</sub>, ClP<sub>5</sub> and XeOP<sub>4</sub>. The fundamental frequencies are taken from Begun, et al., except for ν<sub>9</sub> which was beyond the range of their infrared measurements. The value ν<sub>9</sub> = 245 cm.<sup>-1</sup> for the gas has been observed by R. S. McDowell and L. E. Asprey, J. Chem. Phys. 37, 165 (1962) and is confirmed by 237 cm.<sup>-1</sup> found in the Raman spectra of the liquid. Raman values from the liquid were used for the infrared inactive fundamentals ν<sub>4</sub> and ν<sub>6</sub>. One Raman active frequency, presumably ν<sub>5</sub>, is not observed in any of the four molecules. The value ν<sub>5</sub> = 261 cm.<sup>-1</sup> was obtained from the normal coordinate calculation. Previous Raman studies were reported by C. V. Stephenson and E. A. Jones, J. Chem. Phys. 20, 1830 (1952).

A tetragonal pyramidal structure (C<sub>4v</sub> symmetry) with the above parameters was used by Begun, et al., in the analysis of the spectra. This symmetry is consistent with the NMR spectra of H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. 19, 1259 (1951), with the dipole moment determined by M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speirs, J. Am. Chem. Soc. 78, 44 (1956), and with the X-ray crystal structure obtained by R. D. Robinson and P. N. Bensey, Jr., J. Chem. Phys. 27, 982 (1957). Bond distances were based on those in the crystal and the bond angle was assumed to be 90°, slightly larger than those in the crystal (80.5-86.5°). Begun, et al., indicate that the angle in the gaseous molecule is probably not exactly 90° but that the normal coordinate calculations are not sensitive to this angle. The three principal moments of inertia are: I<sub>A</sub> = 2.81497 X 10<sup>-38</sup>, I<sub>B</sub> = 2.81497 X 10<sup>-38</sup> and I<sub>C</sub> = 4.04277 X 10<sup>-38</sup> g. cm.<sup>2</sup>

(IDEAL GAS)

HYDROGEN BROMIDE (HBr)

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

$S_{298.15}^{\circ} = 47.465 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^{\circ} = -6.84 \pm 0.13 \text{ kcal. mole}^{-1}$

$\Delta H_f^{\circ} = 47.465 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^{\circ} = -8.71 \pm 0.10 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{\epsilon_1}{0} \text{ cm.}^{-1} \frac{g_1}{1}$$

$\sigma = 1$

$\omega_e x_e = 45.246 \pm 0.008 \text{ cm.}^{-1}$

$\omega_e = 2649.218 \pm 0.016 \text{ cm.}^{-1}$

$\alpha_e = 0.23248 \pm 7 \times 10^{-5} \text{ cm.}^{-1}$

$B_e = 8.46571 \pm 1.8 \times 10^{-4} \text{ cm.}^{-1}$

$r_e = 1.414 \text{ \AA}$

Heat of Formation.

The enthalpy change,  $\Delta H_f^{\circ}$ , 376.2 = -12.47 ± 0.13 kcal. mole<sup>-1</sup>, for the reaction (1) 1/2 H<sub>2</sub>(g) + 1/2 Br<sub>2</sub>(g) = HBr(g) was reported by J. R. Lacher, L. Casali and J. D. Park, J. Phys. Chem. 60, 608 (1956). Using  $\Delta H_f^{\circ}$  298.15 (Br<sub>2</sub>, g) = 7.39 kcal. mole<sup>-1</sup>, the  $\Delta H_f^{\circ}$  298.15 (HBr, g) was derived as -8.71 ± 0.13 kcal. mole<sup>-1</sup>.

The heat of oxidation of aqueous sulfur dioxide with gaseous chlorine and liquid bromine were determined by calorimetric methods by W. H. Johnson and J. R. Ambrose, J. Res. Natl. Bur. Std. 67A, 427 (1963) and W. H. Johnson and S. Sunner, Acta Chem. Scand., 11, 1917 (1963), respectively. The results were given as  $\Delta H_f^{\circ}$  298.15 = -77.28 ± 0.14 kcal. mole<sup>-1</sup> (X<sub>2</sub> = Cl<sub>2</sub>(g)) and -55.47 ± 0.11 kcal. mole<sup>-1</sup> (X<sub>2</sub> = Br<sub>2</sub>(l)) for the reaction X<sub>2</sub> + 802.2500 H<sub>2</sub>O + 2 H<sub>2</sub>O(l) = H<sub>2</sub>SO<sub>4</sub>.2500 H<sub>2</sub>O + 2 (HX.1250 H<sub>2</sub>O). The enthalpy change for the reaction Cl<sub>2</sub>(g) + 2 (HBr.1250 H<sub>2</sub>O = Br<sub>2</sub>(l) + 2 (HCl.1250 H<sub>2</sub>O) was calculated to be -21.92 ± 0.18 kcal. mole<sup>-1</sup>. Using  $\Delta H_f^{\circ}$  298.15 (HCl.1250 H<sub>2</sub>O) = -59.95 ± 0.05 kcal. mole<sup>-1</sup>, the heat of formation for HBr.1250 H<sub>2</sub>O was derived to be -28.352 ± 0.10 kcal. mole<sup>-1</sup>. Employing  $\Delta H_f^{\circ}$  (HBr.1250 H<sub>2</sub>O) = -0.084 kcal. mole<sup>-1</sup>, leads to  $\Delta H_f^{\circ}$  298.15 (HBr.∞H<sub>2</sub>O) = -29.016 ± 0.10 kcal. mole<sup>-1</sup>. Based on the value,  $\Delta H_f^{\circ}$  298.15 = -20.350 ± 0.012 kcal. mole<sup>-1</sup> for the reaction HBr(g) = HBr(∞H<sub>2</sub>O) reported by C. E. Vandervee and J. D. Nutter, J. Phys. Chem. 67, 2521 (1963), the heat of formation ( $\Delta H_f^{\circ}$  298.15) for HBr(g) was evaluated as -8.67 ± 0.10 kcal. mole<sup>-1</sup>.

The heats of oxidation of As<sub>2</sub>O<sub>3</sub> to As<sub>2</sub>O<sub>5</sub> in aqueous solution with Br<sub>2</sub>(l) and Cl<sub>2</sub>(g) were measured by L. Bjellerup, S. Sunner and I. Wedsö, Acta Chem. Scand., 11, 1761 (1957) and S. Sunner and S. Thoren, Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July, 1963. Using the values  $\Delta H_f^{\circ}$  = -56.61 ± 0.11 kcal. mole<sup>-1</sup> (X<sub>2</sub> = Br<sub>2</sub>(l)) and -100.09 ± 0.08 kcal. mole<sup>-1</sup> (X<sub>2</sub> = Cl<sub>2</sub>(g)) for the reaction As<sub>2</sub>O<sub>3</sub>(aq.) + 2X<sub>2</sub> + 2 H<sub>2</sub>O(aq.) → As<sub>2</sub>O<sub>5</sub>(aq.) + 4 HX(aq.) obtained from H. A. Skinner, Pure Appl. Chem. 9, 95 (1964), the enthalpy change for the reaction 2Br<sub>2</sub>(l) + 4HCl(aq.) = 2Cl<sub>2</sub> + 4HBr(aq.) was calculated to be +45.48 ± 0.14 kcal. mole<sup>-1</sup>. Based on  $\Delta H_f^{\circ}$  298.15 (HCl, ∞H<sub>2</sub>O) = -39.95 ± 0.05 kcal. mole<sup>-1</sup>, the value of  $\Delta H_f^{\circ}$  298.15 (HBr, ∞H<sub>2</sub>O) was derived to be -29.06 ± 0.06 kcal. mole<sup>-1</sup>, yielding  $\Delta H_f^{\circ}$  298.15 (HBr, g) = -8.71 ± 0.06 kcal. mole<sup>-1</sup>.

The value of  $\Delta H_f^{\circ}$  298.15 (HBr, g) adopted is -8.71 ± 0.10 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The values of  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$  and  $\alpha_e$  were taken from T. C. James and R. J. Thibault, J. Chem. Phys. 42, 1450 (1965), and corrected to the average isotopic species. Submillimeter-wave spectra of HBr were measured by G. Jones and W. Gordy, Phys. Rev. 135, A 1229 (1964). The molecular constants derived were close to the values adopted. The ground state configuration was obtained from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950, in which molecular constants for HBr(g) were also given. A precise measurement of the infrared fundamental bands of HBr has been made by E. K. Plyler, J. Res. Natl. Bur. Std., 64, 377 (1960). The corresponding rotational and vibrational constants have been calculated from the observed data. The moment of inertia is 3.30614 × 10<sup>-40</sup> g. cm<sup>2</sup>.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.959	39.861	-2.067	6.836	6.836	6.836	INFINITE
200	6.961	48.685	-1.379	6.861	6.861	6.861	19.435
298	6.965	47.465	-0.000	6.836	6.836	6.836	12.572
300	6.965	47.508	+0.013	6.720	12.810	12.810	9.332
400	6.984	49.514	7.739	7.10	12.440	13.405	7.324
500	7.040	51.078	48.256	1.411	12.590	13.625	5.955
600	7.139	52.369	48.837	2.120	12.665	13.825	5.036
700	7.272	53.479	49.222	2.840	12.743	14.012	4.374
800	7.423	54.460	49.992	3.575	12.809	14.189	3.876
900	7.576	55.343	50.538	4.325	12.864	14.358	3.486
1000	7.725	56.140	51.060	5.090	12.908	14.521	3.173
1100	7.863	56.892	51.557	5.869	12.942	14.681	2.917
1200	7.989	57.582	52.010	6.662	12.968	14.838	2.702
1300	8.103	58.226	52.482	7.466	12.988	14.993	2.520
1400	8.205	58.830	52.914	8.282	13.003	15.146	2.364
1500	8.296	59.399	53.328	9.107	13.014	15.298	2.229
1600	8.378	59.937	53.724	9.941	13.024	15.451	2.110
1700	8.451	60.448	54.105	10.782	13.031	15.602	2.006
1800	8.517	60.933	54.471	11.631	13.037	15.755	1.913
1900	8.577	61.395	54.823	12.486	13.041	15.904	1.829
2000	8.630	61.836	55.163	13.346	13.044	16.055	1.754
2100	8.679	62.258	55.491	14.212	13.048	16.205	1.686
2200	8.724	62.663	55.806	15.082	13.052	16.356	1.625
2300	8.765	63.052	56.114	15.956	13.056	16.506	1.568
2400	8.803	63.426	56.411	16.835	13.060	16.655	1.517
2500	8.838	63.786	56.699	17.717	13.065	16.806	1.469
2600	8.870	64.133	56.978	18.602	13.070	16.954	1.425
2700	8.899	64.468	57.250	19.481	13.075	17.105	1.384
2800	8.925	64.792	57.513	20.362	13.082	17.252	1.347
2900	8.948	65.106	57.770	21.246	13.088	17.400	1.311
3000	8.968	65.410	58.019	22.131	13.095	17.550	1.278
3100	8.984	65.705	58.262	23.017	13.101	17.696	1.248
3200	8.997	65.991	58.500	23.904	13.111	17.846	1.218
3300	9.008	66.269	58.731	24.791	13.111	17.993	1.192
3400	9.016	66.540	58.957	25.678	13.111	18.144	1.164
3500	9.022	66.803	59.177	26.561	13.112	18.289	1.142
3600	9.107	67.059	59.392	27.446	13.155	18.436	1.119
3700	9.125	67.309	59.603	28.331	13.168	18.583	1.098
3800	9.143	67.553	59.809	29.216	13.182	18.730	1.077
3900	9.160	67.790	60.011	30.101	13.198	18.872	1.058
4000	9.176	68.023	60.208	31.028	13.215	19.023	1.039
4100	9.192	68.249	60.401	32.176	13.232	19.165	1.025
4200	9.208	68.471	60.591	33.096	13.251	19.310	1.005
4300	9.223	68.688	60.777	34.018	13.271	19.454	0.989
4400	9.238	68.900	60.959	34.941	13.292	19.597	0.973
4500	9.252	69.108	61.138	35.866	13.314	19.743	0.959
4600	9.266	69.311	61.313	36.791	13.338	19.881	0.945
4700	9.280	69.511	61.485	37.719	13.362	20.024	0.931
4800	9.294	69.706	61.655	38.647	13.388	20.166	0.918
4900	9.307	69.898	61.821	39.578	13.414	20.306	0.906
5000	9.320	70.086	61.984	40.509	13.442	20.447	0.894
5100	9.333	70.271	62.145	41.442	13.471	20.589	0.882
5200	9.346	70.452	62.303	42.375	13.501	20.726	0.871
5300	9.358	70.630	62.459	43.311	13.532	20.862	0.860
5400	9.371	70.805	62.612	44.247	13.564	21.003	0.850
5500	9.383	70.977	62.762	45.185	13.597	21.138	0.840
5600	9.395	71.147	62.910	46.124	13.632	21.281	0.831
5700	9.407	71.313	63.056	47.064	13.667	21.413	0.821
5800	9.419	71.477	63.200	48.005	13.703	21.551	0.812
5900	9.430	71.638	63.342	48.948	13.741	21.685	0.803
6000	9.442	71.796	63.481	49.891	13.779	21.819	0.795

Sept. 30, 1961; Sept. 30, 1965

(CRYSTAL)

AMMONIUM BROMIDE (NH<sub>4</sub>Br)

$\Delta H_f^0 = -60.9 \pm 0.3 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -64.9 \pm 0.3 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 = 0.77 \text{ kcal. mole}^{-1}$   
 $\Delta H_m = \text{Unknown}$

$S_{298.15}^0 = 26.97 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_c = 411^\circ \text{K.}$   
 $T_m = 815.2^\circ \text{K.}$   
 $T_d = 670^\circ \text{K.}$

Heat of Formation.

The equilibrium pressures for the reaction  $\text{NH}_3(\text{g}) + \text{HBr}(\text{g}) \rightarrow \text{NH}_4\text{Br}(\text{s})$  have been measured by several investigators. Using the densi-tensimeter, A. Saito and R. Purcell, J. Chem. Soc. 2944 (1928), determined both the equilibrium pressures and vapor densities of the decomposition products, simultaneously, at several temperatures. In order to check the density values obtained, the authors applied the "extrapolation method", from which it was calculated that the corresponding vapor density agreed with complete dissociation. Based on this conclusion, the reported equilibrium pressures were employed to evaluate the enthalpy changes ( $\Delta H_f^0$ ) of the decomposition reaction by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	Equipment Used
Smith and Calvert (1)	576.40-676.02	45.12 ± 0.13	44.93	Isoteniscope
Saito and Purcell (2)	604.95-668.15	45.50 ± 0.17	45.08	Densi-tensimeter
Johnson (3)	573.15-667.75	45.41 ± 0.44	44.85	Spiral Manometer

- (1) A. Saito and R. P. Calvert, J. Am. Chem. Soc. 56, 1363 (1934).  
 (2) A. Saito and R. Purcell, J. Chem. Soc. 2944 (1928).  
 (3) F. M. G. Johnson, Z. physik. Chem. 65, 38 (1909).

The value of  $\Delta H_f^0$  298.15 adopted is  $45.2 \pm 0.2 \text{ kcal. mole}^{-1}$ . Using  $\Delta H_f^0$  298.15 = -10.37 and -8.71 kcal. mole<sup>-1</sup> for  $\text{NH}_3(\text{g})$  and  $\text{HBr}(\text{g})$ , respectively, the value of  $\Delta H_f^0$  298.15 for  $\text{NH}_4\text{Br}(\text{s})$  is evaluated as  $-64.9 \pm 0.3 \text{ kcal. mole}^{-1}$ . The corresponding  $\Delta H_f^0$  298.15 value evaluated from solution data, selected by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NBS-RS-2, National Bureau of Standards, April 1, 1965, is  $45.5 \pm 0.2 \text{ kcal. mole}^{-1}$ .

The vapor densities (573-661°K.) of dissociation products of  $\text{NH}_4\text{Br}(\text{s})$  were also measured by A. Saito and R. H. Lombard, J. Am. Chem. Soc. 57, 38 (1935). Using the equilibrium pressures reported by A. Saito and R. P. Calvert, loc. cit., they derived the corresponding degrees of dissociation of  $\text{NH}_4\text{Br}(\text{s})$  at different temperatures. The calculated results indicated that only 48% of  $\text{NH}_4\text{Br}(\text{s})$  decomposed at 573°K. and as reaction temperatures increased to 661°K. the degree of dissociation decreased to 10%. This conclusion was stated to be erroneous by Saito and Purcell, loc. cit., probably because of incorrect density determinations.

Heat Capacity and Entropy.

The low temperature (13-305°K.) heat capacities and  $S_{298.15}^0$  were obtained from M. Sorai, H. Suga and S. Seki, Bull. Chem. Soc. Japan, 39, 1125 (1965). The  $C_p$  values above 305°K. were estimated by comparison with those for  $\text{NaCl}(\text{s})$ ,  $\text{NaBr}(\text{s})$  and  $\text{NH}_4\text{Cl}(\text{s})$ . The low temperature heat capacities were also measured by R. Ewald, Ann. Physik, 44, 1213 (1914), 139-301°K., and F. Simon and M. Ruhemann, Z. phys. Chem. 129, 339 (1927), 201.2-277.1°K.

Transition Data.

The temperature ( $T_c$ ) and heat of transition ( $\Delta H_c^0$ ) were given by F. W. Bridgman, Proc. Am. Acad. Arts Sci. 52, 91 (1916-17).  $T_c = 419.5 \pm 0.6^\circ \text{K.}$  was reported by M. M. Markowitz and D. A. Boryta, J. Phys. Chem. 65, 1477 (1962), which was determined by differential thermal analysis. According to Sorai, Suga and Seki, loc. cit., there are 3 solid phase transitions, namely Phase IV (CsCl) → Phase III (tetragonal) at 108°K., Phase III (tetragonal) → Phase II (CaCl) at 235°K. and Phase II (CaCl) → Phase I (NaCl) at 411°K.

Melting Temperature.

The value of  $T_m$  was taken from H. Rasmussen, Z. anorg. Chem. 114, 117 (1920), determined under pressure.

Temperature of Decomposition.

The temperature of decomposition ( $T_d$ ) was calculated as the temperature at which the total pressure of the decomposition products for the reaction  $\text{NH}_4\text{Br}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HBr}(\text{g})$  equals 1 atm.  $T_d = 674$  and  $668.4^\circ \text{K.}$  were reported by N. W. Luft, Ind. Chemist, 31, 502 (1965) and M. M. Markowitz and D. A. Boryta, loc. cit., respectively.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	10.264	8.530	43.950	4.052	60.939	60.939	INFINITE
200	18.603	18.010	28.875	3.542	62.623	56.604	12.480
298	21.194	26.970	26.970	2.053	63.277	49.203	55.864
				0.700	64.976	42.585	30.847
300	21.246	27.101	26.970	0.039	64.910	41.943	30.554
400	27.100	33.381	27.820	2.224	68.581	33.532	18.320
500	32.850	39.597	29.714	4.942	68.055	24.908	10.887
600	38.480	45.729	31.707	7.213	67.984	16.279	5.929
700	44.000	51.781	33.717	9.814	67.567	7.687	2.400
800	49.500	57.750	35.737	12.707	66.935	8.877	2.226
900	55.000	63.634	37.679	15.859	66.036	9.247	2.245
1000	60.500	69.461	39.621	19.241	64.927	17.554	3.836
1100	66.000	75.234	41.576	22.829	63.636	25.741	5.114
1200	71.500	80.961	43.443	26.602	62.183	33.805	6.156
1300	77.000	86.644	45.221	30.542	60.589	41.739	7.017
1400	82.500	92.281	46.916	34.634	58.868	49.547	7.734
1500	88.000	97.877	48.525	38.868	57.035	57.228	8.338

CARBON UNINEGATIVE ION (C<sup>-</sup>) (IDEAL GAS)

Ground State Configuration 4S<sup>2</sup> 3/2

$\Delta H_f^0 = 140.8 \pm 0.8$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = 140.5 \pm 0.8$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 36.156$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Electronic Levels and Quantum Weight

$\epsilon_1$ , cm. <sup>-1</sup>	$\epsilon_2$	$\epsilon_1$ , cm. <sup>-1</sup>	$\epsilon_2$
0	4	86223.2	4
19223.9	6	96751.7	4
19233.1	4	96788.2	4
28840.0	6	96864.2	6
83285.5	2	97770.1	2
83319.3	4	97805.8	4
83366.0	6	99863.0	10
86131.4	2		

Heat of Formation.

The heat of formation was calculated from the equation:  $C(g) + e^- \rightarrow C^-(g)$  with the JANAP auxiliary value for C(g); using an electron affinity = 1.25 e.v. (28.83 kcal/mole) obtained from M. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962). Other values for the electron affinity are: 1.17 e.v. reported by E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 1.12 e.v. reported by E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964); and 1.24 e.v. reported by B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case nitrogen. The electronic levels above  $1 \times 10^5$  cm.<sup>-1</sup> were omitted because their contribution is negligible below 6000°K. The  $H_{298}^0$  value at 0°K. is -1.481 kcal/mole.

T. °K.	C <sub>p</sub>	S°	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0							
100	4.968	36.156	36.156	.000	140.500	131.612	96.470
200	4.968	36.187	36.156	.009	140.496	131.557	95.835
300	4.968	36.216	36.151	.506	140.250	128.613	70.267
400	4.968	36.244	36.139	1.003	139.931	125.739	54.958
500	4.968	36.271	36.131	1.500	139.553	122.935	44.777
600	4.968	36.296	36.128	1.996	139.200	120.200	37.526
700	4.968	36.321	36.125	2.493	138.869	117.527	32.105
800	4.968	36.345	36.122	2.990	138.561	114.911	27.903
900	4.968	36.368	36.119	3.487	138.272	112.353	24.554
1000	4.968	36.390	36.116	3.984	138.000	109.844	21.823
1100	4.968	36.411	36.113	4.481	137.743	107.386	19.557
1200	4.968	36.431	36.110	4.977	137.500	104.972	17.647
1300	4.968	36.450	36.107	5.474	137.269	102.602	16.016
1400	4.968	36.468	36.104	5.971	137.048	100.272	14.609
1500	4.968	36.485	36.101	6.468	136.837	97.978	13.383
1600	4.968	36.502	36.098	6.965	136.636	95.720	12.303
1700	4.968	36.518	36.095	7.462	136.443	93.503	11.352
1800	4.968	36.534	36.092	7.959	136.258	91.326	10.520
1900	4.968	36.549	36.089	8.456	136.082	89.194	9.791
2000	4.970	36.564	36.086	8.952	135.915	87.106	9.155
2100	4.971	36.578	36.083	9.449	135.757	85.061	8.613
2200	4.972	36.592	36.080	9.946	135.607	83.058	8.161
2300	4.973	36.605	36.077	10.443	135.465	81.095	7.796
2400	4.974	36.618	36.074	10.940	135.330	79.175	7.506
2500	4.975	36.631	36.071	11.437	135.201	77.295	7.281
2600	4.976	36.644	36.068	11.934	135.078	75.454	7.114
2700	4.977	36.656	36.065	12.431	134.961	73.651	6.999
2800	4.978	36.668	36.062	12.928	134.850	71.884	6.924
2900	4.979	36.680	36.059	13.425	134.744	70.154	6.885
3000	4.980	36.692	36.056	13.922	134.643	68.458	6.875
3100	4.981	36.704	36.053	14.419	134.547	66.794	6.885
3200	4.982	36.716	36.050	14.916	134.455	65.162	6.905
3300	4.983	36.728	36.047	15.413	134.367	63.562	6.934
3400	4.984	36.740	36.044	15.910	134.282	62.000	6.971
3500	4.985	36.752	36.041	16.407	134.200	60.476	7.016
3600	4.986	36.764	36.038	16.904	134.121	58.998	7.068
3700	4.987	36.776	36.035	17.401	134.045	57.565	7.126
3800	4.988	36.788	36.032	17.898	133.972	56.176	7.190
3900	4.989	36.800	36.029	18.395	133.902	54.830	7.259
4000	4.990	36.812	36.026	18.892	133.834	53.526	7.332
4100	4.991	36.824	36.023	19.389	133.769	52.262	7.408
4200	4.992	36.836	36.020	19.886	133.706	51.038	7.487
4300	4.993	36.848	36.017	20.383	133.645	49.853	7.568
4400	4.994	36.860	36.014	20.880	133.586	48.706	7.650
4500	4.995	36.872	36.011	21.377	133.529	47.596	7.733
4600	4.996	36.884	36.008	21.874	133.474	46.522	7.817
4700	4.997	36.896	36.005	22.371	133.421	45.484	7.902
4800	4.998	36.908	36.002	22.868	133.369	44.481	7.987
4900	4.999	36.920	36.000	23.365	133.319	43.512	8.072
5000	5.000	36.932	36.000	23.862	133.270	42.576	8.157
5100	5.001	36.944	36.000	24.359	133.222	41.672	8.242
5200	5.002	36.956	36.000	24.856	133.175	40.798	8.327
5300	5.003	36.968	36.000	25.353	133.129	39.954	8.412
5400	5.004	36.980	36.000	25.850	133.084	39.139	8.497
5500	5.005	36.992	36.000	26.347	133.040	38.352	8.582
5600	5.006	37.004	36.000	26.844	133.000	37.592	8.667
5700	5.007	37.016	36.000	27.341	132.961	36.858	8.752
5800	5.008	37.028	36.000	27.838	132.923	36.149	8.837
5900	5.009	37.040	36.000	28.335	132.886	35.464	8.922
6000	5.010	37.052	36.000	28.832	132.850	34.794	9.007

T, °K.	cal. mole <sup>-1</sup> deg <sup>-1</sup>		kcal. mole <sup>-1</sup>		Log K <sub>p</sub>
	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔF <sup>‡</sup>	
0	∞	∞	∞	∞	∞
100	6.212	13.228	1.312	9.219	20.135
200	6.355	12.499	0.949	9.213	10.039
298	6.483	6.483	0.000	9.261	6.707
300	6.483	6.483	0.024	9.296	6.666
400	6.562	11.057	1.596	9.105	4.974
500	6.686	8.304	3.591	9.234	3.965
600	6.848	6.848	5.846	9.257	3.291
700	7.048	5.048	8.263	9.329	2.808
800	7.270	3.315	10.790	9.441	2.442
900	7.527	1.767	13.403	9.579	2.154
1000	7.818	0.318	16.095	9.733	1.919
1100	8.044	35.239	18.864	9.903	1.725
1200	8.276	37.708	21.703	10.076	1.559
1300	8.512	40.033	24.608	10.256	1.417
1400	8.753	42.233	27.577	10.431	1.292
1500	9.001	44.324	30.608	10.608	1.183
1600	9.257	46.319	33.699	10.779	1.085
1700	9.521	48.229	36.850	10.942	0.998
1800	9.792	50.063	40.059	11.092	0.920
1900	10.069	51.829	43.325	11.220	0.869
2000	10.352	53.534	46.649	11.317	0.784
2100	10.641	55.183	50.030	11.383	0.724
2200	10.935	56.782	53.467	11.417	0.670
2300	11.234	58.334	56.959	11.417	0.630
2400	11.538	59.844	60.508	11.383	0.564
2500	11.847	61.316	64.112	11.317	0.496
2600	12.161	62.751	67.771	11.211	0.386
2700	12.480	64.152	71.486	11.076	0.285
2800	12.804	65.524	75.256	10.912	0.191
2900	13.133	66.866	79.081	10.719	0.104
3000	13.467	68.161	82.961	10.501	0.024
3100	13.806	69.471	86.895	10.256	0.049
3200	14.150	70.788	90.888	10.000	0.118
3300	14.500	72.111	94.938	9.733	0.181
3400	14.856	73.440	99.048	9.457	0.240
3500	15.218	74.769	103.219	9.172	0.293

TETRABORON MONOCARBIDE (B<sub>4</sub>C)

(CRYSTAL)

MOL. WT. = 55.25515

$$\Delta H_f^{\circ} = -9.2 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} = -9.3 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = [25] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{\circ} = 6.483 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 2743 \pm 20 \text{ }^{\circ}\text{K.}$$

Heat of Formation.

The  $\Delta H_f^{\circ}$  298.15 was calculated from  $\Delta H_f^{\circ}$  298.15 = -683.3 ± 2.2 kcal. mole<sup>-1</sup> for the reaction B<sub>3</sub>C(c) + 4O<sub>2</sub>(g) → 2B<sub>2</sub>O<sub>3</sub>(amorph) + CO<sub>2</sub>(g) measured by D. Smith, A. S. Dworkin and E. R. Van Artsdalen, J. Am. Chem. Soc. 77, 2684-6 (1955) and the heat of formation for B<sub>2</sub>O<sub>3</sub>(amorph) (Dec. 31, 1964) and for CO<sub>2</sub>(g) (March 31, 1961) in JANAF Tables.

Heat Capacity and Entropy.

The low temperature heat capacities, 54-294°K., were taken from K. K. Kelley, J. Am. Chem. Soc. 63, 1137 (1941). Above 298°K., C<sub>p</sub> was calculated using the equation  $C_p = 22.99 + 5.40 \times 10^{-5}T - 10.72 \times 10^{-8}T^2$  obtained from the enthalpy data in the range 298 to 1726°K. reported by E. G. King, Ind. Eng. Chem. 41, 1288 (1949).

The values from the two sources join smoothly at 298°K. The  $S_{298.15}^{\circ}$  was calculated based on the low temperature heat capacities measured by K. K. Kelley, loc. cit., using  $S_{53.1}^{\circ} = 0.047 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Melting Data.

T<sub>m</sub> was determined by Dolloff, WADD Tech. Rept. 60-143, 1960 and  $\Delta H_m^{\circ}$  was estimated.

$\Delta H_f^{298.15} = 16.592 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{298.15} = 18.1 \pm 2.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^0 = [25] \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 16.592 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 2743 \pm 20^\circ \text{K.}$

Heat of Formation.

The  $\Delta H_f^{298.15}$  was obtained from  $\Delta H_f^{298.15}(c)$  by adding  $\Delta H_m^0$  and the difference between  $H_m^0$  and  $H_{298.15}^0$  for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 1750°K. The heat capacity below 1750°K. was obtained from the heat capacity of the crystal. Above 1750°K. the heat capacity was assumed constant and estimated as 32.50 cal. deg.<sup>-1</sup> mole<sup>-1</sup> or 6.5 cal. deg.<sup>-1</sup> per g-atom.

The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See B<sub>4</sub>C(c) table.

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0						
100						
200						
298	17.545	16.592	.000	18.095	15.226	- 11.161
300	17.700	16.670	.023	18.094	15.208	- 11.078
400	18.450	17.115	1.617	18.154	14.240	- 7.780
500	21.400	18.442	3.618	18.184	13.256	- 5.794
600	24.200	19.983	5.955	18.143	12.273	- 4.470
700	26.540	21.645	8.249	18.048	11.303	- 3.529
800	28.540	23.331	10.161	17.921	10.347	- 2.827
900	29.850	24.995	13.371	17.780	9.406	- 2.284
1000	27.320	26.628	16.064	17.627	8.487	- 1.855
1100	28.040	28.210	18.932	17.456	7.578	- 1.506
1200	28.750	29.740	21.671	17.283	6.692	- 1.219
1300	29.380	30.220	24.277	17.104	5.813	- .977
1400	30.000	32.669	27.246	16.929	4.956	- .774
1500	30.610	34.031	30.276	16.751	4.100	- .597
1600	31.210	35.266	33.667	16.580	3.267	- .446
1700	31.800	36.663	36.818	16.417	2.438	- .313
1800	32.500	37.817	39.040	16.280	1.618	- .196
1900	32.500	39.135	43.290	16.136	.807	- .093
2000	32.500	40.316	46.940	15.965	.007	- .001
2100	32.500	41.462	49.790	15.768	-.784	-.082
2200	32.500	42.574	53.000	15.500	- 1.509	-.152
2300	32.500	43.654	56.560	15.265	- 2.200	-.222
2400	32.500	44.703	59.540	15.000	- 2.822	-.282
2500	32.500	45.722	62.790	14.790	- 3.415	-.298
2600	32.500	46.713	66.040	14.559	- 3.278	-.276
2700	32.500	47.130	69.200	14.320	- 3.122	-.253
2800	32.500	47.601	72.500	14.000	- 2.953	-.231
2900	32.500	48.062	75.700	13.690	- 2.787	-.210
3000	32.500	48.517	79.040	13.449	- 2.614	-.190
3100	32.500	49.829	82.200	13.171	- 2.426	-.171
3200	32.500	49.861	85.540	12.870	- 2.226	-.152
3300	32.500	50.955	88.700	12.540	- 2.016	-.134
3400	32.500	50.831	93.761	12.190	- 1.797	-.116
3500	32.500	51.773	95.500	11.854	- 1.584	-.099



T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH° <sub>f</sub>	ΔF°	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	8.576	53.008	72.619	2.761	15.374	15.374	INFINITE
200	9.951	54.461	64.505	1.951	15.286	16.230	35.468
298	10.773	63.542	63.542	1.021	15.134	17.231	18.828
				.000	15.000	18.291	13.407
300	10.784	63.609	63.543	.020	14.998	18.311	13.939
400	11.297	66.786	63.072	1.126	14.909	18.616	10.616
500	11.690	69.351	64.900	2.475	14.870	20.566	8.989
600	12.022	71.512	65.743	3.662	14.874	21.706	7.906
700	12.306	73.387	66.704	4.678	14.910	22.841	7.131
800	12.544	75.046	67.645	5.521	14.968	23.971	6.548
900	12.742	76.536	68.551	7.186	15.043	25.093	6.093
1000	12.906	77.887	69.419	8.469	15.126	26.205	5.727
1100	13.041	79.124	70.245	9.766	15.220	27.309	5.426
1200	13.152	80.263	71.033	11.076	15.320	28.403	5.173
1300	13.245	81.320	71.784	12.396	15.429	29.489	4.957
1400	13.323	82.304	72.501	13.724	15.540	30.565	4.771
1500	13.389	83.226	73.186	15.060	15.657	31.635	4.609
1600	13.445	84.092	73.841	16.402	15.778	32.698	4.466
1700	13.492	84.908	74.468	17.749	15.900	33.749	4.339
1800	13.533	85.681	75.069	19.100	16.028	34.797	4.225
1900	13.569	86.413	75.647	20.455	16.158	35.834	4.122
2000	13.599	87.110	76.203	21.814	16.292	36.867	4.028
2100	13.626	87.774	76.739	23.175	16.428	37.891	3.943
2200	13.650	88.409	77.255	24.539	16.570	38.913	3.865
2300	13.671	89.016	77.753	25.905	16.714	39.923	3.793
2400	13.689	89.598	78.234	27.273	16.862	40.928	3.727
2500	13.706	90.157	78.700	28.643	17.014	41.929	3.665
2600	13.720	90.695	79.151	30.014	17.171	42.922	3.608
2700	13.734	91.213	79.589	31.387	17.331	43.911	3.554
2800	13.746	91.715	80.013	32.761	17.495	44.891	3.504
2900	13.756	92.195	80.425	34.136	17.664	45.866	3.456
3000	13.765	92.662	80.825	35.512	17.838	46.837	3.412
3100	13.775	93.114	81.214	36.889	18.014	47.801	3.370
3200	13.783	93.551	81.593	38.267	18.197	48.758	3.330
3300	13.791	93.975	81.966	39.646	18.383	49.717	3.292
3400	13.797	94.387	82.331	41.025	18.574	50.656	3.256
3500	13.804	94.787	82.681	42.405	18.769	51.601	3.222
3600	13.809	95.176	83.013	43.786	18.968	52.535	3.189
3700	13.815	95.554	83.347	45.167	19.172	53.462	3.158
3800	13.819	95.923	83.673	46.549	19.379	54.386	3.128
3900	13.824	96.282	83.992	47.931	19.590	55.306	3.100
4000	13.828	96.632	84.304	49.313	19.806	56.218	3.071
4100	13.832	96.974	84.609	50.696	20.025	57.130	3.045
4200	13.836	97.307	84.907	52.080	20.248	58.029	3.018
4300	13.839	97.632	85.199	53.463	20.475	58.923	2.995
4400	13.842	97.951	85.485	54.848	20.702	59.818	2.971
4500	13.845	98.262	85.766	56.232	20.938	60.707	2.948
4600	13.848	98.566	86.041	57.617	21.174	61.583	2.926
4700	13.851	98.864	86.310	59.002	21.414	62.459	2.904
4800	13.853	99.156	86.575	60.387	21.657	63.331	2.883
4900	13.855	99.441	86.835	61.772	21.903	64.195	2.863
5000	13.858	99.721	87.090	63.158	22.151	65.056	2.843
5100	13.860	99.996	87.340	64.544	22.403	65.917	2.825
5200	13.861	100.265	87.586	65.930	22.657	66.766	2.806
5300	13.863	100.529	87.828	67.316	22.914	67.609	2.788
5400	13.865	100.788	88.065	68.702	23.174	68.450	2.770
5500	13.867	101.042	88.299	70.089	23.436	69.281	2.753
5600	13.868	101.292	88.529	71.476	23.701	70.116	2.736
5700	13.870	101.538	88.755	72.863	23.966	70.951	2.720
5800	13.871	101.779	88.977	74.250	24.239	71.767	2.704
5900	13.872	102.016	89.196	75.637	24.512	72.582	2.688
6000	13.874	102.249	89.412	77.024	24.787	73.396	2.673

CARBONYL MONOCHLORIDE (COCl)

MOL. WT. = 83.46355

(IDEAL GAS)

$$\Delta H_f^0 = [-15 \pm 10] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = [-15 \pm 10] \text{ kcal. mole}^{-1}$$

Point Group C<sub>s</sub>

$$S_{298.15}^0 = [64] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

( $\omega$ ), cm.<sup>-1</sup>

570 (1)

201 (1)

1890 (1)

Bond Distance: C-Cl = [1.75] Å C-O = [1.17] Å

Bond Angle: Cl-C-O = [120] °

$\sigma = 1$

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [1.27603 x 10<sup>-115</sup>] g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The enthalpy change ( $\Delta H_f^0$ ) for the reaction  $\text{COCl}_2(\text{g}) = \text{CO}(\text{g}) + 2\text{Cl}(\text{g})$  is calculated to be 82 kcal. mole<sup>-1</sup>, which is the sum of two bond energies, i.e.  $D(\text{Cl-COCl}) + D(\text{Cl-CO})$ . By comparison with the values,  $D(\text{H}_2\text{C-COCH}_2)/D(\text{H}_3\text{C-CO}) = 72/18 = 4.0$  for  $\text{CH}_3\text{COCH}_3(\text{g})$  and  $D(\text{H}_3\text{C-COCl})/D(\text{Cl-CO}) = 4.3$  for  $\text{CH}_3\text{COCl}(\text{g})$ , the ratio of  $D(\text{Cl-COCl})/D(\text{Cl-CO})$  is estimated to be 4.0 for  $\text{COCl}_2(\text{g})$ . Hence the enthalpy change for the reaction  $\text{COCl}_2(\text{g}) = \text{COCl}(\text{g}) + \text{Cl}(\text{g})$  is calculated as  $82 \times (4/5) = 65.6$  kcal. mole<sup>-1</sup>. Using the  $\Delta H_f^0$  value obtained, the heat of formation for  $\text{COCl}(\text{g})$  is derived to be  $-15 \pm 10$  kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The vibrational frequencies were reported by M. E. Jacox and D. E. Milligan, J. Chem. Phys. 43, 866 (1965). The bond distances and angle were estimated by Jacox and Milligan, loc. cit. Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are: I<sub>A</sub> = 1.29987 x 10<sup>-38</sup>, I<sub>B</sub> = 7.1580 x 10<sup>-40</sup>, and I<sub>C</sub> = 1.37145 x 10<sup>-38</sup> g. cm.<sup>2</sup>

MOL. WT. = 47.00895

(IDEAL GAS)

CARBONYL MONOFLUORIDE (COP)

$$\Delta H_f^{\circ} O = [-41 \pm 15] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = [-41 \pm 15] \text{ kcal. mole}^{-1}$$

Point Group  $C_s$ 

$$S_{298.15}^{\circ} = [59] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 2

## Vibrational Frequencies and Degeneracies

 $(\lambda), \text{ cm.}^{-1}$ 

1018 (1)

826 (1)

1855 (1)

C-O = [1.18] Å

 $\sigma^- = 1$ 

Bond Distance: C-F = [1.34] Å

Bond Angle: F-C-O = [135] °

Product of the Moments of Inertia:  $I_A I_B I_C = [2.1986 \times 10^{-116}] \text{ g.}^3 \text{ cm.}^6$ 

## Heat of Formation.

The enthalpy change ( $\Delta H_f^{\circ}$ ) for the reaction  $\text{COP}_2(\text{g}) = \text{CO}(\text{g}) + 2\text{F}(\text{g})$  was calculated as 160.5 kcal. mole<sup>-1</sup>.By analogy with  $\text{D}(\text{Cl-COCl})/\text{D}(\text{Cl-CO})$ , the value of  $\text{D}(\text{F-COP})/\text{D}(\text{F-CO})$  was taken to be 4. Based on  $\Delta H_f^{\circ} = 160.5 \times (4/5) = 128.4 \text{ kcal. mole}^{-1}$  for the reaction  $\text{COP}_2(\text{g}) = \text{COP}(\text{g}) + \text{F}(\text{g})$ , the heat of formation for  $\text{COP}(\text{g})$  was derived as  $-41 \pm 15 \text{ kcal. mole}^{-1}$ .

## Heat Capacity and Entropy.

The vibrational frequencies were reported by D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford and D. E. Mann, J. Chem. Phys. 42, 3187 (1965). The bond distances and angle were estimated by comparison with those for HFCO (g). Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are:  $I_A = 7.8757 \times 10^{-39}$ ,  $I_B = 3.3980 \times 10^{-40}$ , and  $I_C = 8.2155 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	$C_p$	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	7.969	50.185	2.484	41.139	41.139	INFINITE
200	8.476	55.826	1.689	41.062	41.949	91.675
298	9.305	58.363	.000	41.014	42.857	46.830
300	9.320	58.420	.017	41.000	43.784	31.895
400	10.106	62.212	.990	41.014	44.710	24.427
500	10.768	64.541	2.034	41.058	45.629	19.944
600	11.310	66.554	3.139	41.124	46.538	16.951
700	11.748	68.331	4.293	41.210	47.433	14.809
800	12.099	69.923	5.486	41.308	48.315	13.199
900	12.381	71.365	6.810	41.416	49.186	11.943
1000	12.607	72.682	8.272	41.528	50.043	10.936
1100	12.791	73.892	9.809	41.646	50.890	10.110
1200	12.943	75.017	11.417	41.769	51.724	9.420
1300	13.068	76.058	13.087	41.897	52.546	8.852
1400	13.168	77.025	14.819	42.027	53.352	8.390
1500	13.251	77.936	16.609	42.161	54.147	7.992
1600	13.323	78.794	18.459	42.298	54.925	7.508
1700	13.384	79.603	20.366	42.436	55.687	7.187
1800	13.436	80.377	22.329	42.576	56.432	6.884
1900	13.482	81.116	24.346	42.717	57.160	6.591
2000	13.521	81.790	26.414	42.859	57.874	6.315
2100	13.555	82.451	28.532	43.002	58.571	6.121
2200	13.585	83.082	30.700	43.146	59.251	5.918
2300	13.611	83.686	32.918	43.291	59.914	5.730
2400	13.634	84.266	35.186	43.436	60.561	5.559
2500	13.655	84.823	37.504	43.581	61.194	5.400
2600	13.674	85.359	39.872	43.726	61.812	5.253
2700	13.690	85.875	42.290	43.871	62.416	5.116
2800	13.705	86.373	44.758	44.016	63.006	4.988
2900	13.719	86.855	47.276	44.161	63.581	4.869
3000	13.731	87.320	49.844	44.306	64.141	4.758
3100	13.742	87.770	52.462	44.451	64.686	4.653
3200	13.752	88.207	55.130	44.596	65.216	4.554
3300	13.761	88.630	57.848	44.741	65.731	4.461
3400	13.770	89.041	60.616	44.886	66.231	4.373
3500	13.778	89.440	63.434	45.031	66.716	4.289
3600	13.785	89.829	66.302	45.176	67.186	4.210
3700	13.791	90.206	69.220	45.321	67.641	4.135
3800	13.797	90.574	72.178	45.466	68.081	4.063
3900	13.803	90.933	75.176	45.611	68.506	3.995
4000	13.808	91.282	78.214	45.756	68.916	3.930
4100	13.813	91.623	81.292	45.901	69.311	3.868
4200	13.818	91.956	84.410	46.046	69.691	3.808
4300	13.822	92.281	87.568	46.191	70.056	3.751
4400	13.826	92.599	90.766	46.336	70.406	3.696
4500	13.829	92.910	94.004	46.481	70.741	3.644
4600	13.833	93.214	97.282	46.626	71.061	3.593
4700	13.836	93.511	100.600	46.771	71.366	3.544
4800	13.839	93.803	103.958	46.916	71.656	3.497
4900	13.842	94.088	107.356	47.061	71.931	3.452
5000	13.845	94.368	110.794	47.206	72.191	3.409
5100	13.847	94.642	114.272	47.351	72.436	3.367
5200	13.850	94.911	117.790	47.496	72.666	3.326
5300	13.852	95.175	121.348	47.641	72.881	3.286
5400	13.854	95.434	124.946	47.786	73.081	3.248
5500	13.856	95.688	128.584	47.931	73.266	3.211
5600	13.858	95.938	132.262	48.076	73.436	3.175
5700	13.860	96.183	135.980	48.221	73.591	3.141
5800	13.862	96.424	139.738	48.366	73.731	3.107
5900	13.863	96.661	143.536	48.511	73.856	3.074
6000	13.865	96.894	147.374	48.656	73.966	3.042

Dec. 31, 1965

$\Delta H_f^0 = -28.28 \pm 0.2 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -27.12 \pm 0.2 \text{ kcal. mole}^{-1}$   
 $\Delta H_c^0 = 0.279 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^0 = 3.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_g^0 \text{ 298.15 (to dimer)} = 52 \pm 10 \text{ kcal. mole}^{-1}$   
 $\Delta H_g^0 \text{ 298.15 (to monomer)} = 46 \pm 5 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 30.54 \pm 0.25 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_f = 168.3 \pm 0.1^\circ\text{K.}$   
 $T_m = 895 \pm 2^\circ\text{K.}$

Heat of Formation.

The enthalpy change,  $\Delta H_f^0 \text{ 298.15} = 2.80 \pm 0.10 \text{ kcal. mole}^{-1}$ , for the reaction  $\text{KCN}(c) \rightarrow \text{KCN}(\text{co H}_2\text{O})$  was reported by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RS-NBS 2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heat of formation for  $\text{K}^+(\text{co H}_2\text{O})$  and  $\text{CN}^-(\text{co H}_2\text{O})$  reported by D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of  $\Delta H_f^0 \text{ 298.15}$  for  $\text{KCN}(c)$  was evaluated to be  $-27.12 \pm 0.2 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

The heat capacity for  $\text{KCN}(c)$  has been measured with a heat conduction method by C. E. Messer and W. T. Ziegler, J. Am. Chem. Soc. 63, 2703 (1941), 101.6-345.8°K., and adiabatically by H. Suga, T. Matsuo and S. Seki, Bull. Chem. Soc. Japan, 38, 1115 (1965), 14.23-308.5°K. The data of Suga, Matsuo and Seki were adopted after correction for curvature. The anomalous region between 50-105°K. has been treated as second order by inclusion of the enthalpy in the heat capacity. The  $C_p$  values above 310°K. were estimated by graphical extrapolation. The value of  $S_{298.15}$  was evaluated based on  $S_{15}^0 = 0.193 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . This extrapolated value appears more reasonable than the value,  $S_{15}^0 = 0.307 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  reported by Suga, Matsuo and Seki.

Transition Data.

$T_f$  was taken from Suga, Matsuo and Seki, loc. cit.  $\Delta H_c^0$  was calculated as the difference between the total enthalpy change,  $H_{173.80}^0 - H_{159.02}^0 = 0.533 \text{ kcal. mole}^{-1}$  obtained from  $C_p$  values measured by Messer and Ziegler, loc. cit., and the enthalpy change,  $0.254 \text{ kcal. mole}^{-1}$ , calculated from the arbitrarily smoothed  $C_p$  curve. Suga, et al. reported  $\Delta H_c^0 = 0.339 \text{ kcal. mole}^{-1}$ , however, their  $C_p$  data do not adequately define the total enthalpy change through the transition region. The values of  $T_f$  and  $\Delta H_c^0$  reported by Messer and Ziegler, loc. cit., were 168.3 ± 0.4°K. and 0.30 kcal. mole<sup>-1</sup>, respectively. The lower transition,  $T = 82.9 \pm 0.2^\circ\text{K.}$  and  $\Delta H^0 = 0.095 \pm 0.001 \text{ kcal. mole}^{-1}$  reported by Suga, et al., was treated as second order by inclusion of the enthalpy in the heat capacity.

Melting Data.

See KCN(1) table.

Heat of Sublimation.

The difference between  $\Delta H_f^0 \text{ 298.15}$  for  $(\text{KCN})_2(g)$  and  $2\text{KCN}(c)$  is  $\Delta H_g^0 \text{ 298.15}$  (to dimer) and for  $\text{KCN}(g)$  and  $\text{KCN}(c)$  is  $\Delta H_g^0 \text{ 298.15}$  (to monomer).

T. °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	0.000	0.000	INFINITE	4.445	28.284	28.284	INFINITE
100	13.261	11.767	45.684	3.412	28.322	26.720	56.397
200	15.972	24.186	31.094	1.562	27.521	25.358	27.710
298	15.868	30.540	30.540	0.000	27.120	24.389	17.877
300	15.866	30.638	30.540	0.029	27.114	24.372	17.755
400	15.850	35.198	31.162	1.614	27.438	23.390	12.780
500	15.859	38.736	32.336	3.200	27.266	22.400	9.791
600	15.868	41.628	33.651	4.786	27.139	21.439	7.809
700	15.878	44.075	34.970	6.373	27.057	20.496	6.399
800	15.887	46.196	36.244	7.962	27.011	19.562	5.344
900	15.897	48.068	37.455	9.551	27.001	18.633	4.525
1000	15.906	49.743	38.602	11.141	27.024	17.703	3.869
1100	15.915	51.259	39.685	12.732	45.987	15.744	3.128
1200	15.925	52.645	40.702	14.324	45.829	13.001	2.368
1300	15.934	53.920	41.676	15.917	45.687	10.273	1.727
1400	15.944	55.101	42.593	17.511	45.557	7.551	1.179
1500	15.953	56.201	43.464	19.106	45.438	4.840	0.705
1600	15.962	57.231	44.293	20.702	45.327	2.138	0.292
1700	15.972	58.199	45.082	22.298	45.224	0.556	-0.072
1800	15.981	59.112	45.837	23.896	45.128	3.247	0.394
1900	15.991	59.977	46.558	25.494	45.038	5.932	0.682
2000	16.000	60.797	47.250	27.094	44.952	8.614	0.941

MOL. WT. = 65.11985

(LIQUID)

POTASSIUM CYANIDE (KCN)

$$\Delta H_f^{298.15} = -24.891 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 3.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^0 = [37.55] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 32.104 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 895 \pm 2^\circ \text{ K.}$$

$$T_b = [1698]^\circ \text{ K.}$$

Heat of Formation.

$\Delta H_f^{298.15}(l)$  was obtained from  $\Delta H_f^{298.15}(c)$  by adding  $\Delta H_m^0$  and the difference between  $H_{895}^0 - H_{298.15}^0$  for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity was estimated and assumed constant in the temperature range 298.15-3000°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature was reported by W. Truthe, Z. anorg. Chem. 76, 129 (1912). The value of  $\Delta H_m^0$  was taken from K. K. Kelley, U. S. Bur. Mines Bull. 393, 1956, based on phase diagrams of the systems KCN-AgCN, KCN-Cu<sub>2</sub>(CN)<sub>2</sub>, KCN-KCl, KCN-NaCN, and KCN-Zn(CN)<sub>2</sub> reported by W. Truthe, loc. cit.

Vaporization Data.

$T_b$  is the temperature at which the free energy change for the reaction  $\text{KCN}(l) = \text{KCN}(g)$  becomes zero. The difference between  $\Delta H_f^0$  for  $\text{KCN}(g)$  and  $\text{KCN}(l)$  at  $T_b$  is  $\Delta H_v^0$ .

T, °K.	C <sub>p</sub>	S°	-(H° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0							
100	18.000	32.104	32.104	.000	-24.891	-22.626	16.585
200	18.000	32.215	32.104	.033	-24.881	-22.612	16.473
300	18.000	32.394	32.810	1.833	-24.940	-21.821	11.922
400	18.000	41.610	34.144	3.633	-24.603	-21.075	9.212
500	18.000	44.692	35.636	5.433	-24.263	-20.401	7.431
600	18.000	47.467	37.133	7.233	-23.968	-19.781	6.176
700	18.000	49.870	38.572	9.033	-23.711	-19.201	5.245
800	18.000	51.990	39.853	10.833	-23.486	-18.652	4.526
900	18.000	53.887	41.054	12.633	-23.303	-18.126	3.961
1000	18.000	55.602	42.181	14.433	-23.157	-17.691	3.286
1100	18.000	57.164	43.241	16.233	-23.041	-17.322	2.603
1200	18.000	58.609	44.236	18.033	-22.953	-17.023	2.021
1300	18.000	59.943	45.177	21.833	-22.886	-16.779	1.527
1400	18.000	61.185	46.073	21.633	-22.833	-16.566	1.101
1500	18.000	62.347	47.701	23.433	-22.793	-16.363	.733
1600	18.000	63.438	48.595	25.233	-22.763	-16.183	.420
1700	18.000	64.467	49.565	27.033	-22.741	-16.026	.156
1800	18.000	65.440	50.265	28.833	-22.726	-15.886	.000
1900	18.000	66.364	51.047	30.633	-22.718	-15.758	.158
2000	18.000	67.242	51.797	32.433	-22.716	-15.641	.324
2100	18.000	68.079	52.518	34.233	-22.719	-15.534	.498
2200	18.000	68.879	53.213	36.033	-22.726	-15.437	.673
2300	18.000	69.645	53.881	37.833	-22.737	-15.350	.848
2400	18.000	70.380	54.527	39.633	-22.751	-15.273	1.023
2500	18.000	71.086	55.150	41.433	-22.767	-15.206	1.198
2600	18.000	71.765	55.753	43.233	-22.784	-15.149	1.373
2700	18.000	72.420	56.337	45.033	-22.803	-15.102	1.548
2800	18.000	73.052	56.902	46.833	-22.823	-15.065	1.723
2900	18.000	73.662	57.451	48.633	-22.844	-15.038	1.898
3000	18.000						

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298<sup>o</sup>)/T</sub>	H <sup>o</sup> -H <sub>298<sup>o</sup></sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>P</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	9.223	48.562	2.977	19.004	19.004	19.004	INFINITE
200	11.406	55.760	2.213	18.999	16.919	16.919	36.976
298	12.155	60.477	0.000	18.999	16.224	16.224	16.224
300	12.164	60.452	0.022	18.999	12.767	12.767	9.387
400	12.520	64.104	1.258	18.326	10.811	10.811	5.907
500	12.778	66.926	2.523	18.178	8.948	8.948	3.911
600	13.015	69.277	3.813	18.008	7.119	7.119	2.593
700	13.238	71.303	5.126	17.816	5.318	5.318	1.660
800	13.443	73.082	6.460	17.607	3.547	3.547	0.969
900	13.625	74.676	7.814	17.382	1.802	1.802	0.438
1000	13.782	76.120	9.184	17.139	0.083	0.083	0.18
1100	13.918	77.440	10.570	16.871	2.030	2.030	0.116
1200	14.034	78.656	11.967	16.583	0.451	0.451	0.082
1300	14.133	79.783	13.376	16.276	2.109	2.109	0.053
1400	14.218	80.834	14.793	15.953	0.175	0.175	0.027
1500	14.290	81.817	16.219	15.619	2.205	2.205	0.005
1600	14.352	82.742	17.651	15.271	2.257	2.257	0.016
1700	14.406	83.613	19.089	14.909	2.313	2.313	0.034
1800	14.452	84.432	20.532	14.532	2.371	2.371	0.051
1900	14.490	85.201	21.979	14.149	2.430	2.430	0.066
2000	14.529	85.925	23.431	13.759	2.489	2.489	0.080
2100	14.569	86.605	24.885	13.365	2.548	2.548	0.093
2200	14.609	87.243	26.339	12.969	2.607	2.607	0.106
2300	14.649	87.840	27.803	12.573	2.666	2.666	0.117
2400	14.689	88.424	29.265	12.178	2.724	2.724	0.128
2500	14.729	88.996	30.730	11.783	2.783	2.783	0.138
2600	14.772	89.571	32.196	11.388	2.842	2.842	0.148
2700	14.818	90.151	33.664	10.993	2.901	2.901	0.157
2800	14.866	90.736	35.134	10.598	2.960	2.960	0.166
2900	14.915	91.326	36.605	10.203	3.019	3.019	0.175
3000	14.972	91.921	38.077	9.808	3.078	3.078	0.183
3100	14.738	92.384	39.550	9.413	3.137	3.137	0.192
3200	14.777	92.852	41.024	9.018	3.196	3.196	0.200
3300	14.816	93.326	42.497	8.623	3.255	3.255	0.207
3400	14.855	93.775	43.975	8.228	3.314	3.314	0.215
3500	14.894	94.217	45.452	7.833	3.373	3.373	0.222
3600	14.779	94.591	46.930	7.438	3.432	3.432	0.229
3700	14.786	94.996	48.408	7.043	3.491	3.491	0.237
3800	14.791	95.390	49.887	6.648	3.550	3.550	0.244
3900	14.797	95.775	51.366	6.253	3.609	3.609	0.251
4000	14.802	96.149	52.846	5.858	3.668	3.668	0.259
4100	14.807	96.515	54.327	5.463	3.727	3.727	0.266
4200	14.811	96.872	55.808	5.068	3.786	3.786	0.274
4300	14.815	97.220	57.289	4.673	3.845	3.845	0.281
4400	14.819	97.561	58.771	4.278	3.904	3.904	0.289
4500	14.823	97.894	60.253	3.883	3.963	3.963	0.296
4600	14.826	98.220	61.735	3.488	4.022	4.022	0.304
4700	14.830	98.559	63.218	3.093	4.081	4.081	0.313
4800	14.833	98.891	64.701	2.698	4.140	4.140	0.321
4900	14.835	99.157	66.185	2.303	4.199	4.199	0.330
5000	14.838	99.457	67.668	1.908	4.258	4.258	0.338
5100	14.841	99.751	69.152	1.513	4.317	4.317	0.347
5200	14.845	100.039	70.637	1.118	4.376	4.376	0.357
5300	14.848	100.321	72.121	0.723	4.435	4.435	0.367
5400	14.851	100.599	73.606	0.328	4.494	4.494	0.377
5500	14.854	100.871	75.090	-0.067	4.553	4.553	0.387
5600	14.851	101.139	76.575	-0.462	4.612	4.612	0.398
5700	14.853	101.402	78.061	-0.857	4.671	4.671	0.409
5800	14.855	101.662	79.546	-1.252	4.730	4.730	0.421
5900	14.856	101.914	81.031	-1.647	4.789	4.789	0.433
6000	14.858	102.164	82.517	-2.042	4.848	4.848	0.446

POTASSIUM CYANIDE (KCN)

(IDEAL GAS)

MOL. WT. = 65.11985

Point Group C<sub>∞v</sub>

ΔH<sub>f</sub><sup>o</sup> = [19 ± 5] kcal. mole<sup>-1</sup>

ΔH<sub>f</sub><sup>o</sup> 298.15 = [19 ± 5] kcal. mole<sup>-1</sup>

S<sup>o</sup> 298.15 = [60.48] cal. deg.<sup>-1</sup>. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

( $\nu$ ), cm.<sup>-1</sup>

[370] (1)

207 (2)

2158 (1)

Bond Distance: C-N = 1.16 ± 0.01 Å

K-C = [2.294] Å

Bond Angle: K-C-N = 180°

Rotational Constant: B = 0.11891 cm.<sup>-1</sup>

σ = 1

Heat of Formation.

The vapor pressure of KCN(g) at 870°C. was estimated to be 1-10 mm. Hg by D. S. Villars, J. Am. Chem. Soc. 53, 405 (1931). Assuming the vapor pressure at this temperature to be 1 mm. Hg, the heat of vaporization (ΔH<sub>v</sub><sup>o</sup> 298.15) for KCN(l) was evaluated as 44 kcal. mole<sup>-1</sup>. Based on ΔH<sub>f</sub><sup>o</sup> 298.15 = -24.89 kcal. mole<sup>-1</sup> for KCN(l), the value of ΔH<sub>f</sub><sup>o</sup> 298.15 for KCN(g) was calculated to be 19 ± 5 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The molecular structure of KCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was determined by N. Elliott and J. Hastings, Acta Cryst. 14, 1018 (1961) by use of neutron diffraction measurements. The K-C bond distance was taken from G. E. Leroi, Ph. D. Thesis, Harvard University, 1961, which was estimated. The vibrational frequencies, ν<sub>2</sub> and ν<sub>3</sub>, were obtained from G. E. Leroi and W. Klemperer, J. Chem. Phys. 35, 774 (1961). The value of ν<sub>1</sub> was calculated by valence force method described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is 2.3540 X 10<sup>-38</sup> g. cm.<sup>2</sup>

$\Delta H_f^0 = -273.57 \pm 0.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_{298.15}^0 = -274.9 \pm 0.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^0 = 6.6 \pm 0.1 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 37.17 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 1174 \pm 1^\circ \text{K.}$

Heat of Formation.

The heat of formation was obtained from the heat of solution  $\Delta H_{sol}^0 = -7.6 \pm 0.5 \text{ kcal. mole}^{-1}$  and the heats of formation for  $K^+(aq)$  and  $CO_3^{2-}(aq)$ , -60.32 and -161.84 kcal. mole<sup>-1</sup>, respectively. The standard heat of solution,  $\Delta H_{sol}^0 = -7.6 \pm 0.5 \text{ kcal. mole}^{-1}$ , was calculated by extrapolation to infinite dilution of the calorimetric data of L. Benjamin, J. Chem. Eng. Data 7, 239-40 (1962), using the methods suggested by J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, J. Phys. Chem. 69, 3059-62 (1965). The equilibrium constant for the hydrolysis  $CO_3^{2-}(\infty H_2O) + H_2O(l) \rightleftharpoons HCO_3^-(\infty H_2O) + OH^-(\infty H_2O)$  was taken as  $K = 2.1 \times 10^{-4}$  based on the selected values of D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-1, October 1, 1965. The resulting extrapolations were not so consistent as those of Rupert et al. (loc. cit.) for Na<sub>2</sub>CO<sub>3</sub>. The ionic heats of formation were taken from Wagman et al. (loc. cit.). This procedure was adopted even though it may involve an inconsistency between the extrapolations for  $\Delta H_{sol}^0$  and  $CO_3^{2-}(\infty H_2O)$ . The alternative evaluation of  $\Delta H_f^0$  288.15 for K<sub>2</sub>CO<sub>3</sub>(~1900 H<sub>2</sub>O) from the heats of mixing given by J. A. Muller, Ann. chim. phys. (6), 15, 517 (1888) and M. Berthelot, Ann. chim. phys. (4) 29, 433 (1873) may be subject to significant error if dissolved CO<sub>2</sub> was not excluded from the solutions. Presumably, this path was used by D. D. Wagman, NBS Report 8628, January 1965, in the selection of  $\Delta H_f^0$  298.15 = -274.3 kcal. mole<sup>-1</sup>. This value is 0.6 kcal. mole<sup>-1</sup> less negative than the value adopted here.

Heat Capacity and Entropy.

The low temperature heat capacity, 14.0-315°K. was measured by F. L. Oetting, unpublished data, Thermal Research Laboratory, Dow Chemical Company, Midland, Michigan, 1963. G. I. Janz, E. Neuenschwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963) measured the heat content by drop calorimetry in the temperature range 630-1250°K., and gave enthalpy and heat capacity equations based on their measurements. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity above 298°K. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point. The entropy at 14.0°K. was calculated from the extrapolated low temperature C<sub>p</sub> data, using the cubic law. The value of  $S_{14.0}^0 = 0.109 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Melting Data.

T<sub>m</sub> was obtained from A. Reisman, J. Am. Chem. Soc. 80, 3558 (1958) and  $\Delta H_m^0$  was taken from Janz et al. (loc. cit.).

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg <sup>-1</sup>	S <sup>0</sup> -(F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	-273.569	-273.569	INFINITE
100	17.300	12.690	5.419	-274.673	-267.991	585.693
200	23.495	21.112	4.612	-274.908	-261.183	285.407
298	27.351	31.170	3.717	-274.900	-254.444	186.513
300	27.414	31.339	3.717	-274.899	-254.437	185.270
400	30.425	45.875	2.956	-275.934	-247.254	135.093
500	33.473	52.821	6.164	-275.628	-240.115	104.954
600	36.010	59.152	9.640	-275.114	-233.056	84.891
700	38.356	64.881	13.359	-274.419	-226.099	70.591
800	40.641	70.152	17.309	-273.549	-219.255	59.898
900	42.905	75.070	21.487	-272.503	-212.530	51.609
1000	45.160	79.707	25.890	-271.288	-205.929	45.006
1100	47.400	84.117	30.518	-267.716	-197.413	39.222
1200	49.640	88.337	35.370	-305.666	-187.471	34.143
1300	51.880	92.399	40.446	-303.418	-177.714	29.876
1400	54.120	96.325	45.746	-300.984	-168.132	26.247
1500	56.360	100.136	51.270	-298.305	-158.736	23.128
1600	58.600	103.845	57.018	-295.436	-149.524	20.424
1700	60.840	107.464	62.990	-292.357	-140.499	18.062
1800	63.080	111.005	69.186	-289.070	-131.659	15.986
1900	65.320	114.476	75.606	-285.574	-123.009	14.149
2000	67.560	117.883	82.250	-281.865	-114.547	12.517

$\Delta H_f^{298.15} = 40.719 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_m^c = 6.60 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $T_m = 1174 \pm 1 \text{ }^\circ\text{K.}$

Heat of Formation.

The  $\Delta H_f^{298.15}$  was obtained from  $\Delta H_f^{298.15}(c)$  and the difference between  $H_m^c$  and  $H_m^{298.15}$  for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 800°K. The heat capacity below 800°K. was obtained from the heat capacity of the crystal. Above 800°K. the heat capacity was adopted as 50.0 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, based on the enthalpy measurements in the range 1169-1250°K. reported by G. J. Janz, E. Neunschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See K<sub>2</sub>CO<sub>3</sub>(c) table.

T, °K.	C <sub>p</sub>	S°	-(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0							
100							
200							
298	27.351	40.719	40.719	0.000	-270.220	-250.822	183.858
300	27.614	40.888	40.720	0.051	-270.219	-250.702	182.636
400	30.625	49.224	41.634	2.926	-271.238	-243.984	133.312
500	33.473	50.370	44.043	6.104	-270.948	-237.209	103.684
600	36.010	62.701	46.635	9.640	-270.434	-230.506	83.062
700	38.356	68.143	48.345	13.308	-268.759	-223.993	69.906
800	50.000	75.899	52.082	17.309	-267.001	-217.452	59.394
900	50.000	78.588	54.600	21.309	-265.189	-211.024	51.780
1000	50.000	84.856	57.946	27.309	-263.189	-204.979	44.788
1100	50.000	89.621	60.249	32.309	-301.245	-196.996	39.139
1200	50.000	93.872	62.681	37.309	-296.047	-187.614	34.169
1300	50.000	97.574	65.428	42.309	-296.875	-178.419	29.995
1400	50.000	101.679	67.887	47.309	-294.721	-169.384	26.442
1500	50.000	105.129	70.256	52.309	-292.586	-160.506	23.386
1600	50.000	108.356	72.538	57.309	-290.465	-151.771	20.731
1700	50.000	111.387	74.735	62.309	-288.358	-143.169	18.406
1800	50.000	114.245	76.851	67.309	-286.267	-134.688	16.353
1900	50.000	116.948	78.891	72.309	-284.191	-126.323	14.530
2000	50.000	119.513	80.858	77.309	-282.126	-118.068	12.902
2100	50.000	121.953	82.758	82.309	-280.075	-109.914	11.439
2200	50.000	124.279	84.593	87.309	-278.044	-101.861	10.119
2300	50.000	126.501	86.367	92.309	-276.024	-93.897	8.922
2400	50.000	128.629	88.084	97.309	-274.022	-86.020	7.833
2500	50.000	130.670	89.747	102.309	-272.040	-78.232	6.839

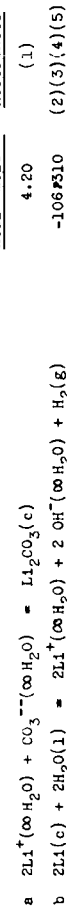
LITHIUM CARBONATE (Li<sub>2</sub>CO<sub>3</sub>) (CRYSTAL)

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	4.000						INFINITE
100	8.320	4.792	37.868	3.306	-288.692	-288.692	619.744
200	17.310	13.507	23.487	1.966	-289.693	-283.571	502.857
298	23.000	21.551	21.551	1.000	-290.640	-270.596	198.133
300	23.080	21.694	21.552	1.043	-290.643	-270.474	197.040
400	26.810	28.860	27.504	2.343	-290.697	-263.738	144.099
500	30.820	35.259	24.424	5.418	-292.074	-259.855	112.271
600	35.700	41.295	26.746	8.746	-291.692	-249.839	91.004
700	33.670	48.035	29.279	13.175	-290.293	-242.954	75.854
800	38.000	52.811	31.406	16.711	-289.749	-236.225	64.534
900	42.210	57.537	33.507	20.721	-288.824	-229.586	55.751
1000	46.340	62.225	37.604	25.161	-287.495	-223.070	48.752
1100	49.220	66.795	39.542	29.978	-285.856	-216.706	43.056
1200	50.830	71.152	41.097	34.986	-284.032	-210.500	38.337
1300	51.760	75.259	44.399	40.418	-282.107	-204.451	34.371
1400	52.420	79.120	46.743	45.329	-280.118	-198.549	30.995
1500	52.840	82.752	49.023	50.592	-278.091	-192.795	28.090
1600	53.200	86.174	51.239	55.896	-276.035	-187.174	25.567
1700	53.400	89.405	53.190	61.226	-274.056	-179.027	23.016
1800	53.600	92.463	55.477	66.576	-272.161	-169.387	20.566
1900	53.800	95.367	57.501	71.946	-270.346	-159.885	18.391
2000	54.000	98.131	59.464	77.336	-268.702	-150.516	16.448

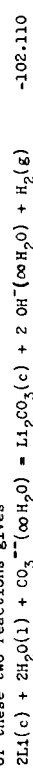
$\Delta H_f^0 = -288.69 \pm 0.04$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -290.64 \pm 0.04$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = 21.551 \pm 0.05$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_{t1} = 623^\circ\text{K.}$   
 $T_{t2} = 683 \pm 3^\circ\text{K.}$   
 $T_m = 983 \pm 1^\circ\text{K.}$

Heat of Formation.

The heat of formation was derived from the following reactions:



Summation of these two reactions gives



Using  $\Delta H_f^0$  of  $\text{H}_2\text{O}(l)$ ,  $\text{CO}_3^{--}(\infty\text{H}_2\text{O})$  and  $\text{OH}^-(\infty\text{H}_2\text{O})$  from Ref. 6 yields  $\Delta H_f^0 \text{Li}_2\text{CO}_3 = -290.64$  kcal. mole<sup>-1</sup>.

References

- (1) O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. **58**, 2228(1936).
- (2) JANAF table for LiOH(c), March 31, 1966.
- (3) S. R. Gunn and L. G. Green, J. Am. Chem. Soc. **80**, 4782 (1958). S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeters," UCRL-7492, Oct. 1964.
- (4) C. B. Messer, L. G. Fasolino and C. E. Thalmeier, J. Am. Chem. Soc. **77**, 4524 (1955).
- (5) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes" NSRDS-NBS 2 Nat'l. Bur. Std., April 1, 1965.
- (6) D. D. Wagman, W. H. Evans, I. Helow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-1, October 1, 1965.

Heat Capacity and Entropy.

The low temperature heat capacity, 16.68-300.20°K., was measured by O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. **58**, 2228 (1936). G. I. Janz, E. Neunschwender and P. J. Kelly, Trans. Faraday Soc. **52**, 841 (1956) measured the heat content by drop calorimetry in the temperature range 560-1150°K., and gave enthalpy and heat capacity equations based on their measurement. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point. The entropy at 16.68°K. was calculated from the extrapolated low temperature  $C_p$  data, using the cubic law. The value of  $S_{16.68}^0 = 0.053$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Transition Data.

$T_t$  were taken from A. Reisman, J. Am. Chem. Soc. **80**, 3558 (1958). The enthalpies of transition were estimated from the relative areas of the transitions and the heat of fusion of the differential analysis curve reported by Reisman loc. cit.

Melting Data.

$T_m$  was obtained from Reisman loc cit. and  $\Delta H_m^0$  was taken from Janz et. al. (loc. cit.).



LITHIUM CARBONATE (Li<sub>2</sub>CO<sub>3</sub>) (LIQUID)

MOL. WT. = 73.88735

$$S_{298.15}^{\circ} = 30.423 \pm 0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad \Delta H_f^{\circ} 298.15 = -281.63 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$T_m = 993.15 \pm 1^{\circ}\text{K.} \quad \Delta H_m^{\circ} = 10.7 \pm 0.1 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The  $\Delta H_f^{\circ} 298.15$  was obtained from  $\Delta H_f^{\circ} 298.15(c)$  by adding  $\Delta H_m^{\circ}$  and the difference between  $H_m^{\circ}$  and  $H_{cr}^{\circ} 298.15$  for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 683.15°K. The heat capacity below 683.15°K. was obtained from the heat capacity of the crystal. Above 683.15°K. the heat capacity was adopted as 44.32 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, based on the enthalpy measurements in the range 996-1150°K. reported by G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See Li<sub>2</sub>CO<sub>3</sub>(c) table.

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0							
100							
200							
298	23.000	30.423	30.423	0.000	-281.629	-264.232	193.687
300	23.080	30.566	30.423	0.043	-281.632	-264.125	192.415
400	26.810	37.732	31.176	2.543	-281.686	-259.275	141.115
500	30.820	44.131	33.296	5.418	-283.063	-252.280	110.271
600	35.700	50.167	35.608	8.736	-282.681	-246.151	89.661
700	44.320	56.387	38.136	12.776	-281.633	-240.142	74.976
800	44.320	62.305	40.795	17.208	-280.241	-234.312	64.011
900	44.320	67.525	43.481	21.640	-278.899	-228.652	55.524
1000	44.320	72.195	46.123	26.072	-277.593	-223.138	48.767
1100	44.320	76.419	48.688	30.504	-276.319	-217.755	43.264
1200	44.320	80.275	51.162	34.936	-275.071	-212.487	38.699
1300	44.320	83.823	53.540	39.368	-273.845	-207.322	34.854
1400	44.320	87.107	55.822	43.800	-272.635	-202.248	31.572
1500	44.320	90.165	58.010	48.232	-271.440	-197.263	28.741
1600	44.320	93.026	60.110	52.664	-270.255	-192.358	26.275
1700	44.320	95.712	62.126	57.096	-339.174	-194.868	23.766
1800	44.320	98.246	64.063	61.528	-337.649	-175.833	21.349
1900	44.320	100.642	65.926	65.960	-336.135	-166.882	19.196
2000	44.320	102.915	67.719	70.392	-334.634	-158.016	17.267

SODIUM CYANIDE (NaCN) (CRYSTAL)

MOL. WT. = 49.00765

$\Delta H_f^0 = -23.49 \pm 0.3 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -21.68 \pm 0.3 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^0 = [2.1] \text{ kcal. mole}^{-1}$   
 $\Delta H_m^{298.15}(\text{to dimer}) = [41.3] \text{ kcal. mole}^{-1}$   
 $\Delta H_g^{298.15}(\text{to monomer}) = 44.21 \text{ kcal. mole}^{-1}$

$S_{298.15}^{298.15} = [28.52 \pm 0.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 835^\circ \text{ K.}$

Heat of Formation.

The enthalpy change for the reaction  $\text{NaCN}(c) \rightarrow \text{NaCN}(\infty \text{ H}_2\text{O})$  was reported to be  $0.29 \pm 0.20 \text{ kcal. mole}^{-1}$  by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heats of formation for  $\text{Na}^+(\infty \text{ H}_2\text{O})$ ,  $-57.39$ , and  $\text{CN}^-(\infty \text{ H}_2\text{O})$ ,  $36.0 \text{ kcal. mole}^{-1}$ , reported by D. D. Wegman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of  $\Delta H_f^{298.15}$  for  $\text{NaCN}(c)$  was derived and adopted.

O. Lord and A. A. Woolf, J. Chem. Soc. 2546 (1954), determined the value,  $\Delta H_f^{298.15}(\text{NaCN}, c) = -21.4 \text{ kcal. mole}^{-1}$ , by solution calorimetry. This value is in agreement with the adopted one.

Heat Capacity and Entropy.

The low temperature heat capacities,  $101.6\text{--}345.8^\circ \text{K.}$ , were reported by C. E. Messer and W. T. Ziegler, J. Am. Chem. Soc. 65, 2705 (1943). The  $C_p$  values above  $345.8^\circ \text{K.}$  were estimated by graphical extrapolation.  $S_{298.15}^{298.15}$  was derived from low temperature heat capacities, based on  $S_{100}^{100} = 8.4 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  which was estimated by comparison with the  $S_{298.15}^{298.15}$  values for NaCl, KCl, and KCN crystals.

Transition Data.

The transition temperatures,  $T_2$  and  $T_1$ , were determined by C. E. Messer and W. T. Ziegler, loc. cit. The corresponding enthalpies of transition were reported to be  $0.15$  and  $0.70 \text{ kcal. mole}^{-1}$ , respectively. However, these quantities were incorporated with  $C_p$  values used to evaluate  $\text{H}^+\text{--H}_2^{298.15}$ . Therefore  $\Delta H_f^0$ 's are not listed.

Melting Data.

See NaCN(1) table for details.

Heat of Sublimation.

The difference between  $\Delta H_f^{298.15}$  for  $(\text{NaCN})_2(g)$  and  $2\text{NaCN}(c)$  is  $\Delta H_g^{298.15}$  (to dimer) and for  $\text{NaCN}(g)$  and  $\text{NaCN}(c)$  is  $\Delta H_g^{298.15}$  (to monomer).

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	0.00	∞	∞	∞	∞	∞	∞
100	11.320	8.400	4.7821	3.942	23.493	23.493	INFINITE
200	16.223	9.7138	3.9812	2.355	21.814	21.814	47.674
298	16.415	28.315	28.315	+0.00	20.339	20.339	21.223
300	16.390	28.416	28.315	+0.30	19.211	19.211	13.995
400	16.410	33.141	28.060	1.672	21.969	18.397	10.052
500	16.432	36.805	30.176	3.315	21.738	17.531	7.663
600	16.455	39.803	31.536	4.959	21.549	16.709	6.086
700	16.478	42.341	32.905	6.606	21.397	15.915	4.969
800	16.502	44.543	34.225	8.255	21.273	15.140	4.136
900	16.526	46.488	35.482	9.906	21.179	14.380	3.492
1000	16.550	48.231	36.671	11.560	21.108	13.629	2.979
1100	16.576	49.809	37.795	13.216	21.064	12.885	2.560
1200	16.602	51.253	38.857	14.875	44.282	11.685	2.128
1300	16.628	52.582	39.862	16.536	44.072	8.976	1.509
1400	16.653	53.816	40.815	18.200	43.872	6.284	0.981
1500	16.678	54.965	41.721	19.867	43.681	3.605	0.525
1600	16.703	56.043	42.583	21.536	43.496	0.941	0.129
1700	16.728	57.056	43.404	23.208	43.316	1.714	0.220
1800	16.752	58.013	44.190	24.882	43.143	4.357	0.529
1900	16.776	58.919	44.941	26.558	42.972	6.994	0.805
2000	16.800	59.780	45.662	28.237	42.805	9.619	1.051

(LIQUID)

SODIUM CYANIDE (NaCN)

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	(F° - H° <sub>298</sub> )	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0							
100	16.415	29.996	29.996	0.000	20.160	18.208	13.347
200	16.390	30.097	29.996	0.030	20.152	18.196	13.256
300	16.410	30.622	30.641	1.672	20.449	17.549	9.588
400	16.432	38.486	31.857	3.315	20.218	16.852	7.366
500	19.000	41.484	33.219	4.959	20.029	16.197	5.900
600	19.000	46.413	34.614	6.959	19.624	15.592	4.868
700	19.000	48.920	35.001	8.159	19.269	15.044	4.109
800	19.000	49.188	37.345	10.659	18.906	14.537	3.530
1000	19.000	51.190	38.631	12.859	18.589	14.069	3.075
1100	19.000	53.001	39.856	14.459	18.302	13.633	2.709
1200	19.000	54.654	41.021	16.359	18.048	13.228	2.424
1300	19.000	56.175	42.129	18.429	17.822	12.846	2.209
1400	19.000	57.584	43.184	20.659	17.622	12.484	2.049
1500	19.000	58.894	44.184	22.059	17.438	12.142	1.924
1600	19.000	60.120	45.146	23.959	17.264	11.822	1.811
1700	19.000	61.272	46.061	25.859	17.102	11.522	1.709
1800	19.000	62.348	46.938	27.759	16.952	11.242	1.617
1900	19.000	63.348	47.775	29.759	16.812	10.982	1.534
2000	19.000	64.260	48.580	31.859	16.682	10.732	1.459
2100	19.000	65.287	49.354	33.459	16.562	10.492	1.390
2200	19.000	66.170	50.098	35.359	16.452	10.262	1.327
2300	19.000	67.015	50.816	37.259	16.352	10.042	1.270
2400	19.000	67.824	51.507	39.159	16.262	9.832	1.218
2500	19.000	68.599	52.176	41.059	16.182	9.632	1.170
2600	19.000	69.345	52.822	42.959	16.112	9.442	1.127
2700	19.000	70.062	53.447	44.859	16.052	9.262	1.089
2800	19.000	70.753	54.043	46.759	16.002	9.092	1.056
2900	19.000	71.419	54.614	48.659	15.962	8.932	1.027
3000	19.000	72.063	55.210	50.559	15.932	8.782	1.001

ΔH<sub>f</sub><sup>o</sup> 298.15 = [-20.160] kcal. mole<sup>-1</sup>  
 ΔH<sub>m</sub><sup>o</sup> = [2.1] kcal. mole<sup>-1</sup>  
 ΔH<sub>v</sub><sup>o</sup> = [35.39] kcal. mole<sup>-1</sup>

S° 298.15 = [29.996] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 T<sub>m</sub> = 855° K.  
 T<sub>b</sub> = [1803]\*K.

Heat of Formation.

ΔH<sub>f</sub><sup>o</sup> 298.15(l) was obtained from ΔH<sub>f</sub><sup>o</sup> 298.15(c) by adding ΔH<sub>m</sub><sup>o</sup> and the difference between H<sub>g35</sub><sup>o</sup>-H<sub>g298.15</sub><sup>o</sup> for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with those for NaCN(c), KCN(c) and KCN(l). A glass transition temperature is assumed at 600°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature was reported by W. Truette, Z. anorg. Chem. 76, 129 (1912). ΔH<sub>m</sub><sup>o</sup> was estimated such that the derived third law value for ΔH<sub>v</sub><sup>o</sup> (NaCN, l) agrees with the second law value. See NaCN(g) table for details.

Vaporization Data.

T<sub>b</sub> is the temperature at which the free energy change for the reaction NaCN(l) = NaCN(g) becomes zero. The difference between ΔH<sub>f</sub><sup>o</sup> for NaCN(g) and NaCN(l) at T<sub>b</sub> is ΔH<sub>v</sub><sup>o</sup>.

$\Delta H_f^0 = 22.46 \pm 0.50$  kcal. mole<sup>-1</sup>

$\Delta H_f^{298.15} = 22.53 \pm 0.50$  kcal. mole<sup>-1</sup>

Point Group C<sub>∞v</sub>

S<sup>298.15</sup> = [58.14] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Group State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_e$ , cm.<sup>-1</sup>  
[400](1)  
239 (2)  
2176 (1)

Bond Distance: Na-C = [1.992] Å C-N = [1.16] Å  
Bond Angle: Na-C-N = [180]°  
Rotational Constant: B = [0.18272] cm.<sup>-1</sup>

σ = 1

Heat of Formation.

The vapor pressures of NaCN(1) at temperatures 805-1353°K. were measured by C. K. Ingold, J. Chem. Soc. 123, 885 (1923). According to the investigation reported by R. F. Porter, J. Chem. Phys. 35, 318 (1961), the vapor consists of NaCN and (NaCN)<sub>2</sub>. Based on his data the dimer/monomer ratios at temperatures 805-1353°K. (1078.2-1626.2°K.) were calculated to be 0.29-0.09. Hence the respective partial pressures for NaCN(g) and (NaCN)<sub>2</sub>(g) were derived. By the second and third law methods, the values of ΔH<sub>f</sub><sup>298.15</sup> (1 → monomer) were evaluated to be 43.43 and 42.69 kcal. mole<sup>-1</sup>, respectively. The heat of formation (ΔH<sub>f</sub><sup>298.15</sup>) for NaCN(g) was calculated from ΔH<sub>f</sub><sup>298.15</sup> (NaCN, c) and the third law value for ΔH<sub>f</sub><sup>298.15</sup>.

Heat Capacity and Entropy.

The molecular structure of NaCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was assumed to be the same as that in KCN(g) and the Na-C bond distance was taken from G. E. Leroi, Ph. D. Dissertation, Harvard University, 1961, which was calculated. The vibrational frequencies,  $\nu_2$  and  $\nu_3$ , were measured by G. E. Leroi and W. Klemperer, J. Chem. Phys. 35, 774 (1961) from infrared absorption spectra. The value of  $\nu_1$  was calculated by valence force method described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is 1.53187 x 10<sup>-38</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S°	-(F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> <sup>298</sup>	ΔF <sub>f</sub> <sup>298</sup>	Log K <sub>p</sub>
0	∞-0	∞-0	∞-0	∞-0	∞-0	∞-0	∞-0
100	8.775	46.583	68.115	2.898	22.461	22.466	INFINITE
200	11.114	52.711	80.214	2.154	22.529	20.366	44.510
298	11.899	56.133	88.139	1.541	22.525	18.211	19.900
				0.000	22.530	16.091	11.796
300	12.003	58.213	88.139	0.222	22.530	16.051	11.693
400	12.419	61.729	88.616	1.245	21.814	13.951	7.622
500	12.707	64.532	89.478	2.502	21.660	12.003	5.246
600	12.960	66.872	90.462	3.786	21.488	10.087	3.674
700	13.194	68.887	91.611	5.093	21.301	8.200	2.560
800	13.405	70.563	92.934	6.424	21.106	6.343	1.733
900	13.592	72.023	94.318	7.774	20.899	4.509	1.095
1000	13.754	73.264	95.752	9.141	20.684	2.699	0.590
1100	13.893	74.311	97.234	10.524	20.453	0.911	0.181
1200	14.012	75.175	98.752	11.919	20.208	0.166	0.072
1300	14.113	75.847	100.304	13.326	19.949	0.453	0.030
1400	14.200	76.420	101.888	14.741	19.677	0.749	0.008
1500	14.274	76.892	103.492	16.165	19.400	1.049	0.040
1600	14.338	77.266	105.116	17.596	19.120	1.352	0.069
1700	14.393	77.541	106.758	19.032	18.838	1.658	0.096
1800	14.441	77.721	108.416	20.474	18.555	1.965	0.119
1900	14.483	77.813	110.088	21.921	18.271	2.273	0.141
2000	14.520	77.821	111.771	23.371	17.987	2.581	0.160
2100	14.552	77.745	113.464	24.824	17.703	2.889	0.179
2200	14.580	77.588	115.164	26.281	17.419	3.196	0.195
2300	14.606	77.352	116.871	27.740	17.135	3.502	0.211
2400	14.628	77.038	118.584	29.202	16.851	3.808	0.226
2500	14.648	76.648	120.301	30.666	16.567	4.114	0.239
2600	14.666	76.183	122.021	32.132	16.282	4.420	0.252
2700	14.682	75.643	123.744	33.599	16.000	4.726	0.264
2800	14.697	75.028	125.468	35.068	15.719	5.032	0.277
2900	14.710	74.338	127.192	36.538	15.438	5.338	0.289
3000	14.722	73.573	128.916	38.010	15.157	5.644	0.297
3100	14.733	72.743	130.640	39.483	14.876	5.950	0.307
3200	14.743	71.848	132.364	40.957	14.595	6.256	0.316
3300	14.753	70.888	134.088	42.432	14.314	6.562	0.324
3400	14.761	70.000	135.812	43.907	14.033	6.868	0.332
3500	14.769	69.173	137.536	45.384	13.752	7.174	0.339
3600	14.776	68.419	139.260	46.861	13.471	7.480	0.343
3700	14.782	67.734	140.984	48.339	13.190	7.786	0.351
3800	14.789	67.118	142.708	49.817	12.909	8.092	0.359
3900	14.794	66.572	144.432	51.297	12.628	8.398	0.367
4000	14.799	66.097	146.156	52.776	12.347	8.704	0.374
4100	14.804	65.693	147.880	54.256	12.066	9.010	0.382
4200	14.809	65.359	149.604	55.737	11.785	9.316	0.389
4300	14.815	65.095	151.328	57.218	11.504	9.622	0.396
4400	14.821	64.891	153.052	58.700	11.223	9.928	0.403
4500	14.827	64.747	154.776	60.182	10.942	10.234	0.409
4600	14.824	64.664	156.500	61.664	10.661	10.540	0.416
4700	14.826	64.641	158.224	63.146	10.380	10.846	0.423
4800	14.828	64.678	159.948	64.629	10.100	11.152	0.430
4900	14.831	64.774	161.672	66.113	9.819	11.458	0.436
5000	14.836	64.930	163.400	67.596	9.538	11.764	0.443
5100	14.839	65.146	165.124	69.080	9.257	12.070	0.449
5200	14.841	65.422	166.848	70.564	8.976	12.376	0.456
5300	14.844	65.758	168.572	72.048	8.695	12.682	0.462
5400	14.846	66.154	170.296	73.533	8.414	12.988	0.469
5500	14.848	66.610	172.020	75.017	8.133	13.294	0.476
5600	14.850	67.126	173.744	76.502	7.852	13.600	0.483
5700	14.852	67.702	175.468	77.987	7.571	13.906	0.490
5800	14.853	68.338	177.192	79.472	7.290	14.212	0.497
5900	14.855	69.034	178.916	80.958	7.009	14.518	0.504
6000	14.857	69.790	180.640	82.443	6.728	14.824	0.511
							0.519

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	$-(H^o - H_{298}^o)/T$	$H^o - H_{298}^o$	$\Delta H_f^o$	$\Delta F_f^o$	Log K <sub>F</sub>
0	.000	.000	INFINITE	-4.974	-268.788	-268.788	INFINITE
100	14.637	10.334	53.814	4.348	-269.885	-263.531	575.947
200	22.500	23.367	35.485	2.424	-270.233	-257.002	280.839
298	26.530	33.173	.000	.000	-270.260	-250.496	183.619
300	26.590	33.338	33.174	.049	-270.258	-250.373	182.397
400	29.900	41.621	34.254	2.867	-271.441	-247.456	133.127
500	33.990	48.520	36.408	6.056	-271.150	-236.735	103.477
600	39.030	55.153	38.493	9.702	-270.456	-229.910	83.745
700	44.830	61.597	41.755	13.690	-269.272	-223.240	69.699
800	50.650	66.889	44.504	17.937	-268.371	-216.743	59.211
900	56.730	71.983	47.322	21.655	-267.641	-210.331	51.075
1000	62.830	75.729	49.494	25.182	-266.640	-204.013	44.587
1100	68.900	79.256	52.484	30.320	-265.376	-197.813	39.302
1200	74.980	84.065	54.946	36.844	-263.840	-190.821	34.753
1300	80.280	87.900	57.337	43.811	-262.302	-180.943	30.419
1400	84.830	91.045	59.657	51.183	-260.816	-171.226	26.730
1500	89.600	93.527	61.907	58.930	-259.393	-161.662	23.594
1600	94.530	96.422	64.087	66.937	-258.166	-152.246	20.786
1700	99.640	101.550	66.199	75.246	-257.195	-142.869	18.360
1800	104.900	106.865	68.246	83.846	-256.426	-133.531	16.249
1900	110.300	112.340	70.234	92.728	-255.814	-124.228	14.388
2000	115.800	117.970	72.154	101.878	-255.320	-115.028	12.668

SODIUM CARBONATE (Na<sub>2</sub>CO<sub>3</sub>)

(CRYSTAL)

MOL. WT. = 105.9885

- $\Delta H_f^o = -268.79 \pm 0.05$  kcal. mole<sup>-1</sup>
- $\Delta H_f^{298.15} = -270.26 \pm 0.05$  kcal. mole<sup>-1</sup>
- $\Delta H_f^o = 0.165$  kcal. mole<sup>-1</sup>
- $\Delta H_m^o = 7.090$  kcal. mole<sup>-1</sup>
- $S_{298.15}^o = 35.17 \pm 0.2$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>
- $T_c = 723.15^\circ\text{K.}$
- $T_m = 1123.15^\circ\text{K.}$

Heat of Formation.

The heat of formation was obtained from the heat of solution  $\Delta H_{sol}^o = -6.36$  kcal. mole<sup>-1</sup> and the heats of formation for Na<sup>+</sup>(aq) and CO<sub>3</sub><sup>2-</sup>(aq), -57.39 and -161.84 kcal. mole<sup>-1</sup>, respectively. The heat of solution was taken from J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, *J. Phys. Chem.* **69**, 3059-62 (1965). The ionic heats of formation were taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm "Selected Values of Chemical Thermodynamic Properties" NBS Technical Note 270-1, October 1, 1965.

A value of  $\Delta H_f^o$  298.15 = -270.9 kcal. mole<sup>-1</sup> has been selected by D. D. Wagman, *Natl. Bur. Std. Rept. No. 8628*, 87, Jan. 1965.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.6-292.1°K., were measured by C. T. Anderson, *J. Am. Chem. Soc.* **55**, 3621 (1933). In the temperature range 473.15-873.15°K. Popov and Galchenko (Source 1) measured the heat capacities (by heat conduction calorimetry) and observed two transformations, one at about 623°K. and the other at about 750°K. Popov and Ginzburg (Source 2) measured enthalpies in the temperature range 480-1350°K. and tabulated their data only in the range 476-872°K. Ginzburg (Source 3) has given heat capacity equations based on the data from Source 1 and 2 and has tabulated thermodynamic functions in the range 500-1500°K. There appear to be inconsistencies among the data, equations and functions. Rolin and Recapet (Source 4) also measured the enthalpy in the temperature range 645-1322°K. Janz, Neuenchwander and Kelly (Source 5) have given an enthalpy equation based on their heat content measured data in the range 707-1127°K. May (Source 6) has tabulated smoothed enthalpy values in the range 400-1500°K. All the above information was used in a Shomate analysis in order to smooth the enthalpies and calculate heat capacities. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point.

The entropy was calculated at 54.60° using the Debye and Einstein function  $D(\frac{3\theta}{T}) + 2E(\frac{2\theta}{T}) + 2D(\frac{1.5}{T})$  given by Anderson, loc. cit. The value of  $S_{54.6}^o = 3.943$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Source

- 1 M. M. Popov and G. L. Galchenko, *Zh. Obshch. Khim.* **21**, 2220 (1951).
- 2 M. M. Popov and D. M. Ginzburg, *Zh. Obshch. Khim.* **25**, 971-80 (1956).
- 3 D. M. Ginzburg, *Zh. Obshch. Khim.* **25**, 968-70 (1956).
- 4 M. Rolin and J. M. Recapet, *Bull. Soc. chim.*, 2504 (1964).
- 5 G. J. Janz, E. Neuenchwander and F. J. Kelly, *Trans. Faraday Soc.* **59**, 841 (1963).
- 6 M. N. May, *Tappi*, **35**, 511 (1952).

Transition Data.

$T_c$  was taken from Ginzburg loc. cit. and  $\Delta H_m^o$  was obtained from the above reported enthalpy measurements by means of Shomate function analysis. The heat of transition at 593.15°K. has been incorporated in the heat capacity.

Melting Data.

$T_m$  was taken from Ginzburg loc. cit. and  $\Delta H_m^o$  was obtained from the above reported enthalpy measurements by means of Shomate function analysis.

CNa<sub>2</sub>O<sub>3</sub>

$\Delta H_f^\circ 298.15 = -265.21 \pm 0.05 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^\circ = 7.090 \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = 37.14 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 1123.15^\circ \text{K.}$

Heat of Formation.

The  $\Delta H_f^\circ 298.15$  was obtained from  $\Delta H_f^\circ 298.15(c)$  by adding  $\Delta H_m^\circ$  and the difference between  $H_m^\circ$  and  $H_f^\circ$  for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 723.15°K. The heat capacity below 723.15°K. was obtained from the heat capacity of the crystal. Above 723.15°K. the heat capacity was adopted as 45.30 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, based on the enthalpy measurements in the range 1127-1210°K. reported by G. J. Janz, E. Neuenschwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See Na<sub>2</sub>CO<sub>3</sub>(c) table.

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0						
100	37.143	37.143	0.000	-265.205	-246.625	180.781
200	37.307	37.314	0.049	-265.203	-246.509	179.581
298	37.590	38.224	2.867	-266.386	-240.189	131.233
300	38.224	40.378	6.054	-266.097	-233.665	102.135
400	52.485	42.952	9.698	-265.405	-227.236	82.771
500	65.564	45.723	13.889	-264.218	-220.963	68.988
600	76.956	48.590	18.424	-262.729	-214.886	58.704
700	81.729	51.451	22.954	-261.287	-208.593	50.750
800	86.046	54.245	27.484	-259.884	-202.257	44.422
900	89.888	56.943	32.014	-258.527	-197.664	39.272
1000	93.614	59.555	36.544	-257.214	-191.273	34.836
1100	96.871	62.018	41.074	-255.943	-181.975	30.593
1200	99.674	64.397	45.604	-254.714	-172.807	26.976
1300	100.096	66.674	50.134	-253.527	-163.757	23.859
1400	103.020	68.855	54.664	-252.381	-154.821	21.147
1500	105.766	70.946	59.194	-251.274	-145.983	18.767
1600	108.355	72.953	63.724	-250.205	-137.244	16.664
1700	110.805	74.881	68.254	-249.174	-128.595	14.792
1800	113.128	76.736	72.784	-248.181	-120.033	13.117
1900	115.338	78.522	77.314	-247.226	-111.547	11.609
2000	117.446	80.244	81.844	-246.305	-103.131	10.246
2100	119.459	81.905	86.374	-245.417	-94.802	9.008
2200	121.387	83.511	90.904	-244.561	-86.527	7.879
2300	123.236	85.063	95.434	-243.736	-78.329	6.847
2400						
2500						

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

$S_{298.15}^0 = 47.21 \pm 0.01$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

$\Delta H_f^0 = 2169.52$  cm.<sup>-1</sup>

$\Delta H_f^0 = 298.15 = -26.42 \pm 0.04$  kcal. mole<sup>-1</sup>

$\omega_e x_e = 13.453$  cm.<sup>-1</sup>

$B_e = 1.9302$  cm.<sup>-1</sup>

$r_e = 1.1281$  Å

$\alpha_e = 0.01746$  cm.<sup>-1</sup>

Heat of Formation.

The enthalpy change ( $\Delta H_f^0$ , 298.15) for the reaction:  $CO(g) + 1/2 O_2(g) = CO_2(g)$  was reported to be  $-67.636 \pm 0.029$  kcal. mole<sup>-1</sup>, based on molecular weight of  $CO_2 = 44.010$ , by F. D. Rossini, J. Research Nat. Bur. Standards 22, 407 (1939). It was recalculated to be  $-67.638 \pm 0.03$  kcal. mole<sup>-1</sup>, using molecular weight of  $CO_2 = 44.011$ , for internal consistency. From the value of  $\Delta H_f^0$ , 298.15, the heat of formation ( $\Delta H_f^0$ , 298.15) for  $CO(g)$  was derived to be  $-26.417 \pm 0.04$  kcal. mole<sup>-1</sup>, which yields  $D_0(CO) = 11.09$  e.v.

The  $D_0(CO)$  value has been proposed to be 6.92 to 11.11 e.v. in the past few decades in order to explain data collected from spectroscopic, flame, shock-wave, detonation, and electron-impact studies. Recent evaluations by L. Brewer and A. Searcy, Ann. Rev. Phys. Chem. 7, 259 (1956); M. A. Fineman and A. W. Petrocelli, J. Chem. Phys. 36, 25 (1962); and C. F. Giese and W. B. Maier II, J. Chem. Phys. 39, 197 (1963) favored the value 11.11 e.v., reported by A. O. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 1953.

The heat of combustion of  $CO(g)$  was also determined by J. H. Abery and E. Griffiths, Proc. Roy. Soc. (London) [A] 141, 1 (1933), R. W. Penning and F. T. Cotton, ibid., [A] 141, 17 (1935), and W. A. Roth and H. Banse, Arch. Eisenhüttenw. 43 (1932-33).

Heat Capacity and Entropy.

The functions adopted here were obtained from J. Belzer, L. G. Svedoff and H. L. Johnston, Ohio State University, TR 316-6, May 1, 1953, assuming the thermodynamic functions for the naturally occurring isotopic mixture to be the same as those for  $C^{12}O^{16}(g)$ . The spectroscopic constants employed for calculation were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950. The tabulated functions include the second order corrections to the rigid-rotator and harmonic-oscillator molecular model for vibrational anharmonicity, rotational stretching and rotational-vibrational interaction.

The spectroscopic constants listed above are for the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

Thermodynamic properties for CO from 70 to 300°K., with pressures to 300 atmospheres were reported by J. G. Hest and R. B. Stewart, NBS-TN-202, National Bureau of Standards, 1963. Calculations of the vapor pressure and heats of vaporization and sublimation of CO and  $CO_2$  below one atmosphere were reported by J. C. Mullins, B. S. Kirk and W. T. Ziegler, U. S. Atomic Energy Commission NP-13862 (1963).

Log K<sub>p</sub>

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	INFINITE	2.072	27.200	27.200	INFINITE
100	6.956	39.401	1.379	26.876	28.741	62.809
200	6.957	44.435	0.683	26.599	30.718	33.566
298	6.965	47.214	0.000	26.417	32.783	24.029
300	6.965	47.257	0.013	26.414	32.823	23.910
400	7.013	49.265	0.711	26.318	34.975	19.109
500	7.121	50.841	1.417	26.296	37.144	16.235
600	7.276	52.132	2.137	26.332	39.311	14.318
700	7.450	53.287	2.873	26.409	41.468	12.946
800	7.624	54.293	3.627	26.514	43.612	11.914
900	7.786	55.200	4.397	26.637	45.744	11.108
1000	7.931	56.028	5.183	26.771	47.859	10.459
1100	8.057	56.790	5.983	26.914	49.962	9.926
1200	8.168	57.496	6.794	27.062	52.049	9.479
1300	8.263	58.154	7.616	27.218	54.126	9.099
1400	8.346	58.769	8.446	27.376	56.189	8.771
1500	8.417	59.348	9.285	27.537	58.241	8.485
1600	8.480	59.893	10.130	27.700	60.284	8.234
1700	8.535	60.409	10.980	27.865	62.315	8.011
1800	8.583	60.898	11.836	28.032	64.337	7.811
1900	8.626	61.363	12.697	28.201	66.349	7.631
2000	8.664	61.807	13.561	28.372	68.353	7.469
2100	8.698	62.230	14.430	28.543	70.346	7.321
2200	8.728	62.635	15.301	28.719	72.335	7.185
2300	8.754	63.024	16.175	28.894	74.311	7.061
2400	8.778	63.397	17.052	29.074	76.282	6.946
2500	8.804	63.756	17.931	29.254	78.247	6.840
2600	8.825	64.102	18.813	29.438	80.202	6.741
2700	8.844	64.435	19.696	29.623	82.153	6.649
2800	8.863	64.757	20.582	29.810	84.093	6.563
2900	8.879	65.069	21.469	30.001	86.028	6.483
3000	8.895	65.370	22.357	30.194	87.957	6.407
3100	8.910	65.662	23.248	30.388	89.878	6.336
3200	8.924	65.945	24.139	30.586	91.795	6.269
3300	8.937	66.220	25.032	30.786	93.707	6.206
3400	8.949	66.487	25.927	30.988	95.609	6.145
3500	8.961	66.746	26.822	31.192	97.509	6.088
3600	8.973	66.999	27.719	31.399	99.400	6.034
3700	8.984	67.245	28.617	31.608	101.286	5.982
3800	8.994	67.485	29.516	31.818	103.164	5.933
3900	9.004	67.718	30.419	32.031	105.039	5.886
4000	9.014	67.946	31.316	32.247	106.908	5.841
4100	9.024	68.169	32.218	32.464	108.774	5.798
4200	9.033	68.387	33.121	32.684	110.630	5.756
4300	9.042	68.599	34.025	32.906	112.483	5.717
4400	9.051	68.807	34.930	33.130	114.333	5.679
4500	9.059	69.011	35.835	33.356	116.177	5.642
4600	9.068	69.210	36.741	33.584	118.012	5.607
4700	9.076	69.405	37.649	33.814	119.845	5.573
4800	9.084	69.596	38.557	34.046	121.672	5.540
4900	9.092	69.784	39.465	34.280	123.501	5.508
5000	9.100	69.967	40.375	34.516	125.335	5.477
5100	9.107	70.148	41.285	34.755	127.132	5.448
5200	9.115	70.325	42.196	34.995	128.941	5.419
5300	9.123	70.498	43.108	35.237	130.741	5.391
5400	9.130	70.669	44.021	35.480	132.542	5.364
5500	9.138	70.836	44.934	35.727	134.346	5.338
5600	9.145	71.001	45.849	35.974	136.129	5.312
5700	9.153	71.165	46.763	36.225	137.919	5.288
5800	9.160	71.328	47.679	36.476	139.696	5.264
5900	9.167	71.491	48.595	36.730	141.473	5.240
6000	9.175	71.653	49.513	36.983	143.249	5.218

(IDEAL GAS)

CARBON DIOXIDE (CO<sub>2</sub>)

$\Delta H_f^0 = -93.965 \pm 0.011 \text{ kcal. mole}^{-1}$

$\Delta H_f^0 = -94.054 \pm 0.011 \text{ kcal. mole}^{-1}$

Point Group D<sub>∞h</sub>

$S_{298.15} = 51.07 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
1342.86 (1)
667.30 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å

Bond Angle: O-C-O = 180°

Rotational Constant: B<sub>0</sub> = 0.39038 cm.<sup>-1</sup>

σ = 2

Heat of Formation.

The enthalpy change ( $\Delta H_f^0$  298.15) of the reaction C(c, graphite) + O<sub>2</sub>(g) = CO<sub>2</sub>(g) has been measured by P. H. Dewey and D. R. Harper, J. Res. Natl. Bur. Std. 21, 457 (1938), R. S. Jessup, *ibid.* 21, 491 (1938), and E. J. Prosen and F. D. Rossini, *ibid.*, 33, 439 (1944). Based on these data, the heat of formation ( $\Delta H_f^0$  298.15) for CO<sub>2</sub>(g) was reported to be -94.0518 ± 0.0108 kcal. mole<sup>-1</sup>, using molecular weight of CO<sub>2</sub> = 44.010, by E. J. Prosen, R. S. Jessup and F. D. Rossini, J. Research Natl. Bur. Standards 53, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole<sup>-1</sup>, based on molecular weight of CO<sub>2</sub> = 44.011, for internal consistency.

Heat Capacity and Entropy.

The functions adopted here were obtained from H. W. Woolley, J. Research Nat. Bur. Standards 52, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., J. Chem. Phys. 30, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtney, Mem. soc. roy. Liege 18, 496 (1957) and V. R. Stull, P. J. Wyatt and G. N. Plass, J. Chem. Phys. 37, 1442 (1962). The high-resolution infrared spectrum of <sup>18</sup>O-enriched CO<sub>2</sub> was examined in the region 5400-1620 cm.<sup>-1</sup>, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm.<sup>-1</sup> by C. V. Berney, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B<sub>0</sub>, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r<sub>e</sub>, was calculated from B<sub>0</sub> which was derived from B<sub>0</sub>, using B<sub>e</sub>-B<sub>0</sub> = 0.0011 cm.<sup>-1</sup> given in G. Herzberg, loc. cit. The principal moment of inertia is I = 7.1495 X 10<sup>-39</sup> g. cm.<sup>2</sup>

Heat capacities of CO<sub>2</sub>(g) at high pressures were reported by M. P. Vukalovich, V. V. Altunin and A. N. Gureev, Teploenergetika, 12 (7), 58 (1965); K. Krueger, Ver. Deut. Ingr. Z., 106 (52) 1620 (1964), and M. P. Vukalovich and A. N. Gureev, Teploenergetika, 11 (8), 80 (1964).

T. °K.	C <sub>p</sub>	S°	-(H°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.491	42.758	58.188	2.238	93.965	93.965	INFINITE
200	7.734	51.849	61.843	8.15	94.028	94.100	205.645
298	8.874	51.072	62.418	20.818	94.054	94.265	102.922
300	8.896	51.127	62.418	21.857	94.054	94.265	69.095
400	9.877	53.830	64.334	9.266	94.055	94.267	68.670
500	10.656	56.122	65.594	10.652	94.070	94.335	51.540
600	11.310	58.126	66.596	11.788	94.091	94.399	41.260
700	11.846	59.910	67.469	12.861	94.124	94.458	34.405
800	12.293	61.522	68.222	13.867	94.169	94.510	29.506
900	12.667	62.992	68.884	14.811	94.218	94.556	25.830
1000	12.980	64.344	69.466	15.709	94.270	94.596	22.970
1100	13.243	65.594	69.977	16.562	94.321	94.628	20.680
1200	13.466	66.756	70.422	17.385	94.371	94.658	18.806
1300	13.656	67.841	70.824	18.181	94.419	94.681	17.243
1400	13.815	68.859	71.188	18.947	94.469	94.701	15.920
1500	13.953	69.817	71.522	19.684	94.515	94.716	14.805
1600	14.074	70.722	71.830	20.397	94.562	94.728	13.881
1700	14.177	71.574	72.112	21.087	94.607	94.739	12.940
1800	14.266	72.381	72.372	21.754	94.656	94.746	12.180
1900	14.342	73.145	72.612	22.401	94.706	94.750	11.584
2000	14.404	73.869	72.824	23.031	94.758	94.751	10.898
2100	14.459	74.554	73.012	23.646	94.811	94.752	10.353
2200	14.507	75.200	73.172	24.246	94.865	94.746	9.860
2300	14.548	75.808	73.307	24.831	94.916	94.735	9.411
2400	14.582	76.381	73.418	25.401	94.964	94.724	9.001
2500	14.609	76.919	73.504	25.956	95.009	94.714	8.625
2600	14.629	77.424	73.567	26.496	95.051	94.704	8.280
2700	14.644	77.897	73.607	27.021	95.090	94.698	7.960
2800	14.655	78.339	73.624	27.531	95.127	94.683	7.664
2900	14.662	78.749	73.618	28.026	95.162	94.669	7.388
3000	14.673	79.128	73.594	28.506	95.195	94.657	7.132
3100	14.682	79.477	73.551	28.971	95.226	94.645	6.892
3200	14.688	79.797	73.491	29.421	95.254	94.631	6.668
3300	14.692	80.089	73.418	29.856	95.280	94.616	6.458
3400	14.696	80.354	73.334	30.276	95.304	94.601	6.260
3500	14.699	80.594	73.241	30.681	95.326	94.585	6.074
3600	14.700	80.809	73.139	31.071	95.346	94.568	5.898
3700	14.700	80.999	73.021	31.446	95.363	94.551	5.732
3800	14.700	81.164	72.888	31.806	95.378	94.534	5.574
3900	14.700	81.314	72.741	32.151	95.391	94.517	5.425
4000	14.700	81.449	72.581	32.481	95.402	94.500	5.283
4100	14.700	81.571	72.406	32.796	95.411	94.483	5.149
4200	14.700	81.681	72.216	33.106	95.418	94.466	5.020
4300	14.700	81.779	72.011	33.411	95.424	94.449	4.898
4400	14.700	81.864	71.791	33.711	95.429	94.432	4.781
4500	14.700	81.936	71.556	34.006	95.433	94.415	4.670
4600	14.700	82.004	71.306	34.296	95.436	94.398	4.563
4700	14.700	82.068	71.041	34.581	95.438	94.381	4.460
4800	14.700	82.128	70.761	34.861	95.439	94.364	4.362
4900	14.700	82.184	70.466	35.136	95.440	94.347	4.268
5000	14.700	82.236	70.156	35.406	95.441	94.330	4.178
5100	14.700	82.284	69.831	35.671	95.441	94.313	4.091
5200	14.700	82.328	69.491	35.931	95.441	94.296	4.008
5300	14.700	82.368	69.136	36.186	95.441	94.279	3.927
5400	14.700	82.404	68.766	36.436	95.441	94.262	3.850
5500	14.700	82.436	68.381	36.681	95.441	94.245	3.775
5600	14.700	82.464	67.981	36.921	95.441	94.228	3.703
5700	14.700	82.488	67.566	37.156	95.441	94.211	3.633
5800	14.700	82.508	67.136	37.386	95.441	94.194	3.566
5900	14.700	82.524	66.691	37.611	95.441	94.177	3.501
6000	14.700	82.536	66.231	37.831	95.441	94.160	3.438
6100	14.700	82.544	65.756	38.046	95.441	94.143	3.377
6200	14.700	82.549	65.266	38.256	95.441	94.126	3.317



Point Group D<sub>3d</sub> ΔH<sub>f</sub><sup>0</sup> = -314.8 kcal. mole<sup>-1</sup>

S<sub>298.15</sub><sup>0</sup> = 79.368 cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>298.15</sup> = -316.8 kcal. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm. <sup>-1</sup>	ω, cm. <sup>-1</sup>	g, cm. <sup>-1</sup>
1228 (1)	1243 (2)	
607 (1)	619 (2)	
348 (1)	376 (2)	
Torsion		
1117 (1)	523 (2)	
714 (1)	220 (2)	

Bond Distances: C-C = 1.56 Å C-F = 1.32 Å

Bond Angle: C-C-F = 109.5°

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 60,070 X 10<sup>-117</sup> g.<sup>3</sup> cm.<sup>6</sup>

Barrier to Internal Rotation: V = 3960 cal. mole<sup>-1</sup>

Reduced Moment of Inertia: I<sub>red</sub> = 73.2 X 10<sup>-40</sup> g. cm.<sup>2</sup>

Heat of Formation.

F. W. Kirkbride and F. G. Davidson, Nature 174, 79 (1954) measured the enthalpy of reaction of C<sub>2</sub>F<sub>6</sub> and elemental potassium to form KP and amorphous carbon. Combining ΔH<sub>f</sub> with their estimate of +2.5 kcal. mole<sup>-1</sup> for the heat of formation of the amorphous carbon and the current JANAF heat of formation of KP(c) of -135.6 kcal. mole<sup>-1</sup> yields for C<sub>2</sub>F<sub>6</sub> a ΔH<sub>f</sub><sup>298</sup>(g) = -309.6 kcal. mole<sup>-1</sup>. E. Tschuikow-Roux, J. Phys. Chem. 69, 1075 (1965) determined the dissociation energy to CF<sub>3</sub> radicals as 95 ± 4 kcal. mole<sup>-1</sup>. Combining with the current JANAF value of -115.7 kcal. mole<sup>-1</sup> for CF<sub>3</sub>, there is derived for C<sub>2</sub>F<sub>6</sub> a ΔH<sub>f</sub><sup>298</sup>(g) = -324.4 kcal. mole<sup>-1</sup>. The enthalpy of reaction of NF<sub>3</sub> and C<sub>2</sub>F<sub>6</sub> to form CF<sub>4</sub> and N<sub>2</sub> was measured by G. C. Sinke, Quarterly Progress Report AR-30-65, Dow Chemical Co., Contract No. APO4(611)-7554(4). Combined with current JANAF values of -30.4 and -220.5 kcal. mole<sup>-1</sup> for NF<sub>3</sub> and CF<sub>4</sub>, respectively, there is derived for C<sub>2</sub>F<sub>6</sub> a ΔH<sub>f</sub><sup>298</sup>(g) = -316.8 kcal. mole<sup>-1</sup>. This last result is close to an average of the first two and is adopted.

Heat Capacity and Entropy.

The vibrational frequencies are from R. A. Carney, E. A. Plotrowski, A. G. Meister, J. H. Braun, and F. P. Cleveland, J. Mol. Spectroscopy 7, 209 (1961). They also reviewed the previous literature on the spectra of C<sub>2</sub>F<sub>6</sub>. Bond distances and angles were determined by electron diffraction by D. A. Swick and I. L. Karle, J. Chem. Phys. 23, 1499 (1955). Low temperature thermal data were reported by E. L. Pace and J. G. Aston, J. Am. Chem. Soc. 70, 566 (1948). They derived a third law entropy of the ideal gas at 194.87°K. of 69.88 cal. mole<sup>-1</sup> deg.<sup>-1</sup> which serves to fix the barrier to internal rotation at 3960 cal. mole<sup>-1</sup>. Thermodynamic functions are calculated on the basis of these parameters. The three principal moments of inertia are I<sub>A</sub> = 2.9303 X 10<sup>-38</sup> and I<sub>B</sub> = I<sub>C</sub> = 4.5275 X 10<sup>-38</sup> g. cm.<sup>2</sup>

T. °K.	C <sub>p</sub>	S <sup>0</sup> - (F <sup>0</sup> - H <sub>298</sub> <sup>0)/T</sup>	H <sup>0</sup> - H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sup>0</sup>	Log K <sub>p</sub>
0		INFINITE	0	314.807	314.807	INFINITE
100	4.000	59.332	4.861	315.931	309.614	676.628
200	7.173	70.413	2.227	316.562	303.030	331.120
298	23.432	79.368	0.000	316.800	296.320	217.198
300	25.0526	79.576	0.047	316.803	296.164	215.767
400	30.0336	87.451	2.834	316.818	289.349	186.066
500	33.2255	94.578	6.007	316.704	282.452	123.454
600	35.5542	100.855	9.453	316.510	275.618	100.389
700	37.1157	106.463	13.093	316.273	268.820	83.925
800	38.1315	111.504	16.869	316.013	262.060	71.588
900	41.1859	116.067	20.744	315.740	255.334	62.001
1000	39.791	120.226	24.692	315.459	248.638	54.337
1100	40.263	124.041	28.695	315.178	241.970	48.073
1200	40.652	127.562	32.742	314.894	235.325	42.856
1300	40.941	130.827	36.822	314.621	228.704	38.447
1400	41.185	133.870	40.928	314.348	222.103	34.670
1500	41.375	136.719	45.057	314.080	215.523	31.400
1600	41.541	139.394	49.203	313.819	208.965	28.542
1700	41.681	141.916	53.363	313.561	202.417	26.021
1800	41.771	144.301	57.535	313.313	195.892	23.783
1900	41.859	146.562	61.717	313.067	189.372	21.782
2000	41.937	148.712	65.908	312.827	182.865	19.982
2100	42.002	150.769	70.107	312.592	176.373	18.353
2200	42.059	152.717	74.312	312.368	169.898	16.875
2300	42.115	154.588	78.523	312.146	163.419	15.528
2400	42.165	156.383	82.739	311.934	156.961	14.293
2500	42.210	158.106	86.960	311.728	150.511	13.157
2600	42.256	159.768	91.185	311.529	144.064	12.109
2700	42.299	161.359	95.413	311.337	137.627	11.140
2800	42.339	162.887	99.643	311.145	131.196	10.240
2900	42.376	164.359	103.879	310.972	124.766	9.402
3000	42.410	165.780	108.110	310.804	118.360	8.622
3100	42.440	167.160	112.355	310.639	111.944	7.892
3200	42.465	168.507	116.607	310.488	105.538	7.207
3300	42.485	169.822	120.864	310.348	99.138	6.565
3400	42.502	171.110	125.130	310.217	92.737	5.961
3500	42.517	172.381	129.409	310.068	86.341	5.391
3600	42.529	173.634	133.682	309.943	79.949	4.853
3700	42.538	174.872	137.951	309.829	73.562	4.345
3800	42.545	176.096	142.218	309.722	67.172	3.863
3900	42.550	177.307	146.483	309.627	60.795	3.407
4000	42.553	178.507	150.748	309.536	54.412	2.973
4100	42.554	179.687	155.013	309.447	48.041	2.561
4200	42.558	180.844	159.278	309.388	41.663	2.168
4300	42.559	181.981	163.543	309.325	35.286	1.793
4400	42.560	183.100	167.808	309.275	28.916	1.436
4500	42.565	184.200	172.073	309.232	22.555	1.095
4600	42.569	185.284	176.338	309.198	16.178	0.769
4700	42.572	186.352	180.603	309.175	9.808	0.456
4800	42.575	187.406	184.868	309.161	3.429	0.156
4900	42.578	188.446	189.133	309.157	-3.039	-0.131
5000	42.580	189.473	193.400	309.163	-9.307	-0.407
5100	42.581	188.377	197.670	309.181	15.958	0.671
5200	42.582	189.242	201.942	309.207	22.644	1.126
5300	42.583	190.075	206.213	309.243	29.329	1.572
5400	42.584	190.878	210.484	309.291	36.014	2.018
5500	42.585	191.653	214.755	309.349	42.700	2.464
5600	42.586	192.400	219.026	309.417	49.386	2.910
5700	42.587	193.114	223.297	309.498	56.072	3.356
5800	42.588	193.814	227.568	309.585	62.758	3.802
5900	42.589	194.490	231.839	309.685	69.444	4.248
6000	42.590	195.143	236.110	309.795	76.130	4.694

MOL. WT. = 28.05418

(IDEAL GAS)

ETHYLENE (C<sub>2</sub>H<sub>4</sub>)

Point Group D<sub>2h</sub>  
 $\Delta H_f^0 = 14.58 \pm 0.07 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 = 52.396 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^0 298.15 = 12.54 \pm 0.07 \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
3026.4 (1)	3102.5 (1)	3105.5 (1)
1622.9 (1)	1222.0 (1)	826.0 (1)
1342.2 (1)	949.3 (1)	2988.7 (1)
1023.0 (1)	943.0 (1)	1443.5 (1)

Bond Distance: H-C = 1.086 Å C-C = 1.337 Å  
 Bond Angle: H-C-H = 117° 22' H-C-C = 121° 19'

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 5.4466 X 10<sup>-117</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The heat of combustion of ethylene was measured by P. D. Rossini and J. W. Knowlton, J. Res. Natl. Bur. Std. 19, 249 (1937). From the value,  $\Delta H_f^0 298.15 = -337.28 \pm 0.07 \text{ kcal. mole}^{-1}$  for the reaction C<sub>2</sub>H<sub>4</sub>(g) + 3 O<sub>2</sub>(g) = 2 CO<sub>2</sub>(g) + 2 H<sub>2</sub>O(l), the heat of formation ( $\Delta H_f^0 298.15$ ) for C<sub>2</sub>H<sub>4</sub>(g) was derived to be 12.54 ± 0.07 kcal. mole<sup>-1</sup>. The values of  $\Delta H_f^0 298.15$  for CO<sub>2</sub>(g) and H<sub>2</sub>O(l) used for calculation were obtained from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and Irving Jaffe, "Selected Values of Chemical Thermodynamic Properties", Circular of the National Bureau of Standards 500, 1952.

Heat Capacity and Entropy.

The molecular structure, bond distances and angles were obtained from H. C. Allen, Jr. and E. K. Plyler, J. Chem. Phys. 40, 2085 (1964). Eight of the vibrational frequencies were taken from W. L. Smith and I. M. Mills, J. Chem. Phys. 18, 118 (1950); B. L. Crawford, J. E. Lancaster and R. Inskoop, J. Chem. Phys. 21, 678 (1953); B. P. Stoicheff, J. Chem. Phys. 21, 755 (1953); T. Feldman, J. Romanko and H. L. Welsh, Can. J. Phys. 34, 737 (1956); and H. C. Allen and E. K. Plyler, loc. cit. G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York, 1945, also reported the vibrational frequencies for ethylene as 3019.3 (1), 1623.3 (1), 1342.4 (1), 825.0 (1), 3272.3 (1), 1050 (1), 949.2 (1), 943 (1), 3105.5 (1), 995 (1), 2989.5 (1) and 1443.5 (1) which are very close to the values adopted. The infrared and Raman spectra of ethylene before 1945 have been summarized by J. Herzberg, loc. cit. The molecular structure of ethylene was also determined by L. S. Bartell and R. A. Bonham, J. Chem. Phys. 27, 1414 (1957). Their results, r<sub>C-H</sub> = 1.085 Å, r<sub>C-C</sub> = 1.334 Å and  $\angle \text{H-C-H} = 116^\circ$  are in excellent agreement with the values adopted. The three principal moments of inertia are I<sub>A</sub> = 0.5762 X 10<sup>-39</sup>, I<sub>B</sub> = 2.7999 X 10<sup>-39</sup> and I<sub>C</sub> = 3.3761 X 10<sup>-39</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> )/T	H <sup>o</sup> -H <sub>298</sub>	ΔF <sup>o</sup>	ΔF <sup>o</sup>	Log K <sub>p</sub>
0	.000	INFINITE	-	2.514	14.578	14.578	INFINITE
100	7.952	43.125	60.316	1.719	13.827	14.434	- 31.544
200	8.451	48.721	53.275	.909	13.275	15.227	- 16.638
298	10.250	52.396	52.396	.000	12.540	16.338	- 11.975
300	10.292	52.459	52.396	.019	12.525	16.361	- 11.918
400	12.679	55.745	52.828	1.167	11.793	17.752	- 9.699
500	14.933	58.821	53.722	2.550	11.140	18.319	- 8.444
600	16.889	61.721	54.816	4.143	10.577	21.008	- 7.652
700	18.574	64.454	55.999	5.918	10.098	22.788	- 7.114
800	20.039	67.033	57.219	7.851	9.701	24.628	- 6.728
900	21.320	69.468	58.466	9.920	9.372	26.514	- 6.438
1000	22.443	71.774	59.665	12.109	9.113	28.431	- 6.213
1100	23.427	73.960	60.866	14.404	8.910	30.373	- 6.034
1200	24.290	76.036	62.044	16.811	8.757	32.330	- 5.899
1300	25.044	78.011	63.197	19.258	8.638	34.302	- 5.786
1400	25.706	79.892	64.323	21.747	8.537	36.286	- 5.694
1500	26.285	81.686	65.421	24.287	8.457	38.286	- 5.625
1600	26.794	83.399	66.492	27.051	8.385	40.246	- 5.567
1700	27.242	85.037	67.535	29.753	8.330	42.237	- 5.520
1800	27.643	86.605	68.548	32.498	8.288	44.224	- 5.480
1900	27.986	88.109	69.541	35.279	8.253	46.215	- 5.446
2000	28.296	89.552	70.506	38.094	8.228	48.204	- 5.421
2100	28.571	90.940	71.446	40.937	8.169	50.192	- 5.223
2200	28.818	92.275	72.362	43.807	8.093	52.174	- 5.183
2300	29.038	93.561	73.256	46.700	8.024	54.163	- 5.146
2400	29.236	94.801	74.128	49.614	7.964	56.148	- 5.113
2500	29.414	95.998	74.979	52.546	7.914	58.124	- 5.081
2600	29.575	97.155	75.810	55.496	7.872	60.109	- 5.052
2700	29.721	98.274	76.621	58.461	7.837	62.085	- 5.025
2800	29.853	99.357	77.414	61.440	7.806	64.064	- 5.000
2900	29.973	100.407	78.189	64.431	7.779	66.047	- 4.977
3000	30.083	101.425	78.947	67.434	7.755	68.019	- 4.955
3100	30.184	102.413	79.688	70.447	7.735	69.996	- 4.934
3200	30.276	103.373	80.413	73.470	7.717	71.971	- 4.915
3300	30.360	104.305	81.123	76.502	7.702	73.947	- 4.897
3400	30.438	105.213	81.819	79.542	7.688	75.920	- 4.880
3500	30.510	106.096	82.499	82.590	7.676	77.894	- 4.864
3600	30.577	106.957	83.167	85.644	7.664	79.864	- 4.848
3700	30.638	107.795	83.821	88.705	7.652	81.834	- 4.834
3800	30.695	108.613	84.463	91.772	7.640	83.802	- 4.821
3900	30.748	109.411	85.092	94.844	7.628	85.768	- 4.808
4000	30.797	110.190	85.710	97.921	7.616	87.735	- 4.796
4100	30.843	110.951	86.317	101.003	7.604	89.706	- 4.784
4200	30.886	111.695	86.912	104.090	7.592	91.679	- 4.773
4300	30.926	112.422	87.497	107.180	7.580	93.653	- 4.762
4400	30.964	113.134	88.071	110.275	7.568	95.628	- 4.752
4500	30.999	113.830	88.636	113.373	7.556	97.603	- 4.742
4600	31.032	114.512	89.191	116.475	7.544	99.578	- 4.734
4700	31.063	115.180	89.737	119.579	7.532	101.553	- 4.725
4800	31.093	115.834	90.274	122.687	7.520	103.528	- 4.718
4900	31.120	116.475	90.802	125.798	7.508	105.503	- 4.710
5000	31.146	117.104	91.322	128.911	7.496	107.478	- 4.703
5100	31.171	117.721	91.834	132.027	7.484	109.453	- 4.696
5200	31.194	118.327	92.337	135.145	7.472	111.428	- 4.688
5300	31.216	118.921	92.833	138.266	7.460	113.403	- 4.681
5400	31.236	119.505	93.322	141.388	7.448	115.378	- 4.674
5500	31.256	120.078	93.803	144.513	7.436	117.353	- 4.667
5600	31.275	120.641	94.277	147.639	7.424	119.328	- 4.661
5700	31.292	121.195	94.745	150.768	7.412	121.303	- 4.655
5800	31.309	121.740	95.205	153.898	7.400	123.278	- 4.650
5900	31.325	122.275	95.660	157.030	7.388	125.253	- 4.645
6000	31.340	122.802	96.108	160.163	7.376	127.228	- 4.640

Dec. 31, 1960; Sept. 30, 1965

$\Delta H_f^0 = -9.59 \pm 0.15 \text{ kcal. mole}^{-1}$

$\Delta H_f^0 = -12.58 \pm 0.15 \text{ kcal. mole}^{-1}$

Point Group C<sub>2v</sub>

$S_{298.15} = 58.06 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
3005 (1)	3065 (1)	1153 (1)
1480 (1)	[1345](1)	892 (1)
1266 (1)	807 (1)	3079 (1)
1120 (1)	3019 (1)	1143 (1)
877 (1)	1470 (1)	832 (1)

Bond Distance: C-H = 1.0802 Å C-O = 1.4363 Å C-C = 1.4728 Å

Bond Angle: H-C-H = 116° 51' H<sub>2</sub>C-C = 158° 51'  
H<sub>2</sub>C-O = 142° 45.6'

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 7.42336 X 10<sup>-116</sup> g.<sup>3</sup> cm.<sup>6</sup>

$\sigma = 2$

Heat of Formation.

The heat of combustion of ethylene oxide (g) was determined by A. S. Fell and G. Pilcher, Trans. Faraday Soc. 51, 71 (1955) and R. S. Crog and H. Hunt, J. Phys. Chem. 45, 1162 (1942), as -312.15 ± 0.14 and -312.55 ± 0.20 kcal. mole<sup>-1</sup>, respectively. The corresponding value of  $\Delta H_f^0$  (C<sub>2</sub>H<sub>4</sub>O, g) was evaluated to be -12.58 ± 0.15 and -12.19 ± 0.22 kcal. mole<sup>-1</sup>. The former value is adopted.

Heat Capacity and Entropy.

The vibrational frequencies were taken from R. C. Lord and B. Molin, J. Chem. Phys. 24, 656 (1956). The infrared and Raman spectra of ethylene oxide have also been examined by J. W. Linnett, J. Chem. Phys. 5, 692 (1938) and H. W. Thompson and W. T. Cave, Trans. Faraday Soc., 47, 946 (1951). The vibrational frequencies assigned were slightly different from the ones reported by R. C. Lord and B. Molin, loc. cit. As a result of analogies between ethylene oxide and ethylene imine, small changes of R. C. Lord and B. Molin's assignment have been made by W. J. Potts, Spectrochim. Acta, 21, 511 (1965). The bond distances and angles were obtained from G. L. Cunningham, A. W. Boyd and W. D. Gwinn, J. Chem. Phys. 11, 211 (1949). The investigation of the structure of ethylene oxide by electron diffraction was reported by P. C. Ackermann and J. E. Mayer, J. Chem. Phys. 4, 377 (1936) and M. Igarashi, Bull. Chem. Soc. Japan, 25, 350 (1953). The three principal moments of inertia are: I<sub>A</sub> = 3.8052 X 10<sup>-39</sup>, I<sub>B</sub> = 3.2786 X 10<sup>-39</sup> and I<sub>C</sub> = 5.9499 X 10<sup>-39</sup> g. cm.<sup>2</sup>

The calculated heat capacities (307.2 - 371.2°K.) are in good agreement with the experimentally measured ones reported by G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. 8, 618 (1940).

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298°)/T</sub>	H° - H <sub>298°</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.0000	INFINITE	2.596	9.587	9.587	INFINITE
100	7.956	48.444	1.801	10.544	18.670	18.670
200	8.772	54.102	.861	11.576	6.077	6.640
298	11.449	58.056	.000	12.580	3.164	2.319
300	11.510	58.056	.021	12.599	3.107	2.263
400	14.913	61.904	1.342	13.514	3.201	1.110
500	18.023	65.575	2.993	14.264	3.719	1.625
600	20.629	69.099	4.930	14.861	7.373	2.685
700	22.793	72.446	7.100	15.330	11.119	3.471
800	24.611	75.612	9.477	15.686	14.922	4.076
900	26.155	78.602	12.017	15.951	18.764	4.556
1000	27.477	81.428	14.701	16.129	22.631	4.946
1100	28.615	84.102	17.507	16.240	26.512	5.267
1200	29.597	86.632	20.418	16.293	30.404	5.537
1300	30.477	89.032	23.432	16.304	34.294	5.765
1400	31.284	91.322	26.504	16.273	38.189	5.961
1500	31.826	93.496	29.655	16.218	42.078	6.131
1600	32.286	95.568	32.867	16.141	45.957	6.277
1700	32.676	97.547	36.130	16.040	49.837	6.407
1800	33.006	99.438	39.440	15.927	53.708	6.521
1900	33.286	101.249	42.790	15.801	57.576	6.622
2000	33.522	102.986	46.175	15.665	61.433	6.713
2100	33.719	104.653	49.593	15.522	65.288	6.794
2200	33.885	106.258	53.038	15.379	69.128	6.867
2300	34.022	107.799	56.509	15.228	72.969	6.933
2400	34.134	109.284	60.002	15.080	76.804	6.994
2500	34.226	110.719	63.515	14.933	80.622	7.048
2600	34.298	112.104	67.046	14.786	84.446	7.098
2700	34.354	113.443	70.594	14.641	88.256	7.143
2800	34.395	114.739	74.157	14.498	92.063	7.186
2900	34.423	115.994	77.733	14.360	95.872	7.225
3000	34.441	117.210	81.321	14.226	99.687	7.260
3100	34.448	118.390	84.921	14.093	103.464	7.294
3200	34.446	119.537	88.530	13.968	107.251	7.325
3300	34.437	120.650	92.150	13.850	111.037	7.353
3400	34.421	121.731	95.777	13.736	114.869	7.380
3500	34.396	122.787	99.413	13.631	118.697	7.405
3600	34.366	123.813	103.056	13.531	122.375	7.429
3700	34.332	124.814	106.706	13.434	126.048	7.451
3800	34.292	125.789	110.363	13.342	129.725	7.472
3900	34.249	126.740	114.025	13.252	133.406	7.492
4000	34.201	127.668	117.692	13.164	137.066	7.510
4100	34.150	128.575	121.365	13.075	140.726	7.528
4200	34.100	129.461	125.042	13.000	144.398	7.545
4300	34.053	130.328	128.724	13.067	148.075	7.560
4400	34.010	131.175	132.410	13.034	151.751	7.575
4500	33.975	132.004	136.099	13.013	155.427	7.589
4600	33.950	132.816	139.793	12.999	160.043	7.603
4700	33.933	133.611	143.489	12.996	164.606	7.617
4800	33.924	134.390	147.189	13.001	169.170	7.629
4900	33.923	135.153	150.892	13.015	173.733	7.641
5000	33.931	135.902	154.608	13.039	178.299	7.653
5100	33.947	136.636	158.306	13.075	182.851	7.664
5200	33.971	137.357	162.017	13.117	187.361	7.675
5300	33.999	138.064	165.730	13.169	191.839	7.686
5400	34.031	138.759	169.446	13.232	196.284	7.695
5500	34.067	139.441	173.164	13.305	200.701	7.705
5600	34.107	140.111	176.883	13.387	205.096	7.714
5700	34.151	140.770	180.605	13.480	209.471	7.723
5800	34.199	141.417	184.328	13.583	213.828	7.733
5900	34.250	142.054	188.054	13.694	218.167	7.742
6000	34.277	142.681	191.780	13.815	222.460	7.749

Point Group [D<sub>2h</sub>]

ΔH<sub>f</sub><sup>0</sup> = [-2 ± 10] kcal. mole<sup>-1</sup>

S<sub>298.15</sub><sup>0</sup> = [89.15] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω <sub>v</sub> , cm. <sup>-1</sup>	ω <sub>v</sub> , cm. <sup>-1</sup>	ω <sub>v</sub> , cm. <sup>-1</sup>
[240] (1)	[220] (1)	[2158] (1)
[150] (1)	[225] (1)	[2158] (1)
[205] (1)	[207] (1)	[2158] (1)
[130] (1)	[207] (1)	[2158] (1)

Bond Distance: K-C = [2.75] Å C-N = [1.16] Å

Bond Angle: N-C-K = [140]° C-K-C = [100]° K-C-K = [80]°

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [2.94818 X 10<sup>-112</sup>] g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation

ΔH<sub>f</sub><sup>0</sup> 298.15 ((KCN)<sub>2</sub>; g) was calculated based on an estimated heat of dissociation, 40 kcal. mole<sup>-1</sup> for the reaction (KCN)<sub>2</sub>(g) → 2KCN(g), which was obtained by comparison with that for (NaCN)<sub>2</sub>(g).

Heat Capacity and Entropy

The molecular structure and bond angles were assumed to be the same as those for KCN(c) reported by J. M. Bljvoest and J. A. Lely, Rec. trav. chim. 59, 908 (1940). The C-N bond distance was assumed to be the same as that for KCN(g), and the K-C bond distance was assumed to be 10% longer than that in KCN(g). The vibrational frequencies were estimated by comparison with those for K<sub>2</sub>P<sub>2</sub>(g). The last six frequencies were adopted from the bending and asymmetric stretching frequencies for KCN(g). The three principal moments of inertia are: I<sub>A</sub> = 4.05745 X 10<sup>-38</sup>, I<sub>B</sub> = 6.73351 X 10<sup>-38</sup> and I<sub>C</sub> = 1.079096 X 10<sup>-37</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub> <sup>0</sup>	S <sup>0</sup>	-(F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	18.534	63.656	111.235	5.924	1.962	1.962	INFINITE
200	24.722	78.921	91.523	4.758	2.337	3.147	6.879
298	26.353	89.153	89.153	4.000	2.198	4.353	3.597
300	26.371	89.153	89.153	4.049	1.998	4.925	3.588
400	27.081	97.009	90.197	2.725	3.139	5.690	3.109
500	27.586	103.108	92.190	5.455	3.232	6.319	2.762
600	28.050	108.170	94.444	8.241	3.370	6.924	2.522
700	28.489	112.156	96.545	11.039	3.525	7.501	2.362
800	28.893	115.337	98.405	13.939	3.723	8.051	2.269
900	29.252	119.791	101.075	16.844	4.018	8.573	2.082
1000	29.565	122.890	103.104	19.786	4.303	9.066	1.866
1100	29.834	125.721	105.033	22.756	4.586	9.529	1.622
1200	30.064	128.337	106.667	25.752	4.868	9.965	1.360
1300	30.261	130.741	108.012	28.768	5.149	10.378	1.081
1400	30.429	132.990	110.274	31.803	5.428	10.767	0.787
1500	30.573	135.094	111.859	34.853	5.705	11.134	0.480
1600	30.697	137.072	113.374	37.917	5.980	11.481	0.164
1700	30.804	138.936	114.823	40.992	6.254	11.810	-0.161
1800	30.897	140.699	116.212	44.077	6.527	12.122	-0.480
1900	30.979	142.372	117.545	47.171	6.800	12.418	-0.793
2000	31.050	143.963	118.827	50.273	7.073	12.699	-1.101
2100	31.112	145.479	120.060	53.381	7.346	12.965	-1.404
2200	31.167	146.928	121.249	56.495	7.619	13.217	-1.702
2300	31.216	148.315	122.395	59.614	7.892	13.456	-1.995
2400	31.260	149.644	123.503	62.738	8.165	13.683	-2.283
2500	31.299	150.921	124.575	65.866	8.438	13.898	-2.566
2600	31.334	152.149	125.612	68.998	8.711	14.103	-2.844
2700	31.365	153.332	126.617	72.133	8.984	14.298	-3.117
2800	31.394	154.474	127.591	75.271	9.257	14.483	-3.386
2900	31.419	155.576	128.537	78.411	9.530	14.658	-3.650
3000	31.443	156.641	129.456	81.554	9.803	14.823	-3.909
3100	31.464	157.673	130.350	84.700	10.076	14.978	-4.164
3200	31.483	158.672	131.220	87.847	10.349	15.123	-4.415
3300	31.501	159.641	132.066	90.996	10.622	15.258	-4.662
3400	31.518	160.582	132.891	94.147	10.895	15.383	-4.905
3500	31.533	161.495	133.695	97.300	11.168	15.500	-5.144
3600	31.547	162.384	134.480	100.454	11.441	15.609	-5.379
3700	31.559	163.248	135.246	103.609	11.714	15.711	-5.610
3800	31.571	164.090	135.994	106.766	11.987	15.807	-5.837
3900	31.582	164.910	136.725	109.923	12.260	15.898	-6.061
4000	31.592	165.710	137.440	113.082	12.533	15.984	-6.282
4100	31.602	166.490	138.139	116.242	12.806	16.066	-6.500
4200	31.611	167.252	138.823	119.402	13.079	16.144	-6.715
4300	31.619	167.996	139.493	122.564	13.352	16.218	-6.927
4400	31.627	168.723	140.149	125.726	13.625	16.288	-7.136
4500	31.634	169.434	140.792	128.889	13.898	16.354	-7.341
4600	31.641	170.129	141.422	132.053	14.171	16.417	-7.543
4700	31.647	170.810	142.040	135.217	14.444	16.477	-7.742
4800	31.653	171.481	142.646	138.382	14.717	16.534	-7.938
4900	31.659	172.145	143.240	141.546	14.990	16.588	-8.131
5000	31.664	172.798	143.826	144.714	15.263	16.640	-8.321
5100	31.669	173.495	144.399	147.881	15.536	16.689	-8.508
5200	31.674	174.190	145.063	151.048	15.809	16.735	-8.692
5300	31.678	174.816	145.715	154.215	16.082	16.778	-8.873
5400	31.682	175.406	146.361	157.383	16.355	16.818	-9.051
5500	31.686	175.987	146.996	160.552	16.628	16.855	-9.227
5600	31.690	176.558	147.122	163.720	16.901	16.889	-9.400
5700	31.694	177.019	147.640	166.890	17.174	16.920	-9.571
5800	31.697	177.412	148.150	170.059	17.447	16.948	-9.739
5900	31.700	177.812	148.651	173.229	17.720	16.973	-9.904
6000	31.703	178.245	149.145	176.399	17.993	16.995	-10.067

$$\Delta H_f^0 = [-2.0 \pm 3] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = [-2.1 \pm 3] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = [82.93] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\text{Ground State Quantum Weight} = 1$$

Vibrational Frequencies and Degeneracies

$\omega_j$ , cm. <sup>-1</sup>	$\omega_j$ , cm. <sup>-1</sup>	$\omega_j$ , cm. <sup>-1</sup>
[295](1)	[250](1)	[2176](1)
[175](1)	[290](1)	[2176](1)
[250](1)	[239](1)	[2176](1)
[170](1)	[239](1)	[2176](1)

$$\text{Bond Distance: N-C} = [1.16] \text{ \AA} \quad \text{C-Na} = [2.19] \text{ \AA}$$

$$\text{Bond Angle: C-Na-C} = [105]^\circ \quad \text{Na-C-Na} = [75]^\circ \quad \text{N-C-Na} = [142.5]^\circ$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = [4.48269 \times 10^{-113}] \text{ g.}^3 \text{ cm.}^6$$

$$\sigma = [4]$$

Heat of Formation.

The mass spectra of vapors from samples of NaCN have been observed by R. F. Porter, J. Chem. Phys. **35**, 318 (1961), at temperatures around 1000°K. The results indicate that the compound evaporates as NaCN(g) and Na<sub>2</sub>CN<sub>2</sub>(g). A comparison of relative ion currents produced by electron bombardment of NaCN vapors effusing from single- and double-oven-type Knudsen cells, yielded information on the partial pressures of monomer and dimer. Based on the partial pressures for NaCN(g) and (NaCN)<sub>2</sub>(g) reported at temperatures, 903-1049°K., the vapor pressures of (NaCN)<sub>2</sub>(g) over NaCN(l), 1078.2-1626.2°K., were calculated from the total vapor pressure measurements reported by C. K. Ingold, J. Chem. Soc. **123**, 885 (1923). By the second and third law methods, the values of  $\Delta H_f^{298.15}(1 \rightarrow \text{dimer})$  were evaluated to be 38.69 and 38.21 kcal. mole<sup>-1</sup>, respectively. Using the third law value, the heat of formation for (NaCN)<sub>2</sub>(g) was evaluated.

Heat Capacity and Entropy.

The molecular structure, bond distances and C-Na-C bond angle were estimated by R. F. Porter, loc. cit. The vibrational frequencies were estimated by comparison with those for NaCl(g). The last six frequencies were the bending and asymmetric stretching frequencies for NaCN(g). The three principal moments of inertia are:  $I_A = 1.3570 \times 10^{-38}$ ,  $I_B = 5.1090 \times 10^{-38}$  and  $I_C = 6.4660 \times 10^{-38}$  g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298<sup>o</sup>)/T</sub>	H <sup>o</sup> -H <sub>298<sup>o</sup></sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0							INFINITE
100	16.1175	56.0048		5.540	1.982	1.982	
200	21.539	73.050	85.231	4.499	2.294	3.207	7.009
298	25.737	82.032	82.032	2.436	4.039	4.039	3.692
300	25.762	83.051	82.032	4.048	2.097	5.054	3.682
400	26.716	85.667	83.056	2.676	3.346	3.948	3.250
500	27.339	86.578	85.91E	5.380	3.465	6.586	2.879
600	27.667	101.710	86.142	8.141	3.614	7.196	2.621
700	28.346	108.043	96.307	10.952	3.793	7.782	2.430
800	28.776	109.656	97.595	13.809	3.987	8.336	2.277
900	29.155	113.268	96.706	16.706	4.203	8.869	2.154
1000	29.482	116.357	96.719	19.638	4.437	9.375	2.049
1100	29.763	119.181	98.635	22.601	4.700	9.861	1.959
1200	30.002	121.781	100.457	25.589	4.940	10.322	1.712
1300	30.206	124.191	102.191	28.600	5.135	10.766	1.592
1400	30.381	126.436	103.843	31.629	5.286	11.192	1.482
1500	30.530	128.537	105.420	34.675	5.400	11.601	1.381
1600	30.659	130.512	106.927	37.735	5.485	12.000	1.289
1700	30.770	132.374	108.370	40.806	5.545	12.390	1.203
1800	30.866	134.135	109.753	43.888	5.590	12.772	1.122
1900	30.950	135.806	111.081	46.979	5.621	13.147	1.046
2000	31.024	137.396	112.357	50.078	5.640	13.514	0.974
2100	31.088	138.911	113.586	53.184	5.650	13.872	0.907
2200	31.145	140.359	114.770	56.295	5.653	14.221	0.844
2300	31.196	141.744	115.913	59.412	5.650	14.562	0.784
2400	31.241	143.073	117.017	62.534	5.642	14.896	0.727
2500	31.282	144.349	118.085	65.661	5.640	15.224	0.673
2600	31.318	145.577	119.115	68.791	5.637	15.547	0.621
2700	31.350	146.759	120.121	71.924	5.630	15.865	0.571
2800	31.379	147.890	121.093	75.060	5.620	16.178	0.522
2900	31.406	148.982	122.036	78.200	5.609	16.486	0.475
3000	31.431	150.037	122.953	81.342	5.595	16.790	0.430
3100	31.453	151.058	123.844	84.486	5.580	17.090	0.386
3200	31.473	152.047	124.712	87.632	5.565	17.386	0.343
3300	31.491	153.005	125.556	90.780	5.550	17.679	0.301
3400	31.508	153.936	126.379	93.930	5.535	17.968	0.260
3500	31.524	154.840	127.182	97.082	5.520	18.254	0.220
3600	31.538	155.817	127.964	100.235	5.505	18.537	0.180
3700	31.551	156.672	128.729	103.389	5.490	18.818	0.141
3800	31.563	157.513	129.475	106.545	5.475	19.097	0.102
3900	31.575	158.333	130.205	109.702	5.460	19.374	0.063
4000	31.585	159.133	130.91E	112.860	5.445	19.649	0.024
4100	31.595	159.913	131.616	116.019	5.430	19.922	0.000
4200	31.604	160.674	132.29E	119.179	5.415	20.193	0.000
4300	31.613	161.418	132.967	122.340	5.400	20.462	0.000
4400	31.621	162.145	133.622	125.482	5.385	20.729	0.000
4500	31.628	162.856	134.264	128.624	5.370	20.994	0.000
4600	31.635	163.551	134.893	131.767	5.355	21.257	0.000
4700	31.642	164.231	135.510	134.901	5.340	21.518	0.000
4800	31.648	164.898	136.115	138.036	5.325	21.777	0.000
4900	31.654	165.550	136.709	141.171	5.310	22.034	0.000
5000	31.659	166.190	137.293	144.306	5.295	22.289	0.000
5100	31.664	166.817	137.865	147.441	5.280	22.542	0.000
5200	31.669	167.432	138.428	150.576	5.265	22.794	0.000
5300	31.674	168.035	138.981	153.711	5.250	23.044	0.000
5400	31.678	168.627	139.524	156.846	5.235	23.292	0.000
5500	31.682	169.208	140.059	160.000	5.220	23.538	0.000
5600	31.686	169.779	140.685	163.160	5.205	23.782	0.000
5700	31.689	170.350	141.302	166.320	5.190	24.024	0.000
5800	31.692	170.900	141.911	169.480	5.175	24.264	0.000
5900	31.695	171.433	142.511	172.640	5.160	24.502	0.000
6000	31.697	171.966	143.100	175.800	5.145	24.738	0.000

$\Delta H_f^0 = -50.35 \pm 1.6$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 298.15 = -51.55 \pm 1.6$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^0 =$  Unknown

$S_{298.15} = 21.26 \pm 0.3$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_m = [2500]^{\circ}K.$

Heat of Formation.

The  $\Delta H_f^0 298.15 = -51.55 \pm 1.6$  kcal. mole<sup>-1</sup> is the average value of  $\Delta H_f^0 298.15 = -49.7 \pm 1.2$  kcal. mole<sup>-1</sup> by R. C. King and G. T. Armstrong, National Bureau of Standards Report No. 8504 (1964) and that of  $\Delta H_f^0 298.15 = -53.4 \pm 2.0$  kcal. mole<sup>-1</sup> by A. D. Mah, United States Bureau of Mines, Report No. 6415 (1964). Both measured the heat of reaction  $Al_4C_3(c) + 6O_2(g) \rightarrow 2Al_2O_3(c, \infty) + 3CO_2(g)$  and used their  $\Delta H_f^0 298.15$  and the  $\Delta H_f^0 298.15$  of  $Al_2O_3(c)$  and  $CO_2(g)$  to calculate the  $\Delta H_f^0 298.15$  of  $Al_4C_3(c)$ . The  $\Delta H_f^0 298.15$  measured by King and Armstrong was  $-1033.3 \pm 1.1$  kcal. mole<sup>-1</sup>, the  $\Delta H_f^0 298.15$  measured by Mah was  $-1029.6 \pm 1.9$  kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The low temperature heat capacities, 10-500°K., were measured by W. G. Saba and G. T. Furukawa, National Bureau of Standards Report 7587, July 1, 1962. The high temperature heat capacities, 273-1173°K., were measured by A. C. Victor, W. R. Thurber, and T. B. Douglas, National Bureau of Standards Report 7437, January 1, 1962. These two sets of heat capacity data were joined smoothly and extrapolated to 2000°K. by W. G. Saba and G. T. Furukawa, loc. cit. The values of  $C_p$  above 2000°K were estimated by extrapolation graphically.  $S_{298.15}$  was reported by W. G. Saba and G. T. Furukawa, loc. cit., using  $S_{20}^0$  (extrap.) = 0.013 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Temperature.

$T_m$  was estimated by O. Ruff and E. Jellinek, Z. anorg. u. allgem. Chem. 97, 312 (1916).

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞
100	7.899	∞	3.926	50.354	50.354	INFINITE
200	19.322	50.086	3.728	50.370	50.370	1.62461
300	27.912	11.258	2.628	50.512	48.812	35.624
298	27.912	21.264	∞	51.550	48.802	35.624
300	28.035	21.265	∞	51.554	48.802	35.392
400	33.104	30.269	22.434	51.598	47.581	25.906
500	36.064	37.997	24.792	51.594	46.579	20.359
600	38.050	44.577	27.568	51.642	45.575	16.600
700	39.479	50.734	30.459	51.786	44.553	13.909
800	40.561	56.079	33.333	52.023	43.503	11.884
900	41.411	60.907	36.133	52.372	42.419	10.300
1000	42.099	65.307	38.834	52.801	40.552	8.862
1100	42.569	69.346	41.426	53.311	38.322	7.613
1200	43.150	73.080	43.911	53.897	36.077	6.570
1300	43.863	76.551	46.290	54.558	33.829	5.687
1400	44.622	79.793	48.568	55.292	31.564	4.927
1500	45.429	82.834	50.752	56.097	29.297	4.268
1600	46.221	85.698	52.848	56.964	27.028	3.692
1700	47.074	88.405	54.860	57.891	24.755	3.182
1800	47.971	90.971	56.796	58.864	22.478	2.729
1900	48.902	93.410	58.659	59.891	20.191	2.322
2000	49.866	95.734	60.455	60.964	17.909	1.957
2100	50.862	97.953	62.188	62.094	15.626	1.626
2200	51.890	100.076	63.863	63.276	13.345	1.326
2300	52.948	102.111	65.482	64.509	11.057	1.051
2400	54.022	104.065	67.049	65.794	8.773	0.799
2500	55.106	105.945	68.567	67.131	6.490	0.567
2600	56.222	107.755	70.040	68.518	4.211	0.354
2700	57.370	109.502	71.469	69.951	1.936	0.157
2800	58.530	111.189	72.858	71.430	0.661	0.084
2900	59.722	112.819	74.208	72.954	0.340	0.047
3000	60.946	114.398	75.522	74.524	0.000	0.000

$\Delta H_f^0 = -24.14 \pm 0.44 \text{ kcal. mole}^{-1}$

$\Delta H_f^0 = 66.049 \pm 0.2 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
2200 (1)	2258 (1)	549 (2)
832 (1)	1575 (1)	63.2(2)
	578 (2)	

Bond Distance: C-C = 1.28 Å C-O = 1.16 Å

Bond Angle: C-C-C = 180° O-C-C = 180°

Rotational Constant: B<sub>0</sub> = 0.073206 cm.<sup>-1</sup>

σ = 2

Heat of Formation.

The heat of combustion of a 99.98 mole percent pure sample, which was the sample used for heat capacity determinations, has been burned in the liquid form under its own pressure by B. D. Kybett, G. K. Johnson, C. K. Barker and J. L. Margrave, J. Phys. Chem. 69, 3603 (1965). The average of four determinations gave  $\Delta H_f^0(298(1)) = -29.03 \pm 0.24 \text{ kcal. mole}^{-1}$ , the heat of vaporization at 298° was calculated to be  $5.65 \pm 0.2 \text{ kcal. mole}^{-1}$  from the data of L. A. McDougall and J. E. Kilpatrick, J. Chem. Phys. 42, 2311 (1965). Thus the heat of formation of the gas was found to be  $-23.38 \pm 0.44 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

There has been considerable controversy as to the configuration of this molecule and the assignment of its vibrational frequencies. However the evidence for the linearity of the molecule from the work of W. J. Lafferty, A. G. Maki and R. K. Plyler, J. Chem. Phys. 40, 224 (1964) and F. A. Miller and W. O. Fateley, Spect. Acta, 20, 253 (1964) seems fairly conclusive. The rotational constant adopted here is that found by Lafferty et al., the vibrational frequencies are those reported by D. A. Long, F. S. Murfin and R. L. Williams, Proc. Roy. Soc. (London) A223, 251 (1954), except for  $\nu_7$ . The low frequency  $\nu_{7a}$  mode is taken from the work of McDougall and Kilpatrick loc. cit. who measured the low temperature entropy of C<sub>3</sub>O<sub>2</sub>(c) and (l) and also the heat of vaporization. From a comparison of the entropy calculated statistically from that measured they conclude  $\nu_7 = 63.2 \text{ cm.}^{-1}$ . This is in accord with the findings of Lafferty et al. (recently F. A. Miller (private communication Oct. 1965) reports the observation of this frequency at 63 cm.<sup>-1</sup> in both gas and liquid). The values adopted are confirmed by third law analysis of the vapor pressure data of McDougall and Kilpatrick which indicated a heat of vaporization in fair agreement with their calorimetric value. The drift in the third law analysis corresponded to the entropy of the solid too low or that of the gas too high by 1 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. Alternately a systematic error in the pressure measurements could have caused this deviation.

The bond distances were taken from the electron diffraction experiments of R. L. Livingston and C. N. R. Rao, J. Am. Chem. Soc. 81, 285 (1959) and are in good accord with rotational constant adopted.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	10.861	51.981	3.593	24.142	24.142	INFINITE
200	13.399	60.186	2.668	23.952	24.935	36.493
298	16.009	66.049	∞	23.668	26.026	28.439
			∞	23.380	27.246	19.971
300	16.050	66.049	∞	23.375	27.271	19.866
400	17.977	74.436	1.030	23.121	28.609	15.650
500	18.310	75.190	6.995	22.945	30.003	13.113
600	20.433	78.813	49.503	22.845	31.426	11.446
700	21.366	82.031	71.067	22.808	32.856	10.258
800	21.815	84.941	91.842	22.808	34.279	9.369
900	21.994	87.488	111.146	22.832	35.773	8.677
1000	22.335	90.018	144.410	22.869	37.310	8.122
1100	23.786	92.264	177.022	22.921	38.892	7.667
1200	24.163	94.350	211.164	22.970	40.511	7.287
1300	24.480	96.297	246.884	23.015	42.169	6.965
1400	24.747	98.121	284.059	23.120	43.836	6.687
1500	24.973	99.837	322.740	23.197	45.499	6.446
1600	25.167	101.455	362.997	23.277	47.158	6.235
1700	25.333	102.986	404.811	23.356	48.814	6.048
1800	25.476	104.438	448.118	23.441	50.468	5.880
1900	25.600	105.818	492.957	23.528	52.121	5.730
2000	25.709	107.134	539.238	23.617	53.774	5.595
2100	25.804	108.391	586.980	23.708	55.427	5.471
2200	25.888	109.594	636.113	23.808	57.076	5.359
2300	25.962	110.746	686.643	23.907	58.721	5.256
2400	26.028	111.852	738.570	24.015	60.362	5.161
2500	26.087	112.916	791.896	24.125	62.000	5.074
2600	26.140	113.940	846.620	24.243	63.635	4.992
2700	26.187	114.928	902.753	24.364	65.268	4.917
2800	26.230	115.881	960.315	24.489	66.898	4.846
2900	26.268	116.802	1019.320	24.624	68.524	4.780
3000	26.304	117.693	1079.788	24.764	70.147	4.718
3100	26.336	118.556	1141.730	24.907	71.766	4.659
3200	26.365	119.393	1205.163	25.058	73.380	4.604
3300	26.391	120.204	1270.092	25.216	74.989	4.553
3400	26.416	120.993	1336.526	25.380	76.594	4.503
3500	26.438	121.759	1404.466	25.550	78.197	4.457
3600	26.459	122.504	1473.913	25.725	79.798	4.412
3700	26.478	123.229	1544.878	25.908	81.396	4.370
3800	26.495	123.935	1617.363	26.095	82.991	4.329
3900	26.512	124.622	1691.378	26.290	84.582	4.290
4000	26.527	125.295	1766.923	26.490	86.170	4.253
4100	26.541	125.950	1844.008	26.698	87.756	4.218
4200	26.555	126.590	1922.633	26.912	89.339	4.184
4300	26.567	127.215	2002.808	27.130	90.920	4.151
4400	26.578	127.826	2084.533	27.354	92.500	4.120
4500	26.589	128.423	2167.808	27.584	94.079	4.090
4600	26.599	129.008	2252.633	27.819	95.658	4.060
4700	26.609	129.580	2339.008	28.060	97.237	4.032
4800	26.618	130.140	2426.933	28.305	98.816	4.004
4900	26.626	130.689	2516.408	28.552	100.395	3.978
5000	26.634	131.227	2607.433	28.800	101.974	3.952
5100	26.641	131.755	2700.008	29.050	103.553	3.928
5200	26.648	132.272	2794.233	29.302	105.132	3.904
5300	26.655	132.780	2890.108	29.555	106.711	3.880
5400	26.661	133.278	2987.633	29.810	108.290	3.857
5500	26.667	133.767	3086.808	30.066	109.869	3.835
5600	26.673	134.248	3187.633	30.323	111.448	3.814
5700	26.678	134.720	3289.108	30.581	113.027	3.793
5800	26.683	135.184	3392.233	30.840	114.606	3.772
5900	26.688	135.640	3496.908	31.100	116.185	3.752
6000	26.692	136.089	3603.233	31.360	117.764	3.733

Dec. 31, 1960; Sept. 30, 1965

CHLORINE UNIPosITIVE ION (Cl<sup>+</sup>) (IDEAL GAS)

MOL. WT. = 35.45245

Ground State Configuration <sup>3</sup>P<sub>2</sub>  
 $\Delta H_f^{\circ} = 40.021 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{\circ} = 328.7 \pm .5 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{\circ} = 330.6 \pm .5 \text{ kcal/mole}$

Electronic Levels and Quantum Weight

$E_i, \text{ cm.}^{-1}$	$g_i$	$E_i, \text{ cm.}^{-1}$	$g_i$
0.0	5	27900.0	1
697.0	3	93366.6	5
986.0	1	93998.7	3
11652.0	5	94332.8	1

Heat of Formation.

The heat of formation was calculated from the equation:  $\text{Cl(g)} - e^- \rightarrow \text{Cl}^+(\text{g})$  with the JANAP auxiliary value for  $\text{Cl(g)}$ ; using an I.P. =  $1.04991 \times 10^5 \text{ cm.}^{-1}$  (300.206 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, loc. cit. The electronic levels above  $1 \times 10^5 \text{ cm.}^{-1}$  were omitted because their contribution is negligible below 6000°K. The  $H^{\circ} - H_{298}^{\circ}$  value at 0°K. is -1.526 kcal./mole.

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S° -(F° - H <sub>298}^{\circ})/T</sub>	H° - H <sub>298}^{\circ}</sub>	ΔH <sub>f}^{\circ}</sub>	ΔF <sub>f}^{\circ}</sub>	Log K <sub>p</sub>
0						
100						
200						
298	5.487	40.021	0.000	330.600	325.125	- 238.311
300	5.491	40.035	0.010	330.612	325.090	- 236.817
400	5.686	41.860	0.568	331.282	323.134	- 176.554
500	5.866	42.954	1.195	331.889	321.055	- 140.326
600	5.992	43.954	1.700	332.516	318.829	- 116.128
700	6.085	44.868	2.156	333.132	316.499	- 98.811
800	6.152	45.709	2.610	333.736	314.082	- 85.799
900	6.202	46.486	3.056	334.335	311.589	- 75.660
1000	6.235	47.212	3.495	334.925	309.029	- 67.555
1100	6.257	47.892	3.926	335.507	306.412	- 60.476
1200	6.270	48.527	4.350	336.084	303.747	- 54.426
1300	6.275	49.117	4.761	336.655	301.032	- 49.404
1400	6.272	49.661	5.158	337.222	298.261	- 45.408
1500	6.261	50.160	5.542	337.786	295.458	- 42.436
1600	6.242	50.623	5.913	338.347	292.617	- 39.498
1700	6.216	51.059	6.269	338.905	289.743	- 37.247
1800	6.183	51.477	6.611	339.460	286.834	- 34.825
1900	6.144	51.876	6.938	340.015	283.896	- 32.254
2000	6.100	52.256	7.252	340.567	280.930	- 30.697
2100	6.052	52.617	7.553	341.118	277.932	- 28.923
2200	6.000	52.961	7.840	341.668	274.911	- 27.309
2300	5.945	53.288	8.113	342.216	271.863	- 25.832
2400	5.888	53.600	8.372	342.765	268.793	- 24.476
2500	5.828	53.898	8.617	343.312	265.700	- 23.226
2600	5.765	54.182	8.848	343.859	262.585	- 22.071
2700	5.699	54.452	9.065	344.406	259.449	- 21.000
2800	5.631	54.708	9.268	344.952	256.293	- 20.004
2900	5.561	54.950	9.457	345.497	253.117	- 19.074
3000	5.489	55.179	9.632	346.043	249.920	- 18.206
3100	5.415	55.395	9.794	346.589	246.707	- 17.392
3200	5.339	55.598	9.942	347.134	243.478	- 16.628
3300	5.261	55.788	10.076	347.679	240.231	- 15.909
3400	5.181	55.964	10.197	348.224	236.967	- 15.231
3500	5.100	56.127	10.305	348.769	233.685	- 14.591
3600	5.017	56.277	10.400	349.314	230.393	- 13.986
3700	4.933	56.414	10.483	349.859	227.077	- 13.412
3800	4.848	56.538	10.555	350.405	223.755	- 12.868
3900	4.763	56.650	10.616	350.951	220.414	- 12.351
4000	4.677	56.751	10.665	351.495	217.059	- 11.859
4100	4.591	56.840	10.703	352.042	213.687	- 11.390
4200	4.505	56.918	10.730	352.588	210.311	- 10.943
4300	4.419	56.985	10.748	353.135	206.916	- 10.516
4400	4.333	57.041	10.757	353.682	203.513	- 10.108
4500	4.247	57.087	10.757	354.229	200.088	- 9.717
4600	4.161	57.124	10.748	354.778	196.660	- 9.343
4700	4.075	57.152	10.729	355.327	193.217	- 8.984
4800	4.000	57.171	10.699	355.876	189.758	- 8.639
4900	3.925	57.181	10.660	356.426	186.293	- 8.309
5000	3.850	57.182	10.612	356.976	182.819	- 7.991
5100	3.775	57.174	10.555	357.528	179.336	- 7.684
5200	3.700	57.157	10.489	358.083	175.843	- 7.390
5300	3.625	57.132	10.414	358.641	172.340	- 7.107
5400	3.550	57.099	10.330	359.203	168.829	- 6.833
5500	3.475	57.058	10.237	359.771	165.306	- 6.567
5600	3.400	57.008	10.135	360.345	161.774	- 6.311
5700	3.325	56.950	10.024	360.926	158.233	- 6.065
5800	3.250	56.884	9.905	361.519	154.683	- 5.826
5900	3.175	56.810	9.778	362.124	151.124	- 5.595
6000	3.100	56.728	9.643	362.741	147.557	- 5.371



Ground State Configuration <sup>1</sup>S<sub>0</sub> ΔH<sub>f</sub><sup>0</sup> = -54.8 ± .5 kcal. mole<sup>-1</sup>  
 S<sub>298.15</sub><sup>0</sup> = 36.628 cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>0</sup> 298.15 = -55.9 ± .5 kcal. mole<sup>-1</sup>

Electronic Levels and Quantum Weight

E <sub>i</sub> , cm. <sup>-1</sup>	g <sub>i</sub>
0.0	1
93143.8	5
93750.639	3
94553.707	1
95399.870	3

Heat of Formation.

The heat of formation was calculated from the equation: Cl(g) + e<sup>-</sup> → Cl<sup>-</sup>(g) with the JANAF auxiliary values for Cl(g); using the measured electron affinity = 3.613 e.v. (83.516 kcal/mole) obtained from R. S. Berry and C. W. Reimann, J. Chem. Phys. **38**, 1540 (1963). Other calculated values for the electron affinity are: 3.70 e.v. reported by B. Edlen, J. Chem. Phys. **33**, 98 (1960) and 3.56 e.v. reported by E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Argon. The electronic levels above 1 X 10<sup>5</sup> cm.<sup>-1</sup> were omitted because their contribution is negligible below 6000°K. The H<sup>0</sup>-H<sub>298</sub><sup>0</sup> value at 0°K. is -1.481 kcal/mole.

T, °K.	C <sub>p</sub>	S <sup>0</sup> - (F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0						
100	4.968	36.628	0.000	-55.000	-57.389	42.066
200	4.968	36.628	0.004	-55.007	-57.398	41.813
300	4.968	36.628	0.009	-55.014	-57.407	41.560
400	4.968	36.628	0.014	-55.021	-57.416	41.307
500	4.968	36.628	0.019	-55.028	-57.425	41.054
600	4.968	40.102	1.500	-57.184	-58.504	21.272
700	4.968	40.868	38.016	1.996	-57.622	18.286
800	4.968	41.634	2.494	-58.065	-58.678	16.029
900	4.968	42.400	38.704	2.990	-58.510	14.260
1000	4.968	42.840	30.153	3.487	-58.958	12.834
1100	4.968	43.113	39.602	3.984	-59.406	11.659
1200	4.968	43.546	30.812	4.481	-59.856	10.672
1300	4.968	43.943	40.115	4.977	-60.307	9.830
1400	4.968	44.312	40.401	5.474	-60.759	9.103
1500	4.968	44.654	40.674	5.971	-61.212	8.469
1600	4.968	44.975	40.933	6.468	-61.664	7.909
1700	4.968	45.276	41.179	6.965	-62.121	7.412
1800	4.968	45.560	41.415	7.461	-62.576	6.967
1900	4.968	45.829	41.640	7.958	-63.032	6.565
2000	4.968	46.084	41.856	8.455	-63.489	6.202
2100	4.968	46.326	42.063	8.952	-63.947	5.870
2200	4.968	46.557	42.262	9.449	-64.406	5.567
2300	4.968	46.778	42.454	9.946	-64.865	5.287
2400	4.968	46.989	42.638	10.442	-65.326	5.030
2500	4.968	47.192	42.817	10.939	-65.788	4.791
2600	4.968	47.387	42.989	11.436	-66.251	4.569
2700	4.968	47.575	43.155	11.933	-66.715	4.362
2800	4.968	47.755	43.316	12.430	-67.180	4.168
2900	4.968	47.930	43.472	12.926	-67.646	3.987
3000	4.968	48.098	43.624	13.423	-68.114	3.817
3100	4.968	48.261	43.771	13.920	-68.584	3.656
3200	4.968	48.419	43.913	14.417	-69.055	3.505
3300	4.968	48.572	44.052	14.914	-69.528	3.361
3400	4.968	48.720	44.187	15.410	-70.001	3.225
3500	4.968	48.864	44.319	15.907	-70.476	3.096
3600	4.968	49.004	44.447	16.404	-70.953	2.974
3700	4.968	49.149	44.572	16.901	-71.431	2.857
3800	4.968	49.279	44.694	17.398	-71.910	2.745
3900	4.968	49.401	44.813	17.895	-72.391	2.639
4000	4.968	49.527	44.929	18.391	-72.872	2.537
4100	4.968	49.650	45.043	18.888	-73.355	2.440
4200	4.968	49.770	45.154	19.385	-73.830	2.347
4300	4.968	49.887	45.263	19.882	-74.324	2.257
4400	4.968	50.001	45.369	20.370	-74.809	2.171
4500	4.968	50.112	45.473	20.875	-75.295	2.088
4600	4.968	50.222	45.575	21.372	-75.782	2.008
4700	4.968	50.328	45.675	21.869	-76.269	1.931
4800	4.968	50.433	45.774	22.366	-76.758	1.857
4900	4.968	50.536	45.870	22.863	-77.246	1.786
5000	4.968	50.636	45.964	23.359	-77.734	1.716
5100	4.968	50.734	46.057	23.856	-78.223	1.649
5200	4.968	50.831	46.147	24.353	-78.712	1.585
5300	4.968	50.925	46.237	24.850	-79.202	1.522
5400	4.968	51.018	46.324	25.347	-79.691	1.462
5500	4.968	51.109	46.411	25.844	-80.181	1.403
5600	4.968	51.199	46.495	26.340	-80.670	1.346
5700	4.968	51.287	46.579	26.837	-81.160	1.290
5800	4.968	51.373	46.660	27.334	-81.649	1.236
5900	4.968	51.458	46.741	27.831	-82.140	1.184
6000	4.968	51.542	46.820	28.328	-82.630	1.133

COPPER MONOCHLORIDE (CuCl)

(CRYSTAL)

MOL. WT. = 98.993

$S_{298.15}^{\circ} = 20.8 \pm 1.0$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_m = 703^{\circ}\text{K}$ .

$\Delta H_f^{\circ} =$  Unknown  
 $\Delta H_f^{\circ} 298.15 = -33.0 \pm 0.4$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^{\circ} = 2.445$  kcal. mole<sup>-1</sup>  
 $\Delta H_s^{\circ} 298.15 = 54.77 \pm 0.5$  kcal. mole<sup>-1</sup> of monomer  
 $\Delta H_s^{\circ} 298.15 = 37.2 \pm 0.2$  kcal. mole<sup>-1</sup> of trimer

Heat of Formation.

There have been three calorimetric determinations of the heat of formation. Thomsen, "Thermochemische Untersuchungen", Barth, Leipzig (1882-1886) reported -32.875 kcal. mole<sup>-1</sup>. Berthelot, Ann. Chim. Phys. 20, 504 (1880) reported -35.6 kcal. mole<sup>-1</sup> and H. V. Wartenberg and H. Werth, Z. physik. Chem. A 151, 109 (1930) reported -32.1 ± 0.4 kcal. mole<sup>-1</sup>. In addition, values of the heat of formation have been derived from several sets of equilibrium data. A. A. Noyes and M. Chow, J. Am. Chem. Soc. 40, 739 (1918) from a study of cell potentials derived a  $\Delta H_f^{\circ} = 7.19$  kcal. for the reaction  $\text{Cu}(c) + \text{HCl}(aq) \rightarrow \text{CuCl}(c) + 1/2 \text{H}_2(g)$  which yields  $\Delta H_f^{\circ}(\text{CuCl}) = -32.76$  kcal. mole<sup>-1</sup>. Several investigators have studied the reaction  $2\text{CuCl}(c) \rightarrow 2\text{Cu}(c) + 2\text{HCl}(g)$  and its reverse reaction. These include A. B. Bagdasarian, Trans. Am. Electrochem. Soc. 51, 449 (1927) who reported equilibrium constants which result in 2nd and 3rd law heats of reaction of 24.3 and 23.2 kcal. mole<sup>-1</sup>; A. F. Kapustinsky, J. Am. Chem. Soc. 59, 460 (1936) who obtained similarly 20.1 and 21.8 kcal. mole<sup>-1</sup>; S. A. Shchukarev and M. A. Oranskaya, Z. Obshchei. Khim. 24, 1926 (1954) obtained 25.4 and 21.5 kcal. mole<sup>-1</sup> for the 2nd and 3rd law heat of reaction. These yield values for  $\Delta H_f^{\circ} 298(\text{CuCl})$  ranging from -32.1 to -34.8. M. Watanabe, Bull. Inst. Phys. Chem. Res. 9, 94 (1929) from cell studies reports  $\Delta H_f^{\circ} 298(\text{CuCl}) = -34.6$  kcal. mole<sup>-1</sup>. A value of  $\Delta H_f^{\circ} 298$  can also be obtained from  $\Delta H_f^{\circ}(\text{CuCl}_2(g))$ , which is fixed independently and known with good precision. Using the 3rd law heat of sublimation of  $\text{CuCl}(c)$  to trimer determined by D. W. Magee, Doctoral Thesis, Ohio State University (1955) [See trimer table], we obtain  $\Delta H_f^{\circ} 298 \text{ CuCl}(c) = -33.01 \pm 0.3$  kcal. mole<sup>-1</sup>. A weighted average of -33.0 ± 0.4 kcal. mole<sup>-1</sup> was adopted.

Heat Capacity and Entropy.

The entropy of CuCl was obtained from the several pieces of equilibrium data reported above and the adopted  $\Delta H_f^{\circ} 298$ . A weighted average of  $20.8 \pm 1$  kcal. mole<sup>-1</sup> was adopted for  $S_{298}^{\circ} \text{ CuCl}(c)$ . The enthalpy and heat capacity above 298°K. have been reported by A. M. Krestovnikov and O. A. Karetnikov, Jour. Gen. Chem. (USSR) 6, 955 (1936). However these values were not adopted since they do not give reasonable heat capacities and other data by these workers is not in agreement with established values. Heat capacities equal to those of AgCl, as given by K. K. Kelley, U. S. Bureau of Mines Bulletin 584, Washington 1960, were adopted here above 298°K.

Melting Data.

The temperature and heat of melting were those selected by K. K. Kelley, U. S. Bur. Mines Bulletin 395 (1936), from phase studies. The heat of melting was reported by Krestovnikov and Karetnikov loc. cit. as 2.54 kcal. mole<sup>-1</sup>.

Sublimation Data.

The heat of sublimation was calculated from the adopted heats of formation at 298° for the reaction  $x \text{ CuCl}(c) \rightarrow (\text{CuCl})_x(g)$  where  $x = 1$  or 3. See the respective gas tables for details.

T, °K.	$C_p$	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	kcal. mole <sup>-1</sup>	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0							
100	11.600	20.800	0.000	- 33.000	- 28.898		21.183
200	11.656	20.807	0.022	- 32.997	- 28.873		21.034
300	13.600	22.758	1.922	- 32.079	- 27.955		15.044
400	14.300	27.650	2.699	- 32.374	- 28.275		11.485
500	14.700	30.300	4.149	- 31.991	- 28.092		9.140
600	15.000	32.589	5.435	- 31.889	- 28.072		7.484
700	15.220	34.607	7.146	- 31.778	- 28.074		6.236
800	15.389	36.410	8.677	- 31.759	- 28.005		5.319
900	15.540	38.039	10.224	- 31.838	- 28.044		4.677
1000	15.662	39.526	11.784	- 29.912	- 20.025		3.979
1200	15.777	40.894	13.356	- 29.486	- 19.146		3.487
1300	15.884	42.161	14.959	- 29.058	- 18.301		3.077
1400	15.983	43.342	16.532	- 31.815	- 17.388		2.714
1500	16.075	44.447	18.135	- 31.415	- 16.371		2.385

COPPER MONOCHLORIDE (CuCl) (LIQUID)

$S_{298.15}^{\circ} = 22.4 \pm 1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{\circ} 298.15 = -31.35 \pm 0.4 \text{ kcal. mole}^{-1}$   
 $T_m = 703^{\circ}\text{K.}$   
 $\Delta H_m^{\circ} = 2.4 \pm 5 \text{ kcal. mole}^{-1}$   
 $T_b = [1485]^{\circ}\text{K. (to equilibrium mixture)}$   
 $\Delta H_v^{\circ} = [5.18] \text{ kcal. mole}^{-1} \text{ (to equilibrium mixture)}$

Heat of Formation.  
 Calculated from  $\Delta H_f^{\circ} 298$  of the crystal plus  $\Delta H_m^{\circ}$  and the difference between  $H_m - H_{298}$  for crystal and liquid.

Heat Capacity and Entropy.  
 The heat capacity was estimated to be constant at 8 cal. deg.<sup>-1</sup> gm. atom<sup>-1</sup>. The entropy was calculated in a manner analogous to that of the heat of formation.

Boiling Data.  
 The boiling point and heat of vaporization were calculated from the respective liquid, monomer and trimer gas tables. The boiling point was taken as the point where the total pressure reached 1 atm. At this point the partial pressures are 0.021 atm. of monomer and 0.979 atm. of trimer.

T, K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	(F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0							
100	16.000	22.407	22.407	0.000	-31.350	-27.727	20.325
200	16.000	22.506	22.407	0.030	-31.339	-27.705	20.183
300	16.000	27.109	23.025	1.330	-30.751	-26.584	14.525
400	16.000	30.679	24.220	3.230	-30.193	-25.606	11.192
500	16.000	33.596	25.547	4.830	-29.661	-24.739	9.011
600	16.000	36.049	26.878	6.430	-29.145	-23.960	7.481
700	16.000	38.138	28.212	8.030	-28.645	-23.254	6.353
800	16.000	40.084	29.544	9.630	-28.157	-22.609	5.490
900	16.000	41.770	30.876	11.230	-27.682	-22.019	4.812
1000	16.000	43.294	31.631	12.830	-27.216	-21.474	4.267
1100	16.000	44.687	32.662	14.430	-26.762	-20.974	3.820
1200	16.000	45.967	33.637	16.030	-26.317	-20.508	3.448
1300	16.000	47.153	34.561	17.630	-25.880	-20.067	3.118
1400	16.000	48.257	35.447	19.230	-25.450	-19.642	2.818
1500	16.000	49.290	36.271	20.830	-25.027	-19.234	2.559
1600	16.000	50.260	37.036	22.430	-24.610	-18.848	2.333
1700	16.000	51.174	37.752	24.030	-24.200	-18.484	2.135
1800	16.000	52.039	38.419	25.630	-23.795	-18.141	1.961
1900	16.000	52.860	39.045	27.230	-23.395	-17.819	1.806
2000	16.000	53.641	39.612	28.830	-23.000	-17.518	1.668
2100	16.000	54.385	40.130	30.430	-22.610	-17.237	1.544
2200	16.000	55.096	41.170	32.030	-22.225	-16.974	1.434
2300	16.000	55.777	41.765	33.630	-21.845	-16.728	1.337
2400	16.000	56.430	42.338	35.230	-21.470	-16.497	1.252
2500	16.000	57.058	42.892	36.830	-21.100	-16.280	1.180
2600	16.000	57.662	43.428	38.430	-20.735	-16.077	1.118
2700	16.000	58.243	43.947	40.030	-20.375	-15.887	1.064
2800	16.000	58.801	44.450	41.630	-20.020	-15.708	1.016
2900	16.000	59.337	44.937	43.230	-19.670	-15.540	0.973
3000	16.000	59.851	45.410	44.830	-19.325	-15.383	0.934

$$\Delta H_f^0 = 21.80 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 56.667 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Electronic Levels and Multiplicities

$$\frac{\epsilon_i \text{ cm.}^{-1}}{0} \frac{g_i}{1}$$

$$\omega_e x_e = 1.577 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$\omega_e = 414.9 \text{ cm.}^{-1}$$

$$r_e = 2.050 \text{ \AA}$$

$$B_e = 0.1761 \text{ cm.}^{-1}$$

$$\alpha_e = 0.0001 \text{ cm.}^{-1}$$

Heat of Formation.

The heat of formation was obtained from the equilibrium data of L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950). They studied the reaction  $\text{Cu}(c) + x \text{HCl}(g) \rightarrow \text{CuCl}_x(g) + x/2 \text{H}_2(g)$  by measuring the amount of CuCl formed when various ratios of HCl:H<sub>2</sub> were passed over heated copper. Brewer and Lofgren analysed the data by a least squares fitting technique and deduced partial pressures of monomer and trimer. The monomer pressures were subjected to second and third law analysis and gave  $\Delta H_f^{298} = 46.85 \pm 3.2$  and  $43.83 \pm 0.4$  kcal. mole<sup>-1</sup> respectively. The 3rd law value yields  $\Delta H_f^{298} \text{ CuCl}(g) = 21.77 \pm 0.4$  kcal. mole<sup>-1</sup>, which was adopted.

Heat Capacity and Entropy.

The molecular constants were corrected for normal isotopic abundance of both copper and chlorine and were calculated from the values for <sup>65,35</sup>CuCl given by R. K. Asundi, P. R. Rao and J. K. Brody, Nature 132, 444 (1961). The rotational constants were in good agreement with those reported by A. Lagerqvist and V. Lazarova-Girasimov for Cu<sup>63,35</sup>Cl, Naturwissenschaften 48, 68 (1961).

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	0.000	INFINITE	- 2.264	21.798	21.798	INFINITE
100	7.146	48.171	1.565	19.669	19.669	42.989
200	7.972	53.387	0.808	17.374	17.374	18.985
298	8.428	56.667	0.000	21.770	15.178	11.126
300	8.433	56.719	0.016	21.767	15.137	11.027
400	8.657	59.179	0.871	21.611	12.950	7.076
500	8.778	61.125	1.744	21.441	10.805	4.723
600	8.854	62.733	2.625	21.255	8.695	3.167
700	8.905	64.101	3.514	21.059	6.618	2.066
800	8.942	65.293	4.406	20.851	4.567	1.248
900	8.972	66.348	5.302	20.635	2.545	0.618
1000	8.996	67.295	6.200	20.409	0.546	0.119
1100	9.017	68.153	7.101	20.175	- 1.428	0.284
1200	9.036	68.928	8.004	19.932	- 3.381	0.616
1300	9.052	69.621	8.910	19.681	- 5.313	1.093
1400	9.069	70.232	9.817	19.427	- 7.223	1.612
1500	9.084	70.760	10.722	19.172	- 9.104	2.180
1600	9.098	71.247	11.631	18.917	- 10.959	2.804
1700	9.112	71.699	12.541	18.662	- 12.788	3.474
1800	9.126	72.120	13.451	18.407	- 14.591	4.178
1900	9.139	72.514	14.361	18.152	- 16.368	4.904
2000	9.151	72.883	15.271	17.897	- 18.120	5.650
2100	9.164	73.230	16.181	17.642	- 19.847	6.414
2200	9.176	73.556	17.091	17.387	- 21.550	7.194
2300	9.188	73.864	18.001	17.132	- 23.228	7.988
2400	9.201	74.156	18.911	16.877	- 24.881	8.794
2500	9.212	74.432	19.821	16.622	- 26.509	9.610
2600	9.224	74.693	20.731	16.367	- 28.112	10.434
2700	9.236	74.940	21.641	16.112	- 29.690	11.264
2800	9.248	75.176	22.551	15.857	- 31.243	12.098
2900	9.260	75.402	23.461	15.602	- 32.771	12.936
3000	9.271	75.616	24.371	15.347	- 34.284	13.778
3100	9.283	75.821	25.281	15.092	- 35.781	14.624
3200	9.294	76.016	26.191	14.837	- 37.264	15.474
3300	9.306	76.202	27.101	14.582	- 38.733	16.328
3400	9.317	76.380	28.011	14.327	- 40.188	17.186
3500	9.329	76.550	28.921	14.072	- 41.629	18.048
3600	9.340	76.713	29.831	13.817	- 43.056	18.914
3700	9.352	76.869	30.741	13.562	- 44.469	19.784
3800	9.363	77.019	31.651	13.307	- 45.868	20.658
3900	9.375	77.162	32.561	13.052	- 47.253	21.536
4000	9.386	77.299	33.471	12.797	- 48.624	22.418
4100	9.397	77.431	34.381	12.542	- 49.981	23.304
4200	9.409	77.558	35.291	12.287	- 51.324	24.194
4300	9.420	77.679	36.201	12.032	- 52.653	25.088
4400	9.431	77.796	37.111	11.777	- 53.968	25.986
4500	9.443	77.910	38.021	11.522	- 55.269	26.888
4600	9.454	78.021	38.931	11.267	- 56.556	27.794
4700	9.465	78.128	39.841	11.012	- 57.829	28.704
4800	9.477	78.232	40.751	10.757	- 59.088	29.618
4900	9.488	78.333	41.661	10.502	- 60.333	30.536
5000	9.499	78.432	42.571	10.247	- 61.564	31.458
5100	9.510	78.528	43.481	9.992	- 62.781	32.384
5200	9.522	78.621	44.391	9.737	- 63.984	33.314
5300	9.533	78.712	45.301	9.482	- 65.173	34.248
5400	9.544	78.800	46.211	9.227	- 66.348	35.186
5500	9.555	78.886	47.121	8.972	- 67.509	36.128
5600	9.567	78.969	48.031	8.717	- 68.656	37.074
5700	9.578	79.050	48.941	8.462	- 69.789	38.024
5800	9.589	79.128	49.851	8.207	- 70.908	38.978
5900	9.601	79.204	50.761	7.952	- 72.013	39.936
6000	9.612	79.278	51.671	7.697	- 73.104	40.898

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	6.961	44.228	21.129	12.117	12.117	INFINITE
200	7.291	48.555	1.434	12.120	12.249	26.768
300	7.568	52.750	.753	12.126	12.376	13.524
400	7.800	56.854	.300	12.143	12.447	9.160
500	8.000	60.884	.014	12.162	12.499	9.105
600	8.180	64.854	.803	12.182	12.616	6.893
700	8.340	68.773	1.623	12.203	12.731	5.565
800	8.480	72.643	2.466	12.223	12.844	4.678
900	8.600	76.463	3.316	12.243	12.956	4.045
1000	8.700	80.233	4.164	12.263	13.068	3.500
1100	8.790	83.953	5.012	12.283	13.179	2.954
1200	8.870	87.623	5.859	12.303	13.290	2.662
1300	8.940	91.243	6.707	12.323	13.401	2.459
1400	9.000	94.813	7.554	12.343	13.512	2.288
1500	9.050	98.333	8.402	12.363	13.623	2.142
1600	9.090	101.803	9.250	12.383	13.734	2.014
1700	9.120	105.223	10.098	12.403	13.845	1.903
1800	9.140	108.593	10.946	12.423	13.956	1.804
1900	9.150	111.913	11.794	12.443	14.067	1.717
2000	9.150	115.183	12.642	12.463	14.178	1.638
2100	9.140	118.403	13.490	12.483	14.289	1.568
2200	9.120	121.573	14.338	12.503	14.400	1.504
2300	9.090	124.703	15.186	12.523	14.511	1.446
2400	9.050	127.783	16.034	12.543	14.622	1.393
2500	9.000	130.813	16.882	12.563	14.733	1.344
2600	8.940	133.793	17.730	12.583	14.844	1.299
2700	8.870	136.723	18.578	12.603	14.955	1.257
2800	8.790	139.603	19.426	12.623	15.066	1.218
2900	8.700	142.433	20.274	12.643	15.177	1.183
3000	8.600	145.213	21.122	12.663	15.288	1.149
3100	8.490	147.943	21.970	12.683	15.399	1.118
3200	8.370	150.623	22.818	12.703	15.510	1.089
3300	8.240	153.253	23.666	12.723	15.621	1.061
3400	8.100	155.833	24.514	12.743	15.732	1.035
3500	7.950	158.363	25.362	12.763	15.843	1.011
3600	7.790	160.843	26.210	12.783	15.954	.988
3700	7.620	163.273	27.058	12.803	16.065	.966
3800	7.440	165.653	27.906	12.823	16.176	.945
3900	7.250	167.983	28.754	12.843	16.287	.926
4000	7.050	170.263	29.602	12.863	16.398	.907
4100	6.840	172.493	30.450	12.883	16.509	.889
4200	6.620	174.673	31.298	12.903	16.620	.872
4300	6.390	176.803	32.146	12.923	16.731	.856
4400	6.150	178.883	32.994	12.943	16.842	.841
4500	5.900	180.913	33.842	12.963	16.953	.826
4600	5.640	182.893	34.690	12.983	17.064	.811
4700	5.370	184.823	35.538	12.999	17.175	.798
4800	5.090	186.703	36.386	13.019	17.286	.785
4900	4.800	188.533	37.234	13.039	17.397	.772
5000	4.500	190.313	38.082	13.059	17.508	.760
5100	4.190	192.043	38.930	13.079	17.619	.748
5200	3.870	193.723	39.778	13.099	17.730	.737
5300	3.540	195.353	40.626	13.119	17.841	.726
5400	3.200	196.933	41.474	13.139	17.952	.715
5500	2.850	198.463	42.322	13.159	18.063	.704
5600	2.500	199.943	43.170	13.179	18.174	.693
5700	2.140	201.373	44.018	13.199	18.285	.682
5800	1.770	202.753	44.866	13.219	18.396	.671
5900	1.400	204.083	45.714	13.239	18.507	.660
6000	1.030	205.463	46.562	13.259	18.618	.651

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

CHLORINE MONOFLUORIDE (ClF) (IDEAL GAS)

MOL. WT. = 54.4514

Ground State Configuration  $1\Sigma^+$   $\Delta H_f^0 = -12.12 \pm 0.6$  kcal. mole<sup>-1</sup>  
 $S_{298.15}^0 = 52.064 \pm 0.01$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  $\Delta H_f^0 = -12.14 \pm 0.6$  kcal. mole<sup>-1</sup>  
 $S_{298.15}^0 = 52.064 \pm 0.01$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Electronic Levels and Quantum Weight

State	E <sub>1</sub> , cm. <sup>-1</sup>	g <sub>1</sub>
1Σ <sup>+</sup>	0	1
3Π <sup>+</sup>	19,582	1
3Π <sup>0</sup>	19,582	2
3Π <sup>-</sup>	19,582	2

$\omega_e = 784.39$  cm.<sup>-1</sup>  $\omega_e x_e = 6.20$  cm.<sup>-1</sup>  $\sigma = 1$   
 $P_e = 0.51403$  cm.<sup>-1</sup>  $\alpha_e = 0.004329$  cm.<sup>-1</sup>  $r_e = 1.62813$  Å

Heat of Formation.

The  $\Delta H_f^0$  298.15 = -12.14 kcal. mole<sup>-1</sup> was calculated from the dissociation energy ( $D_0^0 = 58.95$ ) obtained from the visible band spectra measured by H. Schmitz and H. J. Schumacher, Z. Naturforsch 2a, 359 (1947) and A. L. Währhaftig, J. Chem. Phys. 10, 248 (1941). The convergence limit of 21,512 ± 20 cm.<sup>-1</sup> for the A state leads to the selected  $D_0^0$  assuming that the products are Cl(<sup>2</sup>P<sub>1/2) and F(<sup>2</sup>P<sub>3/2) or to  $D_0^0 = 60.36$  assuming Cl(<sup>2</sup>P<sub>3/2) and F(<sup>2</sup>P<sub>1/2). Calorimetric values bracket the two possibilities but more weight was given to the results of Wicke.</sub></sub></sub></sub>

Method	Reaction	Observation	ΔH <sub>f</sub> <sup>0</sup> 298 kcal. mole <sup>-1</sup>
1 Spectroscopic	ClF = Cl( <sup>2</sup> P <sub>1/2) + F(<sup>2</sup>P<sub>3/2)</sub></sub>	$D_0^0 = 58.99$	-12.14
2 Spectroscopic	ClF = Cl( <sup>2</sup> P <sub>3/2) + F(<sup>2</sup>P<sub>1/2)</sub></sub>	$D_0^0 = 60.36$	-13.51
3 Calorimetric	1/2 Cl <sub>2</sub> + 1/2 F <sub>2</sub> = ClF	$\Delta H_{293}^0 = -11.6 \pm 0.1$	-11.6
4 Explosion method	1/2 Cl <sub>2</sub> + 1/2 F <sub>2</sub> = ClF	$\Delta H_0^0 = -11.7 \pm 0.5$	-11.7
5a Calorimetric	NaCl + ClF = NaF + Cl <sub>2</sub>	$\Delta H_{290}^0 = -24.5 \pm 0.5$	-14.34*
5b Calorimetric	NaCl + 0.5 F <sub>2</sub> = NaF + 0.5 Cl <sub>2</sub>	$\Delta H_{290}^0 = -39.5 \pm 0.5$	-15.0**

Sources

- 1,2 H. Schmitz and H. J. Schumacher, Z. Naturforsch 2a, 359 (1947).
- 3 E. Wicke, Nachr. Acad. Wiss. Gottigen Math-Physik Klasse p. 89 (1946).
- 4 E. Wicke and H. Fritz, Z Electrochem 57, 9 (1953).
- 5a, 5b H. Schmitz and H. J. Schumacher, Z. Naturforsch 2a, 362 (1947).

\*Based on  $\Delta H_f^0$  298(NaCl(c)) = -98.26 and  $\Delta H_f^0$  298(NaF(c)) = -137.1 kcal. mole<sup>-1</sup>

\*\*Based on the difference between the two calorimetric reactions of reference 5a, 5b.

Heat Capacity and Entropy.

The rotational constants were obtained from the microwave spectrum by D. A. Gilbert, A. Roberts and P. A. Griswold, Phys. Rev. 76, 1723 (1949) and by D. A. Gilbert and A. Roberts Phys. Rev. 77, 742 (1950). The vibrational constants were obtained from the analysis vibration-rotation fine structure in the infrared by A. H. Nielsen and E. A. Jones, J. Chem. Phys. 19, 1117 (1951).

The rotational and vibrational constants were adjusted to Cl<sup>35</sup> = 75.4% and Cl<sup>37</sup> = 24.6%.

MOL. WT. = 78.763

(IDEAL GAS)

MAGNESIUM CHLORIDE FLUORIDE (MgClF)

Log K<sub>p</sub>

Point Group C<sub>2v</sub>  
 $\Delta H_f^\circ 0 = [-135.6 \pm 5] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^\circ 298.15 = [-136.0 \pm 5] \text{ kcal. mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_j, \text{ cm.}^{-1}$   
 [719](1)  
 [205](1)  
 [453](1)

Bond Distance: Mg-Cl = [2.18] Å Mg-F = [1.77] Å  
 Bond Angle: Cl-Mg-F = [170]°

Product of the Moments of Inertia:  $I_A I_B I_C = [1.5643 \times 10^{-115}] \text{ g.}^3 \text{ cm.}^6$

U = 2

Heat of Formation

The heat of formation is based on an estimated  $\Delta H_f^\circ 298 = 0$  for the reaction  $\text{MgCl}_2(\text{g}) + \text{MgF}_2(\text{g}) \rightarrow 2\text{MgClF}(\text{g})$ , using  $\Delta H_f^\circ 298.15 = -95.85$  and  $-176.2$  kcal. mole<sup>-1</sup> for  $\text{MgCl}_2(\text{g})$  and  $\text{MgF}_2(\text{g})$ , respectively.

Heat Capacity and Entropy

The bond angle is taken to be the value we have adopted for  $\text{MgCl}_2(\text{g})$ . The Mg-Cl and Mg-F bond distances are assumed to be the same as those in  $\text{MgCl}_2(\text{g})$  and  $\text{MgF}_2(\text{g})$ . The vibration frequencies are the averages of those for  $\text{MgCl}_2(\text{g})$  and  $\text{MgF}_2(\text{g})$ . The three principal moments of inertia are:  $I_A = 0.0977 \times 10^{-39}$ ,  $I_B = 59.955 \times 10^{-39}$  and  $I_C = 40.054 \times 10^{-39} \text{ g. cm.}^2$

T, K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	2.947	-135.599	-135.599	INFINITE
100	9.089	51.367	72.543	2.118	-135.622	-136.237	267.145
200	10.794	58.214	63.814	1.120	-135.896	-137.527	149.457
298	11.929	62.756	62.756	∞	-136.000	-137.215	100.281
300	11.945	62.830	62.756	∞	-136.003	-137.232	99.966
400	12.619	66.367	63.734	1.253	-136.186	-137.422	75.182
500	13.015	69.229	64.156	2.537	-136.375	-137.633	60.290
600	13.279	71.625	65.007	3.851	-136.580	-138.226	50.349
700	13.458	73.692	65.744	5.136	-136.800	-138.482	43.236
800	13.576	75.491	66.315	6.393	-137.056	-138.707	37.893
900	13.653	77.070	66.713	7.890	-137.344	-138.896	33.728
1000	13.699	78.515	69.262	9.253	-139.789	-139.870	30.350
1100	13.701	79.813	70.164	10.621	-140.117	-139.764	27.570
1200	13.733	81.013	71.019	11.993	-140.471	-138.626	25.247
1300	13.759	82.113	71.830	13.368	-140.852	-138.456	23.277
1400	13.779	83.134	72.602	14.745	-141.264	-137.778	21.508
1500	13.796	84.085	73.336	16.123	-141.651	-135.359	19.722
1600	13.809	84.976	74.036	17.504	-141.679	-132.940	18.159
1700	13.821	85.813	74.704	18.885	-141.708	-130.515	16.779
1800	13.830	86.604	75.344	20.268	-141.739	-128.094	15.553
1900	13.838	87.332	75.956	21.651	-141.770	-125.667	14.455
2000	13.845	88.032	76.544	23.035	-141.804	-123.240	13.467
2100	13.851	88.737	77.108	24.420	-141.838	-120.811	12.573
2200	13.856	89.382	77.652	25.806	-141.875	-118.380	11.760
2300	13.861	89.998	78.175	27.192	-141.913	-115.946	11.017
2400	13.865	90.588	78.680	28.578	-141.954	-113.514	10.337
2500	13.869	91.154	79.168	29.965	-141.997	-111.079	9.710
2600	13.872	91.698	79.639	31.352	-142.042	-108.639	9.132
2700	13.874	92.221	80.096	32.739	-142.091	-106.198	8.596
2800	13.877	92.726	80.538	34.126	-142.141	-103.759	8.099
2900	13.879	93.213	80.967	35.514	-142.195	-101.314	7.635
3000	13.881	93.684	81.383	36.902	-142.253	-98.873	7.203
3100	13.883	94.139	81.787	38.291	-142.314	-96.425	6.798
3200	13.885	94.580	82.180	39.679	-142.381	-93.977	6.418
3300	13.886	95.007	82.562	41.067	-142.451	-91.525	6.051
3400	13.888	95.421	82.934	42.456	-142.526	-89.067	5.725
3500	13.889	95.824	83.297	43.845	-142.608	-86.615	5.408
3600	13.890	96.215	83.650	45.234	-142.695	-84.153	5.109
3700	13.891	96.596	83.995	46.623	-142.789	-81.693	4.825
3800	13.892	96.966	84.332	48.012	-142.889	-79.228	4.557
3900	13.893	97.327	84.660	49.401	-142.997	-76.760	4.302
4000	13.894	97.679	84.981	50.791	-143.112	-74.290	4.059
4100	13.895	98.022	85.295	52.180	-143.237	-71.825	3.829
4200	13.895	98.357	85.602	53.570	-143.370	-69.353	3.609
4300	13.896	98.684	85.903	54.959	-143.510	-66.872	3.398
4400	13.897	99.003	86.197	56.348	-143.654	-64.387	3.198
4500	13.897	99.316	86.485	57.739	-143.802	-61.906	3.007
4600	13.898	99.621	86.767	59.128	-143.998	-59.415	2.823
4700	13.898	99.920	87.044	60.518	-144.182	-56.922	2.647
4800	13.899	100.213	87.315	61.908	-144.378	-54.426	2.478
4900	13.899	100.499	87.581	63.298	-144.585	-51.921	2.316
5000	13.900	100.780	87.842	64.688	-144.803	-49.417	2.160
5100	13.900	101.055	88.099	66.078	-145.037	-46.910	2.010
5200	13.900	101.325	88.351	67.468	-145.283	-44.401	1.866
5300	13.901	101.590	88.598	68.858	-145.543	-41.871	1.727
5400	13.901	101.850	88.841	70.248	-145.817	-39.353	1.593
5500	13.902	102.105	89.080	71.638	-146.105	-36.820	1.463
5600	13.902	102.355	89.315	73.028	-146.409	-34.284	1.338
5700	13.902	102.601	89.545	74.418	-146.728	-31.740	1.217
5800	13.902	102.843	89.772	75.809	-147.062	-29.197	1.100
5900	13.903	103.081	89.996	77.199	-147.415	-26.646	0.987
6000	13.903	103.314	90.216	78.589	-147.783	-24.087	0.877

CHLORINE TRIFLUORIDE (ClF<sub>3</sub>) (IDEAL GAS) MOL. WT. = 92.4482

Point Group C<sub>2v</sub>  
 $\Delta H_f^\circ = 67.279 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^\circ = 67.279 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^\circ = -37.97 \pm 0.7 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^\circ = -37.97 \pm 0.7 \text{ kcal. mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_e, \text{cm.}^{-1}$	$\omega_e, \text{cm.}^{-1}$
752 (1)	703 (1)
528 (1)	454 (1)
328 (1)	364 (1)

Bond Distances: Cl-F<sub>1</sub> = Cl-F<sub>2</sub> = 1.698 Å Cl-F<sub>3</sub> = 1.598 Å  
 Bond Angle: F<sub>1</sub>-Cl-F<sub>2</sub> = F<sub>2</sub>-Cl-F<sub>3</sub> = 87° 29' F<sub>1</sub>-Cl-F<sub>3</sub> = 185° 02'  
 Product of Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 2.6925061 x 10<sup>-114</sup> g.<sup>3</sup> cm.<sup>6</sup>  
 $\sigma = 2$

Heat of Formation.

The  $\Delta H_f^\circ = -37.97 \text{ kcal. mole}^{-1}$  was calculated from  $\Delta H_f^\circ = 25.85 \text{ kcal. mole}^{-1}$  obtained by third law analysis of the equilibrium data of H. Schmitz and H. T. Schumacher, Z. Naturforsch. **2a**, 362 (1947) for the reaction ClF<sub>3</sub>(g) = ClF(g) + F<sub>2</sub>(g). Smaller values are obtained from the equilibrium data of K. Schäfer and E. Wicke, Z. Elektrochem. **52**, 205-209 (1948). Calorimetric values scatter widely, as summarized below; these were given little weight.

Source	Method	Reaction	Observation <sup>1</sup> (kcal. mole <sup>-1</sup> )	3rd Law Drift (e.u.)	$\Delta H_f^\circ$ (kcal. mole <sup>-1</sup> )
1a	K <sub>2</sub> (535-623°K)	ClF <sub>3</sub> (g) = ClF(g) + F <sub>2</sub> (g)	$\Delta H_f^\circ = 25.85$	$0.8 \pm 0.3$	-37.97
2a	P(733°K)	ClF <sub>3</sub> (g) = ClF(g) + F <sub>2</sub> (g)	$\Delta H_f^\circ = 25.77$	---	-37.91
2b	K <sub>2</sub> (570-680°K)	ClF <sub>3</sub> (g) = ClF(g) + F <sub>2</sub> (g)	$\Delta H_f^\circ = 26.12$	---	-38.26
1b	Calorimetric	3NaCl + ClF <sub>3</sub> = 3NaF + 2Cl <sub>2</sub>	$\Delta H_f^\circ = 76.5$	6 ± 3	-40.02
1c	Calorimetric	NaCl + 0.5 F <sub>2</sub> = NaF + 0.5 Cl <sub>2</sub>	$\Delta H_f^\circ = 39.5$	---	-42.0*
3	Calorimetric	3NaCl + ClF <sub>3</sub> = 3NaF + 2Cl <sub>2</sub>	$\Delta H_f^\circ = 86.8$	---	-29.7
4	Calorimetric	0.5 F <sub>2</sub> + NaCl = NaF + 0.5 Cl <sub>2</sub>	$\Delta H_f^\circ = 39.3$	---	-31.1**
5	Flow reaction	0.5 Cl <sub>2</sub> (g) + 1.5 F <sub>2</sub> (g) = ClF <sub>3</sub> (g)	$\Delta H_f^\circ = 26.4$	---	-26.4

\*From combination of 1b and 1c. \*\*From combination of 3 and 4.

Sources

- H. Schmitz and H. T. Schumacher, Z. Naturforsch., **2a**, 362 (1947).
- (Hot wire) K. Schäfer and E. Wicke, Z. Elektrochem., **52**, 205 (1948).
- (From the Graph) K. Schäfer and E. Wicke, Z. Elektrochem., **52**, 205 (1948).
- H. V. Wartenberg, Z. anorg. allgem. Chem., **258**, 356 (1949).
- H. V. Wartenberg and O. Pitzner, A. anorg. allgem. Chem., **151**, 313 (1926).
- C. P. Shinehart, private communication from the Marathon Chemical Co., March, 1963.

Heat Capacity and Entropy.

The structural constants were obtained from the microwave study of D. P. Smith, J. Chem. Phys., **21**, 609 (1953). The planar distorted "m" structure is similar to that derived from X-ray studies of the solid by R. D. Burbank and P. H. Boney, J. Chem. Phys., **21**, 602 (1953). Fundamental frequencies are taken from the infrared and Raman spectra of H. H. Claassen, B. Weinstock and J. G. Males, J. Chem. Phys., **29**, 885 (1958). These data confirm the "m" structure as opposed to the pyramidal structure used in earlier spectral analyses.

Claassen, et al., loc. cit., calculate thermodynamic functions virtually identical with the JANAF values. These authors also correct the third law entropy reported by J. W. Oriskany, H. A. Bernhardt and G. D. Oliver, J. Am. Chem. Soc., **73**, 5725 (1951) from measurements of heat capacity (14-285°K.) and vapor pressure (226-303°K.). The entropy at the normal boiling point becomes 5284.91 = 67.04 cal. deg.<sup>-1</sup> mole<sup>-1</sup> when a non-ideality correction consistent with the dimer-monomer vapor equilibrium is applied. The corresponding statistical entropy, 5284.91 = 66.59 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, is consistent with the third law value within the probable error in the entropy of the liquid and the entropy of vaporization. The three principal moments of inertia are: I<sub>A</sub> = 6.1114 x 10<sup>-38</sup>, I<sub>B</sub> = 1.81545 x 10<sup>-38</sup> and I<sub>C</sub> = 2.4285 x 10<sup>-38</sup> g. cm.<sup>2</sup>.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	36.970	36.970	INFINITE
100	8.872	54.430	2.450	36.970	36.970	75.480
200	12.582	61.712	1.377	37.883	31.552	34.977
298	15.260	67.279	∞	37.970	28.830	20.830
300	15.298	67.374	∞	37.970	28.360	20.650
400	16.875	72.012	1.644	37.924	25.160	13.746
500	17.798	75.885	3.382	37.824	21.980	9.607
600	18.366	79.184	5.192	37.696	18.823	6.856
700	18.734	82.045	7.048	37.555	15.688	4.998
800	18.984	84.564	8.935	37.410	12.576	3.435
900	19.121	86.811	10.843	37.262	9.480	2.302
1000	19.231	88.837	12.766	37.113	6.402	1.599
1100	19.309	90.680	14.700	36.965	3.338	∞
1200	19.444	92.370	16.643	36.818	∞	∞
1300	19.523	93.931	18.592	36.674	2.752	∞
1400	19.570	95.379	20.547	36.532	5.780	∞
1500	19.608	96.731	22.506	36.392	8.798	∞
1600	19.640	97.997	24.468	36.257	11.806	∞
1700	19.666	99.189	26.434	36.123	14.807	∞
1800	19.688	100.314	28.402	35.993	17.795	∞
1900	19.707	101.379	30.371	35.866	20.782	∞
2000	19.723	102.390	32.343	35.742	23.762	∞
2100	19.737	103.359	34.316	35.622	26.730	∞
2200	19.749	104.271	36.290	35.506	29.698	∞
2300	19.759	105.149	38.265	35.393	32.661	∞
2400	19.768	105.990	40.242	35.284	35.617	∞
2500	19.776	106.797	42.219	35.180	38.569	∞
2600	19.784	107.573	44.197	35.079	41.517	∞
2700	19.790	108.320	46.176	34.982	44.462	∞
2800	19.796	109.040	48.155	34.888	47.404	∞
2900	19.801	109.743	50.135	34.794	50.347	∞
3000	19.806	110.446	52.113	34.717	53.270	∞
3100	19.810	111.155	54.096	34.637	56.204	∞
3200	19.814	111.868	56.077	34.562	59.138	∞
3300	19.817	112.584	58.059	34.492	62.080	∞
3400	19.820	113.294	60.044	34.425	65.024	∞
3500	19.823	113.999	62.031	34.364	67.971	∞
3600	19.826	114.719	64.005	34.306	70.932	∞
3700	19.829	115.442	65.988	34.253	73.924	∞
3800	19.831	116.169	67.971	34.204	76.931	∞
3900	19.833	116.906	69.954	34.161	79.958	∞
4000	19.835	117.648	71.938	34.120	82.994	∞
4100	19.837	118.398	73.921	34.085	85.416	∞
4200	19.838	119.156	75.905	34.054	88.330	∞
4300	19.840	119.924	77.889	34.024	91.246	∞
4400	19.841	120.699	79.873	34.002	94.159	∞
4500	19.843	121.484	81.857	33.981	97.068	∞
4600	19.844	122.278	83.841	33.964	99.969	∞
4700	19.845	123.080	85.826	33.952	102.893	∞
4800	19.846	123.891	87.811	33.942	105.805	∞
4900	19.847	124.713	89.795	33.937	108.719	∞
5000	19.848	125.546	91.780	33.934	111.628	∞
5100	19.849	126.389	93.765	33.935	114.536	∞
5200	19.850	127.241	95.750	33.939	117.446	∞
5300	19.851	128.102	97.735	33.947	120.368	∞
5400	19.852	128.973	99.720	33.958	123.273	∞
5500	19.853	129.856	101.705	33.972	126.186	∞
5600	19.853	130.750	103.691	33.989	129.102	∞
5700	19.854	131.654	105.676	33.011	132.011	∞
5800	19.855	132.568	107.661	34.033	134.927	∞
5900	19.855	133.492	109.647	34.060	137.831	∞
6000	19.856	134.426	111.632	34.090	140.750	∞

IRON MONOCHLORIDE (FeCl) (IDEAL GAS)

MOL. WT. = 91.300

Ground State Configuration  $6\sum$   
 $S_{298.15} = [61.537] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{\circ} 0 = 60 \pm 20 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{\circ} 298.15 = 60 \pm 20 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\epsilon_1$ , cm. <sup>-1</sup>	$\frac{\epsilon_1}{6}$
0	(8)
[200]	(8)
[1000]	(8)
[4000]	(8)

$\omega_e x_e = 1.19 \text{ cm.}^{-1}$   
 $\omega_e = 404.92 \text{ cm.}^{-1}$   
 $\alpha_e = [0.00075] \text{ cm.}^{-1}$   
 $\sigma^- = 1$   
 $r_e = [2.09]$

Heat of Formation.

The dissociation energy ( $D_0^{\circ}$ ) of FeCl(g) was reported as  $3 \pm 2 \text{ e.v.}$  ( $69 \pm 46 \text{ kcal. mole}^{-1}$ ) by A. O. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The corresponding  $\Delta H_f^{\circ} 298.15$  (FeCl, g) was evaluated to be  $56 \pm 46 \text{ kcal. mole}^{-1}$ . By comparing  $D(\text{Fe-O}) = 101 \text{ kcal. mole}^{-1}$  in FeO(g) with the coordinate bond energies obtained in organic complexes and iron carbonyl halides of  $E(\text{Fe-O}) = 59.4$  and  $E(\text{Fe-Cl}) = 37.3 \text{ kcal. mole}^{-1}$ , reported by M. M. Jones, B. J. Yow and W. R. May, Inorg. Chem. 1, 166 (1962), the  $D(\text{Fe-Cl})$  in FeCl(g) was estimated as  $101 \times (37.3/59.4) = 63.5 \text{ kcal. mole}^{-1}$ , yielding  $\Delta H_f^{\circ} 298.15$  (FeCl, g) =  $64 \text{ kcal. mole}^{-1}$ . The adopted value of  $\Delta H_f^{\circ} 298.15$  for FeCl(g) is  $60 \pm 20 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

The ground state configuration,  $\omega_e$  and  $\omega_e x_e$  (corrected to the average isotopic species) were obtained from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950. The Fe-Cl bond distance was assumed to be the same as that in FeCl<sub>2</sub>(g). Hence the values of  $B_0$  and  $\alpha_e$  were calculated. The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe<sup>+</sup>(g) reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1952, using the reasoning suggested by J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961). The total 30 for the quantum weight was obtained from the ground multiplet of Fe<sup>+</sup> and was split arbitrarily. The entropy values may be in error by a few entropy units due to the uncertainties in the low lying electronic levels. The principal moment of inertia is  $1.5728 \times 10^{-38} \text{ g. cm.}^2$ .

T, °K.	C <sub>v</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	59.692	59.692	INFINITE
100	8.232	52.018	69.431	1.741	57.181	57.181	124.064
200	8.821	62.954	62.343	0.882	54.340	54.340	59.377
298	9.136	61.537	61.537	0.000	60.000	60.000	37.781
300	9.141	61.559	61.557	0.17	59.998	51.491	37.509
400	9.366	64.257	61.898	0.943	59.884	48.671	26.591
500	9.478	66.361	62.588	1.886	59.725	45.886	20.056
600	9.516	68.093	63.365	2.896	59.511	43.137	15.712
700	9.520	69.560	64.148	3.788	59.235	40.429	12.622
800	9.515	70.831	64.906	4.740	58.876	37.765	10.316
900	9.512	71.952	65.628	5.691	58.406	35.154	8.536
1000	9.514	72.954	66.311	6.643	57.753	32.602	7.125
1100	9.522	73.861	66.957	7.595	56.882	30.134	5.987
1200	9.532	74.680	67.567	8.547	55.821	27.725	5.049
1300	9.545	75.453	68.145	9.501	55.901	25.365	4.264
1400	9.559	76.161	68.693	10.456	55.565	23.029	3.595
1500	9.572	76.821	69.213	11.413	55.216	20.716	3.018
1600	9.584	77.436	69.708	12.371	54.851	18.428	2.517
1700	9.595	78.021	70.180	13.330	54.480	16.168	2.078
1800	9.605	78.569	70.631	14.290	53.694	13.948	1.693
1900	9.612	79.089	71.062	15.251	49.522	11.938	1.373
2000	9.619	79.582	71.476	16.212	48.970	9.973	1.090
2100	9.623	80.052	71.873	17.174	48.414	8.036	0.836
2200	9.627	80.509	72.257	18.137	47.854	6.129	0.609
2300	9.630	80.954	72.628	19.100	47.289	4.253	0.405
2400	9.631	81.377	72.976	20.063	46.720	2.485	0.217
2500	9.632	81.730	73.320	21.026	46.145	0.750	0.046
2600	9.633	82.108	73.651	21.989	45.566	-1.264	-0.168
2700	9.633	82.473	73.971	22.952	44.981	-3.056	-0.376
2800	9.633	82.827	74.271	23.916	44.391	-4.822	-0.576
2900	9.632	83.160	74.561	24.879	43.795	-6.570	-0.765
3000	9.631	83.487	74.873	25.842	43.194	-8.298	-0.904
3100	9.631	83.802	75.156	26.805	42.588	-10.000	-1.000
3200	9.630	84.108	75.431	27.768	41.949	-10.244	-1.044
3300	9.629	84.405	75.698	28.731	41.603	-9.270	-0.614
3400	9.629	84.692	75.958	29.694	41.767	-8.286	-0.533
3500	9.628	84.971	76.212	30.657	41.940	-7.300	-0.456
3600	9.628	85.242	76.459	31.620	42.112	-6.304	-0.383
3700	9.628	85.506	76.705	32.582	42.314	-5.308	-0.314
3800	9.628	85.763	76.935	33.545	42.515	-4.310	-0.248
3900	9.629	86.013	77.145	34.508	42.725	-3.296	-0.185
4000	9.629	86.257	77.349	35.471	42.947	-2.287	-0.125
4100	9.630	86.495	77.608	36.434	43.176	-1.266	-0.067
4200	9.631	86.727	77.823	37.397	43.417	-0.243	-0.013
4300	9.632	86.953	78.032	38.360	43.667	0.792	0.040
4400	9.634	87.175	78.238	39.323	43.928	1.826	0.091
4500	9.636	87.391	78.439	40.287	44.199	2.869	0.139
4600	9.638	87.603	78.636	41.251	44.478	3.920	0.186
4700	9.640	87.810	78.829	42.214	44.770	4.977	0.231
4800	9.642	88.013	79.018	43.179	45.071	6.039	0.275
4900	9.645	88.212	79.203	44.143	45.383	7.106	0.317
5000	9.648	88.407	79.386	45.108	45.705	8.178	0.357
5100	9.651	88.598	79.564	46.072	46.037	9.260	0.397
5200	9.654	88.786	79.740	47.038	46.379	10.345	0.435
5300	9.658	88.969	79.912	48.003	46.732	11.443	0.472
5400	9.661	89.150	80.082	48.969	47.096	12.542	0.508
5500	9.665	89.327	80.248	49.936	47.469	13.653	0.542
5600	9.669	89.501	80.412	50.902	47.853	14.766	0.576
5700	9.673	89.673	80.573	51.869	48.247	15.881	0.609
5800	9.678	89.841	80.731	52.837	48.651	17.017	0.641
5900	9.682	90.006	80.887	53.805	49.065	18.151	0.672
6000	9.687	90.169	81.040	54.773	49.488	19.296	0.703



MOL. WT. = 53.49158

(CRYSTAL)

AMMONIUM CHLORIDE (NH<sub>4</sub>Cl)

$\Delta H_f^0 = -74.42 \pm 0.20$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -75.18 \pm 0.20$  kcal. mole<sup>-1</sup>  
 $\Delta H_{298.15}^{\circ} = 0.25$  kcal. mole<sup>-1</sup>  
 $\Delta H_1^{\circ} = 0.944$  kcal. mole<sup>-1</sup>

$S_{298.15}^{\circ} = 22.7 \pm 1.0$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_1 = 242.6$  °K.  
 $T_2 = 457.7$  °K.  
 $T_m = 783.2$  °K.  
 $T_b = 612$  °K.

Heat of Formation.  
 The equilibrium pressures for the reaction NH<sub>4</sub>Cl(c) = NH<sub>3</sub>(g) + HCl(g), at 320-626°K., have been measured by many investigators. A. Saito and W. de Lange, J. Chem. Soc., 2944 (1928), using the densi-tensimeter, determined the vapor pressure of NH<sub>4</sub>Cl(c) and the density of the saturated vapor simultaneously. The results obtained indicate that within the range 527-626°K. the saturated vapor completely dissociates into gaseous NH<sub>3</sub> and HCl. Based on this conclusion, the reported vapor pressure data were employed to evaluate the heat of dissociation of NH<sub>4</sub>Cl(c) by both the second and third law methods. The results are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	Drift, e.u.
Saito and Calvert (1)	521.6-619.1	43.18 ± 0.08	42.11	-0.9 ± 0.2
Saito and Lange (2)	527.9-625.6	42.18 ± 0.22	42.11	-0.2 ± 0.1
Braune and Knoke (3)	525.4-615.0	42.02 ± 0.06	42.20	0.2 ± 0.1
Rodebush and Michalek (4)	471.3-557.0	42.43 ± 0.09	42.08	-0.3 ± 0.2
Wagner and Neumann (5)	519.0-552.7	43.95 ± 0.38	42.17	-4.9 ± 1.1
Markowitz and Boryta (6)	503.4-611.4	41.27 ± 0.38	42.12	1.3 ± 0.8

The value of  $\Delta H_f^{298.15}$  adopted is 42.15 ± 0.10 kcal. mole<sup>-1</sup>, yielding  $\Delta H_f^{\circ} = 298.15$  (NH<sub>4</sub>Cl, c) = -75.6 ± 0.20 kcal. mole<sup>-1</sup>. The corresponding  $\Delta H_f^{298.15}$  value evaluated from solution data, selected by V. B. Parker, Thermal Properties of Aqueous Uni-univalent Electrolytes, NBSDS-NBS2, National Bureau of Standards, is 42.05 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.  
 The heat capacities (20.1-523.2°K.) of NH<sub>4</sub>Cl(c) have been measured by the following investigators: (1) R. Ewald, Ann. Physik, 44, 1213 (1914), 138-301°K.; (2) P. Simon, ibid., 59, 241 (1922), 20.1-230.6°K.; (3) H. Klinkhardt, ibid., 84, 167 (1927), 323.2-523.2°K.; (4) P. Simon, C. v. Simon and M. Ruesenm, Z. phys. Chem. 129, 339 (1927), 204.5-275.8°K.; (5) W. T. Ziegler and C. E. Messer, J. Am. Chem. Soc., 63, 2694 (1941), 107.2-320.2; (6) R. Extermann and J. Weigle, Helv. Phys. Acta, 15, 455 (1942), 228.2-246.2°K.; and (7) M. M. Popov and G. L. Galchenko, J. Gen. Chem., USSR, 21, 2469 (1951), 373.2-523.2°K. These  $C_p$  data were plotted and a smooth  $C_p$  curve was drawn and adopted. The  $C_p$  values above 523°K. were obtained by graphical extrapolation of the previous  $C_p$  curve.  $S_{298.15}$  was derived from the adopted low temperature data, based on  $S_{20.1}^{\circ} = 0.114$  e.u.

Transition Data.

There are two transitions reported in the literature. The low temperature transition data ( $T_1$  and  $\Delta H_1^{\circ}$ ) were derived based on the heat capacity (107-320°K.) data reported by W. T. Ziegler and C. E. Messer, loc. cit., in which the other  $T_2$  values given by previous investigators were reviewed. The high temperature transition data ( $T_2$  and  $\Delta H_2^{\circ}$ ) were taken from H. Klinkhardt, loc. cit. However,  $\Delta H_1^{\circ} = 1030$  and  $\Delta H_2^{\circ} = 1059.1 \pm 8.0$  cal. mole<sup>-1</sup> were reported by E. C. Schaffer, Proc. Acad. Sci. Amsterdam, 24, 1513 (1915/16), and M. M. Popov and G. L. Galchenko, loc. cit., respectively. M. M. Markowitz and D. A. Boryta, loc. cit. determined  $T_1$  to be 459.5 ± 0.5°K.

Melting Temperature.

$T_m$  was obtained from H. Resow, Z. anorg. Chem. 114, 117 (1920), determined under pressure.

Decomposition Temperature.

The value of  $T_d$  was calculated as the temperature at which the vapor pressure of the decomposition products (NH<sub>3</sub> and HCl) equals 1 atm. By differential thermal analysis,  $T_d$  for NH<sub>4</sub>Cl(c) was determined to be 611.4°K. by M. M. Markowitz and D. A. Boryta, loc. cit.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	0.000	0.000	INFINITE	5.425	74.424	74.424	INFINITE
100	9.000	5.868	39.148	3.328	74.538	66.082	144.416
200	16.040	14.281	24.653	2.074	75.202	57.336	62.651
298	20.650	22.672	17.672	1.300	75.180	48.563	35.596
300	20.780	22.800	22.672	1.308	75.182	48.598	35.256
400	24.610	29.312	23.534	2.311	75.060	39.479	21.569
500	21.630	36.647	25.432	5.607	73.940	30.704	13.420
600	24.300	40.926	27.653	7.904	73.834	22.062	8.036
700	26.960	44.772	29.819	10.467	73.478	13.457	4.201
800	29.610	48.545	31.926	13.496	72.876	4.923	1.345
900	32.260	52.189	33.976	16.392	72.028	3.524	0.486
1000	34.550	55.710	35.974	19.735	70.955	11.861	2.592
1100	36.500	59.096	37.923	23.490	69.694	20.084	3.990
1200	38.200	62.351	39.824	27.033	68.270	28.186	5.133
1300	39.000	65.433	41.677	30.494	66.764	36.162	6.079
1400	40.870	68.397	43.480	34.883	65.135	44.018	6.871
1500	42.000	71.259	45.237	39.031	63.385	51.757	7.451

MOL. WT. = 162.3574

(CRYSTAL)

IODINE MONOCHLORIDE (CII)

$$\Delta H_f^0 = -8.689 \pm 0.025 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -8.466 \pm 0.025 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 2.773 \pm 0.002 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^0 \text{ 298.15} = 12.650 \text{ kcal. mole}^{-1}$$

$$S_{298.15} = 23.405 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_m^0 = 300.53^\circ \text{K.}$$

Heat of Formation.

The heat of formation is that adopted by G. V. Calder and W. F. Glauque, J. Phys. Chem. 69, 2443 (1965) from an analysis of the equilibrium data of J. McMorris and D. M. Yost, J. Am. Chem. Soc. 54, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939). This yielded a heat of formation of ICl(g), from which the heat of formation of ICl(c) was calculated by using the heat of vaporization determined by Calder and Glauque loc. cit.

Heat Capacity and Entropy.

The heat capacity has been measured by Calder and Glauque loc. cit. from 17-322°K. The entropy was calculated based on  $S_{15} = 0.592 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$  Above 300° the heat capacity data was extrapolated smoothly.

Melting Data.

All data were measured by Calder and Glauque loc. cit.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.000	INFINITE	-2.907	8.699	8.699	INFINITE
100	9.619	10.921	2.326	8.833	6.937	15.159
200	11.840	18.406	1.233	8.690	5.085	5.557
298	13.200	23.405	.000	8.466	3.362	2.464
300	13.223	23.405	.024	8.461	3.330	2.426
400	14.367	27.453	1.406	10.081	1.597	.872
500	15.387	30.773	2.896	14.779	.961	.420
600	16.287	33.659	4.480	14.077	4.044	1.473
700	17.088	36.231	6.150	13.296	7.004	2.187
800	17.785	38.559	7.894	12.446	9.846	2.690
900	18.383	40.690	9.703	11.533	12.578	3.054
1000	18.880	42.653	11.567	10.569	15.206	3.323

T, °K.	cal. mole <sup>-1</sup> deg. <sup>-1</sup>		kcal. mole <sup>-1</sup>		Log K <sub>f</sub>
	C <sub>p</sub>	S°	H° - H° <sub>298</sub> /T	ΔH <sub>f</sub> °	
0					
100					
200					
298	24.560	32.544	32.544	5.720	3.341
300	24.582	32.544	32.544	5.694	3.326
400	23.500	39.649	33.501	6.281	2.676
500	22.500	44.785	35.267	10.169	1.436
600	21.500	48.799	37.200	8.852	1.185
700	20.500	52.038	39.096	7.641	1.594
800	19.500	54.710	40.886	6.534	2.837
900	18.500	56.949	42.550	5.531	3.947
1000	17.500	58.847	44.088	4.631	4.950

IODINE MONOCHLORIDE (CLI)

(LIQUID)

MOL. WT. = 162.8574

$$S_{298.15}^{\circ} = 32.544 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -5.72 \pm 0.03 \text{ kcal. mole}^{-1}$$

$$T_m^{\circ} = 300.53^{\circ}\text{K.}$$

$$\Delta H_m^{\circ} = 2.773 \pm 0.002 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding  $\Delta H_m^{\circ}$  and the difference between  $H_{300.53} - H_{298.15}$  for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity from 300.53 to 317.76°K. has been measured by G. V. Calder and W. P. Giaquie, J. Phys. Chem. 69, 2443 (1965). Above 318°K. it was extrapolated in a smooth manner. The entropy was obtained in a manner analogous to the heat of formation.

MOL. WT. = 162.3574

(IDEAL GAS)

IODINE MONOCHLORIDE (CI1)

Log K<sub>P</sub>

$$\Delta H_f^{\circ} = 4.574 \pm 0.025 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} = 59.145 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

Ground State Configuration  $1 \Sigma^+ +$

Electronic Levels and Quantum Weight

$$\frac{\epsilon \cdot \text{cm.}^{-1}}{E_1}$$

$$0 \quad 1$$

$$\omega_e x_e = 1.450 \text{ cm.}^{-1}$$

$$B_e = 0.11298 \text{ cm.}^{-1}$$

$$r_e = 2.327 \text{ \AA}$$

$$\sigma^- = 1$$

Heat of Formation.

The dissociation energy from spectroscopic measurements of ICl(g) has been summarized by W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. Standards, 55, 147 (1955) from which they adopt  $D_0^{\circ} = 49.64 \text{ kcal. mole}^{-1}$ . J. Morris and D. M. Yost, J. Am. Chem. Soc. 54, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939) studied the equilibria  $\text{NOCl} = \text{NO} + 1/2 \text{Cl}_2$  and  $\text{NO} + \text{ICl} = \text{NOCl} + 1/2 \text{I}_2(\text{g})$  from which the equilibrium constant of  $\text{ICl} = 1/2 \text{Cl}_2 + 1/2 \text{I}_2(\text{g})$  can be obtained. G. V. Calder and W. F. Glauque, J. Phys. Chem. 59, 2443 (1965) have used 3rd law analysis to obtain  $D_0^{\circ} = 49.578 \pm 0.025 \text{ kcal. mole}^{-1}$ . This value was adopted yielding  $\Delta H_f^{\circ} 298 = 4.184 \pm 0.025 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

The molecular and vibrational constants were obtained from G. Herzberg "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York 1950. The values were then adjusted for the normal isotopic abundance of chlorine.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>P</sub>
0	0.00	INFINITE	2.284	4.574	4.574	INFINITE
100	7.213	50.547	1.584	4.559	4.540	5.440
200	8.673	55.831	0.816	4.491	4.497	5.463
298	8.497	59.145	0.000	4.184	1.368	1.003
300	8.502	59.145	0.016	4.180	1.402	1.022
400	8.706	61.674	0.877	2.040	3.164	1.720
500	8.808	63.628	1.753	3.272	3.959	1.731
600	8.873	65.240	2.637	3.270	4.097	1.492
700	8.918	66.611	3.527	3.269	4.235	1.322
800	8.952	67.805	4.420	3.269	4.374	1.195
900	8.978	68.860	5.317	3.270	4.511	1.095
1000	9.000	69.808	6.216	3.270	4.650	1.016
1100	9.019	70.666	7.117	3.271	4.788	0.951
1200	9.036	71.452	8.020	3.273	4.926	0.897
1300	9.052	72.176	8.924	3.274	5.064	0.851
1400	9.066	72.847	9.830	3.276	5.200	0.812
1500	9.080	73.473	10.737	3.278	5.339	0.778
1600	9.094	74.059	11.646	3.281	5.474	0.748
1700	9.106	74.611	12.556	3.283	5.611	0.721
1800	9.119	75.132	13.467	3.286	5.749	0.698
1900	9.131	75.625	14.380	3.289	5.884	0.677
2000	9.143	76.084	15.293	3.293	6.023	0.658
2100	9.155	76.540	16.208	3.296	6.158	0.641
2200	9.167	76.967	17.124	3.300	6.296	0.625
2300	9.178	77.374	18.042	3.304	6.430	0.611
2400	9.190	77.765	18.960	3.309	6.566	0.598
2500	9.201	78.141	19.880	3.315	6.704	0.586
2600	9.212	78.502	20.800	3.321	6.839	0.575
2700	9.223	78.849	21.722	3.328	6.972	0.564
2800	9.234	79.185	22.645	3.336	7.106	0.555
2900	9.246	79.509	23.569	3.345	7.241	0.546
3000	9.257	79.823	24.494	3.354	7.377	0.537
3100	9.268	80.127	25.420	3.365	7.512	0.530
3200	9.279	80.421	26.348	3.377	7.644	0.522
3300	9.290	80.707	27.276	3.390	7.777	0.515
3400	9.300	80.984	28.205	3.404	7.909	0.508
3500	9.311	81.254	29.136	3.418	8.042	0.502
3600	9.322	81.515	30.068	3.434	8.172	0.496
3700	9.333	81.772	31.000	3.451	8.305	0.491
3800	9.344	82.021	31.931	3.469	8.437	0.485
3900	9.355	82.264	32.864	3.487	8.567	0.480
4000	9.366	82.501	33.805	3.506	8.698	0.475
4100	9.376	82.732	34.742	3.526	8.825	0.470
4200	9.386	82.958	35.681	3.546	8.954	0.466
4300	9.396	83.179	36.620	3.567	9.084	0.462
4400	9.406	83.395	37.560	3.589	9.214	0.458
4500	9.416	83.607	38.502	3.611	9.339	0.454
4600	9.430	83.814	39.444	3.634	9.465	0.450
4700	9.441	84.017	40.388	3.658	9.593	0.446
4800	9.452	84.216	41.332	3.677	9.720	0.443
4900	9.462	84.411	42.278	3.699	9.844	0.440
5000	9.473	84.602	43.225	3.721	9.969	0.436
5100	9.484	84.790	44.173	3.742	10.095	0.433
5200	9.495	84.974	45.121	3.765	10.218	0.429
5300	9.505	85.155	46.071	3.786	10.342	0.426
5400	9.516	85.333	47.022	3.808	10.466	0.424
5500	9.527	85.508	47.975	3.828	10.591	0.421
5600	9.537	85.680	48.928	3.849	10.718	0.418
5700	9.548	85.848	49.882	3.870	10.835	0.415
5800	9.559	86.015	50.837	3.890	10.960	0.413
5900	9.570	86.178	51.794	3.909	11.081	0.410
6000	9.580	86.339	52.751	3.929	11.201	0.408

Mar. 31, 1962; Sept. 30, 1963; Dec. 31, 1963; Sept. 30, 1965

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	•000	•000	INFINITE	2.717	-104.297	-104.297	INFINITE
100	4.364	7.594	30.087	2.249	-104.594	-102.243	223.452
200	11.577	14.964	20.833	1.173	-104.498	-99.919	109.186
298	17.258	19.731	19.731	•000	-104.370	-97.700	71.616
300	17.268	19.807	19.732	•073	-104.368	-97.659	71.144
400	17.700	23.398	20.218	1.272	-104.848	-95.329	52.085
500	18.086	26.274	21.151	2.561	-104.728	-92.963	40.634
600	18.460	28.693	22.212	3.890	-104.561	-90.624	33.010
700	18.863	30.797	23.291	5.254	-104.350	-88.317	27.574
800	19.289	32.679	24.346	6.664	-104.095	-86.044	23.506
900	19.736	34.407	25.372	8.132	-103.784	-83.805	20.351
1000	20.206	36.038	26.357	9.661	-103.403	-81.606	17.835
1100	20.700	37.622	27.310	11.343	-121.827	-78.429	15.982
1200	21.200	39.165	28.234	13.075	-121.002	-76.315	13.571
1300	21.700	40.665	29.132	14.857	-120.068	-74.267	11.682
1400	22.200	42.124	30.006	16.690	-119.106	-68.913	10.446
1500	22.700	43.551	30.857	18.590	-118.074	-63.221	9.421

ΔH<sub>f</sub><sup>o</sup> 0 = -104.30 kcal. mole<sup>-1</sup>  
 ΔH<sub>f</sub><sup>o</sup> 298.15 = -104.37 ± 0.06 kcal. mole<sup>-1</sup>  
 ΔH<sub>m</sub><sup>o</sup> = 6.282 kcal. mole<sup>-1</sup>

S<sub>298.15}^{298.15} = 19.73 ± 0.04 cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 T<sub>m</sub> = 1044°K.</sub>

Heat of Formation.

The heat of formation was calculated from the heat of hydrolysis of K(c), the heats of solution of HCl(g) and KCl(c), and the standard heat of neutralization of a strong acid and strong base. Extensive measurements are available for all these quantities. Values used in the calculation, in addition to the heat of formation for HCl(g), are summarized below.

Source	Reaction	ΔH <sub>f</sub> <sup>o</sup> 298.15 (kcal.)
1,2,3,4	K(c) + H <sub>2</sub> O(l) → KOH(∞H <sub>2</sub> O) + 1/2 H <sub>2</sub> (g)	-46.966 ± 0.05
5,2,6	HCl(g) → HCl(∞H <sub>2</sub> O)	-17.88 ± 0.015
7	KCl(∞H <sub>2</sub> O) → KCl(c)	-4.115 ± 0.010
7	KOH(∞H <sub>2</sub> O) + HCl(∞H <sub>2</sub> O) → KCl(∞H <sub>2</sub> O) + H <sub>2</sub> O(l)	-13.345 ± 0.025

Heat Capacity and Entropy.

Low temperature heat capacities were obtained from the data (2.8-275°K.) of W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **242**, 467 (1957). Previous measurements scatter around the selected values and are in good agreement. These include P. G. Strelkov, E. S. Itskovich, V. N. Kostryukov, and G. G. Mirskaya (12-298°K.), Zhur. Fiz. Khim. **28**, 645 (1954); K. Glusius, J. Goldman, and A. Perlick (10-275°K.), Z. Naturforsch. **4a**, 429 (1949); and J. C. Southard and R. A. Nelson (17-285°K.), J. Am. Chem. Soc. **55**, 4865 (1933). For other less extensive data see the review by K. K. Kelley and E. G. King, USEM Bulletin 592, 1961. The entropy is based on the extrapolation S<sub>2,8}^{2,8} = 0.0006 cal./deg.-mole.</sub>

High temperature values are based on enthalpy data (373-1038°K.) from T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. These values join smoothly with the low temperature values and are in excellent agreement with the enthalpy data (673-933°K.) of S. M. Skuratov and S. A. Lapushkin, J. Gen. Chem. (USSR) **21**, 2485 (1951) and the adiabatic heat capacities (354-721°K.) of A. Mustajoki, Ann. Acad. Scient. Fennicae, Series A, I, **98**, 7 (1951).

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of T<sub>m</sub> = 1043° and 1045°K. have been reported by E. Aukrust, B. Ejlorge, H. Flood, and T. Forland, Ann. New York Acad. Sci. **79**, 830 (1960) and J. W. Johnson and M. A. Bredig, J. Phys. Chem. **52**, 604 (1958), respectively. The heat of melting is confirmed by ΔH<sub>m</sub><sup>o</sup> = 6.34 kcal./mole obtained from enthalpy data by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **64**, 269 (1960) and ΔH<sub>m</sub><sup>o</sup> = 6.4 and 6.5 kcal./mole based on enthalpy and phase diagram studies of Aukrust et al., loc. cit., respectively.

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POTASSIUM CHLORIDE (KCl)

(LIQUID)

MOD. WT. = 74.555

$\Delta H_f^{298.15} = 20.71$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_m^{298.15} = -100.81$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^{\circ} = 6.282$  kcal. mole<sup>-1</sup>  
 $\Delta H_v^{\circ} = 29.7$  kcal. mole<sup>-1</sup> (equilibrium vapor)  
 $\Delta H_v^{\circ} = [37.14]$  kcal. mole<sup>-1</sup> (monomer)

$S_{298.15}^{\circ} = 20.71$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_m = 1044^{\circ}\text{K.}$   
 $T_b = 1710^{\circ}\text{K.}$  (to equilibrium vapor)  
 $T_b = [1750^{\circ}\text{K.}]$  (to monomer only)

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding  $\Delta H_m^{\circ}$  and the difference between ( $H_{1044}^{\circ} - H_{298}^{\circ}$ ) for the crystal and liquid.

Heat Capacity and Entropy.

The constant heat capacity, 17.59 cal./deg.-mole, was derived from enthalpy data (1053-1173°K.) of T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. This value was extrapolated above and below the experimental range. A lower value of 16.7 cal./deg.-mole was derived by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1, 1964, from enthalpy data (1050-1110°K.) obtained in a heat of melting study. The entropy of the liquid was obtained in a manner analogous to the heat of formation.

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of  $T_m = 1043^{\circ}$  and  $1045^{\circ}\text{K.}$  have been reported by E. Auksrust, B. Björge, H. Flood, and T. Forland, Ann. New York Acad. Sci. 72, 83C (1960) and J. W. Johnson and M. A. Bredig, J. Phys. Chem. 62, 604 (1958), respectively. The heat of melting is confirmed by  $\Delta H_m^{\circ} = 6.34$  kcal./mole obtained from enthalpy data by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960) and  $\Delta H_m^{\circ} = 6.4$  and  $6.5$  kcal./mole based on enthalpy and phase diagram studies of Auksrust et al., loc. cit., respectively.

Vaporization Data.

$T_b$  (to equilibrium vapor) is the temperature resulting in unit total pressure based on the calculated partial pressures of KCl(g) and K<sub>2</sub>Cl<sub>2</sub>(g). This value may be compared with boiling points of 1688° and 1690°K. observed respectively by O. Ruff and S. Mugdan, Z. anorg. allgem. Chem. 117, 147 (1921), and H. von Wartenburg and P. Albrecht, Z. Elektrochem. 27, 162 (1921).  $\Delta H_v^{\circ}$  (equilibrium vapor) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 22.3 mole percent of dimer. According to the selected functions, the amount of dimer at lower temperatures increases gradually to about 32 mole percent at the melting point then decreases rapidly over the crystal.  $T_b$  (to monomer only) is taken as the temperature at which the calculated free energy change is zero for KCl(l) → KCl(g), while  $\Delta H_v^{\circ}$  (monomer) is the corresponding heat of reaction.

Data on vapor pressures and dimer-monomer equilibrium are reviewed on the tables for KCl(g) and K<sub>2</sub>Cl<sub>2</sub>(g), respectively.

T. °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>p</sub>
0							
100	17.590	20.714	20.714	0.000	-100.810	-94.433	69.221
200	17.590	20.823	20.714	0.133	-100.798	-94.394	68.766
300	17.590	21.004	21.004	1.792	-100.768	-92.264	50.400
400	17.590	21.257	21.257	3.551	-100.178	-90.180	39.418
500	17.590	21.580	21.580	5.310	-99.580	-88.236	32.140
600	17.590	21.977	21.977	7.069	-98.976	-86.394	26.973
700	17.590	22.441	22.441	8.828	-98.372	-84.639	23.122
800	17.590	22.977	22.977	10.587	-97.770	-82.957	20.145
900	17.590	23.580	23.580	12.346	-97.179	-81.344	17.778
1000	17.590	24.241	24.241	14.105	-115.505	-78.764	15.649
1100	17.590	24.968	24.968	15.864	-114.693	-75.460	13.743
1200	17.590	25.757	25.757	17.623	-113.882	-72.225	12.142
1300	17.590	26.600	26.600	19.382	-113.072	-69.053	10.779
1400	17.590	27.497	27.497	21.141	-112.265	-65.933	9.600
1500	17.590	28.441	28.441	22.900	-111.455	-62.870	8.588
1600	17.590	29.430	29.430	24.659	-110.640	-59.858	7.695
1700	17.590	30.461	30.461	26.418	-109.823	-56.885	6.908
1800	17.590	31.530	31.530	28.177	-109.003	-53.935	6.208
1900	17.590	32.641	32.641	29.936	-108.179	-51.030	5.584
2000	17.590	33.793	33.793				

POTASSIUM CHLORIDE (KCl) (IDEAL GAS) MOL. WT. = 74.555

Ground State Configuration  $1^1\Sigma$   
 $\Delta H_f^0 = -50.88 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = 57.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{298.15} = -51.31 \pm 0.1 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weights

$$\frac{E_i \text{ cm.}^{-1}}{\sigma} \frac{g_i}{1}$$

$\omega_e = 278.6 \text{ cm.}^{-1}$   
 $\nu_e = 1.157 \text{ cm.}^{-1}$   
 $\nu_e = 0.000799$   
 $\nu_e = 2.667 \text{ \AA}$

Heat of Formation.

The heat of formation was calculated from that of the liquid based on  $\Delta H_v^{298.15} = 49.5 \text{ kcal./mole}$  as selected from vapor pressure analyses summarized below. Partial pressures for the monomer were obtained from data of the first four sources by combination of total vapor pressures with PVT data or with transpiration data. Mass spectrometric values (source 5) are based on temperature variation of ion intensity. These same five studies were used in selection of  $\Delta H_f^{298.15} = 45.0 \text{ kcal./mole}$  for the dimer-monomer equilibrium (see  $K_2Cl_2$ ).

The resulting tables were tested by comparison with total pressure data over the range 819-1691 K. Dimer-monomer ratios calculated from the tables were used to convert observed total pressures to the monomer pressures which are analyzed below (sources 6-11). The results are consistent except near the boiling point where the observed pressures (sources 10 and 11) are 6-18 percent larger than those calculated. Knudsen effusion and transpiration studies over the crystal were not analyzed since they are in essential agreement with the torsion effusion data of source 6.

Source	Method	No. of Points	Temp. Range K.	$\Delta H_f^{298}$ kcal./mole	$\Delta H_f^{298}$ kcal./mole	Drift eu
1. Datz (1960)	PVT + Vap. Press. (a)	15	1310-1404	51.04±0.40	49.67	-1.0±0.4
2. Schrier (1961)	Trans. + Vap. Press.	10	1253-1352	50.75±0.80	49.49	-1.0±0.6
3. Beuman (1967)	Trans. + Vap. Press. (b)	5	1261-1372	50.26±0.77	49.28	-0.8±0.6
4. J. L. Barton and H. Bloom, J. Phys. Chem. 65, 1785 (1959)	Mass Spectrometry	7	1770-1816	49.6±0.66	49.46	-0.1±0.5
5. Milne et al. (1959)	Mass Spectrometry	137	819-945	49.5	49.57	0.06
6. Pugh et al. (1966)	Total Vap. Press.	9	847-936	49.0	49.44	-0.8±0.2
7. Dietz (1936)	Total Vap. Press.	9	1179-1378	50.3	49.42	-1.2±0.2
8. Flock et al. (1928)	Total Vap. Press.	9	1370-1466	51.0	49.48	-2.7±0.4
9. Novikov et al. (1961)	Total Vap. Press.	7	1393-1868	53.6	49.48	-0.8±0.5
10. O. Ruff and S. Muggdan, Z. anorg. Chem. 117, 149 (1921)	Total Vap. Press.	16	1369-1691	50.2	49.22	-0.8±0.5
11. Wartenburg et al. (1921)	Total Vap. Press.	16	1369-1691	50.2	49.22	-0.8±0.5

(a) Total vapor pressure from sources 2, 5 and 8. (b) 1235°K. was omitted.

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 7. V. Dietz, Z. phys. Chem. 135, 575 (1928).  
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 10. O. Ruff and S. Muggdan, Z. anorg. Chem. 117, 149 (1921).  
 11. H. von Wartenburg and P. Albrecht, Z. elektrochem. 27, 162 (1921).

Heat Capacity and Entropy.

Rotational and vibrational constants are based on the microwave studies of P. L. Clouser and W. Gordy, Phys. Rev. 135, 4885 (1964). Earlier microwave data of C. A. Lee, B. P. Fabricand, R. O. Carlson, and C. H. Townes, Phys. Rev. 96, 629 (1954) and electric resonance data of C. A. Lee, B. P. Fabricand, R. O. Carlson, and I. I. Rabi, Phys. Rev. 91, 1395 (1953) are in excellent agreement. Infrared spectra of S. A. Rice and W. Klempner, J. Chem. Phys. 21, 573 (1957) yield  $\omega_e = 281.6 \text{ cm.}^{-1}$  which is also in good agreement. The constants were adjusted to a natural isotopic composition of 24.47%  $^{37}\text{Cl}$  and 6.9%  $^{41}\text{K}$ .

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	7.576	48.122	-2.362	-50.882	-50.882	-50.882	IMFINITE
200	8.530	53.687	-1.652	-50.926	-50.926	-50.926	115.040
298	8.723	57.116	-0.000	-51.109	-51.109	-51.109	59.307
				-51.310	-51.310	-51.310	40.893
300	8.726	57.117	0.16	-51.314	-51.314	-51.314	40.661
400	8.857	59.701	8.06	-52.163	-52.163	-52.163	31.234
500	8.930	61.685	1.786	-52.443	-52.443	-52.443	25.520
600	8.979	63.318	2.681	-52.708	-52.708	-52.708	21.690
700	9.015	64.705	3.581	-52.964	-52.964	-52.964	18.941
800	9.042	65.911	4.484	-53.215	-53.215	-53.215	16.869
900	9.072	66.978	5.390	-53.467	-53.467	-53.467	15.250
1000	9.097	67.935	6.298	-53.726	-53.726	-53.726	13.949
1100	9.119	68.803	7.209	-53.991	-53.991	-53.991	12.676
1200	9.141	69.598	8.122	-54.262	-54.262	-54.262	11.468
1300	9.162	70.330	9.037	-54.538	-54.538	-54.538	10.318
1400	9.182	71.010	9.955	-54.819	-54.819	-54.819	9.217
1500	9.202	71.644	10.874	-55.104	-55.104	-55.104	8.161
1600	9.221	72.238	11.795	-55.393	-55.393	-55.393	7.145
1700	9.240	72.798	12.718	-55.686	-55.686	-55.686	6.168
1800	9.259	73.327	13.643	-55.983	-55.983	-55.983	5.229
1900	9.278	73.828	14.570	-56.284	-56.284	-56.284	4.328
2000	9.297	74.304	15.499	-56.589	-56.589	-56.589	3.461
2100	9.316	74.758	16.429	-56.898	-56.898	-56.898	2.628
2200	9.335	75.192	17.362	-57.211	-57.211	-57.211	1.829
2300	9.353	75.606	18.296	-57.528	-57.528	-57.528	1.064
2400	9.372	76.006	19.232	-57.848	-57.848	-57.848	0.334
2500	9.390	76.389	20.171	-58.171	-58.171	-58.171	-0.361
2600	9.408	76.758	21.110	-58.498	-58.498	-58.498	-1.096
2700	9.427	77.113	22.052	-58.828	-58.828	-58.828	-1.790
2800	9.445	77.456	22.996	-59.161	-59.161	-59.161	-2.442
2900	9.463	77.788	23.941	-59.497	-59.497	-59.497	-3.052
3000	9.482	78.109	24.888	-59.836	-59.836	-59.836	-3.624
3100	9.500	78.420	25.838	-60.178	-60.178	-60.178	-4.157
3200	9.518	78.722	26.788	-60.523	-60.523	-60.523	-4.654
3300	9.536	79.015	27.741	-60.871	-60.871	-60.871	-5.114
3400	9.553	79.300	28.695	-61.222	-61.222	-61.222	-5.542
3500	9.571	79.577	29.652	-61.576	-61.576	-61.576	-5.939
3600	9.591	79.847	30.610	-61.933	-61.933	-61.933	-6.304
3700	9.609	80.110	31.570	-62.293	-62.293	-62.293	-6.638
3800	9.627	80.367	32.532	-62.656	-62.656	-62.656	-6.941
3900	9.646	80.617	33.496	-63.022	-63.022	-63.022	-7.214
4000	9.664	80.862	34.461	-63.391	-63.391	-63.391	-7.467
4100	9.682	81.101	35.429	-63.762	-63.762	-63.762	-7.699
4200	9.700	81.334	36.398	-64.136	-64.136	-64.136	-7.911
4300	9.718	81.562	37.369	-64.513	-64.513	-64.513	-8.103
4400	9.736	81.786	38.341	-64.893	-64.893	-64.893	-8.275
4500	9.755	82.005	39.316	-65.276	-65.276	-65.276	-8.428
4600	9.773	82.220	40.292	-65.662	-65.662	-65.662	-8.562
4700	9.791	82.430	41.270	-66.051	-66.051	-66.051	-8.677
4800	9.809	82.636	42.250	-66.443	-66.443	-66.443	-8.773
4900	9.827	82.839	43.237	-66.838	-66.838	-66.838	-8.851
5000	9.845	83.038	44.226	-67.236	-67.236	-67.236	-8.911
5100	9.863	83.232	45.219	-67.637	-67.637	-67.637	-8.951
5200	9.881	83.424	46.218	-68.041	-68.041	-68.041	-8.981
5300	9.900	83.613	47.218	-68.448	-68.448	-68.448	-8.999
5400	9.918	83.801	48.218	-68.858	-68.858	-68.858	-9.011
5500	9.936	83.989	49.218	-69.270	-69.270	-69.270	-9.017
5600	9.954	84.179	50.216	-69.684	-69.684	-69.684	-9.011
5700	9.972	84.366	51.215	-70.101	-70.101	-70.101	-8.991
5800	9.990	84.550	52.215	-70.521	-70.521	-70.521	-8.951
5900	10.008	84.734	53.215	-70.943	-70.943	-70.943	-8.891
6000	10.026	84.918	54.215	-71.368	-71.368	-71.368	-8.811

Ground State Configuration  $2 \sum$   
 $\Delta H_f^0 = -10.34 \pm 10 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 298.15 = -10.4 \pm 10 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weights

$$\frac{\epsilon_l, \text{ cm.}^{-1}}{0} \frac{g_l}{2}$$

$$\sigma = 1$$

$$\omega_e x_e = 2.02 \text{ cm.}^{-1}$$

$$r_e = 2.199 \text{ \AA}$$

$$\alpha_e = [0.0014] \text{ cm.}^{-1}$$

$$\omega_e = 462.4 \text{ cm.}^{-1}$$

$$B_e = [0.2417] \text{ cm.}^{-1}$$

Heat of Formation.

The heat of formation is calculated from  $D_0^0 = 3.2 \text{ e.v.}$  reported by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Co., Inc., New York, 1950.  $D_0^0 = 2.7 \pm 0.7 \text{ e.v.}$  reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd Edn., Chapman and Hall, London, 1953, yields  $\Delta H_f^0 298 \text{ (MgCl, g)} = 1.0 \pm 16 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

Spectroscopic constants were reported by Herzberg loc. cit. and adjusted for natural isotopic abundance. The bond length was reported by E. Morgan and R. P. Barrow, Nature 192, 1182, (1961).  $B_e$  and  $\alpha_e$  were estimated by the method suggested by Herzberg loc. cit. The moment of inertia (I) is  $11.578 \times 10^{-59} \text{ g. cm.}^2$

T. °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	7.077	62.801	2.237	10.344	10.344	10.344	INFINITE
200	7.830	57.531	1.540	10.152	12.405	27.411	27.411
298	8.324	55.760	.795	10.329	16.078	16.078	16.078
300	8.330	55.812	.815	10.403	16.791	12.232	12.232
400	8.587	56.091	.863	10.585	18.894	12.323	12.323
500	8.730	56.180	1.729	10.787	20.946	9.156	9.156
600	8.819	57.476	2.607	11.013	22.959	8.363	8.363
700	8.878	58.145	3.492	11.260	24.930	7.784	7.784
800	8.922	58.833	4.382	11.537	26.865	7.339	7.339
900	8.956	59.524	5.276	11.849	28.762	6.984	6.984
1000	8.983	60.158	6.173	12.191	30.622	6.653	6.653
1100	9.007	60.759	7.073	12.569	32.438	6.365	6.365
1200	9.027	61.328	7.974	12.985	34.210	6.120	6.120
1300	9.046	61.867	8.878	13.445	35.932	5.900	5.900
1400	9.063	62.379	9.783	13.953	37.615	5.643	5.643
1500	9.079	62.866	10.691	14.511	39.259	5.412	5.412
1600	9.094	63.330	11.599	15.124	40.866	5.201	5.201
1700	9.109	63.773	12.509	15.792	42.437	5.007	5.007
1800	9.123	64.196	13.421	16.516	43.974	4.837	4.837
1900	9.136	64.602	14.344	17.294	45.478	4.689	4.689
2000	9.150	65.000	15.268	18.126	46.950	4.561	4.561
2100	9.163	65.385	16.194	19.011	48.383	4.452	4.452
2200	9.175	65.757	17.081	19.950	49.778	4.361	4.361
2300	9.188	66.116	18.027	20.943	51.135	4.289	4.289
2400	9.200	66.463	18.938	22.000	52.455	4.234	4.234
2500	9.212	66.798	19.839	23.122	53.734	4.194	4.194
2600	9.225	67.025	20.761	24.315	54.976	4.166	4.166
2700	9.237	67.243	21.684	25.578	56.183	4.149	4.149
2800	9.249	67.451	22.608	26.911	57.356	4.142	4.142
2900	9.261	67.634	23.534	28.324	58.496	4.144	4.144
3000	9.272	67.799	24.460	29.817	59.603	4.154	4.154
3100	9.284	67.946	25.388	31.390	60.678	4.171	4.171
3200	9.296	68.078	26.317	33.043	61.722	4.194	4.194
3300	9.308	68.194	27.247	34.776	62.734	4.222	4.222
3400	9.319	68.295	28.179	36.589	63.714	4.254	4.254
3500	9.331	68.382	29.111	38.482	64.662	4.290	4.290
3600	9.343	68.455	30.045	40.455	65.578	4.329	4.329
3700	9.354	68.515	30.980	42.508	66.462	4.370	4.370
3800	9.366	68.561	31.916	44.641	67.314	4.413	4.413
3900	9.377	68.594	32.853	46.854	68.132	4.458	4.458
4000	9.389	68.615	33.791	49.147	68.914	4.505	4.505
4100	9.400	68.624	34.731	51.520	69.662	4.554	4.554
4200	9.412	68.621	35.671	53.973	70.376	4.604	4.604
4300	9.423	68.606	36.613	56.506	71.059	4.655	4.655
4400	9.435	68.579	37.556	59.119	71.709	4.707	4.707
4500	9.446	68.541	38.500	61.812	72.326	4.760	4.760
4600	9.457	68.499	39.445	64.585	72.910	4.814	4.814
4700	9.469	68.452	40.391	67.448	73.461	4.869	4.869
4800	9.480	68.399	41.339	70.401	73.979	4.925	4.925
4900	9.492	68.342	42.287	73.444	74.464	4.982	4.982
5000	9.503	68.281	43.237	76.577	74.916	5.039	5.039
5100	9.515	68.216	44.188	79.800	75.334	5.096	5.096
5200	9.526	68.147	45.140	83.213	75.718	5.153	5.153
5300	9.537	68.074	46.093	86.816	76.068	5.210	5.210
5400	9.549	68.000	47.047	90.509	76.384	5.267	5.267
5500	9.560	67.925	48.003	94.292	76.666	5.324	5.324
5600	9.571	67.849	48.959	98.165	76.915	5.381	5.381
5700	9.583	67.772	49.917	102.128	77.132	5.438	5.438
5800	9.594	67.695	50.876	106.181	77.317	5.495	5.495
5900	9.605	67.618	51.836	110.324	77.470	5.552	5.552
6000	9.617	67.541	52.797	114.557	77.592	5.609	5.609



T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298°)/T</sub>	H° - H <sub>298°</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0	∞	INFINITE	2.713	12.828	12.828	INFINITE
100	8.021	52.010	1.913	12.578	12.578	1.913
200	8.645	67.095	1.910	12.378	12.378	1.910
298	10.680	82.527	0.000	12.370	12.370	1.958
300	10.694	82.593	0.020	12.369	12.369	1.958
400	11.311	65.757	1.231	12.352	12.352	1.925
500	11.790	68.334	2.277	12.364	12.364	1.925
600	12.196	70.521	3.477	12.396	12.396	1.925
700	12.535	72.427	4.714	12.441	12.441	1.925
800	12.827	74.120	5.982	12.496	12.496	1.925
900	13.069	75.645	7.277	12.559	12.559	1.925
1000	13.273	77.033	8.595	12.629	12.629	1.925
1100	13.446	78.306	9.931	12.703	12.703	1.925
1200	13.597	79.483	11.283	12.781	12.781	1.925
1300	13.726	80.577	12.649	12.862	12.862	1.925
1400	13.841	81.598	14.028	12.946	12.946	1.925
1500	13.943	82.557	15.417	13.033	13.033	1.925
1600	14.035	83.459	16.816	13.121	13.121	1.925
1700	14.120	84.313	18.224	13.212	13.212	1.925
1800	14.195	85.122	19.640	13.303	13.303	1.925
1900	14.266	85.891	21.063	13.396	13.396	1.925
2000	14.335	86.625	22.493	13.490	13.490	1.925
2100	14.396	87.326	23.929	13.585	13.585	1.925
2200	14.458	87.997	25.372	13.680	13.680	1.925
2300	14.515	88.641	26.821	13.777	13.777	1.925
2400	14.570	89.260	28.275	13.874	13.874	1.925
2500	14.623	89.856	29.735	13.972	13.972	1.925
2600	14.675	90.430	31.200	14.068	14.068	1.925
2700	14.724	90.985	32.670	14.165	14.165	1.925
2800	14.771	91.521	34.144	14.263	14.263	1.925
2900	14.820	92.041	35.624	14.361	14.361	1.925
3000	14.866	92.544	37.108	14.458	14.458	1.925
3100	14.910	93.032	38.597	14.556	14.556	1.925
3200	14.957	93.507	40.090	14.653	14.653	1.925
3300	14.997	93.969	41.588	14.751	14.751	1.925
3400	15.044	94.415	43.090	14.849	14.849	1.925
3500	15.083	94.852	44.597	14.947	14.947	1.925
3600	15.126	95.277	46.107	15.044	15.044	1.925
3700	15.169	95.692	47.622	15.143	15.143	1.925
3800	15.210	96.098	49.141	15.243	15.243	1.925
3900	15.251	96.493	50.664	15.343	15.343	1.925
4000	15.292	96.880	52.191	15.443	15.443	1.925
4100	15.333	97.258	53.722	15.545	15.545	1.925
4200	15.371	97.628	55.257	15.648	15.648	1.925
4300	15.411	97.990	56.796	15.752	15.752	1.925
4400	15.454	98.345	58.340	15.858	15.858	1.925
4500	15.491	98.693	59.887	15.964	15.964	1.925
4600	15.530	99.033	61.438	16.074	16.074	1.925
4700	15.570	99.368	62.993	16.184	16.184	1.925
4800	15.608	99.696	64.552	16.297	16.297	1.925
4900	15.647	100.018	66.115	16.412	16.412	1.925
5000	15.688	100.335	67.681	16.529	16.529	1.925
5100	15.721	100.646	69.252	16.648	16.648	1.925
5200	15.756	100.952	70.826	16.771	16.771	1.925
5300	15.798	101.252	72.404	16.895	16.895	1.925
5400	15.838	101.548	73.986	17.022	17.022	1.925
5500	15.878	101.839	75.572	17.152	17.152	1.925
5600	15.911	102.125	77.161	17.283	17.283	1.925
5700	15.951	102.407	78.754	17.418	17.418	1.925
5800	16.002	102.685	80.352	17.557	17.557	1.925
5900	16.027	102.959	81.954	17.698	17.698	1.925
6000	16.066	103.228	83.558	17.841	17.841	1.925

NITROSYL CHLORIDE (NOCl)

(IDEAL GAS)

MOL. WT. = 65.4591

$$\Delta H_f^\circ = 12.83 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = 62.53 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$S_{298.15}^\circ = 12.37 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\text{Ground State Quantum Weight} = 1$$

Vibrational Frequencies & Degeneracies

$\omega_j, \text{ cm.}^{-1}$

1800 (1)

594.9 (1)

331.5 (1)

N-O = 1.17 ± 0.06 Å

Bond Distance: N-Cl = 1.95 ± 0.06 Å

O = 1

Bond Angle: Cl-N-O = 114 ± 3°

Product of the Moments of Inertia:  $I_A I_B I_C = 2.278778 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The equilibrium constants for the reaction  $2\text{NOCl(g)} = 2\text{NO(g)} + \text{Cl}_2\text{(g)}$  have been measured in the temperature range from 372° to 491°K. by C. M. Beeson and D. M. Yost, *J. Chem. Phys.* **7**, 44 (1938). Using the reported equilibrium constants, the heat of reaction ( $\Delta H_f^\circ$ , 298) has been calculated by both the second and the third law methods, as 18.53 ± 0.1 kcal. mole<sup>-1</sup> and 18.42 ± 0.1 kcal. mole<sup>-1</sup>, respectively. The third law value is adopted to calculate the heat of formation of nitrosyl chloride (g) as  $\Delta H_f^\circ$  298 = 12.37 ± 0.2 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The selected bond distances and angle were obtained from the microwave measurements by J. D. Rogers and D. Williams, *J. Chem. Phys.* **34**, 2195 (1961). J. A. A. Ketelaar and K. J. Palmer, *J. Am. Chem. Soc.* **59**, 2629 (1937), reported the bond distance N-Cl = 1.95 Å and the angle O-N-Cl = 116° by the electron diffraction method. These two are in good agreement. The three principal moments of inertia are  $I_A = 0.9895 \times 10^{-39}$ ,  $I_B = 14.6885 \times 10^{-39}$  and  $I_C = 15.6780 \times 10^{-39} \text{ g. cm.}^2$ . The selected vibrational frequencies which were obtained from the infrared spectrum by L. Landau and W. H. Fletcher, *J. Mol. Spectry.* **4**, 276 (1960), have been modified to natural isotopic mixture. W. G. Burns and J. J. Bernstein, *J. Chem. Phys.* **18**, 1669 (1950), reported the vibrational frequencies as 1799, 592 and 332 cm<sup>-1</sup>.

J. S. Gordon, *J. Chem. Eng. Data* **7**, 82 (1962), has calculated the thermodynamic functions from 298.15° to 6000°K. by the method of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.* **22**, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from Landau and Fletcher, loc. cit., and J. D. Rogers, W. J. Pletenpol and D. Williams, *Phys. Rev.* **83**, 431 (1951). These calculated functions have been adopted in the tabulation. Below 298°K. the rigid-rotator harmonic oscillator method was used to calculate the functions.

(IDEAL GAS)

NITRYL CHLORIDE (NO<sub>2</sub>Cl)

MOL. WT. = 81.4585

Point Group C<sub>2v</sub>  
 $\Delta H_f^0 = 4.20 \pm 0.4$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 65.0$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>  
 $\Delta H_f^0 = 2.90 \pm 0.4$  kcal. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
1293 (1)	1685 (1)
794 (1)	411 (1)
367 (1)	651 (1)

Bond Distances: N-Cl = 1.83 Å, N-O = 1.21 Å  
 Bond Angle: O-N-O = 129.5°  
 Product of Moments of Inertia:  $I_A I_B I_C = 2.36698 \times 10^{-114}$  g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The selected heat of formation was obtained from the recalculation of the heat of reaction ClNO<sub>2</sub> + NO = ClNO + NO<sub>2</sub> which has been measured calorimetrically as -9.27 kcal. mole<sup>-1</sup> by J. Ray and R. Ogg, Jr., J. Chem. Phys. 31, 168 (1959). Not only the thermal effects of 2NO<sub>2</sub> = N<sub>2</sub>O<sub>4</sub> but also NO + NO<sub>2</sub> = N<sub>2</sub>O<sub>3</sub> (a minor one) have been considered in calculation. Using all JANAF auxiliary data for ClNO, NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub>, the recalculation gives  $\Delta H_f^0 = 2.90 \pm 0.4$  kcal. mole<sup>-1</sup> for NO<sub>2</sub>Cl(g). For the reaction ClNO + N<sub>2</sub>O<sub>3</sub> = ClNO<sub>2</sub> + 2NO<sub>2</sub> also measured by Ray and Ogg, loc. cit., the recalculation gives  $\Delta H_f^0 = 2.56 \pm 0.4$  kcal. mole<sup>-1</sup>.

H. Martin and E. Koehlein, Z. physik. Chem. 17, 375 (1958), have determined kinetically the heat of reaction,  $\Delta H_f^0 = 2.75$  kcal. mole<sup>-1</sup> for the reaction NO<sub>2</sub> + NOCl = NO + NO<sub>2</sub>Cl which gives  $\Delta H_f^0 = 1.90 \pm 1$  kcal. mole<sup>-1</sup> for NO<sub>2</sub>Cl(g). H. Cordes and H. Johnston, J. Am. Chem. Soc., 76, 4264 (1954), have also determined kinetically the  $\Delta H_f^0 = 29.5$  kcal. mole<sup>-1</sup> for the reaction NO<sub>2</sub>Cl = NO<sub>2</sub> + Cl which gives  $\Delta H_f^0 = 6.5 \pm 0.3$  kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The selected bond distances and bond angles were obtained from microwave spectrum studies by L. Clayton, Q. Williams and T. L. Weatherly, J. Chem. Phys. 30, 1328 (1959). D. J. Millen and K. M. Simmott, J. Chem. Soc. 350 (1958), reported bond distance N-Cl = 1.840 Å, N-O = 1.202 Å and angle ONO = 130° 35' from the microwave measurement. These two are in good agreement.

The selected vibrational frequencies were obtained from infrared and Raman spectrum measurements by R. Ryason and M. K. Wilson, J. Chem. Phys. 22, 2000 (1954). However, the assignment of the fundamental frequencies has been revised by R. E. Dodd, J. A. Rolfe and L. A. Woodward, Trans. Faraday Soc. 52, 145 (1956), and Y. Morino and T. Tanaka, J. Mol. Spectry. 15, 179 (1965). Morino and Tanaka's assignment was adopted. The three principal moments of inertia are  $I_A = 6.3658 \times 10^{-39}$ ,  $I_B = 16.3609 \times 10^{-39}$  and  $I_C = 22.7267 \times 10^{-39}$  g. cm.<sup>2</sup>

Dec. 31, 1962; Dec. 31, 1965

T, °K.	C <sub>v</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF°	Log K <sub>p</sub>
0	6.00	INFINITE	-	2.916	4.192	4.192	INFINITE
100	8.43	53.818	-	2.412	6.523	6.523	-14.261
200	10.74	60.535	-	1.156	9.642	9.642	-10.538
298	12.712	65.030	-	0.000	2.900	12.889	-9.447
300	12.744	65.030	0.024	2.897	2.897	12.951	-9.434
400	14.254	68.549	1.377	2.775	2.775	16.324	-8.918
500	15.448	72.332	2.657	2.663	2.752	19.716	-8.617
600	16.291	75.193	4.450	2.794	2.794	23.106	-8.416
700	16.566	77.023	6.414	2.877	2.877	26.485	-8.269
800	17.485	80.058	7.838	2.988	2.988	29.849	-8.154
900	17.886	82.141	9.607	3.119	3.119	33.200	-8.062
1000	18.250	84.043	11.412	3.263	3.263	36.534	-7.984
1100	18.448	85.790	13.245	3.414	3.414	39.853	-7.918
1200	18.648	87.404	15.100	3.571	3.571	43.159	-7.860
1300	18.809	88.903	16.973	3.731	3.731	46.452	-7.809
1400	18.942	90.302	18.861	3.892	3.892	49.731	-7.763
1500	19.052	91.613	20.761	4.053	4.053	53.000	-7.722
1600	19.144	92.845	22.671	4.214	4.214	56.259	-7.684
1700	19.222	94.008	24.589	4.375	4.375	59.508	-7.650
1800	19.288	95.108	26.515	4.531	4.531	62.745	-7.618
1900	19.345	96.153	28.446	4.685	4.685	65.977	-7.589
2000	19.394	97.147	30.383	4.836	4.836	69.197	-7.561
2100	19.436	98.094	32.325	4.984	4.984	72.412	-7.536
2200	19.474	98.999	34.270	5.125	5.125	75.619	-7.512
2300	19.506	99.865	36.220	5.265	5.265	78.821	-7.489
2400	19.535	100.696	38.172	5.399	5.399	82.017	-7.468
2500	19.561	101.494	40.126	5.526	5.526	85.205	-7.448
2600	19.584	102.262	42.084	5.650	5.650	88.390	-7.429
2700	19.604	103.001	44.043	5.780	5.780	91.571	-7.412
2800	19.622	103.715	46.004	5.880	5.880	94.745	-7.395
2900	19.639	104.404	47.967	5.988	5.988	97.919	-7.379
3000	19.654	105.070	49.932	6.089	6.089	101.086	-7.364
3100	19.668	105.714	51.898	6.186	6.186	104.253	-7.349
3200	19.680	106.339	53.866	6.276	6.276	107.420	-7.334
3300	19.691	106.945	55.834	6.361	6.361	110.578	-7.320
3400	19.702	107.533	57.804	6.441	6.441	113.728	-7.306
3500	19.711	108.104	59.774	6.516	6.516	116.868	-7.298
3600	19.720	108.659	61.746	6.587	6.587	120.037	-7.287
3700	19.728	109.200	63.718	6.652	6.652	123.185	-7.276
3800	19.735	109.726	65.692	6.713	6.713	126.335	-7.266
3900	19.742	110.239	67.665	6.770	6.770	129.480	-7.256
4000	19.748	110.738	69.640	6.822	6.822	132.628	-7.246
4100	19.754	111.226	71.615	6.870	6.870	135.772	-7.237
4200	19.760	111.702	73.591	6.915	6.915	138.914	-7.228
4300	19.765	112.167	75.567	6.957	6.957	142.050	-7.220
4400	19.770	112.622	77.544	6.994	6.994	145.198	-7.212
4500	19.774	113.066	79.521	7.028	7.028	148.339	-7.204
4600	19.778	113.501	81.499	7.061	7.061	151.482	-7.197
4700	19.782	113.926	83.477	7.089	7.089	154.622	-7.190
4800	19.786	114.343	85.455	7.116	7.116	157.759	-7.183
4900	19.789	114.751	87.434	7.140	7.140	160.892	-7.176
5000	19.793	115.151	89.413	7.162	7.162	164.029	-7.169
5100	19.796	115.542	91.392	7.182	7.182	167.174	-7.164
5200	19.799	115.927	93.372	7.201	7.201	170.306	-7.157
5300	19.801	116.304	95.352	7.217	7.217	173.446	-7.152
5400	19.804	116.674	97.332	7.232	7.232	176.579	-7.146
5500	19.807	117.038	99.313	7.246	7.246	179.718	-7.141
5600	19.809	117.395	101.294	7.257	7.257	182.848	-7.136
5700	19.811	117.745	103.275	7.268	7.268	185.985	-7.131
5800	19.813	118.090	105.256	7.277	7.277	189.125	-7.126
5900	19.815	118.428	107.237	7.285	7.285	192.259	-7.121
6000	19.817	118.762	109.219	7.292	7.292	195.392	-7.117

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (F <sup>o</sup> - H <sub>298<sup>o</sup>)/T</sub>	H <sup>o</sup> - H <sub>298<sup>o</sup></sub>	ΔH <sub>f</sub> <sup>o</sup> kcal. mole <sup>-1</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	.000	INFINITE	2.194	.000	.000	.000
100	7.001	45.150	60.130	.000	.000	.000
200	7.576	54.016	.772	.000	.000	.000
298	8.111	53.289	.000	.000	.000	.000
300	8.119	53.339	.015	.000	.000	.000
400	8.437	55.724	8.45	.000	.000	.000
500	8.624	57.628	1.698	.000	.000	.000
600	8.741	59.212	2.567	.000	.000	.000
700	8.821	60.565	3.445	.000	.000	.000
800	8.878	61.747	4.331	.000	.000	.000
900	8.922	62.796	5.221	.000	.000	.000
1000	8.956	63.737	6.115	.000	.000	.000
1100	8.985	64.592	7.012	.000	.000	.000
1200	9.010	65.375	7.912	.000	.000	.000
1300	9.032	66.097	8.814	.000	.000	.000
1400	9.051	66.767	9.718	.000	.000	.000
1500	9.069	67.392	10.624	.000	.000	.000
1600	9.086	67.978	11.532	.000	.000	.000
1700	9.102	68.530	12.441	.000	.000	.000
1800	9.117	69.050	13.352	.000	.000	.000
1900	9.133	69.534	14.264	.000	.000	.000
2000	9.149	70.013	15.179	.000	.000	.000
2100	9.166	70.489	16.094	.000	.000	.000
2200	9.182	70.962	17.012	.000	.000	.000
2300	9.203	71.439	17.931	.000	.000	.000
2400	9.223	71.918	18.852	.000	.000	.000
2500	9.245	72.404	19.776	.000	.000	.000
2600	9.268	72.827	20.701	.000	.000	.000
2700	9.293	73.277	21.629	.000	.000	.000
2800	9.319	73.716	22.560	.000	.000	.000
2900	9.346	74.143	23.493	.000	.000	.000
3000	9.374	74.560	24.429	.000	.000	.000
3100	9.403	74.968	25.368	.000	.000	.000
3200	9.432	75.367	26.310	.000	.000	.000
3300	9.461	75.758	27.255	.000	.000	.000
3400	9.490	76.141	28.202	.000	.000	.000
3500	9.518	76.516	29.153	.000	.000	.000
3600	9.546	76.885	30.106	.000	.000	.000
3700	9.573	77.247	31.062	.000	.000	.000
3800	9.598	77.602	32.020	.000	.000	.000
3900	9.622	77.952	32.981	.000	.000	.000
4000	9.645	78.296	33.945	.000	.000	.000
4100	9.666	78.634	34.910	.000	.000	.000
4200	9.685	78.967	35.878	.000	.000	.000
4300	9.702	79.295	36.847	.000	.000	.000
4400	9.718	79.619	37.818	.000	.000	.000
4500	9.732	79.937	38.791	.000	.000	.000
4600	9.743	80.251	39.764	.000	.000	.000
4700	9.754	80.561	40.739	.000	.000	.000
4800	9.762	80.866	41.715	.000	.000	.000
4900	9.768	81.166	42.692	.000	.000	.000
5000	9.774	81.461	43.669	.000	.000	.000
5100	9.778	81.751	44.646	.000	.000	.000
5200	9.783	82.036	45.624	.000	.000	.000
5300	9.787	82.315	46.603	.000	.000	.000
5400	9.790	82.589	47.582	.000	.000	.000
5500	9.792	82.858	48.561	.000	.000	.000
5600	9.794	83.122	49.540	.000	.000	.000
5700	9.795	83.381	50.520	.000	.000	.000
5800	9.797	83.635	51.500	.000	.000	.000
5900	9.797	83.884	52.480	.000	.000	.000
6000	9.798	84.128	53.459	.000	.000	.000

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

CHLORINE, DIATOMIC (Cl<sub>2</sub>) (IDEAL GAS - REFERENCE STATE) MOL. WT. = 70.906

Ground State Configuration 1Σ<sup>+</sup> + ΔH<sub>f</sub><sup>o</sup> 0 = 0  
 S<sub>298.15</sub><sup>o</sup> = 53.29 ± 0.01 cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>o</sup> 298 = 0

Electronic Levels and Multiplicities

State	E <sub>cm.</sub> <sup>-1</sup>	g <sub>1</sub>
1Σ <sup>+</sup>	0	1
3Π <sup>0</sup>	18,147 ± 500	1
3Π <sub>1</sub>	17,841 ± 500	2
3Π <sub>2</sub>	17,560 ± 500	2

ω<sub>e</sub> = 561.1 cm.<sup>-1</sup> ω<sub>e</sub>x<sub>e</sub> = 4.0 cm.<sup>-1</sup> σ<sup>-</sup> = 2  
 B<sub>e</sub> = 0.2408 cm.<sup>-1</sup> α<sub>e</sub> = 0.0017 cm.<sup>-1</sup> r<sub>e</sub> = 1.986 Å

Heat of Formation.

The heat of formation (ΔH<sub>f</sub><sup>o</sup>) for Cl<sub>2</sub>(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here were calculated by R. L. Potter, J. Chem. Phys. 31, 1100 (1959) using a direct summation over the energy levels not including those of non-bonding states. The functions are for the naturally occurring isotopic composition.

The absorption spectrum of chlorine has been observed by A. Elliott, Proc. Roy. Soc. A 127, 638 (1930); C. F. Goodeve and B. A. Stephens, Trans. Faraday Soc. 52, 1517 (1956); H. Stammreich, R. Forneris and V. Tavares, Spectrochim. Acta, 17, 775 (1961); Y. V. Rao and P. Venkateswarlu, J. Mol. Spectr. 9, 173 (1962); and A. E. Douglas, C. K. Moller and B. P. Stoicheff, Can. J. Phys. 41, 1174 (1963). There is disagreement over the vibrational assignments. The listed ground state spectroscopic constants for the naturally occurring isotopic composition are based upon the abundances given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 595 (1958).

The molecular structure of gaseous chlorine was determined by the sector-microphotometer method of electron diffraction by S. Shibata, J. Phys. Chem. 57, 2256 (1953). The value of r<sub>e</sub>(Cl-Cl) was found to be 1.986 Å. The other r<sub>e</sub> values, 1.983 - 1.989 Å, were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., 1950; W. G. Richards and R. F. Barrow, Proc. Chem. Soc., 297 (1962), and L. S. Bartell and K. Kuchitsu, presented at the International Conference on Magnetism and Crystallography, 1961, quoted by S. Shihata, loc. cit.

MOL. WT. = 134.446

COPPER DICHLORIDE (CuCl<sub>2</sub>) (CRYSTAL)

$\Delta H_f^0 = -49.39 \pm 1.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -49.2 \pm 1.5 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 25.833 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_D = [766]^{\circ}\text{K.}$

Heat of Formation.

S. A. Shchukarev and M. A. Oranskaya, Zhur. Obshchei Khim. 24, 1926 (1954) have reported equilibrium constants for the dissociation  $\text{CuCl}_2(c) \rightarrow \text{CuCl}(c/1) + 0.5 \text{ Cl}_2(g)$ , which are in general agreement with earlier reports by P. Ephraim, Ber. 50, 1069 (1917) and D. I. Tarsasenkov, A. I. Grigorovich and A. V. Boroslovskaya, Collected Works of the Central State Institute for Non-Ferrous Metallurgy, Part 1, 1, 69 (1929). These data were subjected to third law analysis which revealed a significant trend of  $13 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}$ , indicating that equilibrium conditions were not reached. However an average value of  $\Delta H_f^{298} = 16.5 \pm 1.9 \text{ kcal. mole}^{-1}$  yields a heat of formation of  $\text{CuCl}_2(c) = -49.5 \pm 2.5 \text{ kcal. mole}^{-1}$  which is in good agreement with the adopted value taken from Natl. Bureau Std. Circular 500, Washington, 1952.

Heat Capacity and Entropy.

The low temperature heat capacity has been measured from 11-300°K. by J. W. Stout and R. C. Chisholm, J. Chem. Phys. 36, 979 (1962). The integration of this data from  $S_{10} = 0.111 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  gave  $S_{298} = 25.833 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . The heat capacity above 298° was obtained by smooth extrapolation of the above data, since the heat capacities of A. N. Krestovnikov and G. A. Karetnikov, Journ. Gen. Chem. (USSR) 5, 955 (1936) were not compatible with the low temperature data.

Decomposition Data.

The temperature of decomposition was estimated from the table for  $\text{CuCl}_2(c)$ ,  $\text{CuCl}(l)$  and  $\text{Cl}_2(g)$  so that the pressure of  $\text{Cl}_2$  is 1 atm.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.000	INFINITE	3.581	-49.392	-49.392	INFINITE
100	11.180	9.804	3.012	-49.683	-45.905	100.326
200	15.690	19.246	1.624	-49.497	-42.183	46.095
298	17.180	25.833	.000	-49.200	-38.655	28.335
300	17.190	25.833	.032	-49.194	-38.590	28.112
400	17.940	30.994	1.791	-48.862	-35.104	19.180
500	18.470	35.057	3.612	-48.510	-31.704	13.858
600	18.830	38.458	5.478	-48.146	-28.378	10.337
700	19.110	41.302	7.376	-47.771	-25.112	7.640
800	19.332	43.849	9.298	-47.392	-21.902	5.683
900	19.516	46.236	11.240	-47.007	-18.798	4.450
1000	19.667	48.501	13.201	-46.618	-15.618	3.413
1100	19.838	50.185	15.177	-46.225	-12.538	2.491
1200	19.983	51.071	17.178	-45.830	-9.483	1.729
1300	20.122	52.022	19.193	-45.431	-6.487	1.089
1400	20.256	53.012	21.192	-45.031	-3.527	.530
1500	20.384	54.040	23.224	-44.638	-.520	.031

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	+0.00	INFINITE	3.889	-	82.320	-	INFINITE
100	12.164	10.703	43.476	-	82.512	-	172.465
200	16.806	11.138	20.828	-	82.116	-	82.446
298	19.323	78.190	28.190	+0.00	81.700	-	52.073
300	18.340	78.303	28.190	+0.34	81.692	-	52.604
400	19.041	33.681	28.919	1.905	81.277	-	37.761
500	19.512	37.983	30.316	3.834	80.876	-	28.900
600	19.863	41.572	31.001	5.803	80.506	-	21.021
700	20.166	44.657	33.508	7.804	80.172	-	18.840
800	20.437	47.368	35.074	9.835	79.895	-	15.718
900	20.675	49.780	36.577	11.891	79.705	-	13.295
1000	20.878	51.978	38.005	13.969	79.678	-	11.361
1100	21.036	53.976	39.371	16.065	79.854	-	9.775
1200	21.165	55.812	40.666	18.175	79.807	-	8.455
1300	21.262	57.510	41.897	20.296	79.411	-	7.339
1400	21.340	59.088	43.069	22.427	78.023	-	6.388
1500	21.393	60.563	44.187	24.563	78.646	-	5.568
1600	21.435	61.945	45.254	26.705	78.281	-	4.853
1700	21.467	63.245	46.275	28.850	78.220	-	4.225
1800	21.488	64.473	47.252	30.998	77.974	-	3.667
1900	21.499	65.634	48.189	33.147	81.414	-	27.368
2000	21.500	66.738	49.089	35.297	81.235	-	2.680

IRON DICHLORIDE (FeCl<sub>2</sub>)

(CRYSTAL)

MOL. WT. = 126.753

ΔH<sub>f</sub>° 0 = -82.32 ± 0.12 kcal. mole<sup>-1</sup>

ΔH<sub>f</sub>° 298.15 = -81.70 ± 0.12 kcal. mole<sup>-1</sup>

ΔH<sub>m</sub>° = 10.28 ± 0.05 kcal. mole<sup>-1</sup>

ΔH<sub>B</sub>° 298.15 = 46.2 ± 0.7 kcal. mole<sup>-1</sup>

S°<sub>298.15</sub> = 28.190 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = 950°K.

Heat of Formation.

The enthalpy change, ΔH<sub>f</sub>° 298.15 = -4.06 ± 0.05 kcal. mole<sup>-1</sup>, for the reaction Fe(∞) + 2(HCl·12.731 H<sub>2</sub>O) (l) = FeCl<sub>2</sub>(c) + H<sub>2</sub>(g) + 25.462 H<sub>2</sub>O (l) was reported by M. P. Koehler and J. P. Coughlin, J. Phys. Chem. 63, 605 (1959). The value of ΔH<sub>f</sub>° 298.15(FeCl<sub>2</sub>, c) was then derived. The enthalpy change, ΔH<sub>f</sub>° 298.15 = -19.5 ± 0.2 kcal. mole<sup>-1</sup>, for the reaction FeCl<sub>2</sub>(c) = Fe<sup>++</sup>(aq.) + 2 Cl<sup>-</sup>(aq.) was determined by J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. 74, 4670 (1952), yielding ΔH<sub>f</sub>° 298.15 = -81.4 ± 0.2 kcal. mole<sup>-1</sup> which is in agreement with the adopted value reported by M. P. Koehler and J. P. Coughlin. The equilibrium constants for the reaction FeCl<sub>2</sub>(c) + H<sub>2</sub>(g) = Fe (c) + 2HCl (g) were determined by W. Kangro and E. Petersen, Z. Anorg. Chem. 261, 157 (1950). By use of the second and third law methods the enthalpy change (ΔH<sub>f</sub>° 298.15) of this reaction was evaluated as 37.81 ± 0.68 and 36.24 kcal. mole<sup>-1</sup>, respectively. Based on the third law value for ΔH<sub>f</sub>° 298.15, the value of ΔH<sub>f</sub>° 298.15(FeCl<sub>2</sub>, c) was derived to be -82.37 kcal. mole<sup>-1</sup> which is in reasonable agreement with the adopted value.

Heat Capacity and Entropy.

The low temperature (53.2-295.0°K.) heat capacities were determined by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. 65, 1264 (1943). The high temperature (670.5-941.0°K.) heat capacities were measured by G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). The two sets of C<sub>p</sub> data were plotted and joined smoothly at 298°K. The C<sub>p</sub> values above 941.0°K. were obtained by graphical extrapolation. The C<sub>p</sub> values, 60-500°K., were also reported by F. L. Oetting and N. W. Gregory, J. Phys. Chem. 65, 138 (1961) which are in good agreement with those determined by G. E. Moore, loc. cit. S°<sub>298.15</sub> was derived from the smoothed C<sub>p</sub> values, using S°<sub>53.2</sub> = 4.930 e.u. The S°<sub>298.15</sub> value was determined by E. P. Westrum, Jr. quoted by L. E. Wilson and N. W. Gregory in J. Phys. Chem. 62, 437 (1958). The entropy at 298° is assumed to include the uncoupling energy of Fe<sup>++</sup> which is calculated to be 3.2 e.u. which corresponds to R ln 5.

Melting Data.

T<sub>m</sub> and ΔH<sub>m</sub>° were taken from G. E. Moore, loc. cit.

Heat of Sublimation.

The difference between ΔH<sub>f</sub>° 298.15 for FeCl<sub>2</sub>(g) and FeCl<sub>2</sub>(c) is ΔH<sub>s</sub>° 298.15. The former was obtained by the second and third law analyses on the equilibrium pressure data as described in FeCl<sub>2</sub>(g) table.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0						
100	33.432	33.432	0.000	74.411	66.544	48.776
200	33.432	33.432	0.045	74.392	66.495	48.439
300	33.432	33.432	2.487	73.406	64.014	34.974
400	36.057	36.057	4.929	72.492	61.772	26.999
500	38.224	38.224	7.371	71.649	59.709	21.748
600	40.255	40.255	9.813	70.874	57.762	18.039
700	42.216	42.216	12.255	70.186	55.961	15.287
800	44.091	44.091	14.697	69.610	54.217	13.165
900	45.845	45.845	17.139	69.219	52.532	11.480
1000	47.510	47.510	19.581	69.049	50.867	10.106
1100	49.084	49.084	22.023	69.070	49.236	8.967
1200	50.572	50.572	24.465	69.253	47.646	8.010
1300	51.981	51.981	26.907	67.254	46.110	7.198
1400	53.319	53.319	29.349	66.571	44.624	6.501
1500	54.592	54.592	31.791	65.906	43.183	5.898
1600	55.805	55.805	34.233	65.548	41.775	5.370
1700	56.965	56.965	36.675	65.008	40.393	4.904
1800	58.070	58.070	39.117	64.195	38.893	4.469
1900	59.131	59.131	41.559	67.684	37.326	4.079
2000	60.149	60.149	44.001	67.217	35.818	3.727
2100	61.126	61.126	46.443	66.757	34.333	3.411
2200	62.069	62.069	48.885	66.302	32.871	3.123
2300	62.977	62.977	51.327	65.853	31.427	2.862
2400	63.852	63.852	53.769	65.411	30.001	2.623
2500	64.698	64.698	56.211	64.974	28.595	2.403
2600	65.516	65.516	58.653	64.541	27.203	2.202
2700	66.305	66.305	61.095	64.121	25.825	2.016
2800	67.075	67.075	63.537	63.704	24.467	1.844
2900	67.819	67.819	65.979	63.294	23.121	1.684
3000						

$\Delta H_f^{298.15} = 33.432 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_m^{298.15} = -74.411 \pm 0.13 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^o = 10.28 \pm 0.05 \text{ kcal. mole}^{-1}$   
 $\Delta H_v^o = 29.83 \text{ kcal. mole}^{-1}$

$S_{298.15}^o = 33.432 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 950^\circ\text{K.}$   
 $T_b = 1347^\circ\text{K.}$

Heat of Formation.

The value of  $\Delta H_f^{298.15}(\text{FeCl}_2, l)$  was obtained from  $\Delta H_f^{298.15}(\text{FeCl}_2, c)$  by adding  $\Delta H_m^o$  and the difference between  $H_m^o - H_{298.15}^o$  for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity (950-1100°K.) for FeCl<sub>2</sub>(l) was reported as 24.42 cal. deg.<sup>-1</sup> mole<sup>-1</sup> by G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). A constant C<sub>p</sub> was assumed for all the other temperatures. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T<sub>m</sub> and  $\Delta H_m^o$  were taken from G. M. Moore, loc. cit.

Vaporization Data.

The boiling point (T<sub>b</sub>) is determined as the temperature at which the free energy change ( $\Delta H_v^o$ ) for the reaction FeCl<sub>2</sub>(l) = FeCl<sub>2</sub>(g) approaches zero. The corresponding enthalpy change ( $\Delta H_v^o$ ) at T<sub>b</sub> is the heat of vaporization ( $\Delta H_v^o$ ).

IRON DICHLORIDE (FeCl<sub>2</sub>) (IDEAL GAS) MOL. WT. = 126.753

Point Group [D<sub>2h</sub>h]  
 $\Delta H_f^0 = -35.63 \pm 2.0$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 298.15 = -35.50 \pm 2.0$  kcal. mole<sup>-1</sup>  
 $S^0_{298.15} = [68.71]$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Electronic Levels and Quantum Weight

E <sub>i</sub> , cm. <sup>-1</sup>	g <sub>i</sub>
0	[5]
[800]	[10]
[3000]	[5]
[5000]	[5]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	g
327 (1)	[135] (2)
492 (1)	

Bond Distance: Fe-Cl = [2.09] Å

Bond Angle: Cl-Fe-Cl = [180]°

Rotational Constant: B<sub>0</sub> = [0.05442] cm.<sup>-1</sup>

Heat of Formation.

The equilibrium pressures for the reactions: (1) FeCl<sub>2</sub>(g) = FeCl<sub>2</sub>(l); (2) FeCl<sub>2</sub>(g) = FeCl<sub>2</sub>(c); and (3) Fe(c) + 2HCl(g) = FeCl<sub>2</sub>(g) + H<sub>2</sub>(g) were determined by several investigators. Using the reported data, the corresponding enthalpy changes ( $\Delta H_f^0 298.15$ ) for these reactions were evaluated by both the second and third law methods. Hence the respective  $\Delta H_f^0 298.15$  values for FeCl<sub>2</sub>(g) were derived, based on the third law values for  $\Delta H_f^0 298.15$ . The results obtained are presented as follows.

Investigator	Reaction	Temperature, K.	Second Law Value	Third Law Value	$\Delta H_f^0 298.15$ , kcal. mole <sup>-1</sup>
Beumann <sup>1</sup>	(1)	960.2-1167.2	37.07 ± 0.61	36.42	-35.45 ± 0.30
Schoonmaker and Porter <sup>2</sup>	(2)	621.0-701.0	45.61 ± 0.10	46.14	-35.56 ± 0.20
H. Schäfer, et al. <sup>3</sup>	(1)	981.0-1107.0	38.95 ± 0.10	37.77	-36.10 ± 0.30
Schäfer and Krehl <sup>4</sup>	(1)	990.7-1106.7	40.56 ± 1.45	37.76	-36.11 ± 0.50
C. G. Maier <sup>5</sup>	(1)	972.1-1268.0	38.68 ± 0.16	37.95	-35.92 ± 0.30
Schäfer and Krehl <sup>4</sup>	(3)	1205.2-1373.2	4.10 ± 0.13	8.01	-36.13 ± 0.50

<sup>1</sup> C. Beumann, "Activities in the KCl-FeCl<sub>2</sub> and LiCl-FeCl<sub>2</sub> Systems", ORNL-2323, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1957.

<sup>2</sup> R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. **29**, 116 (1958).

<sup>3</sup> H. Schäfer, L. Bayer, G. Brell, K. Etzel and K. Krehl, Z. anorg. allgem. Chem. **278**, 300 (1955).

<sup>4</sup> H. Schäfer and K. Krehl, Z. anorg. allgem. Chem. **258**, 35 (1952).

The value of  $\Delta H_f^0 298.15$  for FeCl<sub>2</sub>(g) adopted is  $-35.5 \pm 2.0$  kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The molecular structure, bond distance and angle, and two vibrational frequencies ( $\nu_1$  and  $\nu_2$ ) were obtained from L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963). The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe<sup>2+</sup>(g) reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1962, using the reasoning suggested by J. T. Hougen, O. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1670 (1961). The total 25 for the quantum weight was obtained from the ground multiplet of Fe<sup>2+</sup> and was split arbitrarily. The bending frequency ( $\nu_2$ ) was derived such that the calculated free energy functions are consistent with the experimental equilibrium data. In other words, the free energy functions were adjusted by choosing a proper value for  $\nu_2$  in order to make the second and third law values of  $\Delta H_f^0$  for the reactions in reasonable agreement. The moment of inertia (I) is 5.1426 x 10<sup>-38</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	<0.00	INFINITE	-	3.294	-35.625	-35.625	INFINITE
100	10.380	55.044	80.642	2.560	-35.595	-36.634	79.422
200	13.688	63.128	70.0718	1.576	-35.586	-37.280	40.747
298	14.830	68.710	68.710	0.000	-35.500	-38.151	27.964
300	14.854	68.802	68.711	0.027	-35.499	-38.168	27.804
400	15.667	73.206	69.305	1.560	-35.422	-39.346	17.478
500	15.897	76.734	70.431	3.141	-35.369	-39.988	14.901
600	15.892	79.633	71.747	4.732	-35.377	-40.911	13.059
700	15.826	82.078	73.053	6.318	-35.458	-41.829	11.673
800	15.759	84.187	74.311	7.897	-35.633	-42.730	10.587
900	15.708	86.040	75.518	9.470	-35.926	-43.599	9.710
1000	15.675	87.693	76.654	11.039	-36.408	-44.430	8.979
1100	15.654	89.186	77.726	12.606	-37.113	-45.193	8.361
1200	15.642	90.548	78.739	14.170	-37.612	-45.912	7.833
1300	15.635	91.799	79.696	15.734	-37.773	-46.596	7.379
1400	15.631	92.958	80.603	17.297	-37.953	-47.268	6.983
1500	15.627	94.036	81.463	18.860	-38.149	-47.927	6.634
1600	15.624	95.045	82.280	20.423	-38.363	-48.573	6.324
1700	15.619	95.992	83.059	21.985	-38.685	-49.197	6.045
1800	15.614	96.884	83.803	23.547	-39.225	-50.793	5.772
1900	15.606	97.728	84.514	25.108	-43.253	-50.184	5.523
2000	15.598	98.529	85.195	26.668	-43.664	-50.542	5.294
2100	15.588	99.289	85.848	28.227	-44.080	-50.873	5.085
2200	15.576	100.014	86.475	29.785	-44.504	-51.187	4.892
2300	15.564	100.706	87.079	31.343	-44.933	-51.482	4.713
2400	15.551	101.369	87.661	32.898	-45.371	-51.759	4.547
2500	15.538	102.003	88.222	34.453	-45.816	-52.014	4.392
2600	15.524	102.612	88.784	36.006	-46.268	-52.253	4.247
2700	15.509	103.198	89.328	37.558	-46.728	-52.477	4.112
2800	15.495	103.762	89.795	39.108	-47.197	-52.680	3.984
2900	15.480	104.305	90.286	40.656	-47.674	-52.867	3.864
3000	15.465	104.830	90.782	42.204	-48.158	-53.039	3.750
3100	15.451	105.337	91.274	43.750	-48.651	-53.193	3.642
3200	15.436	105.827	91.762	45.294	-49.148	-53.331	3.538
3300	15.422	106.302	92.219	46.837	-49.649	-53.456	3.437
3400	15.408	106.762	92.653	48.378	-50.154	-53.568	3.337
3500	15.394	107.208	92.946	49.918	-50.664	-53.667	3.239
3600	15.380	107.642	93.318	51.457	-51.182	-53.753	3.142
3700	15.366	108.062	93.676	52.994	-51.712	-53.826	3.047
3800	15.354	108.473	94.022	54.530	-52.253	-53.886	2.953
3900	15.342	108.871	94.356	56.065	-52.796	-53.933	2.860
4000	15.330	109.259	94.680	57.599	-53.341	-53.967	2.768
4100	15.318	109.638	95.016	59.131	-53.894	-53.987	2.677
4200	15.307	110.007	95.343	60.662	-54.451	-53.993	2.587
4300	15.295	110.367	95.666	62.193	-55.012	-53.988	2.497
4400	15.285	110.718	96.236	63.722	-55.577	-53.973	2.407
4500	15.274	111.062	96.562	65.250	-56.146	-53.948	2.317
4600	15.264	111.397	96.881	66.776	-56.719	-53.903	2.227
4700	15.255	111.726	97.199	68.302	-57.296	-53.838	2.137
4800	15.245	112.049	97.499	69.827	-57.877	-53.753	2.047
4900	15.236	112.361	97.799	71.351	-58.462	-53.648	1.957
5000	15.227	112.669	98.094	72.875	-59.051	-53.523	1.867
5100	15.219	112.970	98.392	74.397	-59.644	-53.378	1.777
5200	15.211	113.266	98.686	75.918	-60.242	-53.213	1.687
5300	15.203	113.555	98.944	77.439	-60.844	-53.028	1.597
5400	15.195	113.839	99.217	78.959	-61.451	-52.823	1.507
5500	15.188	114.118	99.486	80.478	-62.062	-52.598	1.417
5600	15.181	114.392	99.749	81.997	-62.676	-52.353	1.327
5700	15.174	114.662	100.009	83.514	-63.294	-52.088	1.237
5800	15.167	114.924	100.264	85.031	-63.916	-51.803	1.147
5900	15.160	115.183	100.514	86.548	-64.542	-51.498	1.057
6000	15.154	115.438	100.761	88.063	-65.172	-51.173	0.967

MOL. WT. = 149.11

(IDEAL GAS)

POTASSIUM CHLORIDE, DIMERIC (K<sub>2</sub>Cl<sub>2</sub>)

Point Group D<sub>2h</sub>  
 $\Delta H_f^0 = -146.85 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -147.62 \pm 1.0 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = [84.3] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_j$ , cm <sup>-1</sup>	$\omega_j$ , cm <sup>-1</sup>
[219](1)	[104](1)
[108](1)	[164](1)
[180](1)	[100](1)

Bond Distances: Cl-K = [2.932] Å

$\sigma = 4$

Bond Angle: Cl-K-Cl = [100.8°]

Product of the Moments of Inertia:  $I_A I_B I_C = [2.873 \times 10^{-112}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation is calculated from that of KCl(g) using  $\Delta H_f^{298} = 45.0 \text{ kcal./mole}$  for K<sub>2</sub>Cl<sub>2</sub>(g) - 2KCl(g) as selected from data analyses summarized below. The three experimental techniques include PVT measurements (source 1), combination of total vapor pressure and transpiration data (sources 2,3,4), and mass spectrometric studies of the variation of ion intensities with temperature (source 5). The results are reasonably consistent, considering the uncertainties inherent in the problem.

The resulting tables were tested by comparison with other data. Calculated total vapor pressures are in satisfactory agreement with the observed values over the range 820-1500°K.; however, near the boiling point they are lower by 6-18 percent [see KCl(g)]. Knudsen effusion data and transpiration data over KCl(c) have been reviewed by A. C. P. Pugh and R. P. Barrow, *Trans. Faraday Soc.* 54, 671 (1958). These data suggest negligible dimer formation when combined with the total vapor pressures of Pugh and Barrow but significant dimer formation when combined with the lower (20-30 percent) total pressures of V. Dietz, *J. Chem. Phys.* 4, 575 (1936). Calculated dimer formation (22 mole percent at 900°K.) agrees with the latter combination but calculated total pressures agree with those of Pugh & Barrow. Velocity distribution studies of R. C. Miller and P. Kusch, *J. Chem. Phys.* 27, 981 (1957); 25, 860 (1956) suggest about 10 mole percent of dimer at 900°K. Thus, while minor inconsistencies do exist, it is not apparent that they exceed the combined experimental errors.

Source	Method	No. of Points	Temp. Range, K.	$\Delta H_f^{298}$ , kcal./mole	$\Delta H_f^{298}$ , kcal./mole	Drift, eu
1. Datz (1960)	PVT data	15	1310-1404	46.70±2.1	46.01	-0.5±1.6
2. Schrier (1961)	Trans. + Vap. Press.	10	1253-1352	46.24±3.5	44.98	-1.0±2.7
3. Beaman (1957)	Trans. + Vap. Press.	5	1261-1372	43.0±4.5	44.16	0.7±3.4
4. Barton et al. (1959)	Trans. + Vap. Press.	7	1250-1475	42.54±2.9	45.21	2.5±2.3
5. Milne et al. (1960)	Mass Spectrometry	—	774-1016	41.9±3	—	—

- S. Datz, ORNL-2933, Oak Ridge, Tenn., May 1960.
- E. E. Schrier, Ph.D. Thesis, Rensselaer Polytechnic Inst., Troy, N.Y., Jun 1961.
- C. C. Beaman, ORNL-2323, Oak Ridge, Tenn., Jun 1957.
- J. L. Barton and H. Bloom, *J. Phys. Chem.* 63, 1785 (1959); 60, 1413 (1956).
- T. A. Milne and H. M. Klein, *AIChE J.* 6, 512, Menlo Park, Calif., Jun 1960.

Heat Capacity and Entropy.

The structure and vibrational frequencies are those calculated from an ionic model by J. Berkowitz, *J. Chem. Phys.* 32, 1519 (1960); 23, 1386 (1958). The sixth fundamental was arbitrarily lowered from 206 to 100 cm<sup>-1</sup> since the resulting entropy increase (1.4 eu at 1300°K.) improved the overall agreement with the equilibrium data. Based on electron diffraction studies of the monomer-dimer vapor, P. A. Akhiehin and N. G. Rambidi, *Zhur. Neorg. Khim.* 4, 718 (1959) have derived the bond distance and angle to be 2.81 Å and 98°. Interpretation of the diffraction data, however, is complicated by the presence of only about 30 mole percent of dimer at the temperature of measurement. Adoption of this dimer structure would reduce the entropy by 0.23 eu. Principal moments of inertia for the Berkowitz structure are  $I_A = 45.31 \times 10^{-39}$ ,  $I_B = 60.13 \times 10^{-39}$ , and  $I_C = 106.45 \times 10^{-39}$  g. cm.<sup>2</sup>

Dec. 31, 1961; Mar. 31, 1966

T, K.	C <sub>p</sub>	S°	$-(F^0 - H_{298}^0)/T$	H° - H <sub>298</sub>	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	0.000	INFINITE	-	4.812	-146.852	-146.852	INFINITE
100	16.145	64.482	100.078	3.650	-147.219	-147.446	322.243
200	18.714	76.700	86.082	1.872	-147.402	-147.597	161.286
298	19.327	84.309	84.309	0.000	-147.620	-147.652	108.231
300	19.333	84.429	84.430	0.036	-147.625	-147.652	107.564
400	19.504	90.027	85.071	1.982	-149.157	-147.392	80.531
500	19.673	94.905	86.516	3.245	-149.513	-146.912	64.215
600	19.733	97.998	88.139	5.915	-149.864	-146.357	53.311
700	19.770	101.043	91.348	7.400	-150.208	-145.746	45.544
800	19.793	103.682	94.748	9.860	-150.539	-145.089	39.297
900	19.810	106.017	92.651	11.849	-150.864	-144.388	35.062
1000	19.822	108.105	94.274	13.831	-151.218	-143.652	31.399
1100	19.830	109.994	95.619	15.813	-151.587	-142.889	27.960
1200	19.837	111.720	96.889	17.797	-151.967	-142.115	24.845
1300	19.842	113.308	98.092	19.781	-152.359	-141.341	22.193
1400	19.846	114.764	99.232	21.765	-152.762	-140.568	19.921
1500	19.849	116.148	100.315	23.750	-153.176	-139.793	17.953
1600	19.852	117.429	101.345	25.735	-153.605	-139.022	16.232
1700	19.854	118.633	102.327	27.720	-154.054	-138.253	14.714
1800	19.856	119.767	103.254	29.706	-154.524	-137.495	13.365
1900	19.858	120.841	104.161	31.691	-155.015	-136.743	12.159
2000	19.859	121.860	105.021	33.677	-155.528	-136.000	11.073
2100	19.860	122.829	105.846	35.663	-156.065	-135.269	10.092
2200	19.861	123.753	106.639	37.649	-156.628	-134.552	9.200
2300	19.862	124.635	107.403	39.635	-157.218	-133.850	8.385
2400	19.863	125.468	108.138	41.622	-157.835	-133.163	7.639
2500	19.864	126.262	108.848	43.608	-158.478	-132.495	6.953
2600	19.864	127.071	109.534	45.594	-159.148	-131.855	6.319
2700	19.865	127.820	110.198	47.580	-159.845	-131.245	5.733
2800	19.865	128.543	110.840	49.567	-160.568	-130.665	5.188
2900	19.866	129.240	111.463	51.554	-161.328	-130.115	4.681
3000	19.866	129.913	112.067	53.540	-162.125	-129.595	4.208
3100	19.866	130.565	112.653	55.527	-162.950	-129.105	3.765
3200	19.867	131.196	113.222	57.514	-163.802	-128.645	3.350
3300	19.867	131.806	113.777	59.500	-164.681	-128.215	2.959
3400	19.868	132.400	114.318	61.487	-165.588	-127.815	2.592
3500	19.868	132.976	114.841	63.474	-166.522	-127.445	2.245
3600	19.868	133.536	115.352	65.461	-167.483	-127.105	1.917
3700	19.868	134.080	115.851	67.447	-168.470	-126.795	1.606
3800	19.868	134.610	116.338	69.434	-169.482	-126.515	1.312
3900	19.868	135.126	116.813	71.421	-170.520	-126.265	1.032
4000	19.869	135.629	117.277	73.408	-171.585	-126.045	0.765
4100	19.869	136.120	117.731	75.395	-172.678	-125.855	0.511
4200	19.869	136.598	118.174	77.382	-173.798	-125.695	0.268
4300	19.869	137.066	118.608	79.369	-174.945	-125.565	0.037
4400	19.869	137.523	119.033	81.355	-176.118	-125.465	0.000
4500	19.869	137.969	119.449	83.342	-177.318	-125.395	0.000
4600	19.869	138.406	119.856	85.329	-178.545	-125.345	0.000
4700	19.869	138.833	120.255	87.316	-179.800	-125.315	0.000
4800	19.869	139.252	120.647	89.303	-181.085	-125.305	0.000
4900	19.870	139.661	121.031	91.290	-182.400	-125.315	0.000
5000	19.870	140.063	121.407	93.277	-183.745	-125.345	0.000
5100	19.870	140.456	121.777	95.264	-185.120	-125.395	0.000
5200	19.870	140.842	122.140	97.251	-186.525	-125.465	0.000
5300	19.870	141.222	122.496	99.238	-187.960	-125.555	0.000
5400	19.870	141.592	122.846	101.225	-189.425	-125.665	0.000
5500	19.870	141.956	123.191	103.212	-190.920	-125.795	0.000
5600	19.870	142.314	123.529	105.199	-192.445	-125.945	0.000
5700	19.870	142.666	123.862	107.186	-194.000	-126.115	0.000
5800	19.870	143.012	124.189	109.173	-195.585	-126.305	0.000
5900	19.870	143.351	124.511	111.160	-197.200	-126.515	0.000
6000	19.870	143.685	124.828	113.147	-198.845	-126.745	0.000



T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	9.630	6.204	35.079	3.288	153.248	153.248	INFINITE
200	15.495	14.977	22.092	2.988	149.577	149.577	326.884
298	17.000	21.427	21.427	1.500	153.688	145.545	159.037
300	17.088	21.527	21.422	∞	153.350	141.519	103.731
400	18.045	26.594	22.106	∞	153.344	141.446	103.038
500	18.677	30.701	23.428	1.766	153.024	137.528	75.138
600	19.090	34.144	24.934	3.636	152.679	133.692	58.434
700	19.420	37.111	26.667	5.525	152.378	129.928	47.324
800	19.730	39.725	27.064	7.451	151.973	126.222	39.406
900	20.040	42.067	29.403	9.409	151.626	122.569	33.483
1000	20.350	44.194	30.777	11.397	151.289	118.956	28.885
				13.417	153.082	115.200	25.176
1100	20.654	46.148	32.087	15.467	152.731	111.430	22.138
1200	20.951	47.958	33.325	17.547	152.378	107.692	19.612
1300	21.242	49.646	34.526	19.657	152.023	103.982	17.480
1400	21.526	51.231	35.663	21.795	182.033	99.820	15.582
1500	21.805	52.726	36.751	23.962	181.269	93.975	13.691
1600	22.076	54.147	37.784	26.156	180.480	88.182	12.045
1700	22.342	55.488	38.766	28.377	179.665	82.435	10.597
1800	22.601	56.772	39.759	30.624	178.826	76.741	9.317
1900	22.854	58.001	40.687	32.897	177.961	71.092	8.177
2000	23.100	59.180	41.582	35.195	177.075	65.491	7.156

MAGNESIUM DICHLORIDE (MgCl<sub>2</sub>)

(CRYSTAL)

MOL. WT. = 95.218

$$\Delta H_f^{\circ} 0 = -153.25 \pm 0.11 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -153.35 \pm 0.11 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 10.30 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$T_m = 987^{\circ}\text{K.}$$

$$\Delta H_g^{\circ} 298.15 = 57.5 \pm 1.5 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The adopted  $\Delta H_f^{\circ} 298.15 = -153.35 \pm 0.11 \text{ kcal. mole}^{-1}$  is from heat of solution measurements reported by C. H. Shomate and E. H. Huffman, *J. Am. Chem. Soc.* 65, 1625 (1943). Shomate and Huffmans heat of solution of Mg in 1 M HCl ( $\Delta H = -111.322 \pm 0.041 \text{ kcal. mole}^{-1}$ ) has been substituted for calibration purposes by S. R. Gunn and B. B. Cunningham, *J. Am. Chem. Soc.*, 79, 1563 (1957) ( $\Delta H = -111.3 \text{ kcal. mole}^{-1}$ ) and by E. F. Westrum Jr. and L. Eyring, *J. Am. Chem. Soc.*, 74, 2045 (1952) ( $\Delta H = -111.27 \text{ kcal. mole}^{-1}$ ). Auxiliary heat of dilution and heat of formation data for HCl were taken from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NSRDS-NBS 2, Nat'l. Bur. Stds., April 1965 and from D. D. Wagman et al., N.B.S. Technical Note 270-1, Oct. 1965.

Heat Capacity and Entropy.

High temperature heat content data by G. E. Moore, *J. Am. Chem. Soc.* 65, 1700 (1943) were joined by Shomate correlation with low temperature heat capacity data reported by K. K. Kelley and G. E. Moore, *J. Am. Chem. Soc.* 65, 1264 (1943).  $C_p(c)$  above  $T_m$  is a linear extrapolation from 700°K.  $S_{298.15}^{\circ}$  is derived from the low temperature data and is based on  $S_{53.6}^{\circ} = 2.006 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Melting Data.

$\Delta H_m^{\circ} = 10.30 \pm 0.05 \text{ kcal. mole}^{-1}$  is taken from heat content measurements of Moore loc. cit.  $T_m = 987^{\circ}\text{K.}$  is from National Bureau of Standards Circular 500, 1952.

Sublimation Data.

The value of  $\Delta H_g^{\circ} 298.15$  was derived by 2nd and 3rd law analyses of vapor pressure data. See the MgCl<sub>2</sub>(g) table for details.

(LIQUID)

MAGNESIUM DICHLORIDE (MgCl<sub>2</sub>)

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0						
100	17.060	30.949	0.000	-143.779	-134.789	98.798
200	17.088	31.055	0.032	-143.773	-134.733	98.148
300	18.095	36.123	1.706	-143.653	-131.768	71.991
400	18.677	40.228	3.636	-143.108	-128.884	56.332
500	19.090	43.634	5.505	-142.777	-126.072	45.919
600	22.000	46.807	7.569	-142.284	-123.321	38.501
700	22.000	49.745	9.769	-141.695	-120.654	32.959
800	22.000	52.336	11.969	-141.146	-118.056	28.667
900	22.000	54.655	14.169	-142.759	-115.337	25.206
1000	22.000	56.751	16.369	-142.258	-112.621	22.375
1100	22.000	58.665	18.569	-141.785	-109.948	20.023
1200	22.000	60.426	20.769	-141.340	-107.313	18.040
1300	22.000	62.056	22.969	-171.288	-104.231	16.270
1400	22.000	63.574	25.169	-170.491	-99.469	14.492
1500	22.000	64.994	27.369	-169.696	-94.762	12.943
1600	22.000	66.328	29.569	-168.902	-90.101	11.583
1700	22.000	67.585	31.769	-168.110	-85.489	10.379
1800	22.000	68.775	33.969	-167.318	-80.920	9.307
1900	22.000	69.903	36.169	-166.530	-76.392	8.347
2000	22.000	70.977	38.369	-165.742	-71.908	7.483
2100	22.000	72.000	40.569	-164.957	-67.456	6.701
2200	22.000	72.978	42.769	-164.173	-63.040	5.990
2300	22.000	73.914	44.969	-163.391	-58.660	5.341
2400	22.000	74.812	47.169	-162.613	-54.313	4.748
2500	22.000	75.675	49.369	-161.836	-49.995	4.202
2600	22.000	76.506	51.569	-161.063	-45.711	3.700
2700	22.000	77.306	53.769	-160.293	-41.459	3.233
2800	22.000	78.078	55.969	-159.526	-37.222	2.803
2900	22.000	78.824	58.169	-158.764	-33.019	2.405
3000	22.000					

S°<sub>298.15</sub> = 30.949 cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 ΔH<sub>f</sub>°<sub>298.15</sub> = -143.779 kcal. mole<sup>-1</sup>  
 ΔH<sub>m</sub>° = 10.30 ± 0.05 kcal. mole<sup>-1</sup>  
 ΔH<sub>v</sub>° = [37.34] kcal. mole<sup>-1</sup>

T<sub>m</sub> = 987°K.  
 T<sub>b</sub> = [1710]°K.

Heat of Formation.

ΔH<sub>f</sub>°<sub>298.15(1)</sub> was calculated from ΔH<sub>f</sub>°<sub>298.15(c)</sub> by adding ΔH<sub>m</sub>° and the difference between H<sub>m</sub>° - H<sub>m</sub>°<sub>298</sub> for crystal and liquid.

Heat Capacity and Entropy.

A constant C<sub>p</sub>(1) = 22.0 cal. deg.<sup>-1</sup> mole<sup>-1</sup> over the temperature range 1006-1428°K. is from the high temperature heat content data of G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). This constant value was assumed to hold from an assumed glass transition of 660°K. to 3000°K. C<sub>p</sub>(1) below 660°K. is taken to be that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See MgCl<sub>2</sub>(c) table for details.

Vaporization Data.

T<sub>b</sub> is calculated as the temperature at which the free energy change of the reaction MgCl<sub>2</sub>(l) = MgCl<sub>2</sub>(g) approaches zero. The difference between ΔH<sub>f</sub>° for MgCl<sub>2</sub>(l) and MgCl<sub>2</sub>(g) at T<sub>b</sub> is ΔH<sub>v</sub>°.

$\Delta H_f^0 = -95.524 \pm 2.0 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -95.85 \pm 2.0 \text{ kcal. mole}^{-1}$

Point Group C<sub>2v</sub>  
 $S_{298.15} = [64.873] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_e, \text{ cm.}^{-1}$   
 597 (1)  
 [170] (2)  
 [375] (1)

Bond Distance: Mg-Cl = 2.18 Å

Bond Angle: Cl-Mg-Cl = 170°

Product of the Moments of Inertia:  $I_A I_B I_C = 335.307 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation

From Knudsen effusion-mass spectrometer measurements, J. R. Marquart, J. Chem. Phys. 37, 1853 (1962) reported a monomer pressure of  $3.84 \times 10^{-5}$  atm. at 920.6°K. for the reaction  $\text{MgCl}_2(\text{c}) \rightarrow \text{MgCl}_2(\text{g})$ . This yields a 3rd law heat of sublimation  $\Delta H_m^{298} = 55.88 \text{ kcal. mole}^{-1}$ . The 2nd law heat of sublimation is  $\Delta H_m^{298} = 57.35 \text{ kcal. mole}^{-1}$ .

D. L. Hildenbrand et al., Aeronautic Publication No. U-2289, Sept. 1953, reported vapor pressure results from torsion-effusion measurements over the temperature range 802 to 985°K. Their vapor pressure equation yields 2nd and 3rd law heats of sublimation of 61.77 and 57.74 kcal. mole<sup>-1</sup>, respectively. Monomeric vapor was assumed.

Transpiration studies by E. E. Schrier, Ph.D. Thesis, Rensselaer Polytechnic Institute, 1961 showed the gaseous species over MgCl<sub>2</sub>(l) to exhibit about 50% dimerization in the range 1255 to 1346°K. His vapor pressure data for the monomer yielded 2nd and 3rd law heats of sublimation of 57.26 and 57.76 kcal. mole<sup>-1</sup>, respectively, when adjusted for the heat of melting.

W. Fischer, T. Fetzl and S. Lauter, Z. Anorg. Allgem. Chem. 333, 226 (1964) reported a vapor pressure equation obtained from bell method measurements. Their equation yielded 2nd and 3rd law heats of sublimation of 37.246 and 57.65 kcal. mole<sup>-1</sup>, respectively, when adjusted for  $\Delta H_m^{298} = 9.571 \text{ kcal. mole}^{-1}$ .

Liquid vapor pressures by C. G. Meier, U. S. Bur. Mines Tech. Paper 350 (1929) yielded 2nd and 3rd law heats of sublimation of 52.83 and 56.08 kcal. mole<sup>-1</sup>, respectively, when adjusted for the heat of melting.

The adopted heat of sublimation  $\Delta H_m^{298} = 57.5 \text{ kcal. mole}^{-1}$  is an average of the 2nd and 3rd law results of Schrier.  $\Delta H_m^{298}(\text{g}) = 95.85 \text{ kcal. mole}^{-1}$  is calculated from  $\Delta H_m^{298}$  and  $\Delta H_f^{298}(\text{c})$ .

Heat Capacity and Entropy

A. Büchler and V. Klempner, J. Chem. Phys. 29, 121 (1958) reported bending and asymmetric stretch frequencies of 285 and 597 cm<sup>-1</sup>. However, as in the case of BeCl<sub>2</sub> and BeCl<sub>2</sub>, their bending assignments are suspected. Electron diffraction data by F. A. Akshin and V. P. Spiridonov, Kristallografiya 2, 475 (1957) indicated a linear structure for MgCl<sub>2</sub> with 2.18 Å bond length. The equilibrium data reported above, however, indicated a slightly bent structure to be more consistent.

The magnitude of isotopic shifts of Mg<sup>2+</sup> from infrared absorption spectra by D. White, Structure and Thermodynamic Properties of Polyatomic Molecules at Elevated Temperatures, Report No. 32, Ohio State University, Sept. 1964, suggested a linear or slightly bent molecular configuration for MgCl<sub>2</sub>(g). D. E. Mann and G. V. Calder, N.B.S. Report 8919, July 1965 reported  $\nu_2 = 240 \text{ cm.}^{-1}$  and  $\nu_3 = 840 \text{ cm.}^{-1}$  for MgCl<sub>2</sub>(g). Using these two frequencies and an estimated 170° bond angle,  $\nu_1$  was adjusted until consistent force constants K and  $K_f/2$  were obtained.  $\nu_1 = 530 \text{ cm.}^{-1}$  was thus obtained.

Using a 170° bond angle for Cl-Mg-Cl, Büchler and Klempner's asymmetric stretch frequency  $\nu_2 = 597 \text{ cm.}^{-1}$  and the force constant ratio established for MgCl<sub>2</sub> we calculated  $\nu_1 = 375 \text{ cm.}^{-1}$  and  $\nu_3 = 170 \text{ cm.}^{-1}$  for MgCl<sub>2</sub>(g).

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	9.476	52.942	INFINITE	3.064	95.524	-	INFINITE
100	11.340	60.127	75.916	2.177	95.524	-	209.978
200	12.390	64.873	64.873	1.170	95.850	-	105.615
298	12.900	66.949	64.873	0.000	95.850	-	96.974
300	12.900	66.949	64.873	0.000	95.850	-	70.647
400	12.959	68.507	65.367	1.294	96.026	-	53.177
500	13.205	71.530	68.517	2.607	96.208	-	42.675
600	13.448	73.966	71.904	3.943	96.410	-	35.660
700	13.684	76.046	74.685	5.294	96.630	-	30.638
800	13.911	77.841	76.857	6.654	96.881	-	26.863
900	14.131	79.473	79.562	8.021	97.165	-	23.918
1000	14.346	80.920	81.927	9.393	97.486	-	21.515
1100	14.551	82.230	84.000	10.768	97.843	-	19.533
1200	14.748	83.420	85.800	12.146	98.237	-	17.876
1300	14.930	84.500	87.333	13.526	98.664	-	16.469
1400	15.098	85.480	88.667	14.907	99.121	-	15.183
1500	15.255	86.370	89.817	16.290	99.606	-	13.815
1600	15.401	87.170	90.883	17.673	100.117	-	12.619
1700	15.538	87.880	91.863	19.058	100.654	-	11.562
1800	15.667	88.500	92.750	20.443	101.217	-	10.623
1900	15.788	89.030	93.543	21.829	101.801	-	9.782
2000	15.902	89.476	94.243	23.215	102.403	-	9.026
2100	16.010	89.830	94.850	24.602	103.021	-	8.341
2200	16.112	90.100	95.367	25.989	103.654	-	7.719
2300	16.209	90.290	95.793	27.377	104.301	-	7.150
2400	16.302	90.400	96.133	28.765	104.961	-	6.629
2500	16.391	90.430	96.383	30.153	105.633	-	6.150
2600	16.476	90.380	96.543	31.541	106.315	-	5.707
2700	16.558	90.250	96.617	32.930	107.006	-	5.297
2800	16.637	90.040	96.600	34.318	107.706	-	4.916
2900	16.713	89.750	96.493	35.707	108.415	-	4.561
3000	16.786	89.380	96.293	37.096	109.133	-	4.229
3100	16.856	88.930	96.000	38.485	109.860	-	3.919
3200	16.923	88.400	95.617	39.875	110.595	-	3.629
3300	16.987	87.790	95.143	41.264	111.338	-	3.356
3400	17.049	87.100	94.580	42.653	112.089	-	3.098
3500	17.108	86.330	93.927	44.043	112.847	-	2.855
3600	17.165	85.490	93.183	45.433	113.612	-	2.626
3700	17.219	84.580	92.343	46.822	114.383	-	2.409
3800	17.271	83.600	91.417	48.212	115.160	-	2.203
3900	17.320	82.550	90.400	49.602	115.943	-	2.008
4000	17.367	81.430	89.293	50.992	116.732	-	1.822
4100	17.411	80.250	88.093	52.382	117.527	-	1.645
4200	17.453	79.010	86.800	53.772	118.328	-	1.476
4300	17.493	77.710	85.417	55.162	119.134	-	1.315
4400	17.531	76.350	83.943	56.552	119.945	-	1.161
4500	17.567	74.930	82.380	57.942	120.761	-	1.014
4600	17.601	73.460	80.727	59.333	121.582	-	0.873
4700	17.633	71.940	78.983	60.723	122.408	-	0.738
4800	17.663	70.370	77.143	62.113	123.239	-	0.609
4900	17.691	68.750	75.207	63.503	124.075	-	0.484
5000	17.717	67.080	73.173	64.894	124.916	-	0.364
5100	17.741	65.360	71.043	66.284	125.761	-	0.249
5200	17.763	63.590	68.817	67.675	126.610	-	0.136
5300	17.783	61.770	66.500	69.065	127.463	-	0.027
5400	17.801	59.910	64.083	70.455	128.320	-	0.000
5500	17.817	58.010	61.567	71.846	129.181	-	0.172
5600	17.831	56.070	59.050	73.236	130.046	-	0.346
5700	17.843	54.090	56.533	74.627	130.915	-	0.521
5800	17.854	52.070	54.017	76.018	131.788	-	0.696
5900	17.863	50.010	51.500	77.409	132.665	-	0.871
6000	17.871	47.910	49.000	78.799	133.546	-	1.046

DICHLORINE MONOXIDE (Cl<sub>2</sub>O) (IDEAL GAS) MOL. WT. = 86.9054

$\Delta H_f^0 = 21.4 \pm 0.6 \text{ kcal. mole}^{-1}$

$\Delta H_f^{298.15} = 64.019 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^{298.15} = 21.0 \pm 0.6 \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

( $\nu$ ), cm.<sup>-1</sup>

640 (1)

500 (1)

686 (1)

Bond Distance: Cl-O = 1.701 ± 0.02 Å

Bond Angle: Cl-O-Cl = 110.8 ± 1°

Product of the Moments of Inertia:  $I_A I_B I_C = 1.171535 \times 10^{-114} \text{ g.}^3 \text{ cm.}^3$

$\sigma^- = 2$

Heat of Formation.

V. A. Kustodina, K. P. Mishchenko and I. E. Flis, Zh. Prikl. Khim. 35, 1374 (1962) (Source 1) derived the heat of formation of Cl<sub>2</sub>O dissolved in CCl<sub>4</sub> from solution calorimetry at 275, 283, 298 and 308°K. The heat of formation in CCl<sub>4</sub> was interpolated to 285°K. D. M. Yost and R. C. Fehl, J. Am. Chem. Soc. 56, 68 (1934) (Source 2) measured the partial vapor pressures of Cl<sub>2</sub>O above its CCl<sub>4</sub> solution at 273 and 298°K which yield the heat of solution -6.59 kcal. mole<sup>-1</sup> at 285°K. The  $\Delta H_f^{298.15} = 21.0 \text{ kcal. mole}^{-1}$  was calculated from these two values. J. I. Wallace and C. P. Goodeve, Trans. Faraday Soc. 27, 648 (1931) (Source 3) obtained the heat of explosion of Cl<sub>2</sub>O(g); their data gave  $\Delta H_f^{298.15} \text{ Cl}_2\text{O(g)} = 21.4 \text{ kcal. mole}^{-1}$  which is in very good agreement with the above. Also P. Günther and K. Wekus, Z. Physik Chem. 154, 193 (1933) (Source 4) measured the heat of explosion; their data give  $\Delta H_f^{298.15} \text{ Cl}_2\text{O(g)} = 24.7 \text{ kcal. mole}^{-1}$ .

$\Delta H_f^{298.15}$   
kcal. mole<sup>-1</sup>

$\Delta H_f^\ddagger$   
kcal. mole<sup>-1</sup>

T, °K

Reaction

1 Cl<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g) → Cl<sub>2</sub>O(in CCl<sub>4</sub>)

2 Cl<sub>2</sub>O(in CCl<sub>4</sub>) → Cl<sub>2</sub>O(g)

3 Cl<sub>2</sub>O(g) → Cl<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g)

4 Cl<sub>2</sub>O(g) → Cl<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g)

Source

1

2

3

4

4.176

4.141

4.108

4.077

4.213

285

285

298

298

14.38

6.59

-21.4

-24.7

21.0

21.4

24.7

Heat Capacity and Entropy.

The vibrational frequencies were obtained from M. M. Rochkind and G. C. Pimentel, J. Chem. Phys. 42, 1361 (1965). The infrared spectrum of Cl<sub>2</sub>O(g) has been investigated previously beginning with the work of C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. (London) A142, 192 (1933). K. Hedberg, J. Chem. Phys. 19, 509 (1951) proposed stretching frequencies at 688 cm.<sup>-1</sup> ( $\nu_1$ ) and 969 cm.<sup>-1</sup> ( $\nu_2$ ), but left the bending frequency unknown. Previous evidence concerning the bending mode ( $\nu_2$ ) was shown by Hedberg (loc. cit.) to be spurious. Rochkind and Pimentel (loc. cit.) present infrared studies of Cl<sub>2</sub>O gas and condensed phases which reveal the bending frequency and require reassignment of the stretching fundamentals. The bond distance and bond angle were obtained from J. D. Dunitz and K. Hedberg, J. Am. Chem. Soc. 72, 3108 (1950).

The three principal moments of inertia are:  $I_A = 2.022 \times 10^{-39}$ ,  $I_B = 2.30806 \times 10^{-38}$ , and  $I_C = 2.51026 \times 10^{-38} \text{ g. cm.}^2$

\*G. B. M. Sutherland and W. B. Penny, Proc. Roy. Soc. (London) A156, 678 (1936).

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S° -(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub> kcal. mole <sup>-1</sup>	$\Delta H_f^\ddagger$	$\Delta F_f^\ddagger$	Log K <sub>p</sub>
0	4.00C	INFINITE	-2.795	21.436	21.436	INFINITE
100	8.484	53.356	73.241	21.185	22.445	48.051
200	10.059	59.722	1.061	23.763	25.106	28.965
298	11.427	64.019	4.000	21.000	25.106	18.402
300	11.447	64.019	4.021	21.000	25.131	18.307
400	12.280	67.508	64.48C	21.004	26.509	14.483
500	12.777	70.536	65.374	21.004	27.882	12.187
600	13.086	72.665	66.307	21.088	29.246	10.652
700	13.287	74.098	67.441	21.141	30.602	9.554
800	13.454	74.862	68.462	21.192	31.948	8.727
900	13.581	75.009	69.445	21.242	33.290	8.084
1000	13.682	75.497	70.378	21.290	34.626	7.567
1100	13.645	71.267	10.481	21.336	35.958	7.144
1200	13.686	81.984	11.648	21.379	37.285	6.790
1300	13.719	83.081	13.218	21.418	38.609	6.490
1400	13.745	84.059	14.591	21.456	39.929	6.233
1500	13.766	85.048	15.967	21.490	41.248	6.009
1600	13.783	85.937	17.344	21.521	42.564	5.814
1700	13.797	86.773	18.723	21.550	43.880	5.641
1800	13.809	87.562	20.103	21.574	45.191	5.487
1900	13.820	88.309	21.485	21.596	46.505	5.349
2000	13.829	89.018	22.867	21.614	47.814	5.225
2100	13.836	89.693	24.251	21.630	49.123	5.112
2200	13.843	90.337	25.635	21.640	50.431	5.010
2300	13.848	90.952	27.019	21.647	51.742	4.916
2400	13.853	91.542	28.404	21.650	53.049	4.831
2500	13.858	92.107	29.790	21.648	54.358	4.752
2600	13.862	92.651	31.176	21.643	55.666	4.679
2700	13.865	93.174	32.542	21.632	56.975	4.612
2800	13.869	93.678	33.949	21.616	58.287	4.549
2900	13.871	94.165	35.336	21.596	59.595	4.491
3000	13.874	94.635	36.723	21.571	60.906	4.437
3100	13.876	95.090	38.111	21.541	62.218	4.386
3200	13.878	95.531	39.498	21.506	63.528	4.339
3300	13.880	95.958	40.886	21.466	64.843	4.293
3400	13.882	96.372	42.275	21.422	66.160	4.254
3500	13.884	96.775	43.663	21.372	67.472	4.213
3600	13.885	97.166	45.051	21.318	68.793	4.176
3700	13.887	97.546	46.440	21.260	70.115	4.141
3800	13.888	97.917	47.829	21.198	71.432	4.108
3900	13.889	98.277	49.217	21.132	72.758	4.077
4000	13.890	98.629	50.606	21.061	74.081	4.047
4100	13.891	98.972	51.995	20.987	75.407	4.019
4200	13.892	99.307	53.385	20.910	76.732	3.993
4300	13.893	99.634	54.774	20.830	78.063	3.967
4400	13.894	99.953	56.163	20.747	79.399	3.944
4500	13.894	100.265	57.553	20.661	80.732	3.921
4600	13.895	100.571	58.942	20.574	82.067	3.899
4700	13.896	100.870	60.332	20.484	83.405	3.878
4800	13.896	101.162	61.721	20.392	84.745	3.858
4900	13.897	101.449	63.111	20.298	86.085	3.839
5000	13.898	101.729	64.501	20.203	87.431	3.821
5100	13.898	102.005	65.890	20.107	88.776	3.804
5200	13.899	102.275	67.280	20.010	90.122	3.788
5300	13.899	102.539	68.670	19.912	91.475	3.772
5400	13.899	102.799	69.825	19.812	92.823	3.757
5500	13.900	103.054	70.963	19.712	94.168	3.742
5600	13.900	103.295	72.040	19.611	95.518	3.728
5700	13.901	103.551	73.250	19.510	96.868	3.714
5800	13.901	103.792	74.460	19.408	98.210	3.702
5900	13.901	104.020	75.620	19.305	99.564	3.689
6000	13.902	104.264	76.840	19.202	100.967	3.678

Dec. 31, 1960; Dec. 31, 1965

Point Group D<sub>3h</sub>  
 $\Delta H_f^0 = -61.8 \pm 0.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -61.8 \pm 0.5 \text{ kcal. mole}^{-1}$   
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
[100](1)	350 (2)
[150](1)	[300](2)
[250](1)	[60](2)
[200](1)	[80](2)

Bond Distance: Cu-Cl = 2.16 Å  
 Bond Angle: Cl-Cu-Cl = 150° Cu-Cl-Cu = 90°  
 Product of the Moments of Inertia:  $I_A I_B I_C = 2.02847 \times 10^{-111} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of sublimation was determined by second and third law analysis of the following vapor pressure data. D. W. Magee, Doctoral Thesis, Ohio State University (1955), measured both vapor pressure by torsion effusion and vapor density in the range 533-644°K. and found only trimer present. The 2nd and 3rd law analyses gave  $\Delta H_f^{298} = 37.37 \pm 0.04$  and  $37.24 \pm 0.02 \text{ kcal. mole}^{-1}$  with a drift of  $-0.25 \pm 0.07 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . R. A. J. Shelton, Trans. Faraday Soc. 57, 213 (1961) using Knudsen effusion in the range 547-657°K. obtained  $\Delta H_f^{298} = 40.35 \pm 1.4$  and  $37.42 \pm 0.4 \text{ kcal. mole}^{-1}$  with a drift of  $-4.9 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . P. I. Pedorov and M. N. Shakhovaya, Izv. Vysokhkh Uchebn. Zavedeni, Khim. Tekhnol. 4, 550 (1961), using transport methods obtained vapor pressures over the liquid from 751-1057°K. Using 2nd and 3rd law analysis these gave  $\Delta H_f^{298} = 36.6 \pm 1.0$  and  $39.27 \pm 0.5 \text{ kcal. mole}^{-1}$ .

L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950) obtained equilibrium constants for the reaction  $3\text{CuCl}(g) + 3\text{HCl}(g) \rightarrow \text{Cu}_3\text{Cl}_3(g) + 1.5 \text{H}_2(g)$ . Second and third law analysis of these constants gave  $\Delta H_f^{298} = 3.9 \pm 0.6$  and  $4.39 \pm 0.3 \text{ kcal. mole}^{-1}$  which leads to  $\Delta H_f^{298} = -61.8 \pm 0.5 \text{ kcal. mole}^{-1}$ . This was the value adopted since it is dependent only on  $\text{HCl}(g)$  and does not involve three times the uncertainty of  $\text{CuCl}(c)$  as do the sublimation experiments, which yield values in good agreement but of larger uncertainty.

Heat Capacity and Entropy.

The structure of the trimer has been investigated by C-H. Wong and V. Schomaker, J. Phys. Chem. 61, 358 (1957). They conclude that the molecule is planar with D<sub>3h</sub> symmetry and a Cu-Cl bond length of 2.16 Å. They also state that a very large amplitude of the symmetric in-plane bending appears plausible from the diffraction pattern. The infra-red spectrum has been investigated by W. Klempner, S. A. Rice and R. S. Berry, J. Am. Chem. Soc. 79, 1810 (1957). They observed one strong absorption with a maximum at 350 cm.<sup>-1</sup> they attribute this to bond stretching motion of type E'. They also suggest that the broad absorption may involve another mode of approximately equal frequency.

In order to estimate the remaining frequencies we assumed that the other infra-red active E' mode would be close to the observed 350 cm.<sup>-1</sup> and this was estimated as 300 cm.<sup>-1</sup>. The in-plane bending is the third E' mode and since this has a very large amplitude it was estimated as 60 cm.<sup>-1</sup>. By analogy with other D<sub>3h</sub> rings the A<sub>2</sub>' mode was assumed to be in the same region as the E' stretches and was taken to be 250 cm.<sup>-1</sup>. The 2A<sub>1</sub>' stretches were estimated as 100 and 150 cm.<sup>-1</sup>, while the out of plane A<sub>2</sub>' was taken as 200 cm.<sup>-1</sup> and the E'' as 80 cm.<sup>-1</sup>. These values gave calculated entropies in excellent agreement with the equilibrium data and thus support the estimates.

The individual moments of inertia were  $I_A = 1.00472 \times 10^{-39} \text{ g. cm.}^2$ ,  $I_B = 200.944 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C <sub>v</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sup>298</sup> )/T	H <sup>o</sup> -H <sup>298</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	21.756	73.970	127.517	6.865	-61.789	-61.789	INFINITE
200	27.780	91.104	105.304	5.373	-61.825	-61.708	134.863
298	29.773	102.631	102.631	2.840	-61.817	-61.594	67.307
				∞	-61.800	-61.489	45.073
300	29.795	102.815	102.632	∞	-61.800	-61.488	44.794
400	30.621	111.515	103.812	3.081	-61.810	-61.384	33.539
500	31.028	118.397	106.095	6.166	-61.853	-61.271	26.781
600	31.256	124.076	108.607	9.281	-61.940	-61.148	22.273
700	31.356	128.905	111.171	12.414	-62.059	-61.005	19.047
800	31.448	133.104	113.656	15.559	-62.215	-60.848	16.623
900	31.532	136.817	116.057	18.711	-62.399	-60.664	14.731
1000	31.598	140.144	118.275	21.869	-62.616	-60.462	13.214
1100	31.632	143.157	120.402	25.030	-62.858	-60.234	11.967
1200	31.657	145.910	122.415	28.195	-63.131	-59.986	10.925
1300	31.678	148.445	124.321	31.361	-63.430	-59.710	10.038
1400	31.694	150.793	126.129	34.530	-63.749	-59.406	9.277
1500	31.707	152.980	127.847	37.700	-64.078	-59.078	8.622
1600	31.717	155.027	129.483	40.871	-64.419	-58.720	7.989
1700	31.726	156.950	131.042	44.043	-64.772	-58.333	7.390
1800	31.733	158.764	132.532	47.216	-65.136	-57.916	6.826
1900	31.740	160.480	133.959	50.390	-65.510	-57.470	6.291
2000	31.745	162.108	135.326	53.564	-65.894	-57.000	5.782
2100	31.750	163.657	136.638	56.738	-66.287	-56.510	5.300
2200	31.754	165.134	137.900	59.914	-66.690	-56.000	4.843
2300	31.757	166.546	139.115	63.090	-67.103	-55.470	4.408
2400	31.760	167.897	140.286	66.266	-67.526	-54.920	4.000
2500	31.763	169.194	141.417	69.442	-67.960	-54.350	3.615
2600	31.765	170.440	142.509	72.618	-68.403	-53.770	3.252
2700	31.767	171.638	143.566	75.794	-68.856	-53.180	2.909
2800	31.769	172.794	144.590	78.972	-69.320	-52.580	2.585
2900	31.771	173.909	145.581	82.149	-69.790	-51.980	2.278
3000	31.773	174.986	146.544	85.326	-70.260	-51.380	1.995
3100	31.774	176.028	147.478	88.503	-70.740	-50.780	1.733
3200	31.775	177.036	148.386	91.681	-71.230	-50.180	1.490
3300	31.776	178.014	149.269	94.858	-71.730	-49.580	1.265
3400	31.777	178.963	150.129	98.036	-72.240	-48.980	1.058
3500	31.778	179.884	150.966	101.214	-72.760	-48.380	0.865
3600	31.779	180.779	151.782	104.392	-73.290	-47.780	0.685
3700	31.780	181.650	152.577	107.570	-73.830	-47.180	0.515
3800	31.781	182.497	153.353	110.748	-74.380	-46.580	0.360
3900	31.782	183.323	154.111	113.926	-74.940	-45.980	0.215
4000	31.782	184.128	154.852	117.104	-75.510	-45.380	0.080
4100	31.783	184.912	155.575	120.282	-76.090	-44.780	0.000
4200	31.783	185.678	156.283	123.461	-76.680	-44.180	∞
4300	31.784	186.426	156.975	126.639	-77.280	-43.580	∞
4400	31.784	187.157	157.653	129.817	-77.890	-42.980	∞
4500	31.785	187.871	158.317	132.996	-78.510	-42.380	∞
4600	31.785	188.570	158.967	136.174	-79.140	-41.780	∞
4700	31.786	189.253	159.604	139.352	-79.780	-41.180	∞
4800	31.786	189.923	160.229	142.531	-80.430	-40.580	∞
4900	31.787	190.578	160.841	145.710	-81.090	-39.980	∞
5000	31.787	191.220	161.442	148.889	-81.760	-39.380	∞
5100	31.787	191.850	162.033	152.067	-82.440	-38.780	∞
5200	31.787	192.467	162.612	155.246	-83.130	-38.180	∞
5300	31.788	193.072	163.181	158.425	-83.830	-37.580	∞
5400	31.788	193.667	163.740	161.604	-84.540	-36.980	∞
5500	31.788	194.250	164.289	164.782	-85.260	-36.380	∞
5600	31.788	194.823	164.921	167.961	-86.000	-35.780	∞
5700	31.788	195.386	165.540	171.140	-86.760	-35.180	∞
5800	31.788	195.938	166.153	174.319	-87.530	-34.580	∞
5900	31.788	196.482	166.762	177.498	-88.310	-33.980	∞
6000	31.789	197.016	167.366	180.677	-89.100	-33.380	∞

MOL. WT. = 162.206

(CRYSTAL)

IRON TRICHLORIDE (FeCl<sub>3</sub>)

$$\Delta H_f^0 = -85.80 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -95.46 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 10.30 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 \text{ (to dimer)} = 34.52 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 34.019 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 577^\circ\text{K.}$$

Heat of Formation.

The enthalpy change,  $\Delta H_f^{298.15} = -24.49 \pm 0.07 \text{ kcal. mole}^{-1}$ , for the reaction  $\text{Fe}(\text{OH})_2 + 3(\text{HCl} \cdot 12.731 \text{ H}_2\text{O})(\text{l}) + 1/2(\text{H}_2\text{O}_2 \cdot 12.580 \text{ H}_2\text{O})(\text{l}) = \text{FeCl}_3(\text{c}) + \text{H}_2(\text{g}) + 45.483 \text{ H}_2\text{O}(\text{l})$  was determined by M. P. Koehler and J. P. Coughlin, *J. Phys. Chem.* **63**, 605 (1959). This leads to  $\Delta H_f^{298.15} = -85.46 \pm 0.20 \text{ kcal. mole}^{-1}$  for  $\text{FeCl}_3(\text{c})$ , using  $\Delta H_f^{298.15} = -38.9 \pm 0.05$  and  $-68.32 \pm 0.01 \text{ kcal. mole}^{-1}$  for hydrochloric acid and hydrogen peroxide solution, respectively, obtained from P. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, National Bureau of Standards Circular 500, 1952. From  $\Delta H_f^{298.15} = -38.0 \pm 0.2 \text{ kcal. mole}^{-1}$  for the reaction  $\text{FeCl}_3(\text{c}) = \text{Fe}^{+++}(\text{aq.})$  reported by J. O. M. Li and N. W. Gregory, *J. Am. Chem. Soc.* **74**, 4670 (1952), the value of  $\Delta H_f^{298.15}(\text{FeCl}_3, \text{c})$  was calculated as  $-95.26 \pm 0.2 \text{ kcal. mole}^{-1}$ . The former  $\Delta H_f^{298.15}$  value is adopted.

The equilibrium pressures of the reaction  $2 \text{FeCl}_2(\text{c}) + \text{Cl}_2(\text{g}) = 2\text{FeCl}_3(\text{c})$ , in the temperature range of 435.7-482.2°K., were measured by H. Schäfer and E. Oehler, *Z. anorg. allgem. Chem.* **271**, 206 (1953). Using the reported partial pressures for  $\text{Cl}_2(\text{g})$ , the enthalpy change ( $\Delta H_r^{298.15}$ ) of the reaction was evaluated as  $-27.49 \pm 0.44$  and  $-27.21 \text{ kcal. mole}^{-1}$  by the second and third law methods, respectively. Based on the third law value for  $\Delta H_f^{298.15}$ , the value of  $\Delta H_f^{298.15}(\text{FeCl}_3, \text{c})$  was derived to be  $-95.36 \pm 0.12 \text{ kcal. mole}^{-1}$  which is in good agreement with the adopted value.

Heat Capacity and Entropy.

The low temperature (51-298.16°K.) heat capacities and high temperature (339.6-560.9°K.) heat content of  $\text{FeCl}_3(\text{c})$  were determined by S. S. Todd and J. P. Coughlin, *J. Am. Chem. Soc.* **73**, 4184 (1951). The low temperature  $C_p$  and the derived high temperature  $C_p$  were plotted. The two  $C_p$  curves were joined smoothly at 298°K. The  $C_p$  values above 560.9°K. were obtained by graphical extrapolation. The value of  $S_{298.15}^0$  was derived from the low temperature data reported by S. S. Todd and J. P. Coughlin, *loc. cit.*, using  $S_{51}^0 = 6.29 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . The value of  $S_{51}^0$  was selected to make the second and third law values of  $\Delta H_r^0$  derived from the equilibrium data reported by H. Schäfer and E. Oehler, *loc. cit.*, in good agreement. The difference in  $S_{51}^0$  between the selected value, 6.29, and the reported value, 4.50  $\text{cal. deg.}^{-1} \text{ mole}^{-1}$ , by S. S. Todd and J. P. Coughlin, *loc. cit.*, is assumed to be the magnetic entropy remaining at 51°K. which was unaccounted for in the report.

Melting Data.

$T_m$  and  $\Delta H_m^0$  were obtained from S. S. Todd and J. P. Coughlin, *loc. cit.*

Heat of Sublimation.

The difference between  $\Delta H_f^{298.15}$  for  $\text{Fe}_2\text{Cl}_6(\text{g})$  and  $2\text{FeCl}_3(\text{c})$  is the heat of sublimation at 298.15°K. The former is obtained by the second and third law analyses of related equilibrium data. See  $\text{Fe}_2\text{Cl}_6(\text{g})$  table for details.

T, °K.	C <sub>p</sub>	S <sup>0</sup>	$-(H^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	Log K <sub>p</sub>
0	0.000	0.000	INFINITE	4.710	95.804	INFINITE
100	13.923	13.127	52.582	3.946	90.582	197.957
200	28.667	25.503	36.055	2.150	85.055	92.940
298	29.100	34.019	34.019	0.000	79.824	58.510
300	23.150	34.162	34.020	0.043	79.727	58.078
400	25.500	41.141	34.865	2.475	74.567	40.739
500	28.650	47.131	36.000	5.465	69.564	30.405
600	29.500	52.382	38.070	8.047	64.726	23.575
700	30.750	57.029	41.225	11.063	60.034	16.743
800	31.500	61.188	43.645	14.170	55.477	11.134
900	31.900	64.924	45.645	17.351	51.026	12.390
1000	32.000	68.291	47.744	20.547	46.669	10.199
1100	32.000	71.341	49.753	23.747	42.363	8.415
1200	32.000	74.126	51.670	26.947	38.120	6.842
1300	32.000	76.687	53.497	30.147	33.942	5.706
1400	32.000	79.058	55.239	33.347	29.841	4.858
1500	32.000	81.266	56.902	36.547	25.814	3.761

IRON TRICHLORIDE (FeCl<sub>3</sub>) (LIQUID) MOL. WT. = 162.206

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S° -(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> ° kcal. mole <sup>-1</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0						
100						
200						
298	32.000	47.955	+0.00	- 86.713	- 75.232	55.144
300	32.000	48.153	+0.059	- 86.687	- 75.161	54.752
400	32.000	57.359	3.259	- 85.358	- 71.522	39.076
500	32.000	64.499	6.459	- 84.113	- 68.207	29.812
600	32.000	70.324	9.659	- 82.946	- 65.139	22.725
700	32.000	75.286	12.859	- 81.852	- 62.257	19.437
800	32.000	79.539	16.059	- 80.849	- 59.529	16.262
900	32.000	83.304	19.259	- 79.960	- 56.918	13.821
1000	32.000	86.680	22.459	- 79.238	- 54.599	11.888
1100	32.000	89.730	25.659	- 78.779	- 51.931	10.317
1200	32.000	92.514	28.859	- 78.492	- 49.326	9.020
1300	32.000	95.074	32.059	- 78.368	- 47.166	7.893
1400	32.000	97.447	35.259	- 78.393	- 45.413	7.013
1500	32.000	99.655	38.459	- 78.675	- 42.738	6.227

S<sub>298.15</sub><sup>o</sup> = 47.955 cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 ΔH<sub>f</sub><sup>o</sup> 298.15 = -86.713 kcal. mole<sup>-1</sup>  
 ΔH<sub>m</sub><sup>o</sup> = 10.30 kcal. mole<sup>-1</sup>  
 ΔH<sub>v</sub><sup>o</sup>(to dimer) = 10.46 kcal. mole<sup>-1</sup>  
 T<sub>m</sub> = 577°K.  
 T<sub>b</sub> = 605°K.

Heat of Formation.

The value of ΔH<sub>f</sub><sup>o</sup> 298.15(FeCl<sub>3</sub>, l) was obtained from ΔH<sub>f</sub><sup>o</sup> 298.15(FeCl<sub>3</sub>, c) by adding ΔH<sub>m</sub><sup>o</sup> and the difference between H<sub>m</sub><sup>o</sup> - H<sub>l</sub><sup>o</sup> - 298.15 for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for FeCl<sub>3</sub>(l) was taken from S. S. Todd and J. P. Coughlin, J. Am. Chem. Soc. 73, 4184 (1951) and assumed as constant between 298.15° and 1500°K. The entropy (S<sub>298.15</sub><sup>o</sup>) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T<sub>m</sub> and ΔH<sub>m</sub><sup>o</sup> were reported by S. S. Todd and J. P. Coughlin, loc. cit.

Vaporization Data.

The boiling point (T<sub>b</sub>) is determined as the temperature at which the free energy change (ΔF<sub>T</sub><sup>o</sup>) of the reaction 2FeCl<sub>3</sub>(l) = Fe<sub>2</sub>Cl<sub>6</sub>(g) approaches zero. The corresponding enthalpy change at T<sub>b</sub> is the heat of vaporization (ΔH<sub>v</sub><sup>o</sup>).

IRON TRICHLORIDE (FeCl<sub>3</sub>) (IDEAL GAS)

MOL. WT. = 162.206

$\Delta H_f^0 = -60.5 \pm 1.2 \text{ kcal. mole}^{-1}$

$\Delta H_f^{298.15} = -60.5 \pm 1.2 \text{ kcal. mole}^{-1}$

Point Group [D<sub>3h</sub>]

Ground State Quantum Weight = [6]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
[350] (1)
[160] (1)
[310] (2)
[130] (2)

Bond Distance: Fe-Cl = [2.17] Å

Bond Angle: Cl-Fe-Cl = [120]°

Product of the Moments of Inertia:  $I_A I_B I_C = [1.43769 \times 10^{-112}] \text{ g.}^3 \text{ cm.}^5$

$\sigma^- = [6]$

Heat of Formation.

The equilibrium pressures for the reaction  $\text{Fe}_2\text{Cl}_6(\text{g}) = 2\text{FeCl}_3(\text{g})$  were determined by Kangro and Bernstorff<sup>1</sup> and Schäfer<sup>2</sup>, respectively. Using their vapor pressure data the corresponding values of  $\Delta H_f^{298.15}$  for that reaction were evaluated by both the second and third law methods. Based on the third law values for  $\Delta H_f^{298.15}$ , the heats of formation ( $\Delta H_f^{298.15}$ ) for  $\text{FeCl}_3(\text{g})$  were derived. The results obtained are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	$\Delta H_f^{298.15}$ , kcal. mole <sup>-1</sup>
Kangro and Bernstorff <sup>1</sup>	760.2-1014.2	34.99 ± 0.44	35.73	-60.34 ± 0.30
Schäfer <sup>2</sup>	673.2-1073.2	34.81 ± 0.02	34.93	-60.74 ± 0.20

<sup>1</sup> W. Kangro and H. Bernstorff, Z. anorg. allgem. Chem. **263**, 316 (1950).

<sup>2</sup> H. Schäfer, Z. anorg. allgem. Chem. **259**, 53 (1949).

The adopted value of  $\Delta H_f^{298.15}(\text{FeCl}_3 \text{ g})$  is  $-60.5 \pm 1.2 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that of  $\text{AlCl}_3(\text{g})$  due to the similarities in structure between  $\text{Fe}_2\text{Cl}_6(\text{g})$  and  $\text{Al}_2\text{Cl}_6(\text{g})$ . The Fe-Cl bond distance was estimated by comparison with those for  $\text{Fe}_2\text{Cl}_6(\text{g})$  reported by E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., **4**, 910 (1963) and O. Hassel and H. Viervoll, Acta Chem. Scand. **1**, 149 (1947). Both the ground state quantum weight and vibrational frequencies were estimated so that the second and third law values of  $\Delta H_f^{298.15}$ , derived from the vapor pressure data, for the reaction  $\text{Fe}_2\text{Cl}_6(\text{g}) = 2\text{FeCl}_3(\text{g})$  are in reasonable agreement. The three principal moments of inertia are:  $I_A I_B = 4.11594 \times 10^{-36}$  and  $I_C = 8.31598 \times 10^{-36} \text{ g. cm.}^2$

T, °K.	C <sub>v</sub> <sup>o</sup>	S <sup>o</sup>	$-(F^o - H_{298}^o)/T$	H <sup>o</sup> - H <sub>298</sub> <sup>o</sup>	$\Delta H_f^o$	$\Delta F_f^o$	Log K <sub>p</sub>
0	+000						
100	13.511	64.295		4.353	60.487	60.487	INFINITE
200	17.298	75.058		3.345	60.633	60.138	13.425
298	18.572	82.243		1.770	60.562	59.666	65.197
300	18.586	82.358		+034	60.499	59.234	43.150
400	19.117	87.787		1.923	60.482	58.817	32.134
500	19.379	92.084		3.849	60.510	58.397	25.524
600	19.526	95.632		5.795	60.598	57.968	21.114
700	19.616	98.659		7.752	60.746	57.619	17.683
800	19.675	101.272		9.717	60.978	57.353	14.853
900	19.716	103.592		11.687	61.320	56.832	13.757
1000	19.746	105.671		13.660	61.845	55.976	12.233
1100	19.767	107.524		15.636	62.580	55.348	10.996
1200	19.779	109.169		17.613	63.525	54.673	9.957
1300	19.787	110.656		19.592	64.672	53.960	9.071
1400	19.807	112.026		21.573	66.028	53.230	8.309
1500	19.816	113.293		23.554	67.595	52.487	7.647
1600	19.823	114.472		25.536	69.374	51.727	7.065
1700	19.828	115.574		27.518	71.366	50.943	6.549
1800	19.833	116.608		29.501	73.572	50.133	6.087
1900	19.837	117.583		31.485	76.000	49.305	5.649
2000	19.841	118.508		33.469	78.653	48.456	5.251
2100	19.844	120.366		35.453	81.531	47.588	4.888
2200	19.846	122.189		37.437	84.644	46.694	4.557
2300	19.848	123.977		39.422	87.991	45.777	4.252
2400	19.850	125.730		41.407	91.584	44.840	3.971
2500	19.852	127.447		43.392	95.425	43.883	3.710
2600	19.854	129.122		45.378	99.521	42.916	3.468
2700	19.855	130.755		47.363	103.872	41.939	3.241
2800	19.856	132.346		49.349	108.485	40.952	3.031
2900	19.857	133.894		51.334	113.358	39.956	2.834
3000	19.858	135.408		53.320	118.493	38.950	2.648
3100	19.859	136.888		55.306	123.893	37.934	2.473
3200	19.860	138.334		57.292	129.562	36.908	2.209
3300	19.861	139.746		59.278	135.505	35.872	1.880
3400	19.862	141.124		61.264	141.728	34.827	1.571
3500	19.862	142.467		63.250	148.236	33.772	1.279
3600	19.863	143.776		65.236	155.027	32.707	1.003
3700	19.863	145.051		67.223	162.098	31.631	0.742
3800	19.864	146.292		69.209	169.446	30.545	0.494
3900	19.864	147.500		71.195	177.068	29.449	0.259
4000	19.865	148.675		73.182	184.971	28.343	0.036
4100	19.865	149.816		75.168	193.158	27.227	0.177
4200	19.865	150.923		77.155	201.628	26.101	0.380
4300	19.866	151.996		79.141	210.381	24.965	0.574
4400	19.866	153.034		81.128	219.416	23.819	0.759
4500	19.866	154.037		83.115	228.733	22.663	0.936
4600	19.867	155.007		85.101	238.333	21.497	1.106
4700	19.867	155.944		87.088	248.216	20.321	1.269
4800	19.867	156.848		89.075	258.381	19.135	1.425
4900	19.867	157.719		91.061	268.828	17.939	1.575
5000	19.867	158.556		93.048	279.557	16.733	1.719
5100	19.868	159.359		95.035	290.568	15.517	1.859
5200	19.868	160.128		97.022	301.861	14.291	1.992
5300	19.868	160.862		99.008	313.436	13.055	2.118
5400	19.868	161.561		100.995	325.293	11.809	2.236
5500	19.868	162.226		102.982	337.433	10.553	2.346
5600	19.869	162.856		104.969	349.856	9.287	2.482
5700	19.869	163.451		106.956	362.563	8.011	2.594
5800	19.869	164.011		108.943	375.554	6.725	2.703
5900	19.869	164.536		110.930	388.829	5.429	2.808
6000	19.869	165.026		112.916	402.387	4.123	2.910



MOL. WT. = 324.412

(IDEAL GAS)

Point Group:  $I_{2h}$   
 $\Delta H_f^\circ = -157.34 \pm 2.0$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^\circ(298.15) = -156.40 \pm 2.0$  kcal. mole<sup>-1</sup>  
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies table with columns for  $\omega_e$  (cm<sup>-1</sup>),  $\omega_e x_e$  (cm<sup>-1</sup>), and  $\omega_e y_e$  (cm<sup>-1</sup>)

Bond Distance: Fe-Cl = 2.11 ± 0.03 Å Fe-Cl bridge = 2.28 ± 0.03 Å  
Bond Angle: Cl-Fe-Cl = 129 ± 3° Cl-bridge-Fe-Cl bridge = 42 ± 3°  
Product of the Moments of Inertia:  $I_A I_B I_C = 7.3510 \times 10^{-41}$  e.s.u.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation... The vaporization of FeCl<sub>3</sub>(c) is complex. It involves three possible chemical reactions... Wilson and Gregory have investigated the vaporization and thermal decomposition equilibria of FeCl<sub>3</sub>(c) by gas saturation flow and chlorine gas techniques...

Table with columns: Investigator, Temperature, K., Second Law Value, Third Law Value, ΔH° 298.15, kcal. mole<sup>-1</sup>

\*Based on the third law values for ΔH° 298.15.  
1. C. G. Meyer, U. S. Bur. Mines Tech. Paper 360 (1925).  
2. H. F. Johnston, H. C. Veitgartner and M. E. Winische, J. Am. Chem. Soc. 64, 241 (1942).  
3. L. E. Wilson and M. W. Gregory, J. Phys. Chem. 62, 433 (1958).  
4. E. Stirmmann, Neues Jahrb. Mineral., Geol., Palaeont., 526, 334 (1925).  
5. K. Sano, J. Chem. Soc. Japan, 55, 1073 (1938).

The value of ΔH° 298.15 for FeCl<sub>3</sub>(g) is selected as -156.4 ± 2.0 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The molecular structure, bond distances and angles were obtained from E. Zaslavin, M. G. Rambidi and P. A. Akinshin, Zh. Strukt. Khim., 3, 310 (1963). The vibrational frequencies were estimated by comparison with those for Al<sub>2</sub>Cl<sub>6</sub>(g) such that the values of ΔH° derived from the equilibrium data by the second and third law methods are in reasonable agreement. The three principal moments of inertia are:  $I_A = 2.79595 \times 10^{-47}$ ,  $I_B = 1.16345 \times 10^{-37}$  and  $I_C = 2.26382 \times 10^{-37}$  e. cm.<sup>2</sup>

Main thermodynamic data table with columns: T, K., Cp, S°, -(F°-H°298)/T, H°-H°298, ΔH°, ΔF°, Log Kp

(REFERENCE STATE)

0 to 1356.6°K. Crystal  
 1356.6 to 2848°K. Liquid  
 2848 to 6000°K. Ideal Monatomic Gas

COPPER (Cu)

See crystal, liquid and monatomic gas tables for details.

T, °K.	C <sub>v</sub>	S°	$-(F^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
		cal. mole <sup>-1</sup> deg <sup>-1</sup>		kcal. mole <sup>-1</sup>			
0	.000	INFINITE	-	1.195	.000	.000	.000
100	3.826	2.392	12.749	1.036	.000	.000	.000
200	5.399	5.661	8.437	.555	.000	.000	.000
298	5.843	7.913	7.913	.000	.000	.000	.000
300	5.846	7.949	7.913	.011	.000	.000	.000
400	6.077	9.665	8.146	.208	.000	.000	.000
500	6.250	11.040	8.591	1.224	.000	.000	.000
600	6.394	12.193	9.098	1.857	.000	.000	.000
700	6.516	13.188	9.673	2.502	.000	.000	.000
800	6.620	14.064	10.116	3.159	.000	.000	.000
900	6.725	14.850	10.529	3.826	.000	.000	.000
1000	6.822	15.564	11.080	4.504	.000	.000	.000
1100	6.910	16.218	11.500	5.190	.000	.000	.000
1200	6.998	16.823	11.918	5.886	.000	.000	.000
1300	7.086	17.387	12.312	6.590	.000	.000	.000
1400	7.170	17.912	12.692	7.300	.000	.000	.000
1500	7.250	18.400	13.058	8.016	.000	.000	.000
1600	7.326	18.854	13.406	8.738	.000	.000	.000
1700	7.400	19.276	13.738	9.466	.000	.000	.000
1800	7.470	19.668	14.056	10.200	.000	.000	.000
1900	7.538	20.032	14.364	10.940	.000	.000	.000
2000	7.604	20.370	14.654	11.686	.000	.000	.000
2100	7.668	20.684	14.928	12.438	.000	.000	.000
2200	7.730	20.974	15.188	13.196	.000	.000	.000
2300	7.790	21.242	15.434	13.960	.000	.000	.000
2400	7.848	21.488	15.666	14.730	.000	.000	.000
2500	7.904	21.714	15.884	15.506	.000	.000	.000
2600	7.958	21.922	16.088	16.288	.000	.000	.000
2700	8.010	22.114	16.278	17.076	.000	.000	.000
2800	8.060	22.292	16.454	17.870	.000	.000	.000
2900	8.108	22.458	16.616	18.670	.000	.000	.000
3000	8.154	22.616	16.766	19.476	.000	.000	.000
3100	8.198	22.766	16.904	20.288	.000	.000	.000
3200	8.240	22.908	17.032	21.106	.000	.000	.000
3300	8.280	23.048	17.152	21.930	.000	.000	.000
3400	8.318	23.180	17.264	22.760	.000	.000	.000
3500	8.354	23.304	17.368	23.596	.000	.000	.000
3600	8.388	23.420	17.464	24.438	.000	.000	.000
3700	8.420	23.528	17.552	25.286	.000	.000	.000
3800	8.450	23.628	17.632	26.140	.000	.000	.000
3900	8.478	23.720	17.704	27.000	.000	.000	.000
4000	8.504	23.804	17.768	27.866	.000	.000	.000
4100	8.528	23.880	17.824	28.738	.000	.000	.000
4200	8.550	23.948	17.872	29.616	.000	.000	.000
4300	8.570	24.008	17.912	30.500	.000	.000	.000
4400	8.588	24.060	17.944	31.390	.000	.000	.000
4500	8.604	24.104	17.968	32.286	.000	.000	.000
4600	8.618	24.140	17.984	33.188	.000	.000	.000
4700	8.630	24.168	17.992	34.096	.000	.000	.000
4800	8.640	24.188	17.996	35.010	.000	.000	.000
4900	8.648	24.200	17.996	35.930	.000	.000	.000
5000	8.654	24.204	17.992	36.856	.000	.000	.000
5100	8.658	24.200	17.984	37.788	.000	.000	.000
5200	8.660	24.188	17.972	38.726	.000	.000	.000
5300	8.660	24.168	17.956	39.670	.000	.000	.000
5400	8.658	24.140	17.928	40.620	.000	.000	.000
5500	8.654	24.104	17.888	41.576	.000	.000	.000
5600	8.648	24.060	17.836	42.538	.000	.000	.000
5700	8.640	24.008	17.772	43.506	.000	.000	.000
5800	8.630	23.948	17.696	44.480	.000	.000	.000
5900	8.618	23.880	17.608	45.460	.000	.000	.000
6000	8.604	23.804	17.512	46.446	.000	.000	.000

Dec. 31, 1965

$\Delta H_f^0 = 0 \text{ kcal. mole}^{-1}$

$\Delta H_f^{298.15} = 0 \text{ kcal. mole}^{-1}$

$\Delta H_m^0 = 3.17 \pm 0.15 \text{ kcal. mole}^{-1}$

$\Delta H_m^{298.15} = 81 \pm 0.4 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 7.913 \pm 0.04 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 1356.6^\circ\text{K.}$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature specific heat of copper has been measured by several workers and generally there is good agreement. The selected values lie close to the determinations of J. A. Kok and W. H. Keessom (1.2-20°K), Physica 3, 1035 (1936); D. L. Martin (20-300°K), Can. J. Phys. 38, 17 (1960); C. B. Satterthwaite, R. S. Craig and W. E. Wallace, J. Am. Chem. Soc. 76, 232 (1954), and S. M. Dockety, Can. J. Research 9, 84 (1953) and 15A, 59 (1937). Several other workers have reported values of  $C_p$  slightly higher than the adopted values especially W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. 63, 1897 (1941), however these measurements were not used for workers, the values of R. E. Pawel and E. E. Stansbury, J. Phys. Chem. Solids 25, 607 (1965) join well with the low temperature data and are adopted. These values lie within 1% of the values adopted by R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York, 1963. Several determinations of the solid enthalpy are also in good agreement with selected heat capacity curve. For references to these determinations refer to Hultgren et al. loc. cit.

Melting Data.

The melting point of copper is well established and the recent determination of W. Heyne, Exptl. Tech. Physik. 12, 87 (1964) is adopted. The heat of fusion was obtained from the calculated enthalpy of the solid at the melting point and the liquid enthalpy measurements of F. Wust, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The liquid enthalpies of I. B. Fieldhouse, J. C. Hedge, J. I. Lang and T. E. Waterman, ASTIA Doc. No. A. D. 150954 are somewhat higher than the adopted values.

Sublimation Data.

See Cu(g) for details.

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞.00	INFINITE	1.105	∞.00	∞.00	INFINITE
100	3.826	2.292	1.036	∞.00	∞.00	∞.001
200	5.259	3.691	4.555	∞.00	∞.00	∞.000
298	5.843	4.913	4.000	∞.00	∞.00	∞.000
300	5.846	7.949	∞.11	∞.00	∞.00	∞.000
400	6.077	9.665	6.608	∞.00	∞.00	∞.000
500	6.220	11.040	1.224	∞.00	∞.00	∞.000
600	6.334	12.193	9.098	∞.00	∞.00	∞.000
700	6.516	13.188	2.502	∞.00	∞.00	∞.000
800	6.620	14.064	10.116	∞.00	∞.00	∞.000
900	6.725	14.850	3.826	∞.00	∞.00	∞.000
1000	6.822	15.564	4.504	∞.00	∞.00	∞.000
1100	6.910	16.218	5.190	∞.00	∞.00	∞.000
1200	6.998	16.823	11.918	∞.00	∞.00	∞.000
1300	7.086	17.387	6.500	∞.00	∞.00	∞.000
1400	7.174	17.915	7.503	3.185	1.102	∞.016
1500	7.262	18.413	8.025	3.213	.337	∞.049
1600	7.350	18.885	13.413	3.233	.574	∞.078
1700	7.438	19.333	13.748	3.243	.813	∞.105
1800	7.526	19.761	10.243	3.245	1.052	∞.128
1900	7.614	20.170	16.380	3.238	1.290	∞.148
2000	7.702	20.563	11.766	3.222	1.528	∞.167

$$\Delta H_f^{298.15} = 8.663 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = 2.224 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 3.17 \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 76.743 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 8.663 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m^0 = 1356.6^\circ \text{K.}$$

$$T_b^0 = 2848^\circ \text{K.}$$

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding  $\Delta H_m^0$  and the difference between  $H_{1356.6}^0 - H_{298}^0$  for (c) and (1).

Heat Capacity and Entropy.

The heat capacity was calculated from the enthalpy data of F. Wust, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See crystal table for details.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0						
100						
200						
298	7.500	8.663	0.000	2.224	2.000	1.466
300	7.500	8.709	0.14	2.227	1.999	1.456
400	7.500	10.867	0.764	2.380	1.899	1.038
500	7.500	12.541	1.514	2.514	1.763	0.771
600	7.500	13.908	2.264	2.631	1.602	0.583
700	7.500	15.064	3.014	2.736	1.423	0.444
800	7.500	16.066	3.764	2.829	1.227	0.335
900	7.500	16.949	4.514	2.912	1.023	0.248
1000	7.500	17.739	5.264	2.984	0.809	0.177
1100	7.500	18.454	6.014	3.048	0.588	0.117
1200	7.500	19.107	6.764	3.102	0.361	0.066
1300	7.500	19.707	7.514	3.148	0.132	0.022
1400	7.500	20.263	8.264	3.186	0.000	0.000
1500	7.500	20.780	9.014	3.216	0.000	0.000
1600	7.500	21.264	9.764	3.239	0.000	0.000
1700	7.500	21.719	10.514	3.256	0.000	0.000
1800	7.500	22.148	11.264	3.267	0.000	0.000
1900	7.500	22.553	12.014	3.273	0.000	0.000
2000	7.500	22.938	12.764	3.275	0.000	0.000
2100	7.500	23.304	13.514	3.273	0.000	0.000
2200	7.500	23.653	14.264	3.267	0.000	0.000
2300	7.500	23.986	15.014	3.256	0.000	0.000
2400	7.500	24.305	15.764	3.239	0.000	0.000
2500	7.500	24.611	16.514	3.216	0.000	0.000
2600	7.500	24.906	17.264	3.186	0.000	0.000
2700	7.500	25.189	18.014	3.148	0.000	0.000
2800	7.500	25.461	18.764	3.102	0.000	0.000
2900	7.500	25.725	19.514	3.048	0.000	0.000
3000	7.500	25.979	20.264	3.000	0.000	0.000
3100	7.500	26.225	21.014	2.956	0.000	0.000
3200	7.500	26.463	21.764	2.916	0.000	0.000
3300	7.500	26.694	22.514	2.880	0.000	0.000
3400	7.500	26.918	23.264	2.848	0.000	0.000
3500	7.500	27.135	24.014	2.820	0.000	0.000
3600	7.500	27.346	24.764	2.796	0.000	0.000
3700	7.500	27.552	25.514	2.776	0.000	0.000
3800	7.500	27.752	26.264	2.760	0.000	0.000
3900	7.500	27.947	27.014	2.748	0.000	0.000
4000	7.500	28.136	27.764	2.740	0.000	0.000

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0	0.000	INFINITE	1.481	80.714	80.714	INFINITE
100	4.868	34.317	0.984	81.052	77.859	-1.70153
200	4.968	37.760	0.198	81.067	74.648	-1.81567
298	4.968	39.744	0.000	81.000	71.510	-2.42415
300	4.968	39.775	0.009	80.998	71.450	-2.42049
400	4.968	41.204	39.939	80.898	68.282	-37.306
500	4.968	42.313	40.307	80.779	65.142	-28.472
600	4.968	43.218	40.719	80.643	62.028	-22.592
700	4.968	44.048	41.132	80.494	58.937	-18.400
800	4.968	44.848	41.531	80.334	55.867	-15.261
900	4.968	45.633	41.911	80.164	52.819	-12.1826
1000	4.968	46.412	42.269	79.983	49.791	-10.1881
1100	4.969	46.230	42.608	79.794	46.781	-9.294
1200	4.970	46.062	42.928	79.595	43.788	-8.474
1300	4.972	45.900	43.231	79.388	40.813	-7.730
1400	4.977	45.729	43.518	79.172	37.855	-7.042
1500	4.985	45.572	43.790	78.947	34.924	-6.413
1600	4.997	45.424	44.049	78.713	32.028	-5.838
1700	5.016	45.288	44.296	78.471	29.167	-5.317
1800	5.041	45.166	44.532	78.222	26.342	-4.841
1900	5.074	45.059	44.758	77.967	23.552	-4.408
2000	5.116	44.970	44.975	77.703	20.795	-4.015
2100	5.168	44.897	45.183	77.430	18.070	-3.660
2200	5.229	44.843	45.383	77.149	15.384	-3.342
2300	5.300	44.807	45.577	76.861	12.737	-3.059
2400	5.380	44.784	45.763	76.567	10.130	-2.809
2500	5.468	44.772	45.944	76.267	7.564	-2.588
2600	5.565	44.770	46.120	75.962	5.041	-2.391
2700	5.668	44.773	46.290	75.652	2.559	-2.218
2800	5.778	44.781	46.456	75.337	0.118	-2.067
2900	5.892	44.794	46.617	75.017	-0.280	-1.935
3000	6.010	44.812	46.774	74.692	-0.660	-1.820
3100	6.131	44.837	46.928	74.362	-1.020	-1.720
3200	6.253	44.864	47.078	74.027	-1.360	-1.635
3300	6.375	44.892	47.225	73.687	-1.680	-1.565
3400	6.496	44.920	47.369	73.342	-1.990	-1.507
3500	6.616	44.948	47.511	72.992	-2.290	-1.460
3600	6.732	44.976	47.649	72.637	-2.580	-1.423
3700	6.846	44.998	47.786	72.277	-2.860	-1.395
3800	6.954	44.998	47.920	71.912	-3.130	-1.375
3900	7.059	44.984	48.051	71.543	-3.390	-1.363
4000	7.158	44.959	48.181	71.170	-3.640	-1.357
4100	7.251	44.924	48.309	70.793	-3.880	-1.357
4200	7.339	44.879	48.435	70.412	-4.110	-1.363
4300	7.421	44.824	48.559	70.027	-4.330	-1.375
4400	7.498	44.759	48.681	69.638	-4.540	-1.392
4500	7.568	44.684	48.802	69.244	-4.740	-1.415
4600	7.633	44.600	48.921	68.846	-4.930	-1.443
4700	7.693	44.509	49.039	68.444	-5.110	-1.476
4800	7.747	44.413	49.155	68.038	-5.280	-1.514
4900	7.797	44.313	49.269	67.628	-5.440	-1.557
5000	7.842	44.210	49.383	67.214	-5.590	-1.605
5100	7.884	44.104	49.495	66.796	-5.730	-1.657
5200	7.921	44.000	49.605	66.374	-5.860	-1.714
5300	7.955	43.897	49.712	65.948	-5.980	-1.775
5400	7.987	43.791	49.817	65.518	-6.090	-1.840
5500	8.016	43.684	49.920	65.084	-6.190	-1.909
5600	8.043	43.576	50.023	64.646	-6.280	-2.082
5700	8.069	43.468	50.123	64.204	-6.360	-2.259
5800	8.094	43.361	50.220	63.758	-6.430	-2.440
5900	8.118	43.254	50.314	63.308	-6.490	-2.625
6000	8.142	43.148	50.405	62.854	-6.540	-2.814

COPPER (Cu)

(IDEAL GAS)

AT. WT. = 63.54

Ground State Configuration  $3s^1/2$   
 $\Delta H_f^o = 80.714 \pm 0.5$  kcal. mole<sup>-1</sup>  
 $\Delta F_f^o = 39.744$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^o = 81.0 \pm 0.5$  kcal. mole<sup>-1</sup>

Electronic Levels and Quantum Weight

E <sub>1</sub> , cm. <sup>-1</sup>	E <sub>1</sub>	E <sub>2</sub> , cm. <sup>-1</sup>	E <sub>2</sub>	E <sub>3</sub> , cm. <sup>-1</sup>	E <sub>3</sub>	E <sub>4</sub> , cm. <sup>-1</sup>	E <sub>4</sub>
0.0	54784.0	44406.3	4	57948.7	4	57948.7	4
11202.6	55027.7	44544.2	4	57983.1	4	57983.1	4
13245.4	55087.7	44915.6	2	57985.1	6	57985.1	6
30335.3	55391.3	43726.2	6	57985.2	6	57985.2	6
35018.7	55486.3	45823.0	6	57987.7	6	57987.7	6
40114.0	56030.0	45879.3	4	58249.5	4	58249.5	4
40943.7	58130.0	46172.8	4	58250.7	6	58250.7	6
40933.1	58343.7	46598.4	6	58275.3	4	58275.3	4
41582.9	58383.5	46598.4	6	58275.3	4	58275.3	4
42302.5	58630.9	49355.2	4	60070.0	16	60070.0	16
43137.2	58671.4	49942.1	6	60595.0	16	60595.0	16
43514.0	58846.8	52646.8	2	61150.0	26	61150.0	26

Heat of Formation

The heat of sublimation has been determined by second and third law analysis of the vapor pressure data of a large number of investigators. The results are summarized below:

Ref.	Range °K.	Method	Points	ΔH <sub>subl.</sub> , 298.15 kcal. mole <sup>-1</sup>	3rd law	Drift
1.	1342-1340	Knudsen	6	83.0 ± 0.2	81.34 ± 0.04	0.3 ± 0.2
2.	1370-1563	Knudsen	10*	80.6 ± 0.6	80.20 ± 0.3	-1.0 ± 0.5
3.	1605-1879	Transport	21*	79.7 ± 0.6	80.55 ± 0.25	0.5 ± 1.4
4.	1192-1360	Knudsen	13	80.6 ± 4.0	81.16 ± 1.2	0.4 ± 3.1
5.	1475-1707	Knudsen	8	83.2 ± 1.3	81.01 ± 0.2	-0.6 ± 0.8
6.	987-1350	Knudsen	14	80.5 ± 2.3	82.14 ± 1.7	2.7 ± 2.0
7.	1366-1466	Langmuir	5	79.1 ± 2.3	79.96 ± 0.3	1.1 ± 1.8
8.	1268-1320	Langmuir	7*	92.5 ± 3.3	81.26 ± 0.5	-8.9 ± 2.6
9.	1419-1463	Knudsen	7	63.0 ± 11.7	81.40 ± 0.4	12.3 ± 0.6
10.	1083-2643	Transport	1	98.5 ± 4.3	77.25 ± 2.8	-6.3 ± 1.7
11.	2138-2643	Boiling	4	120.0 ± 8.0	76.1 ± 2.8	-18.0 ± 3.3
12.	2378-2573	Boiling	5	66.2 ± 2.5	73.5 ± 1.0	-0.9 ± 5.9
13.	1768-2316	Boiling	6	66.2 ± 2.5	73.5 ± 1.0	3.3 ± 1.3

\* Point rejected due to failure of statistical test.

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The first eight references may be considered to have reasonable drifts and second and third law agreement. The three Langmuir values are grouped closely together at about 80.3 kcal. mole<sup>-1</sup>. The Knudsen values all lie a little higher averaging 81.4 kcal. mole<sup>-1</sup>, the single transport determination is at 80.55 kcal. mole<sup>-1</sup>. If the evaporation coefficient is not unity in the Langmuir experiments then one would observe lower pressures and higher heats of sublimation, thus it appears that the coefficient must be unity and that all techniques are measuring valid heats of sublimation. A value of 81 ± 0.5 kcal. mole<sup>-1</sup> was chosen weighted toward the more precise Knudsen work of Hersh.

Heat Capacity and Entropy

The electronic ground state configuration and higher electronic levels were taken from C. Z. Moore "Atomic Energy Levels", Natl. Bur. Stds. Circular 467, Washington 1962.

AT. WT. = 63.55945

(IDEAL GAS)

COPPER UNIPOSITIVE ION (Cu<sup>+</sup>)Ground State Configuration 1S<sub>0</sub>  $\Delta H_f^{\circ} = 258.9 \pm 0.5$  kcal. mole<sup>-1</sup> $S_{298.15}^{\circ} = 38.367$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  $\Delta H_f^{\circ} 298.15 = 260.668 \pm 0.5$  kcal. mole<sup>-1</sup>

## Electronic Levels and Quantum Weight

$\epsilon_1$ , cm. <sup>-1</sup>	$g_1$	$\epsilon_1$ , cm. <sup>-1</sup>	$g_1$
0.0	1	68694.7	39
21928.6	7	72095.4	42
22847.0	5	85388.8	5
23998.3	3	88505.7	9
26264.5	5	95565.7	9

## Heat of Formation.

The heat of formation was obtained from the dissociation limit of Cu(g) which was given as 62317.2 cm.<sup>-1</sup> (or 178.187 kcal. mole<sup>-1</sup>) by C. E. Moore "Atomic Energy Levels", Nat. Bur. Stds. Circ. 467, Washington 1952. This value applies to 0°K, the enthalpy of Cu, Cu<sup>+</sup> and e<sup>-</sup> between 298°K. and zero are all 1.481 kcal. mole<sup>-1</sup>, thus at 298°K. the dissociation energy is 179.668 kcal. mole<sup>-1</sup>. The heat of formation was then obtained from the reaction Cu(g) → Cu<sup>+</sup> + e<sup>-</sup> as  $\Delta H_f^{\circ} 298.15 = 260.668 \pm 0.5$  kcal. mole<sup>-1</sup>, the uncertainty is that due to Cu(g).

## Heat Capacity and Entropy.

The ground state configuration and higher electronic levels were taken from C. E. Moore, loc. cit. Levels above 100,000 cm.<sup>-1</sup> were not included since they do not affect the thermodynamic function, levels above 30,000 cm.<sup>-1</sup> were averaged.

T, °K.	C <sub>v</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> )/T	H <sup>o</sup> -H <sub>298</sub>	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>P</sub>
0							
100	4.968	38.367	38.367	0.000	260.668	250.101	-183.320
200	4.968	38.397	38.417	0.009	260.675	250.035	-182.142
300	4.968	38.427	38.452	0.006	260.672	249.972	-136.636
400	4.968	38.453	38.477	1.003	261.450	242.724	-106.089
500	4.968	41.841	39.342	1.500	261.811	238.944	-87.031
600	4.968	42.607	39.775	1.906	262.158	235.105	-73.400
700	4.968	43.270	40.154	2.403	262.495	231.217	-63.162
800	4.968	43.855	40.533	2.900	262.822	227.288	-55.190
900	4.968	44.379	40.892	3.487	263.138	223.322	-48.805
1000	4.968	44.852	41.233	3.984	263.446	219.327	-43.574
1100	4.968	45.285	41.551	4.481	263.744	215.302	-39.210
1200	4.968	45.682	41.854	4.977	264.032	211.254	-35.513
1300	4.968	46.050	42.140	5.474	264.310	207.188	-32.357
1400	4.968	46.393	42.413	5.971	264.579	203.103	-29.638
1500	4.968	46.714	42.672	6.468	264.838	199.000	-27.257
1600	4.968	47.015	42.918	6.965	265.087	194.879	-25.154
1700	4.968	47.299	43.154	7.461	265.327	190.743	-23.283
1800	4.968	47.568	43.379	7.958	265.558	186.593	-21.608
1900	4.969	47.823	43.595	8.455	265.780	182.428	-20.098
2000	4.970	48.065	43.802	8.952	266.000	178.249	-18.731
2100	4.971	48.296	44.001	9.449	266.218	174.054	-17.488
2200	4.973	48.517	44.193	9.946	266.432	170.840	-16.351
2300	4.976	48.729	44.377	10.444	266.642	167.608	-15.308
2400	4.981	48.932	44.556	10.942	266.848	164.358	-14.347
2500	4.987	49.128	44.728	11.440	267.050	161.094	-13.460
2600	4.996	49.316	44.894	11.939	267.248	157.815	-12.638
2700	5.008	49.498	45.055	12.439	267.442	154.524	-11.873
2800	5.024	49.674	45.212	12.941	267.632	151.221	-11.261
2900	5.044	49.845	45.363	13.444	267.818	147.906	-10.777
3000	5.069	50.010	45.510	13.950	268.000	144.585	-10.325
3100	5.099	50.172	45.654	14.458	268.178	141.257	-9.899
3200	5.136	50.329	45.793	14.970	268.352	137.921	-9.493
3300	5.180	50.483	45.929	15.486	268.522	134.576	-9.104
3400	5.232	50.634	46.061	16.006	268.688	131.221	-8.739
3500	5.291	50.782	46.190	16.532	268.850	127.856	-8.397
3600	5.359	50.928	46.316	17.065	269.008	124.481	-8.077
3700	5.436	51.072	46.439	17.604	269.162	121.096	-7.783
3800	5.522	51.214	46.560	18.152	269.312	117.699	-7.515
3900	5.617	51.355	46.678	18.709	269.458	114.291	-7.240
4000	5.721	51.495	46.794	19.276	269.600	110.871	-6.970
4100	5.835	51.634	46.907	19.853	269.738	107.436	-6.729
4200	5.958	51.773	47.019	20.443	269.872	103.985	-6.501
4300	6.090	51.912	47.129	21.045	269.992	100.518	-6.283
4400	6.231	52.050	47.236	21.661	270.108	97.035	-6.084
4500	6.380	52.189	47.343	22.292	270.220	93.538	-5.903
4600	6.537	52.328	47.447	22.938	270.328	90.026	-5.734
4700	6.702	52.467	47.549	23.600	270.432	86.500	-5.577
4800	6.872	52.607	47.649	24.278	270.532	82.960	-5.432
4900	7.049	52.747	47.747	24.974	270.628	79.406	-5.299
5000	7.230	52.889	47.843	25.688	270.720	75.838	-5.177
5100	7.416	53.031	47.936	26.420	270.808	72.254	-5.066
5200	7.605	53.171	48.027	27.171	270.892	68.656	-4.965
5300	7.796	53.311	48.116	27.941	270.972	65.042	-4.873
5400	7.989	53.451	48.203	28.731	271.048	61.416	-4.789
5500	8.182	53.591	48.287	29.539	271.120	57.778	-4.712
5600	8.376	53.731	48.369	30.367	271.188	54.126	-4.642
5700	8.565	53.870	48.449	31.214	271.252	50.462	-4.577
5800	8.755	54.009	48.527	32.080	271.312	46.786	-4.517
5900	8.944	54.149	48.603	32.965	271.368	43.100	-4.461
6000							

Dec. 31, 1965

FLUORINE, MONATOMIC (F) (IDEAL GAS) MOL. WT. = 18.9984

Ground State Configuration  $2p^2_{3/2}$   $\Delta H_f^\circ = 18.36 \pm 0.40$  kcal. mole $^{-1}$   
 $S_{298.15} = 37.917$  cal. deg $^{-1}$  mole $^{-1}$   $\Delta H_f^\circ(298.15) = 18.86 \pm 0.40$  kcal. mole $^{-1}$

Electronic Levels and Quantum Weight			
$\epsilon_i$ , cm $^{-1}$	$g_i$	$\epsilon_i$ , cm $^{-1}$	$g_i$
0	4	116,597.23	14
		126,346.36	80
404	2	117,465.88	22
		132,766.07	16
103,327.14	18	119,427.73	10
		135,531.81	22
115,918.7	6	125,118.7	12
		134,978.71	88

**Heat of Formation.**  
 The dissociation energy ( $D_0$ ) of fluorine has been discussed by numerous investigators for many years. Until about fifteen years ago, high values of  $D_0(F_2)$ , about 63 kcal. mole $^{-1}$ , were widely accepted. These values were obtained from extrapolations of the spectroscopic data for the halogens, e.g.  $D_0 = 63.3$  kcal. mole $^{-1}$  was reported by H. V. Hartberg, G. Sprenger and J. Taylor, Z. Physik. Chem., Bodenstein-Festschrift, 61 (1931). However, meanwhile many indirect determinations as well as estimation have been carried out, which yield appreciably lower values. In 1950 the available data were examined critically by M. O. Evans, E. Warriner and E. Whittle, J. Chem. Soc. 1524 (1950) and shown to support a value,  $D_0(F_2) = 37 \pm 8$  kcal. mole $^{-1}$ . The indirect determinations include (1) the thermal conductivity measurements by E. U. Franck and E. Wicke, Z. Elektrochem. 55, 643 (1951); (2) the explosion method by H. Fritz, Dissertation, 1952; (3) estimation by use of the relations between  $D_0$  and the vibrational frequencies by A. Bocken and E. Wicke, Nachrichten, 57, 235 (1950); and (4) spectroscopic data on the dissociation energy of diatomic fluorides. Recently more direct methods have been used to determine  $D_0(F_2)$ . They gave still lower values. The  $D_0$  values reported by the previous investigators have been reviewed by L. Hser and C. W. Beckett, National Bureau of Standards Report 1455 (1952), and E. Wicke and H. Fritz, Z. Elektrochem. 57, 9 (1953).

The low bond dissociation energy of  $F_2(g)$  has been attributed to the repulsion between the unpaired electrons on the bound fluorine atoms by K. S. Pitzer, J. Am. Chem. Soc. 70, 2140 (1948), or to the absence in fluorine of strengthening of the bond by hybridization of the p- or d- orbitals as may take place in the higher halogens by R. S. Mulliken, J. Am. Chem. Soc. 77, 884 (1955). M. O. Evans, Trans. Faraday Soc. 55, 9 (1959) suggests that the observed low  $D_0$  value results from the large energy required to promote the P atoms to the valence state from which the bond may be formed.

The equilibrium pressures for the reaction  $F_2(g) \rightarrow 2F(g)$  have been measured by several investigators. Using the reported equilibrium constants, the dissociation energy,  $D_{298.15}$ , was evaluated by both the second and third law methods. The results obtained are presented as follows.

Temperature, $^{\circ}K$ .	$D_{298.15}$ , kcal. mole $^{-1}$		Reference
	2nd Law Value	3rd Law Value	
259 - 1115	36.91 $\pm$ 0.41	37.76	1
810 - 860	36.7 $\pm$ 18.2	35.1	2
513 - 790	34.4 $\pm$ 1.8	38.0	3
725 - 820	41.8 $\pm$ 0.2		4

1. R. M. Doerschner, J. Chem. Phys. 20, 330 (1952).
2. P. W. Gilles and J. L. Margrave, J. Chem. Phys. 21, 381 (1953).
3. K. Wise, J. Phys. Chem. 59, 389 (1954).
4. M. Fréchet, et al. "Study of Rocket Engine Exhaust Products," Thirtieth Quarterly Report, June 1 - Oct. 31, 1964, Rocket Corporation, Pasadena, California.

By use of  $H_2$ - $F_2$  mixture explosion method,  $D_0(F_2)$  was reported as  $37 \pm 2$  kcal. mole $^{-1}$  by E. Wicke and H. Fritz, loc. cit. K. L. Wray and D. F. Hornig, J. Chem. Phys. 25, 1271 (1956), using shock wave method, obtained  $D_0 = 31.0 \pm 4.3$  kcal. mole $^{-1}$ . The continuous absorption electronic spectrum of  $F_2(g)$  and the Raman displacement for the  $0 \rightarrow 1$  vibrational transition have been used by A. L. G. Rees, J. Chem. Phys. 26, 1567 (1957) to compute the potential energy curve for the repulsive  $1/\bar{r}$  state dissociating to two normal  $F(g)$ . This curve is consistent with the value,  $D_0 = 37.1 \pm 0.85$  kcal. mole $^{-1}$ . The absorption spectrum of  $F_2(g)$  has been observed in the vacuum UV region by R. P. Izkowski and J. L. Margrave, J. Chem. Phys. 30, 403 (1959). From a progression of bands at 8744, the value,  $D_0 = 37.5 \pm 2$  kcal. mole $^{-1}$  is deduced.

The  $F_2$  dissociation energy is selected as  $37.76 \pm 0.80$  kcal. mole $^{-1}$ , yielding  $\Delta H_f^\circ(298.15)(F, g) = 18.86 \pm 0.40$  kcal. mole $^{-1}$ .

**Heat Capacity and Entropy.**

The ground state configuration, electronic levels and quantum weights were taken from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

T, $^{\circ}K$ .	$C_p$	$S^\circ$	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\Delta H_f^\circ$	$\Delta F_f^\circ$	Log K <sub>p</sub>
0	0.000	INFINITE	INFINITE	1.598	18.357	18.357	INFINITE
100	5.068	42.710	1.059	18.508	17.675	17.675	37.875
200	5.403	36.744	0.534	18.684	16.089	16.089	17.580
298	5.437	37.917	0.000	18.860	14.777	14.777	10.632
300	5.436	37.951	0.010	18.863	14.752	14.752	10.746
400	5.361	39.505	0.550	19.018	13.358	13.358	7.298
500	5.282	40.693	1.082	19.147	11.927	11.927	5.213
600	5.218	41.650	1.607	19.256	10.472	10.472	3.814
700	5.169	42.450	2.126	19.349	9.001	9.001	2.810
800	5.133	43.138	2.641	19.431	7.517	7.517	2.053
900	5.105	43.741	3.153	19.505	6.023	6.023	1.462
1000	5.083	44.277	3.663	19.572	4.522	4.522	0.988
1100	5.066	44.761	4.170	19.633	3.013	3.013	0.599
1200	5.052	45.201	4.676	19.691	1.500	1.500	0.273
1300	5.041	45.605	5.180	19.744	0.018	0.018	0.003
1400	5.032	45.978	5.684	19.794	-1.540	-1.540	0.240
1500	5.025	46.325	6.187	19.841	-3.065	-3.065	0.447
1600	5.018	46.649	6.689	19.886	-4.594	-4.594	0.627
1700	5.013	46.954	7.191	19.929	-6.126	-6.126	0.788
1800	5.009	47.240	7.692	19.969	-7.660	-7.660	0.930
1900	5.005	47.511	8.199	20.007	-9.197	-9.197	1.058
2000	5.001	47.767	8.721	20.044	-10.733	-10.733	1.173
2100	4.999	48.011	9.243	20.079	-12.273	-12.273	1.277
2200	4.996	48.244	9.768	20.112	-13.816	-13.816	1.372
2300	4.994	48.466	10.294	20.144	-15.368	-15.368	1.459
2400	4.992	48.678	10.824	20.175	-16.902	-16.902	1.539
2500	4.990	48.882	11.356	20.203	-18.448	-18.448	1.613
2600	4.988	49.078	11.889	20.231	-19.995	-19.995	1.681
2700	4.987	49.266	12.422	20.257	-21.552	-21.552	1.744
2800	4.986	49.447	12.957	20.282	-23.122	-23.122	1.802
2900	4.985	49.622	13.491	20.306	-24.699	-24.699	1.857
3000	4.984	49.791	14.023	20.327	-26.281	-26.281	1.908
3100	4.983	49.954	14.556	20.349	-27.868	-27.868	1.956
3200	4.982	50.113	15.089	20.369	-29.460	-29.460	2.001
3300	4.981	50.266	15.622	20.387	-31.058	-31.058	2.043
3400	4.980	50.415	16.155	20.405	-32.661	-32.661	2.082
3500	4.980	50.559	16.688	20.421	-33.950	-33.950	2.120
3600	4.979	50.699	17.221	20.436	-35.502	-35.502	2.155
3700	4.978	50.836	17.754	20.450	-37.059	-37.059	2.189
3800	4.978	50.968	18.287	20.463	-38.610	-38.610	2.220
3900	4.977	51.098	18.820	20.474	-40.169	-40.169	2.245
4000	4.977	51.224	19.353	20.485	-41.723	-41.723	2.280
4100	4.977	51.347	19.886	20.494	-43.279	-43.279	2.307
4200	4.976	51.467	20.419	20.502	-44.835	-44.835	2.333
4300	4.976	51.584	20.952	20.510	-46.390	-46.390	2.358
4400	4.975	51.698	21.485	20.515	-47.944	-47.944	2.381
4500	4.975	51.810	22.018	20.520	-49.502	-49.502	2.404
4600	4.975	51.919	22.551	20.524	-51.056	-51.056	2.426
4700	4.975	52.026	23.084	20.527	-52.612	-52.612	2.446
4800	4.974	52.131	23.617	20.529	-54.169	-54.169	2.466
4900	4.974	52.233	24.150	20.529	-55.722	-55.722	2.485
5000	4.974	52.334	24.683	20.529	-57.281	-57.281	2.504
5100	4.974	52.432	25.216	20.527	-58.837	-58.837	2.521
5200	4.973	52.529	25.751	20.524	-60.393	-60.393	2.538
5300	4.973	52.624	26.284	20.521	-61.950	-61.950	2.554
5400	4.973	52.717	26.817	20.515	-63.509	-63.509	2.570
5500	4.973	52.808	27.350	20.510	-65.062	-65.062	2.585
5600	4.973	52.898	27.883	20.503	-66.619	-66.619	2.600
5700	4.973	52.986	28.416	20.494	-68.175	-68.175	2.614
5800	4.972	53.072	28.949	20.486	-69.728	-69.728	2.627
5900	4.972	53.157	29.482	20.475	-71.284	-71.284	2.640
6000	4.972	53.241	30.015	20.464	-72.842	-72.842	2.653

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

FLUORINE UNINEGATIVE ION (F<sup>-</sup>) (IDEAL GAS)

MOL. WT. = 18.99895

$\Delta H_f^{\circ} = -61.1 \pm .5 \text{ kcal/mole}$   
 $\Delta H_f^{\circ} 298.15 = -62.2 \pm .5 \text{ kcal/mole}$

Ground State Configuration  $1s^2$   
 $S_{298.15} = 34.769 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{E_i, \text{ cm.}^{-1}}{0.00} \frac{g_i}{1}$$

Heat of Formation.

The heat of formation was calculated from the equation:  $F(g) + e^- \rightarrow F^-(g)$  with the JANAF auxiliary value for  $F(g)$ ; using the measured electron affinity = 3.448 e.v. (79.511 kcal/mole) obtained from R. S. Berry and C. W. Reinmann, J. Chem. Phys. 38, 1540 (1963). Other calculated values for the electron affinity are: 3.37 reported by E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 3.08 e.v. E. Clementi, A. D. McLean, D. L. Reimondi, and M. Yoshimine, 133, A1274 (1964); 3.50 e.v. B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Neon. The electronic levels above  $1 \times 10^5 \text{ cm}^{-1}$  were omitted because their contribution is negligible below 6000°K. The  $H^{\circ} - H^{\circ} 298$  value at 0°K. is -1.461 kcal/mole.

T, °K.	C <sub>p</sub>	S°	-(F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>p</sub>
0							
100							
200							
298	4.968	34.768	34.768	0.000	-62.200	-63.857	46.806
300	4.968	34.768	34.768	0.009	-62.207	-63.867	46.825
400	4.968	36.228	34.963	1.506	-62.592	-64.363	35.164
500	4.968	37.337	35.331	1.003	-62.996	-64.759	28.305
600	4.968	38.242	35.742	1.500	-63.412	-65.073	23.702
700	4.968	39.052	36.155	1.999	-63.837	-65.315	20.301
800	4.968	39.785	36.532	2.498	-64.270	-65.498	17.892
900	4.968	40.427	36.934	2.998	-64.708	-65.625	15.935
1000	4.968	40.976	37.293	3.487	-65.151	-65.703	14.259
1100	4.968	41.542	37.632	3.984	-65.597	-65.738	13.060
1200	4.968	42.124	37.952	4.481	-66.045	-65.731	11.971
1300	4.968	42.724	38.255	4.977	-66.496	-65.686	11.042
1400	4.968	43.342	38.542	5.471	-66.950	-65.607	10.241
1500	4.968	43.979	38.814	5.971	-67.406	-65.495	9.542
1600	4.968	44.635	39.073	6.468	-67.863	-65.351	8.926
1700	4.968	45.311	39.320	6.965	-68.322	-65.180	8.379
1800	4.968	46.008	39.555	7.461	-68.783	-64.982	7.899
1900	4.968	46.724	39.781	7.958	-69.245	-64.760	7.449
2000	4.968	47.458	39.996	8.455	-69.708	-64.511	7.049
2100	4.968	48.210	40.203	8.952	-70.174	-64.239	6.685
2200	4.968	48.979	40.403	9.449	-70.640	-63.946	6.352
2300	4.968	49.764	40.594	9.945	-71.107	-63.630	6.046
2400	4.968	50.565	40.779	10.442	-71.576	-63.297	5.764
2500	4.968	51.382	40.957	10.939	-72.047	-62.941	5.502
2600	4.968	52.215	41.129	11.436	-72.519	-62.567	5.259
2700	4.968	53.064	41.295	11.933	-72.991	-62.178	5.033
2800	4.968	53.928	41.456	12.430	-73.465	-61.769	4.821
2900	4.968	54.807	41.612	12.926	-73.939	-61.342	4.623
3000	4.968	55.700	41.763	13.423	-74.416	-60.898	4.436
3100	4.968	56.607	41.911	13.920	-74.893	-60.439	4.261
3200	4.968	57.528	42.054	14.417	-75.372	-59.966	4.095
3300	4.968	58.462	42.193	14.914	-75.851	-59.480	3.937
3400	4.968	59.409	42.328	15.410	-76.331	-58.982	3.781
3500	4.968	60.368	42.459	15.907	-76.813	-58.475	3.650
3600	4.968	61.338	42.587	16.404	-77.296	-57.926	3.516
3700	4.968	62.318	42.712	16.901	-77.780	-57.378	3.380
3800	4.968	63.308	42.834	17.398	-78.265	-56.824	3.268
3900	4.968	64.308	42.953	17.895	-78.752	-56.255	3.152
4000	4.968	65.318	43.070	18.391	-79.238	-55.670	3.042
4100	4.968	66.338	43.183	18.888	-79.727	-55.071	2.935
4200	4.968	67.368	43.294	19.385	-80.217	-54.456	2.832
4300	4.968	68.408	43.403	19.882	-80.707	-53.826	2.737
4400	4.968	69.458	43.510	20.379	-81.199	-53.181	2.643
4500	4.968	70.518	43.614	20.875	-81.691	-52.528	2.553
4600	4.968	71.588	43.716	21.372	-82.184	-51.825	2.467
4700	4.968	72.668	43.816	21.868	-82.678	-51.122	2.384
4800	4.968	73.758	43.914	22.365	-83.175	-50.413	2.303
4900	4.968	74.858	44.010	22.862	-83.675	-49.704	2.226
5000	4.968	75.968	44.104	23.359	-84.170	-49.210	2.151
5100	4.968	77.088	44.197	23.856	-84.669	-48.507	2.079
5200	4.968	78.218	44.288	24.353	-85.169	-47.791	2.009
5300	4.968	79.358	44.377	24.850	-85.670	-47.068	1.941
5400	4.968	80.508	44.465	25.347	-86.173	-46.337	1.875
5500	4.968	81.668	44.551	25.844	-86.676	-45.594	1.812
5600	4.968	82.838	44.636	26.340	-87.180	-44.835	1.750
5700	4.968	84.018	44.719	26.837	-87.685	-44.060	1.690
5800	4.968	85.208	44.801	27.334	-88.191	-43.211	1.632
5900	4.968	86.408	44.881	27.831	-88.699	-42.289	1.575
6000	4.968	87.618	44.961	28.328	-89.208	-41.248	1.521



$$\Delta H_f^0 = [11.4 \pm 5.0] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = [11.4 \pm 5.0] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = [57.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$S_{298.15}^0 = [11.4 \pm 5.0] \text{ kcal. mole}^{-1}$$

Electronic Levels and Quantum Weight

$$\frac{E_i}{\sigma}, \text{ cm.}^{-1} \quad \frac{g_i}{[g]}$$

$$\omega_e x_e = [2.7] \text{ cm.}^{-1}$$

$$\omega_e = [630.0] \text{ cm.}^{-1}$$

$$B_e = [0.3670] \text{ cm.}^{-1}$$

$$r_e = [1.8] \text{ \AA}$$

Heat of Formation

The Dissociation energy ( $D_0$ ) of FeF(g) was estimated as  $4.64 \pm 0.22$  e.v. or  $107 \pm 5$  kcal. mole<sup>-1</sup> by J. L. Margrave, "Optical Spectra and Molecular Parameters of Light Element Molecules", Progress Report No. 8, Jan. 1 to Mar 31, 1965, William Marsh Rice University, Houston, Texas. From the value of  $D^0$  (Fe-F) the heat of formation ( $\Delta H_f^0$ ) for FeF(g) was derived to be  $11.4 \pm 5.0$  kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy

The ground state configuration and bond distance ( $r_e$ ) were estimated by comparison with those for FeCl(g). The value of  $B_e$  was calculated using the relationship  $B_e = \frac{2.79889 \times 10^{-39}}{I}$  where  $I$  = moment of inertia of FeF(g), and  $\omega_e$  was estimated by comparison with those for AlF(g), AlCl(g) and FeCl(g). The value of  $\omega_e$  was derived from the bond distance, reduced mass and number of valence electrons according to the method given by K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946), and the  $\omega_e x_e$  was estimated from those for AlF(g), AlCl(g) and FeCl(g). The moment of inertia is  $7.6259 \times 10^{-59}$  g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0	0.000	0.000	INFINITE	2.467	11.363	11.363	INFINITE
100	6.978	45.406	64.122	1.672	11.698	8.849	19.337
200	7.421	54.350	58.119	0.756	11.552	6.697	6.662
298	7.950	57.417	57.417	0.000	11.400	3.450	2.529
300	7.959	57.467	57.418	0.15	11.397	3.400	2.477
400	8.306	59.808	57.735	0.29	11.200	0.764	0.417
500	8.518	61.686	58.343	1.672	10.964	1.819	0.795
600	8.652	63.252	59.035	2.931	10.677	4.349	1.584
700	8.743	64.593	59.735	3.401	10.333	6.827	2.131
800	8.807	65.765	60.417	4.278	9.909	9.252	2.527
900	8.854	66.805	61.070	5.151	9.378	11.616	2.821
1000	8.891	67.740	61.691	6.049	8.666	13.913	3.041
1100	8.921	68.589	62.280	6.939	7.736	16.122	3.203
1200	8.946	69.366	62.839	7.833	7.018	18.264	3.326
1300	8.967	70.083	63.369	8.728	6.639	20.355	3.422
1400	8.985	70.748	63.872	9.626	6.244	22.416	3.499
1500	9.002	71.369	64.342	10.525	5.835	24.450	3.562
1600	9.017	71.950	64.805	11.426	5.409	26.455	3.613
1700	9.030	72.497	65.245	12.329	4.978	28.427	3.654
1800	9.043	73.014	65.662	13.232	4.543	30.360	3.686
1900	9.055	73.503	66.062	14.137	4.105	32.275	3.689
2000	9.067	73.958	66.446	15.043	3.687	33.743	3.687
2100	9.078	74.380	66.815	15.950	3.286	35.377	3.682
2200	9.088	74.783	67.170	16.859	2.904	36.984	3.674
2300	9.099	75.167	67.512	17.768	2.584	38.563	3.664
2400	9.108	75.524	67.842	18.678	2.215	40.114	3.653
2500	9.118	75.866	68.161	19.590	1.850	41.636	3.640
2600	9.126	76.194	68.469	20.502	1.489	43.137	3.626
2700	9.137	76.509	68.767	21.415	1.133	44.612	3.611
2800	9.146	76.811	69.057	22.330	0.780	46.061	3.595
2900	9.155	77.102	69.345	23.245	0.432	47.487	3.579
3000	9.164	77.383	69.639	24.161	0.088	48.893	3.562
3100	9.173	77.664	69.934	25.077	0.749	50.276	3.544
3200	9.182	77.925	70.232	25.995	0.428	51.642	3.528
3300	9.190	78.178	70.532	26.914	0.144	52.988	3.238
3400	9.199	78.412	70.836	27.833	0.258	54.317	3.058
3500	9.208	78.639	71.144	28.754	0.480	55.626	2.889
3600	9.216	78.864	71.459	29.675	0.710	56.910	2.728
3700	9.225	79.091	71.777	30.597	0.948	58.176	2.576
3800	9.233	79.317	72.097	31.520	1.195	59.424	2.431
3900	9.241	79.544	72.418	32.443	1.451	60.654	2.293
4000	9.250	79.771	72.740	33.368	1.716	61.876	2.162
4100	9.258	80.000	73.064	34.293	1.989	63.091	2.037
4200	9.266	80.225	73.382	35.220	2.272	64.292	1.918
4300	9.274	80.451	73.697	36.147	2.564	65.480	1.803
4400	9.283	80.676	74.012	37.074	2.866	66.656	1.694
4500	9.291	80.903	74.328	38.003	3.178	67.821	1.589
4600	9.299	81.130	74.644	38.933	3.499	68.976	1.488
4700	9.307	81.357	74.960	39.863	3.832	70.121	1.392
4800	9.315	81.583	75.276	40.793	4.173	71.256	1.299
4900	9.323	81.809	75.592	41.726	4.526	72.381	1.209
5000	9.332	82.035	75.908	42.659	4.889	73.496	1.123
5100	9.340	82.261	76.224	43.592	5.263	74.601	1.040
5200	9.348	82.487	76.540	44.527	5.647	75.696	0.959
5300	9.356	82.713	76.856	45.462	6.042	76.781	0.882
5400	9.364	82.939	77.172	46.398	6.449	77.856	0.807
5500	9.372	83.165	77.491	47.335	6.865	78.921	0.734
5600	9.380	83.391	77.810	48.272	7.293	80.000	0.664
5700	9.388	83.617	78.129	49.210	7.731	81.075	0.596
5800	9.395	83.843	78.448	50.150	8.180	82.150	0.530
5900	9.404	84.069	78.767	51.090	8.639	83.225	0.466
6000	9.412	84.295	79.086	52.030	9.109	84.300	0.404

MOL. WT. = 36.00577

(IDEAL GAS)

HYPOFLUOROUS ACID (HFO)

$\Delta H_f^0 = [-30 \pm 10] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = [-51 \pm 10] \text{ kcal. mole}^{-1}$

Point Group  $C_s$

$S_{298.15}^0 = [53.954] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , $\text{cm.}^{-1}$
[1500] (1)
[1065] (1)
[3645] (1)

Bond Distance: H-O = [0.96] Å O-P = [1.41] Å

Bond Angle: H-O-P = [104]°

$\sigma^- = 1$

Product of the Moments of Inertia:  $I_A I_B I_C = [1.2826 \times 10^{-117}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The value of  $\Delta H_f^0$  298.15 for HFO(g) was calculated based on an estimated value for the heat of atomization i.e.  $\Delta H_f^0 = 161.6 \text{ kcal. mole}^{-1}$  for the reaction  $\text{HFO(g)} = \text{H(g)} + \text{F(g)} + \text{O(g)}$ . The  $\Delta H_f^0$  value was assumed to be the sum of the P-O and H-O bond energies which were obtained from the corresponding bond energies in  $\text{F}_2\text{O(g)}$  and  $\text{H}_2\text{O(g)}$  molecules.

Heat Capacity and Entropy.

The H-O and P-O bond distances were assumed to be the same as those in the  $\text{H}_2\text{O(g)}$  and  $\text{F}_2\text{O(g)}$  molecules. The vibrational frequencies and H-O-P bond angle were estimated by comparison with the corresponding values for  $\text{H}_2\text{O(g)}$ ,  $\text{F}_2\text{O(g)}$  and  $\text{Cl}_2\text{O(g)}$ . The three principal moments of inertia are  $I_A = 0.1332 \times 10^{-39}$ ,  $I_B = 3.0366 \times 10^{-39}$  and  $I_C = 3.1699 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C <sub>v</sub>	S°	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	+0.00	INFINITE	-	2.391	- 30.287	-	INFINITE
100	7.949	45.187	61.148	1.596	- 30.575	- 29.764	65.045
200	8.009	50.705	54.700	- 8.00	- 30.770	- 28.882	31.559
298	8.335	53.954	53.054	+0.00	- 31.000	- 27.907	20.455
300	8.344	54.006	53.954	+0.15	- 31.005	- 27.888	20.315
400	8.876	56.477	54.288	1.876	- 31.232	- 26.814	14.050
500	9.421	58.517	54.935	1.791	- 31.435	- 25.685	11.227
600	9.904	60.278	55.682	2.758	- 31.612	- 24.518	8.930
700	10.315	61.837	56.457	3.769	- 31.766	- 23.323	7.281
800	10.668	63.238	57.234	4.819	- 31.901	- 22.109	6.040
900	10.975	64.512	57.995	5.901	- 32.020	- 20.876	5.069
1000	11.248	65.683	58.670	7.013	- 32.123	- 19.633	4.291
1100	11.480	66.766	59.258	8.150	- 32.215	- 18.379	3.651
1200	11.705	67.770	60.000	9.310	- 32.294	- 17.118	3.117
1300	11.922	68.721	60.851	10.480	- 32.366	- 15.850	2.665
1400	12.135	69.626	61.800	11.680	- 32.429	- 14.577	2.275
1500	12.342	70.448	62.844	12.905	- 32.487	- 13.299	1.938
1600	12.542	71.262	62.607	14.135	- 32.542	- 12.020	1.642
1700	12.697	71.996	62.909	15.379	- 32.592	- 10.734	1.380
1800	12.810	72.713	63.422	16.635	- 32.640	- 9.447	1.147
1900	12.911	73.398	63.976	17.901	- 32.687	- 8.158	0.938
2000	12.981	74.057	64.464	19.176	- 32.732	- 6.865	0.750
2100	12.883	74.679	64.936	20.461	- 32.777	- 5.572	0.580
2200	12.956	75.280	65.392	21.753	- 32.824	- 4.276	0.425
2300	13.023	75.857	65.835	23.052	- 32.870	- 2.976	0.283
2400	13.083	76.413	66.264	24.357	- 32.918	- 1.675	0.153
2500	13.138	76.948	66.681	25.668	- 32.969	- 0.374	0.033
2600	13.188	77.464	67.086	26.984	- 33.020	+0.933	0.078
2700	13.235	77.963	67.479	28.306	- 33.074	2.239	0.181
2800	13.275	78.445	67.862	29.631	- 33.130	3.547	0.277
2900	13.313	78.911	68.235	30.960	- 33.189	4.862	0.366
3000	13.347	79.363	68.599	32.293	- 33.251	6.172	0.450
3100	13.379	79.801	68.953	33.630	- 33.314	7.488	0.528
3200	13.409	80.227	69.299	34.969	- 33.381	8.803	0.601
3300	13.436	80.640	69.636	36.311	- 33.451	10.123	0.670
3400	13.461	81.041	69.966	37.656	- 33.523	11.445	0.736
3500	13.484	81.432	70.288	39.004	- 33.599	12.769	0.797
3600	13.506	81.812	70.603	40.353	- 33.678	14.096	0.856
3700	13.525	82.182	70.911	41.705	- 33.761	15.425	0.911
3800	13.544	82.543	71.212	43.058	- 33.846	16.757	0.964
3900	13.561	82.895	71.507	44.413	- 33.935	18.087	1.014
4000	13.577	83.239	71.796	45.770	- 34.027	19.421	1.061
4100	13.592	83.574	72.079	47.129	- 34.123	20.760	1.107
4200	13.606	83.902	72.357	48.489	- 34.221	22.099	1.150
4300	13.620	84.222	72.629	49.850	- 34.322	23.444	1.191
4400	13.632	84.535	72.896	51.213	- 34.428	24.787	1.231
4500	13.644	84.842	73.158	52.576	- 34.536	26.131	1.269
4600	13.655	85.142	73.416	53.941	- 34.647	27.483	1.306
4700	13.665	85.436	73.668	55.307	- 34.762	28.834	1.341
4800	13.674	85.723	73.916	56.674	- 34.878	30.193	1.375
4900	13.684	86.006	74.160	58.042	- 34.998	31.544	1.407
5000	13.692	86.282	74.400	59.411	- 35.122	32.903	1.438
5100	13.700	86.553	74.635	60.781	- 35.248	34.268	1.468
5200	13.708	86.819	74.867	62.151	- 35.376	35.632	1.498
5300	13.715	87.081	75.095	63.522	- 35.508	36.999	1.526
5400	13.722	87.337	75.320	64.894	- 35.643	38.363	1.553
5500	13.729	87.589	75.540	66.267	- 35.779	39.738	1.579
5600	13.735	87.836	75.758	67.640	- 35.920	41.113	1.604
5700	13.741	88.079	75.972	69.014	- 36.063	42.492	1.629
5800	13.746	88.318	76.183	70.388	- 36.208	43.873	1.653
5900	13.752	88.553	76.390	71.763	- 36.356	45.253	1.676
6000	13.757	88.785	76.595	73.138	- 36.507	46.632	1.698

Dec. 31, 1960; Sept. 30, 1965

(IDEAL GAS)

IODINE MONOFLUORIDE (IF)

(IF)

$$\Delta H_f^{\circ} 0 = -22.192 \pm 0.9 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = 56.451 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Electronic Levels and Quantum Weight

$\epsilon$	$1, \text{ cm.}^{-1}$	$\frac{\epsilon_1}{\epsilon}$
	0	1

$$\omega_e x_e = 4 \text{ cm.}^{-1}$$

$$\omega_e = 612 \text{ cm.}^{-1}$$

$$\alpha_e = 0.00763 \text{ cm.}^{-1}$$

$$B_e = 0.2799 \text{ cm.}^{-1}$$

$$r_e = 1.906 \text{ \AA}$$

$$\sigma = 1$$

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

$$^2 298.15 = -22.648 \pm 0.9 \text{ kcal. mole}^{-1}$$

Heat of Formation.

R. A. Durie and A. G. Gaydon, J. Phys. Chem. **56**, 316 (1952), have obtained the dissociation limit (from the spectra) of IF as 23570  $\text{cm.}^{-1}$ . The first excited states of F and I are 404 and 7598  $\text{cm.}^{-1}$  above the ground state respectively. There are two sets of dissociation products possible:  $I(^2P_{1/2}) + F(^2P_{3/2})$  or  $I(^2P_{3/2}) + F(^2P_{1/2})$ . When corrected to the normal atoms, the observed limit gives  $D_0(\text{IF}(g)) 2.87 \pm 0.04 \text{ e.v.}$  or 66.18  $\pm 0.9 \text{ kcal. mole}^{-1}$  and 1.98  $\pm 0.04 \text{ e.v.}$  or 45.66  $\pm 0.9 \text{ kcal. mole}^{-1}$  for dissociation energy respectively. Durie and Gaydon, loc. cit., favored the lower value. However L. Slutsky and S. H. Bauer, J. Am. Chem. Soc. **76**, 270 (1954) have pointed out a numerical error in their calculations, which removes the chief support for the lower value and presented additional evidence favoring the higher value. More weight was given to the higher value which gives  $\Delta H_f^{\circ} 298.15 = -22.648 \pm 0.9 \text{ kcal. mole}^{-1}$  for the reaction  $1/2 I_2(c) + 1/2 F_2(g) = \text{IF}(g)$ .

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Standards **55**, 147 (1955) except  $r_e = 1.906 \text{ \AA}$  was obtained from L. G. Cole and G. W. Elverun Jr., J. Chem. Phys. **20**, 1543 (1952) and ground state configuration was estimated by comparison with that for IBr and ICl from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	$-(F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.936	48.396	63.204	2.176	22.192	22.192	INFINITE
200	7.473	53.359	67.169	1.681	22.209	24.285	53.071
298	8.021	56.451	70.000	1.762	22.629	26.277	28.713
300	8.030	56.501	70.015	1.805	22.652	28.119	20.611
400	8.384	58.864	76.771	1.687	24.801	28.153	20.508
500	8.601	60.760	77.385	1.687	30.116	30.650	16.328
600	8.743	62.341	78.083	2.555	30.103	30.757	13.397
700	8.841	63.636	78.791	3.434	30.118	30.865	11.203
800	8.915	64.882	79.479	4.322	30.104	30.973	9.636
900	8.973	65.936	80.139	5.217	30.099	31.083	8.461
1000	9.020	66.883	80.767	6.116	30.095	31.192	7.568
1100	9.061	67.745	81.363	7.020	30.090	31.302	6.817
1200	9.097	68.535	81.926	7.928	30.085	31.412	6.219
1300	9.130	69.265	82.465	8.840	30.080	31.523	5.721
1400	9.160	69.942	82.975	9.754	30.075	31.634	5.299
1500	9.188	70.575	83.461	10.672	30.069	31.745	4.938
1600	9.215	71.169	83.924	11.592	30.064	31.857	4.625
1700	9.241	71.729	84.367	12.515	30.058	31.970	4.351
1800	9.266	72.258	84.791	13.440	30.052	32.084	4.110
1900	9.290	72.759	85.197	14.368	30.046	32.195	3.895
2000	9.313	73.236	85.587	15.298	30.039	32.309	3.703
2100	9.336	73.691	85.962	16.231	30.032	32.423	3.530
2200	9.356	74.126	86.324	17.165	30.025	32.538	3.374
2300	9.381	74.543	86.672	18.102	30.018	32.652	3.232
2400	9.403	74.949	87.008	19.042	30.010	32.765	3.103
2500	9.425	75.327	87.333	19.983	30.003	32.878	2.984
2600	9.447	75.697	87.648	20.927	29.994	32.997	2.874
2700	9.468	76.053	87.953	21.872	29.986	33.113	2.774
2800	9.490	76.398	88.248	22.820	29.977	33.227	2.680
2900	9.511	76.732	88.535	23.770	29.968	33.344	2.593
3000	9.532	77.055	88.814	24.722	29.960	33.464	2.513
3100	9.553	77.367	89.085	25.677	29.950	33.577	2.438
3200	9.574	77.671	89.348	26.633	29.940	33.695	2.367
3300	9.595	77.966	89.605	27.591	29.930	33.812	2.301
3400	9.616	78.253	89.855	28.552	29.920	33.932	2.239
3500	9.636	78.532	90.099	29.515	29.909	34.048	2.181
3600	9.657	78.804	90.337	30.479	29.898	34.167	2.126
3700	9.678	79.072	90.567	31.446	29.887	34.284	2.074
3800	9.698	79.337	90.797	32.415	29.875	34.404	2.025
3900	9.719	79.595	91.019	33.386	29.863	34.524	1.979
4000	9.739	79.825	91.236	34.359	29.851	34.643	1.935
4100	9.760	80.056	91.448	35.333	29.839	34.763	1.893
4200	9.780	80.281	91.656	36.311	29.827	34.883	1.853
4300	9.801	80.502	91.860	37.290	29.815	35.003	1.815
4400	9.821	80.717	92.059	38.271	29.800	35.124	1.779
4500	9.842	80.928	92.255	39.254	29.786	35.245	1.745
4600	9.862	81.135	92.447	40.239	29.772	35.368	1.712
4700	9.882	81.337	92.636	41.226	29.758	35.489	1.680
4800	9.903	81.535	92.821	42.215	29.743	35.609	1.650
4900	9.923	81.729	93.002	43.207	29.728	35.733	1.621
5000	9.943	82.021	93.180	44.200	29.713	35.858	1.594
5100	9.964	82.218	93.356	45.195	29.698	35.983	1.567
5200	9.984	82.411	93.528	46.193	29.682	36.102	1.542
5300	10.004	82.602	93.697	47.192	29.666	36.227	1.517
5400	10.025	82.789	93.864	48.194	29.650	36.351	1.494
5500	10.045	82.973	94.028	49.197	29.633	36.475	1.471
5600	10.065	83.154	94.189	50.203	29.616	36.600	1.449
5700	10.085	83.332	94.348	51.210	29.599	36.721	1.428
5800	10.106	83.508	94.505	52.220	29.581	36.849	1.408
5900	10.126	83.681	94.659	53.231	29.563	36.977	1.388
6000	10.146	83.851	94.811	54.245	29.545	37.099	1.370

$\Delta H_f^0 = [-21 \pm 10] \text{ kcal. mole}^{-1}$

$\Delta H_f^{298.15} = [-22 \pm 10] \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = [58.775] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
[800] (1)
[500] (1)
[950] (1)

Bond Distance: Li-O = [1.59] Å F-O = [1.41] Å

Bond Angle: F-O-Li = [104]°  $\sigma = 1$

Product of the Moments of Inertia:  $I_A I_B I_C = [4.21664 \times 10^{-116}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation ( $\Delta H_f^{298.15}$ ) for LiFO(g) was calculated from  $\Delta H_f^{298.15} = 139 \text{ kcal. mole}^{-1}$  for the reaction  $\text{LiFO(g)} = \text{Li(g)} + \text{O(g)}$  where the value of  $\Delta H_f^{298.15}$  was estimated to be the sum of the F-O and Li-O bond energies. The values of the F-O and Li-O bond energies were obtained from those in  $\text{F}_2\text{O(g)}$  and  $\text{Li}_2\text{O(g)}$  molecules, respectively.

Heat Capacity and Entropy.

The F-O and Li-O bond distances were assumed to be the same as those in  $\text{F}_2\text{O(g)}$  and  $\text{Li}_2\text{O(g)}$  molecules, respectively. The F-O-Li bond angle and vibrational frequencies were estimated by comparison with the corresponding values for the same oxide molecules. The three principal moments of inertia are:  $I_A = 5.1543 \times 10^{-39}$ ,  $I_B = 1.2729 \times 10^{-39}$  and  $I_C = 6.4272 \times 10^{-39} \text{ g. cm.}^2$

T. °K.	C <sub>v</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	0.00	INFINITE	- 2.588	- 21.396	- 21.390	INFINITE
100	8.025	49.124	- 1.792	- 21.417	- 22.043	46.173
200	9.604	54.938	- 1.948	- 21.703	- 22.656	24.856
298	10.285	58.775	- 2.000	- 22.000	- 22.823	16.802
300	10.307	58.839	- 2.019	- 22.005	- 22.829	16.751
400	11.331	59.193	- 1.104	- 22.282	- 23.194	12.602
500	12.031	60.013	- 2.274	- 23.299	- 23.315	10.191
600	12.502	60.982	- 3.502	- 23.577	- 23.291	8.483
700	12.824	61.939	- 4.770	- 23.824	- 23.225	7.251
800	13.052	62.900	- 6.084	- 24.054	- 23.127	6.317
900	13.217	63.830	- 7.378	- 24.276	- 23.004	5.523
1000	13.339	64.721	- 8.706	- 24.494	- 22.859	4.891
1100	13.433	65.571	- 10.045	- 24.709	- 22.664	4.450
1200	13.505	66.382	- 11.392	- 24.922	- 22.469	4.092
1300	13.565	67.154	- 12.745	- 25.135	- 22.255	3.741
1400	13.609	67.891	- 14.104	- 25.346	- 22.026	3.438
1500	13.646	68.594	- 15.467	- 25.558	- 21.781	3.173
1600	13.678	69.267	- 16.833	- 25.768	- 21.522	2.940
1700	13.704	69.910	- 18.202	- 25.972	- 21.251	2.741
1800	13.725	70.527	- 19.574	- 26.177	- 20.977	2.561
1900	13.744	71.119	- 20.947	- 26.382	- 20.703	2.415
2000	13.760	71.688	- 22.322	- 26.591	- 20.426	2.283
2100	13.774	72.236	- 23.699	- 26.805	- 20.147	2.165
2200	13.786	72.763	- 25.077	- 27.024	- 19.865	2.061
2300	13.796	73.272	- 26.456	- 27.247	- 19.582	1.968
2400	13.805	73.764	- 27.836	- 27.474	- 19.300	1.884
2500	13.814	74.239	- 29.217	- 27.706	- 19.020	1.809
2600	13.821	74.699	- 30.599	- 27.942	- 18.744	1.742
2700	13.827	75.145	- 31.981	- 28.181	- 18.472	1.682
2800	13.833	75.573	- 33.364	- 28.423	- 18.204	1.628
2900	13.838	75.986	- 34.748	- 28.668	- 17.941	1.579
3000	13.843	76.384	- 36.132	- 28.916	- 17.683	1.535
3100	13.847	76.769	- 37.517	- 29.166	- 17.431	1.496
3200	13.851	77.144	- 38.902	- 29.419	- 17.184	1.461
3300	13.855	77.509	- 40.287	- 29.676	- 16.942	1.429
3400	13.858	77.864	- 41.673	- 29.936	- 16.704	1.400
3500	13.861	78.210	- 43.058	- 30.200	- 16.470	1.374
3600	13.864	78.547	- 44.445	- 30.468	- 16.240	1.350
3700	13.866	78.966	- 45.831	- 30.740	- 16.014	1.327
3800	13.868	79.377	- 47.218	- 31.016	- 15.792	1.305
3900	13.871	79.780	- 48.605	- 31.296	- 15.574	1.284
4000	13.873	80.174	- 49.992	- 31.579	- 15.360	1.264
4100	13.874	80.559	- 51.379	- 31.865	- 15.150	1.245
4200	13.876	80.944	- 52.767	- 32.154	- 14.944	1.227
4300	13.878	81.318	- 54.155	- 32.446	- 14.742	1.210
4400	13.879	81.684	- 55.542	- 32.741	- 14.544	1.194
4500	13.881	82.049	- 56.930	- 33.038	- 14.350	1.179
4600	13.882	82.414	- 58.319	- 33.338	- 14.160	1.164
4700	13.883	82.777	- 59.709	- 33.641	- 13.974	1.150
4800	13.884	83.138	- 61.099	- 33.947	- 13.792	1.137
4900	13.885	83.496	- 62.492	- 34.256	- 13.614	1.124
5000	13.886	83.852	- 63.887	- 34.568	- 13.440	1.112
5100	13.887	84.206	- 65.281	- 34.882	- 13.270	1.100
5200	13.888	84.557	- 66.676	- 35.200	- 13.104	1.089
5300	13.889	84.904	- 68.072	- 35.521	- 12.942	1.078
5400	13.890	85.247	- 69.468	- 35.846	- 12.784	1.067
5500	13.891	85.586	- 70.864	- 36.174	- 12.630	1.057
5600	13.891	85.921	- 72.260	- 36.506	- 12.480	1.047
5700	13.892	86.252	- 73.656	- 36.841	- 12.334	1.037
5800	13.893	86.579	- 75.052	- 37.179	- 12.192	1.027
5900	13.893	86.902	- 76.448	- 37.521	- 12.054	1.017
6000	13.894	87.221	- 77.844	- 37.867	- 11.920	1.007

Dec. 31, 1960; Sept. 30, 1965

T. °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	59.501	59.501	INFINITE
100	6.957	43.760	57.713	1.395	59.070	59.070	-129.091
200	7.007	48.590	52.081	0.688	58.636	58.636	-64.072
298	7.253	51.427	51.427	0.000	58.212	58.212	-42.669
300	7.259	51.472	51.427	0.13	58.204	58.204	-42.400
400	7.694	53.607	51.716	0.786	57.772	57.772	-31.563
500	7.913	55.354	52.773	1.533	57.334	57.334	-25.060
600	8.156	56.804	52.909	2.337	56.893	56.893	-20.722
700	8.340	58.075	53.556	3.162	56.445	56.445	-17.622
800	8.480	59.139	54.194	4.053	55.991	55.991	-15.295
900	8.598	60.004	54.807	4.957	55.531	55.531	-13.485
1000	8.674	61.113	55.393	5.720	55.071	55.071	-12.035
1100	8.743	61.943	55.951	6.501	54.607	54.607	-10.849
1200	8.799	62.707	56.483	7.268	54.139	54.139	-9.840
1300	8.846	63.413	56.975	8.021	53.670	53.670	-9.022
1400	8.887	64.070	57.425	8.761	53.198	53.198	-8.304
1500	8.922	64.684	57.832	9.478	52.726	52.726	-7.682
1600	8.953	65.261	58.173	11.022	52.251	52.251	-7.137
1700	8.981	65.805	58.704	11.818	51.775	51.775	-6.566
1800	9.006	66.319	59.198	12.818	51.298	51.298	-6.028
1900	9.029	66.806	59.586	13.719	50.823	50.823	-5.846
2000	9.050	67.270	59.958	14.623	50.345	50.345	-5.501
2100	9.070	67.712	60.317	15.529	49.865	49.865	-5.189
2200	9.088	68.134	60.663	16.437	49.387	49.387	-4.906
2300	9.106	68.539	60.997	17.347	48.907	48.907	-4.647
2400	9.122	68.927	61.319	18.258	48.427	48.427	-4.410
2500	9.138	69.299	61.631	19.171	47.949	47.949	-4.191
2600	9.154	69.658	61.933	20.086	47.469	47.469	-3.990
2700	9.169	70.004	62.225	21.002	46.989	46.989	-3.803
2800	9.183	70.338	62.509	21.920	46.507	46.507	-3.630
2900	9.197	70.660	62.785	22.839	46.029	46.029	-3.469
3000	9.211	70.972	63.052	23.759	45.547	45.547	-3.318
3100	9.224	71.274	63.313	24.681	45.067	45.067	-3.177
3200	9.237	71.567	63.566	25.604	44.587	44.587	-3.045
3300	9.250	71.852	63.811	26.528	44.105	44.105	-2.921
3400	9.263	72.128	64.053	27.454	43.626	43.626	-2.804
3500	9.276	72.397	64.288	28.381	43.145	43.145	-2.694
3600	9.288	72.658	64.517	29.309	42.666	42.666	-2.590
3700	9.300	72.913	64.740	30.239	42.184	42.184	-2.492
3800	9.312	73.161	64.959	31.169	41.705	41.705	-2.398
3900	9.324	73.403	65.172	32.101	41.224	41.224	-2.310
4000	9.336	73.639	65.381	33.034	40.745	40.745	-2.226
4100	9.348	73.870	65.585	33.968	40.263	40.263	-2.146
4200	9.359	74.095	65.785	34.904	39.785	39.785	-2.070
4300	9.371	74.316	65.981	35.840	39.304	39.304	-1.998
4400	9.383	74.531	66.173	36.778	38.825	38.825	-1.928
4500	9.394	74.742	66.361	37.717	38.345	38.345	-1.862
4600	9.405	74.949	66.545	38.657	37.865	37.865	-1.799
4700	9.417	75.150	66.726	39.598	37.386	37.386	-1.738
4800	9.428	75.350	66.904	40.540	36.906	36.906	-1.680
4900	9.439	75.544	67.078	41.483	36.427	36.427	-1.625
5000	9.450	75.735	67.250	42.428	35.948	35.948	-1.571
5100	9.461	75.922	67.418	43.374	35.467	35.467	-1.520
5200	9.473	76.104	67.583	44.320	34.991	34.991	-1.471
5300	9.484	76.287	67.746	45.269	34.510	34.510	-1.423
5400	9.494	76.464	67.904	46.217	34.031	34.031	-1.377
5500	9.506	76.638	68.063	47.167	33.557	33.557	-1.333
5600	9.517	76.810	68.217	48.118	33.076	33.076	-1.291
5700	9.528	76.978	68.370	49.070	32.601	32.601	-1.250
5800	9.538	77.144	68.519	50.024	32.122	32.122	-1.210
5900	9.550	77.307	68.667	50.978	31.643	31.643	-1.172
6000	9.560	77.468	68.812	51.933	31.163	31.163	-1.135

NITROGEN MONOFLUORIDE (NF)

(IDEAL GAS)

MOL. WT. = 35.0051

Ground State Configuration [ $\frac{3}{2}$ ]  
 $\Delta H_f^0 = 59.5 \pm 8$  kcal./mole  
 $\Delta H_f^0 = 51.427$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^0 = 298.15 = 59.5 \pm 8$  kcal./mole

Electronic Levels and Quantum Weight

$$\frac{\sum_i g_i e^{-\epsilon_i / RT}}{Z}$$

$$\mu_e x_e = [12.175]$$

$$d_e = [-0.120]$$

$$r_e = [1.51 \text{ \AA}]$$

Heat of Formation.

The heat of formation was obtained by taking an average of two estimates of the dissociation energy of NF. The first estimate of 3.15 e.v. (72.4 kcal./mole) was obtained from W. C. Price, T. R. Passmore and D. M. Rossler Discussions Faraday Soc. 35, 201 - 11 (1963). The second estimate of 70.4 kcal./mole was obtained by taking one-half the dissociation energy of NF<sub>2</sub> (g) calculated from JANAF values. The  $\Delta H_f^0$  298.15 for NF (g) was then calculated with auxiliary JANAF data from a dissociation energy of 71.4 kcal./mole.

Heat Capacity and Entropy.

The  $\mu_e$  value was obtained from infrared studies of D. E. Milligen and M. E. Jacox, J. Chem. Phys. 40, 2461 (1964). The  $r_e$  value was estimated from Guggenheimer's relation for single bonded molecules. [K. M. Guggenheimer, Proc. Phys. Soc. (London), 58, 456 (1946)] The anharmonicity constant  $x_e$  was estimated by assuming the separation of the vibrational levels to be a linear function of the vibrational quantum number. The  $\mu_e$  value was then calculated using the Morse potential function;  $E_e$  was determined from the bond length. The ground state configuration was assumed to be the same as that in NBr. The principal moment of inertia is  $3.05247 \times 10^{-39}$  g. cm.<sup>2</sup>

$\Delta H_f^0 = -24.6 \pm 5 \text{ kcal. mole}^{-1}$

$\Delta H_f^0 = -26.0 \pm 5 \text{ kcal. mole}^{-1}$

Point Group C<sub>2v</sub>

$S_{298.15} = 62.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega, \text{cm.}^{-1}$	$\omega, \text{cm.}^{-1}$
1312 (1)	1793 (1)
822 (1)	570 (1)
460 (1)	742 (1)

Bond Distance: N-F = 1.40 Å N-O = 1.21 Å

Bond Angle: O-N-O = 129.5° F-N-O = 115.25°

Product of the Moments of Inertia:  $I_A I_B I_C = 6.401696 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

$\sigma = 2$

Heat of Formation.

The heat of reaction at 25°C for direct synthesis of nitryl fluoride from nitrogen dioxide with fluorine (NO<sub>2</sub>(g) + 1/2 F<sub>2</sub>(g) = NO<sub>2</sub>F(g)) has been measured calorimetrically as -33.9 kcal. mole<sup>-1</sup> by J. D. Breazelle and R. O. MacLaren, "Thermochemistry of Oxygen-Fluorine Bonding" (Final Tech. Summary Report, Contract No. Nonr 3453(00), ARPA Order No. 184-62) United Technology Corporation, Sunnyvale, Calif., Mar. 1963. The heat of formation,  $\Delta H_f^0 = -26.0 \text{ kcal. mole}^{-1}$ , for NO<sub>2</sub>F(g) was then derived. The values of  $\Delta H_f^0 = -20 \pm 5$  and  $-19 \pm 2 \text{ kcal. mole}^{-1}$  were issued in their second and third quarterly tech. reports, and have been quoted in the literature by E. Tschuikow-Roux, J. Phys. Chem. 66, 1636 (1962).

G. Hetherington and P. L. Robinson, Special Publication No. 10, The Chem. Soc., London, 1957 quoted  $\Delta H_f^0 = 26 \text{ kcal. mole}^{-1}$  (presumably it has a minus sign) for NO<sub>2</sub>F(g) which was derived from the heat of solution measured by Nichols and Robinson, a private communication to Hetherington and Robinson.

Heat Capacity and Entropy.

D. F. Smith and D. W. Magnuson, Phys. Rev. 87, 226(1952), have measured the moments of inertia from microwave spectrum of NO<sub>2</sub>F(g). In order to calculate the bond distances, given as N-F = 1.35 Å and N-O = 1.23 Å, the bond angle O-N-O was assumed to be 125°. The selected bond distances and angle were obtained from L. Clayton, G. Williams and T. Weatherly, J. Chem. Phys. 30, 1328 (1959). Clayton et al. assumed the bond angle O-N-O in NO<sub>2</sub>F(g) should be the same as that in NO<sub>2</sub>Cl(g), and then calculated the bond distances N-F and N-O from Smith and Magnuson's data of the moments of inertia.

The selected vibrational frequencies were obtained from the infrared and Raman spectra measurements by R. Dodd, J. Rolfe and L. Woodward, Trans. Faraday Soc. 52, 145 (1956).

The three principal moments of inertia are  $I_A = 6.3658 \times 10^{-39}$ ,  $I_B = 7.3583 \times 10^{-39}$  and  $I_C = 13.7041 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C <sub>v</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0	.000	INFINITE	-	2.755	-24.589	-24.589	INFINITE
100	8.110	51.770	71.350	1.958	-25.195	-22.279	48.689
200	9.856	57.847	63.203	1.071	-25.690	-19.159	20.935
298	11.918	62.177	62.177	.000	-26.000	-15.882	11.641
300	11.923	62.251	62.177	.022	-26.004	-15.820	11.524
400	13.626	65.929	62.668	1.305	-26.166	-12.396	6.773
500	14.903	69.114	63.645	2.734	-26.223	-8.946	3.910
600	15.876	71.921	64.795	4.275	-26.209	-5.491	2.000
700	16.620	74.426	65.995	5.902	-26.150	-4.037	1.241
800	17.193	76.685	67.193	7.594	-26.060	-2.581	0.811
900	17.638	78.737	68.163	9.336	-25.950	-1.171	0.531
1000	17.987	80.614	68.946	11.118	-25.824	0.234	0.341
1100	18.265	82.342	70.586	12.941	-25.690	1.632	0.231
1200	18.488	83.941	71.630	14.769	-25.549	2.735	0.175
1300	18.659	85.426	72.630	16.627	-25.405	3.695	0.132
1400	18.783	86.817	73.601	18.502	-25.258	4.529	0.097
1500	18.874	88.120	74.522	20.390	-25.111	5.242	0.070
1600	18.946	89.346	75.415	22.290	-24.964	5.845	0.048
1700	19.000	90.503	76.268	24.189	-24.817	6.347	0.032
1800	19.040	91.599	77.090	26.116	-24.674	6.753	0.021
1900	19.073	92.636	77.881	28.040	-24.534	7.073	0.013
2000	19.100	93.624	78.644	29.970	-24.396	7.312	0.007
2100	19.126	94.573	79.380	31.906	-24.262	7.475	0.004
2200	19.151	95.476	80.092	33.845	-24.134	7.564	0.002
2300	19.174	96.340	80.779	35.789	-24.008	7.584	0.001
2400	19.196	97.169	81.445	37.736	-23.887	7.532	0.000
2500	19.218	97.965	82.090	39.687	-23.773	7.402	0.000
2600	19.244	98.731	82.715	41.640	-23.662	7.188	0.000
2700	19.267	99.469	83.322	43.595	-23.556	6.874	0.000
2800	19.288	100.181	83.912	45.553	-23.455	6.462	0.000
2900	19.306	100.868	84.485	47.513	-23.360	5.952	0.000
3000	19.323	101.533	85.042	49.474	-23.270	5.341	0.000
3100	19.339	102.177	85.584	51.437	-23.184	4.621	0.000
3200	19.353	102.801	86.113	53.402	-23.104	3.804	0.000
3300	19.366	103.406	86.628	55.368	-23.029	2.891	0.000
3400	19.378	103.993	87.130	57.335	-22.958	1.884	0.000
3500	19.388	104.564	87.620	59.303	-22.892	0.787	0.000
3600	19.398	105.118	88.098	61.273	-22.830	-0.413	0.000
3700	19.407	105.658	88.566	63.243	-22.772	-1.617	0.000
3800	19.416	106.184	89.022	65.214	-22.719	-2.836	0.000
3900	19.424	106.696	89.469	67.186	-22.670	-4.069	0.000
4000	19.431	107.196	89.906	69.159	-22.625	-5.316	0.000
4100	19.438	107.683	90.334	71.132	-22.585	-6.575	0.000
4200	19.444	108.159	90.752	73.107	-22.547	-7.846	0.000
4300	19.450	108.623	91.163	75.081	-22.512	-9.120	0.000
4400	19.455	109.077	91.565	77.057	-22.483	-10.397	0.000
4500	19.460	109.521	91.959	79.032	-22.456	-11.677	0.000
4600	19.465	109.956	92.345	81.009	-22.432	-12.959	0.000
4700	19.470	110.381	92.724	82.985	-22.412	-14.243	0.000
4800	19.474	110.797	93.097	84.963	-22.394	-15.529	0.000
4900	19.478	111.205	93.462	86.940	-22.380	-16.816	0.000
5000	19.482	111.605	93.821	88.918	-22.368	-18.103	0.000
5100	19.486	111.996	94.173	90.896	-22.360	-19.390	0.000
5200	19.488	112.381	94.520	92.875	-22.353	-20.677	0.000
5300	19.491	112.757	94.860	94.854	-22.349	-21.963	0.000
5400	19.494	113.127	95.195	96.833	-22.349	-23.249	0.000
5500	19.497	113.491	95.525	98.813	-22.349	-24.534	0.000
5600	19.500	113.847	95.849	100.793	-22.354	-25.819	0.000
5700	19.502	114.198	96.168	102.773	-22.360	-27.103	0.000
5800	19.505	114.542	96.481	104.753	-22.367	-28.387	0.000
5900	19.507	114.881	96.790	106.734	-22.378	-29.670	0.000
6000	19.509	115.214	97.095	108.715	-22.390	-30.952	0.000

Ground State Configuration [ $2\sum^-$ ]  
 $S^{\circ}_{298.15} = 51.254 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H^{\circ}_0 = 27.1 \pm 8 \text{ kcal./mole}$   
 $\Delta H^{\circ}_{298.15} = 27.1 \pm 8 \text{ kcal./mole}$

Electronic Levels and Quantum Weight

$$\frac{\sum \epsilon_i, \text{ cm.}^{-1}}{0} \quad \frac{\epsilon_i}{2}$$

$\mu_e X_e = [14.155] \text{ cm.}^{-1}$   
 $\sigma = 1$   
 $\epsilon_e = [-0.108] \text{ cm.}^{-1}$   
 $r_e = [1.821 \text{ \AA}]$

$\mu_e = 1028 \text{ cm.}^{-1}$   
 $B_e = [-.774] \text{ cm.}^{-1}$

Heat of Formation

The heat of formation was obtained by taking an average of two estimates of the dissociation energy of OF. The first estimate of 2.25 e.v. (51.9 kcal./mole) was obtained from W. C. Price, T. R. Passmore, and D. M. Roessler, Discussions Faraday Soc. 35, 201 - 11 (1963). The second estimate of 50.8 kcal./mole was obtained by taking one-half the dissociation energy of OF<sub>2</sub> (g) calculated from JANAF values. The  $\Delta H^{\circ}_{298.15}$  for OF (g) was then calculated with auxiliary JANAF data from a dissociation energy of 51.3 kcal./mole. Other observations from kinetics, appearance potential and spectra of OF<sub>2</sub> lead to diverse conclusions on the O-F bond strength ranging from 25-61 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy

The  $\mu_e$  value was obtained from matrix infrared studies of A. Arkell, R. R. Reinhard and L. P. Larson, J.A.C.S. 87, 1016 (1965). The  $r_e$  value was estimated from Guggenheimer's relation for single bonded molecules [K. M. Guggenheimer, Proc. Phys. Soc. (London) 59, 456 (1946)]. The anharmonicity constant  $X_e$  was estimated by assuming the separation of the vibrational levels to be a linear function of the vibrational quantum number. The  $\epsilon_e$  value was then calculated using the Morse potential function.  $B_e$  was determined from the bond length. The ground state configuration of  $2\sum^-$  was assumed because of the unpaired electron. The principal moment of inertia is 3.789297 x 10<sup>-39</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (F <sup>o</sup> -H <sup>o</sup> <sub>298</sub> )/T	H <sup>o</sup> - H <sup>o</sup> <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	∞.000	INFINITE	- 2.097	27.095	26.841	INFINITE
100	6.957	43.558	- 1.602	27.086	26.841	58.659
200	7.037	48.399	- 1.015	27.094	26.846	29.058
298	7.345	51.254	∞.000	27.100	26.846	19.311
300	7.352	51.300	∞.014	27.100	26.841	19.189
400	7.725	53.467	∞.768	27.114	26.886	14.252
500	8.035	55.225	1.556	27.133	25.828	11.289
600	8.269	56.712	2.372	27.156	25.564	9.311
700	8.442	58.000	3.208	27.177	25.298	7.698
800	8.573	59.136	4.059	27.196	25.027	6.837
900	8.673	60.152	4.922	27.214	24.755	6.011
1000	8.752	61.070	5.793	27.229	24.482	5.350
1100	8.817	61.908	6.672	27.242	24.205	4.809
1200	8.870	62.677	7.556	27.254	23.929	4.358
1300	8.916	63.389	8.445	27.263	23.652	3.976
1400	8.955	64.051	9.339	27.271	23.374	3.649
1500	8.989	64.670	10.236	27.278	23.096	3.365
1600	9.020	65.251	11.137	27.282	22.817	3.116
1700	9.048	65.799	12.040	27.286	22.538	2.897
1800	9.074	66.317	12.946	27.286	22.257	2.702
1900	9.098	66.808	13.855	27.285	21.979	2.528
2000	9.120	67.275	14.766	27.283	21.700	2.371
2100	9.141	67.721	15.679	27.278	21.419	2.229
2200	9.162	68.147	16.594	27.271	21.140	2.100
2300	9.181	68.554	17.511	27.263	20.863	1.982
2400	9.200	68.945	18.430	27.252	20.586	1.874
2500	9.218	69.321	19.351	27.238	20.307	1.775
2600	9.235	69.689	20.274	27.223	20.030	1.684
2700	9.252	70.032	21.198	27.206	19.754	1.599
2800	9.269	70.359	22.124	27.187	19.477	1.520
2900	9.285	70.684	23.052	27.166	19.205	1.447
3000	9.300	71.009	23.981	27.142	18.930	1.379
3100	9.317	71.315	24.912	27.117	18.654	1.315
3200	9.332	71.611	25.844	27.090	18.382	1.255
3300	9.347	71.898	26.776	27.062	18.111	1.199
3400	9.361	72.177	27.714	27.031	17.841	1.147
3500	9.378	72.449	28.651	26.999	17.570	1.097
3600	9.392	72.713	29.589	26.966	17.304	1.050
3700	9.407	72.971	30.529	26.931	17.034	1.006
3800	9.422	73.222	31.471	26.895	16.768	.964
3900	9.436	73.467	32.414	26.858	16.509	.925
4000	9.451	73.706	33.358	26.819	16.255	.887
4100	9.465	73.939	34.304	26.779	15.973	.851
4200	9.479	74.168	35.251	26.738	15.707	.817
4300	9.493	74.391	36.200	26.697	15.448	.785
4400	9.508	74.609	37.150	26.653	15.187	.754
4500	9.522	74.823	38.101	26.610	14.925	.725
4600	9.536	75.033	39.054	26.566	14.665	.697
4700	9.550	75.238	40.008	26.520	14.408	.670
4800	9.564	75.439	40.964	26.475	14.153	.644
4900	9.577	75.636	41.921	26.428	13.896	.620
5000	9.591	75.830	42.880	26.381	13.639	.596
5100	9.605	76.020	43.839	26.333	13.384	.574
5200	9.619	76.207	44.801	26.286	13.130	.552
5300	9.633	76.390	45.763	26.238	12.882	.531
5400	9.646	76.570	46.727	26.189	12.626	.511
5500	9.660	76.747	47.692	26.140	12.379	.492
5600	9.674	76.922	48.659	26.091	12.124	.473
5700	9.687	77.094	49.627	26.041	11.877	.455
5800	9.701	77.261	50.597	25.992	11.634	.438
5900	9.715	77.427	51.567	25.942	11.384	.422
6000	9.728	77.591	52.540	25.893	11.136	.406

IRON DIFLUORIDE (FeF<sub>2</sub>) (CRYSTAL)

T, °K.	C <sub>p</sub>	$-(F^* - H_{298}^*)/T$	$H^* - H_{298}^*$	$\Delta H_f^*$	$\Delta F_f^*$	Log K <sub>p</sub>
0	∞	INFINITE	3.049	-168.564	-168.564	INFINITE
100	7.994	33.204	2.583	-165.417	-165.417	361.502
200	13.530	14.824	1.476	-168.911	-161.907	176.915
298	16.280	20.790	0.000	-168.700	-158.507	116.184
300	16.300	20.891	0.030	-168.695	-158.444	115.421
400	17.200	25.708	1.707	-168.414	-155.069	84.722
500	17.900	29.624	3.463	-168.140	-151.765	66.333
600	18.440	32.938	5.281	-167.884	-148.515	54.094
700	18.850	35.812	7.146	-167.659	-145.364	43.536
800	19.180	38.351	9.048	-167.491	-142.125	38.875
900	19.440	40.626	10.980	-167.411	-138.959	33.742
1000	19.630	42.684	12.934	-167.499	-135.796	29.677
1100	19.760	44.582	14.904	-167.706	-132.697	26.365
1200	19.860	46.287	16.887	-167.873	-129.610	23.568
1300	19.925	47.891	18.879	-167.807	-126.514	21.218
1400	20.020	49.363	20.877	-167.355	-123.420	19.207
1500	20.072	50.746	22.882	-167.114	-119.883	17.466
1600	20.120	52.043	24.892	-166.888	-116.743	15.946
1700	20.164	53.284	26.906	-166.667	-113.609	14.605
1800	20.220	54.478	28.924	-166.462	-110.475	13.413
1900	20.249	55.616	30.944	-170.441	-107.158	12.325
2000	20.250	56.549	32.970	-170.400	-103.830	11.345

$\Delta H_f^0 = -168.6 \pm 10$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -168.7 \pm 10$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^0 = [12.4]$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^{298.15} = 75.6 \pm 2.0$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 20.79 \pm 0.04$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_m = [1373]^\circ K.$

Heat of Formation.

The equilibrium pressures for the reaction  $FeF_2(c) + H_2(g) = Fe(c) + 2HF(g)$  have been measured by K. Jellinek and A. Rudst, Z. anorg. allgem. Chem. 175, 281 (1928) at 773, 873 and 973°K. The enthalpy change ( $\Delta H_f^{298.15}$ ) of the reaction was evaluated by the second and third law methods to be 27.19 and 39.08 kcal. mole<sup>-1</sup>, respectively. Based on the third law value of  $\Delta H_f^{298.15}$ , the  $\Delta H_f^{298.15}$  ( $FeF_2, c$ ) was calculated to be -168.7 ± 10 kcal. mole<sup>-1</sup>. The drift in the third law values of  $\Delta H_f^{298.15}$  was evaluated to be 13.3 ± 1.8 e.u.

Heat Capacity and Entropy.

The low temperature (11.33 - 307.30°K.) heat capacities were determined by E. Catalano and J. W. Stout, J. Chem. Phys. 23, 1803 (1955). The heat capacities above 307°K. were estimated by comparison with those of  $FeCl_2(c)$ ,  $MgCl_2(c)$  and  $MgF_2(c)$ . The value of  $S_{298.15}^0$  was obtained from E. Catalano and J. W. Stout, loc. cit., in which a sharp maximum  $C_p$  of 17.8 cal. deg.<sup>-1</sup> mole<sup>-1</sup> at 78.35°K. was reported. The  $S_{298.15}^0$  value was based on  $S_{15}^0 = 0.039$  e.u.

Melting Data.

$T_m$  was estimated as 1100°C based on the data reported by W. Biliz and E. Rahlfs, Z. anorg. allgem. Chem. 166, 363 (1927). The value of  $\Delta H_m^0$  was calculated using  $\Delta S_m^0 = 9$  e.u. which was assumed to be the same as the corresponding value for  $MgF_2(c)$ .

Heat of Sublimation.

The value of  $\Delta H_s^{298.15}$  was obtained from J. L. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William Marsh Rice University, Houston, Texas. See  $FeF_2(g)$  table for details.



T, °K.	C <sub>p</sub>	S°	$-(F^{\circ}-H_{298}^{\circ})/T$	H° - H <sub>298</sub> °	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
cal. mole <sup>-1</sup> deg. <sup>-1</sup>		cal. mole <sup>-1</sup>		kcal. mole <sup>-1</sup>			
0							
100	23.500	21.951	21.951	0.000	- 161.229	- 151.383	110.961
200	23.500	22.696	21.951	0.643	- 161.211	- 151.322	110.232
300	23.500	23.057	22.696	1.303	- 161.257	- 148.471	80.953
400	23.500	24.151	24.151	4.743	- 159.480	- 145.253	63.487
500	23.500	26.385	26.385	7.093	- 158.601	- 142.500	51.903
600	23.500	28.157	28.157	9.443	- 157.891	- 139.874	43.669
700	23.500	30.404	30.404	11.793	- 157.275	- 137.345	37.519
800	23.500	32.199	32.199	14.143	- 156.777	- 134.884	32.753
900	23.500	33.896	33.896	16.493	- 156.469	- 132.472	28.950
1000	23.500	35.499	35.499	18.843	- 156.386	- 130.071	25.842
1100	23.500	37.013	37.013	21.193	- 156.096	- 127.696	23.256
1200	23.500	38.445	38.445	23.543	- 155.472	- 125.354	21.073
1300	23.500	39.801	39.801	25.893	- 154.868	- 123.061	19.210
1400	23.500	41.089	41.089	28.243	- 154.282	- 120.809	17.601
1500	23.500	42.314	42.314	30.593	- 153.716	- 118.597	16.190
1600	23.500	43.481	43.481	32.943	- 153.459	- 116.412	14.965
1700	23.500	44.595	44.595	35.293	- 153.072	- 114.248	13.871
1800	23.500	45.661	45.661	37.643	- 152.274	- 111.919	12.874
1900	23.500	46.682	46.682	39.993	- 151.906	- 109.596	11.975
2000	23.500	47.825	47.825	42.343	- 151.556	- 107.288	11.165
2100	23.500	48.918	48.918	44.693	- 151.193	- 104.997	10.430
2200	23.500	49.963	49.963	47.043	- 150.866	- 102.725	9.761
2300	23.500	50.383	50.383	49.393	- 150.506	- 100.467	9.148
2400	23.500	51.225	51.225	51.743	- 150.173	- 98.223	8.586
2500	23.500	52.039	52.039	54.093	- 149.846	- 95.990	8.068
2600	23.500	52.826	52.826	56.443	- 149.525	- 93.771	7.590
2700	23.500	53.588	53.588	58.793	- 149.210	- 91.565	7.147
2800	23.500	54.410	54.410	61.143	- 148.902	- 89.365	6.734
2900	23.500	55.043	55.043	63.493	- 148.601	- 87.183	6.351

$\Delta H_f^{\circ} 298.15 = [-161.229]$  kcal. mole<sup>-1</sup>

$\Delta H_m^{\circ} = [12.4]$  kcal. mole<sup>-1</sup>

$\Delta H_v^{\circ} = [53.64]$  kcal. mole<sup>-1</sup>

$S^{\circ} 298.15 = [21.951]$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

$T_m = [1373]^{\circ}K.$

$T_b = [2110]^{\circ}K.$

Heat of Formation.

The value of  $\Delta H_f^{\circ} 298.15$  (FeF<sub>2</sub>, l) was obtained from  $\Delta H_f^{\circ} 298.15$  (FeF<sub>2</sub>, c) by adding  $\Delta H_m^{\circ}$  and the difference between  $H_m^{\circ} - H_c^{\circ} 298.15$  for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for FeF<sub>2</sub>(l) was estimated by comparison with those for FeCl<sub>2</sub>(c), MgCl<sub>2</sub>(c), CaCl<sub>2</sub>(c) and CaF<sub>2</sub>(c). The  $C_p$ (FeF<sub>2</sub>, l) value was assumed to be constant in the temperature range, 298.15 - 3000°K. The entropy ( $S^{\circ} 298.15$ ) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See the FeF<sub>2</sub>(c) table for details.

Vaporization Data.

$T_b$  is calculated as the temperature at which the free energy change of the reaction FeF<sub>2</sub>(l) = FeF<sub>2</sub>(g) approaches zero. The difference between  $\Delta H_f^{\circ}$  for FeF<sub>2</sub>(l) and FeF<sub>2</sub>(g) at  $T_b$  is  $\Delta H_v^{\circ}$ .

IRON DIFLUORIDE (FeF<sub>2</sub>) (IDEAL GAS)

Point Group [D<sub>2h</sub>h]  
 $\Delta H_f^0 = -82.9 \pm 3.4$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 298.15 = -93.1 \pm 3.4$  kcal. mole<sup>-1</sup>  
 $S_{298.15}^0 = [63.4]$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Electronic Levels and Quantum Weights

$\epsilon_i$ , cm. <sup>-1</sup>	$g_i$
0	[5]
[1000]	[10]
[4000]	[5]
[6000]	[5]

Vibrational Frequencies and Degeneracies

$\omega_j$ , cm. <sup>-1</sup>
[550] (1)
[190] (2)
[714] (1)

Bond Distance: Fe-P = [1.8] Å  
 Bond Angle: P-Fe-P = [180]°  
 Rotational Constant: B<sub>0</sub> = 0.13692 cm.<sup>-1</sup>

$\sigma = 2$

Heat of Formation.

The rate of sublimation of FeF<sub>2</sub>(c) was measured between 965 and 1149°K. by the Knudsen technique employing the high temperature magnetic mass spectrometer by John L. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William March Rice University, Houston, Texas. The only vapor species of importance is FeF<sub>2</sub>(g). From the vapor pressure data the third law heat of sublimation ( $\Delta H_s^0 298.15$ ) was reported as  $75.6 \pm 2.0$  kcal. mole<sup>-1</sup>. The sum of the values of  $\Delta H_g^0 298.15$  and  $\Delta H_f^0 298.15$  for FeF<sub>2</sub>(c) is the  $\Delta H_f^0 298.15$  (FeF<sub>2</sub>, g).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The Fe-F bond distance was estimated from that in FeF<sub>2</sub>(c) reported by W. H. Baur, Acta Cryst. 11, 488 (1958). The vibrational frequencies,  $\omega_j$  and  $\omega_j$ , were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The values of  $\omega_j$ , electronic levels and quantum weights were estimated by comparison with those for FeCl<sub>2</sub>(g). See FeCl<sub>2</sub>(g) table for details. The moment of inertia is 2.0440 X 10<sup>-39</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>v</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	cal. mole <sup>-1</sup> deg. <sup>-1</sup>	keal. mole <sup>-1</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	0.00	0.00	INFINITE	0.00	INFINITE	0.00	92.944	92.944	INFINITE
100	9.216	51.319	12.890	3.029	12.890	3.029	92.944	92.944	205.178
200	11.449	63.361	8.322	1.219	8.322	1.219	92.944	92.944	103.555
298	13.324	68.361	5.000	0.000	5.000	0.000	92.944	92.944	70.073
300	13.355	68.361	4.985	0.000	4.985	0.000	92.944	92.944	69.653
400	14.673	71.822	3.603	1.432	3.603	1.432	92.944	92.944	42.697
500	15.365	73.841	2.965	2.398	2.965	2.398	92.944	92.944	22.153
600	15.647	75.618	2.561	3.491	2.561	3.491	92.944	92.944	15.278
700	15.723	77.091	2.303	4.661	2.303	4.661	92.944	92.944	10.303
800	15.714	78.191	2.143	5.882	2.143	5.882	92.944	92.944	7.226
900	15.679	78.840	2.040	7.103	2.040	7.103	92.944	92.944	5.290
1000	15.644	79.021	1.979	8.269	1.979	8.269	92.944	92.944	4.153
1100	15.617	79.179	1.936	9.332	1.936	9.332	92.944	92.944	3.344
1200	15.600	79.317	1.900	10.276	1.900	10.276	92.944	92.944	2.870
1300	15.591	79.436	1.870	11.146	1.870	11.146	92.944	92.944	2.536
1400	15.588	79.531	1.845	11.961	1.845	11.961	92.944	92.944	2.261
1500	15.590	79.604	1.823	12.726	1.823	12.726	92.944	92.944	2.016
1600	15.594	79.658	1.804	13.446	1.804	13.446	92.944	92.944	1.796
1700	15.599	79.696	1.788	14.116	1.788	14.116	92.944	92.944	1.596
1800	15.604	79.721	1.774	14.731	1.774	14.731	92.944	92.944	1.416
1900	15.609	79.734	1.761	15.296	1.761	15.296	92.944	92.944	1.246
2000	15.612	79.739	1.750	15.816	1.750	15.816	92.944	92.944	1.096
2100	15.613	79.739	1.740	16.286	1.740	16.286	92.944	92.944	0.966
2200	15.613	79.739	1.731	16.711	1.731	16.711	92.944	92.944	0.846
2300	15.611	79.739	1.723	17.096	1.723	17.096	92.944	92.944	0.736
2400	15.608	79.739	1.716	17.436	1.716	17.436	92.944	92.944	0.636
2500	15.603	79.739	1.710	17.736	1.710	17.736	92.944	92.944	0.546
2600	15.597	79.739	1.705	18.001	1.705	18.001	92.944	92.944	0.466
2700	15.590	79.739	1.701	18.226	1.701	18.226	92.944	92.944	0.396
2800	15.582	79.739	1.698	18.416	1.698	18.416	92.944	92.944	0.336
2900	15.573	79.739	1.695	18.576	1.695	18.576	92.944	92.944	0.286
3000	15.563	79.739	1.693	18.706	1.693	18.706	92.944	92.944	0.246
3100	15.553	79.739	1.691	18.811	1.691	18.811	92.944	92.944	0.216
3200	15.542	79.739	1.690	18.896	1.690	18.896	92.944	92.944	0.186
3300	15.530	79.739	1.689	18.956	1.689	18.956	92.944	92.944	0.156
3400	15.517	79.739	1.689	19.001	1.689	19.001	92.944	92.944	0.126
3500	15.503	79.739	1.689	19.036	1.689	19.036	92.944	92.944	0.096
3600	15.489	79.739	1.689	19.061	1.689	19.061	92.944	92.944	0.066
3700	15.474	79.739	1.689	19.076	1.689	19.076	92.944	92.944	0.036
3800	15.458	79.739	1.689	19.086	1.689	19.086	92.944	92.944	0.006
3900	15.441	79.739	1.689	19.091	1.689	19.091	92.944	92.944	0.000
4000	15.424	79.739	1.689	19.096	1.689	19.096	92.944	92.944	0.000
4100	15.406	79.739	1.689	19.101	1.689	19.101	92.944	92.944	0.000
4200	15.387	79.739	1.689	19.106	1.689	19.106	92.944	92.944	0.000
4300	15.368	79.739	1.689	19.111	1.689	19.111	92.944	92.944	0.000
4400	15.348	79.739	1.689	19.116	1.689	19.116	92.944	92.944	0.000
4500	15.328	79.739	1.689	19.121	1.689	19.121	92.944	92.944	0.000
4600	15.307	79.739	1.689	19.126	1.689	19.126	92.944	92.944	0.000
4700	15.286	79.739	1.689	19.131	1.689	19.131	92.944	92.944	0.000
4800	15.264	79.739	1.689	19.136	1.689	19.136	92.944	92.944	0.000
4900	15.242	79.739	1.689	19.141	1.689	19.141	92.944	92.944	0.000
5000	15.220	79.739	1.689	19.146	1.689	19.146	92.944	92.944	0.000
5100	15.198	79.739	1.689	19.151	1.689	19.151	92.944	92.944	0.000
5200	15.176	79.739	1.689	19.156	1.689	19.156	92.944	92.944	0.000
5300	15.154	79.739	1.689	19.161	1.689	19.161	92.944	92.944	0.000
5400	15.132	79.739	1.689	19.166	1.689	19.166	92.944	92.944	0.000
5500	15.110	79.739	1.689	19.171	1.689	19.171	92.944	92.944	0.000
5600	15.088	79.739	1.689	19.176	1.689	19.176	92.944	92.944	0.000
5700	15.066	79.739	1.689	19.181	1.689	19.181	92.944	92.944	0.000
5800	15.044	79.739	1.689	19.186	1.689	19.186	92.944	92.944	0.000
5900	15.022	79.739	1.689	19.191	1.689	19.191	92.944	92.944	0.000
6000	15.000	79.739	1.689	19.196	1.689	19.196	92.944	92.944	0.000

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.000	INFINITE	- 2.370	- 267.764	- 267.764	INFINITE
100	5.193	2.552	- 2.492	- 268.435	- 264.394	577.805
200	11.668	8.378	- 1.314	- 268.819	- 260.279	284.408
298	14.720	13.683	.000	- 268.700	- 256.005	187.648
300	14.790	13.775	.027	- 268.698	- 255.927	186.434
400	16.390	18.265	1.582	- 268.517	- 251.695	139.413
500	17.310	22.028	3.280	- 268.278	- 247.516	108.184
600	17.830	25.232	5.038	- 268.021	- 243.388	88.650
700	18.250	28.013	6.843	- 267.760	- 239.302	74.710
800	18.600	30.473	8.585	- 267.506	- 235.256	64.266
900	18.930	32.683	10.262	- 267.269	- 231.238	56.150
1000	19.230	34.693	12.470	- 266.965	- 227.068	49.623
1100	19.520	36.539	14.408	- 266.921	- 222.869	44.278
1200	19.800	38.250	16.374	- 266.679	- 218.693	39.828
1300	20.080	39.846	18.368	- 266.441	- 214.537	36.065
1400	20.350	41.344	20.389	- 266.571	- 209.920	32.768
1500	20.610	42.757	22.437	- 267.931	- 203.609	29.664
1600	20.860	44.096	24.512	- 267.268	- 197.344	26.955
1700	21.110	45.369	26.613	- 266.582	- 191.118	24.569
1800	21.400	46.585	28.740	- 295.874	- 184.936	22.453
1900	21.660	47.769	30.893	- 295.141	- 178.792	20.565
2000	21.920	48.867	33.072	- 294.386	- 172.687	18.869
2100	22.175	49.942	35.277	- 293.608	- 166.624	17.340
2200	22.430	50.980	37.507	- 292.808	- 160.594	15.953
2300	22.686	51.982	39.763	- 291.984	- 154.601	14.690
2400	22.943	52.953	42.044	- 291.138	- 148.648	13.536
2500	23.200	53.895	44.351	- 290.270	- 142.730	12.477

MAGNESIUM DIFLUORIDE (MgF<sub>2</sub>)

(CRYSTAL)

MOL. WT. = 62.3088

$$\Delta H_f^0 = -267.8 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -268.7 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 13.90 \text{ kcal. mole}^{-1}$$

$$\Delta H_s^{298.15} = 95.5 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 13.68 \pm 0.07 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1536^\circ\text{K.}$$

Heat of Formation.

The value of  $\Delta H_f^0$  298.15 for MgF<sub>2</sub>(c) was obtained from E. Rudzitis and W. N. Hubbard, Argonne National Laboratory, Argonne, Illinois, private communication, dated June 18, 1964. This value was determined by fluorine bomb calorimetry which is considered as comparatively the best method available at the present time. The heats of reaction involving MgF<sub>2</sub>(c) were measured by many early investigators. However, the  $\Delta H_f^0$  298.15 (MgF<sub>2</sub>, c) values derived are in reasonable agreement. The results are presented as follows.

Investigator	Chemical Reaction	$\Delta H_r^0$ 298.15, kcal. mole <sup>-1</sup>	$\Delta H_f^0$ 298.15, kcal. mole <sup>-1</sup>
Domange (1)	MgF <sub>2</sub> (c) + H <sub>2</sub> O(g) → 2HF(g) + MgO(c)	+51.76 ± 1.2(1)	-287.5 ± 1.3
Wartenberg (2)	Mg(c) + 2(HF·80H <sub>2</sub> O) → MgF <sub>2</sub> (c) + H <sub>2</sub> (g) + 160H <sub>2</sub> O(l)	-109.5 ± 0.7	-282.1 ± 0.8
Torgeson, et al. (3)	Mg(OH) <sub>2</sub> (c) + 2HF(sol.) → MgF <sub>2</sub> (c) + 2H <sub>2</sub> O(l)	-29.09	-286.5 ± 0.8
Gross, et al. (4)	Mg(c) + PbF <sub>2</sub> (c) → MgF <sub>2</sub> (c) + Pb(c)	-109.5 ± 1.5	-289.1 ± 1.8
(1) L. Domange, Ann. chim. phys. 7(11)225 (1937). The $\Delta H_f^0$ value was calculated by the third law method.			
(2) H. V. Wartenberg, Z. anorg. allgem. Chem. 249, 100 (1942).			
(3) D. R. Torgeson and T. G. Saha, J. Am. Chem. Soc. 70, 2156 (1948).			
(4) P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).			

Heat Capacity and Entropy.

The low temperature heat capacities, 54.22-296.5°K., were measured by S. S. Todd, J. Am. Chem. Soc. 71, 4115 (1949). The high temperature heat capacities, 298-1536°K., were obtained from the heat content measurements determined by B. P. Naylor, J. Am. Chem. Soc. 67, 150 (1945). These two sets of data were joined smoothly at 298°K.  $S_{298.15}^0$  was obtained from  $C_p$  data reported by S. S. Todd, loc. cit., using  $S_{298.15}^0$  (extrap.) = 0.537 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Data.

$T_m$  and  $\Delta H_m^0$  were taken from B. P. Naylor, loc. cit.

Heat of Sublimation.

The vapor pressure of MgF<sub>2</sub>(c) has been measured by seven investigators. Using the reported data, the respective  $\Delta H_s^0$  298.15 for MgF<sub>2</sub>(c) were calculated (see MgF<sub>2</sub>(g) table for detail). The adopted value was selected to be 95.5 ± 1.5 kcal. mole<sup>-1</sup>.

MAGNESIUM DIFLUORIDE (MgF<sub>2</sub>) (LIQUID)

$S_{298.15}^{\circ} = 15.290 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$        $\Delta H_f^{\circ} 298.15 = -259.557 \text{ kcal. mole}^{-1}$   
 $T_m = 1536^{\circ}\text{K.}$        $\Delta H_m^{\circ} = 13.90 \text{ kcal. mole}^{-1}$   
 $T_b = [2499]^{\circ}\text{K.}$        $\Delta H_v^{\circ} = [63.48] \text{ kcal. mole}^{-1}$

Heat of Formation.  
 $\Delta H_f^{\circ} 298.15(1)$  was obtained from  $\Delta H_f^{\circ} 298.15(c)$  by adding  $\Delta H_m^{\circ}$  and the difference between  $H_m^{\circ}$ - $H_m^{\circ} 298.15$  for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity (1691-1800°K.) was reported by B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945). The same value was used for other temperatures. The entropy was obtained in a manner analogous to that of the heat or formation.

Melting Data.

$T_m$  and  $\Delta H_m^{\circ}$  were obtained from B. F. Naylor, loc. cit.

Vaporization Data.

$T_b$  was obtained from equilibrium calculation between the species  $MgF_2(1)$ ,  $MgF_2(g)$ , and  $(MgF_2)_2(g)$ , i.e., the temperature at which the sum of the partial pressures of  $MgF_2(g)$  and  $(MgF_2)_2(g)$  equals one atmosphere. From the difference between the heats of formation of  $MgF_2(1)$  and  $MgF_2(g)$  at the boiling point, the heat of vaporization was calculated. At the boiling point the amount of dimeric species is negligible in comparison with that of the monomeric species.

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (F <sup>o</sup> - H <sup>o</sup> 298) / T	H <sup>o</sup> - H <sup>o</sup> 298	ΔH <sub>f</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100						
200						
298	22.570	15.290	0.000	-259.557	-247.341	181.297
300	22.570	15.290	0.042	-259.540	-247.266	180.124
400	22.570	16.174	2.299	-258.667	-243.308	132.931
500	22.570	17.847	4.556	-257.859	-239.563	104.708
600	22.570	19.719	6.813	-257.103	-235.976	85.950
700	22.570	21.594	9.070	-256.390	-232.511	72.590
800	22.570	23.267	11.327	-255.724	-229.147	62.597
900	22.570	24.642	13.584	-255.104	-225.862	54.844
1000	22.570	25.863	15.841	-254.651	-222.645	48.417
1100	22.570	26.954	18.098	-254.388	-219.074	43.524
1200	22.570	27.936	20.355	-254.255	-215.731	39.268
1300	22.570	28.825	22.612	-254.254	-212.642	35.711
1400	22.570	29.627	24.869	-284.948	-209.692	32.571
1500	22.570	30.351	27.126	-284.999	-206.974	29.610
1600	22.570	31.001	29.383	-283.254	-204.515	27.033
1700	22.570	31.586	31.640	-282.412	-202.266	24.746
1800	22.570	32.107	33.897	-281.574	-200.245	22.746
1900	22.570	32.564	36.154	-280.737	-198.437	20.949
2000	22.570	32.958	38.411	-279.904	-196.847	19.337
2100	22.570	33.299	40.668	-279.074	-195.464	17.883
2200	22.570	33.588	42.925	-278.247	-194.255	16.565
2300	22.570	33.822	45.182	-277.422	-193.170	15.365
2400	22.570	34.003	47.439	-276.600	-192.193	14.268
2500	22.570	34.134	49.696	-275.782	-191.315	13.262
2600	22.570	34.219	51.953	-274.966	-190.466	12.336
2700	22.570	34.258	54.210	-274.153	-189.741	11.481
2800	22.570	34.252	56.467	-273.342	-189.128	10.690
2900	22.570	34.204	58.724	-272.535	-188.618	9.955
3000	22.570	34.119	60.981	-271.733	-188.203	9.272
3100	22.570	34.000	63.238	-270.933	-187.881	8.634
3200	22.570	33.848	65.495	-270.138	-187.650	8.038
3300	22.570	33.667	67.752	-269.347	-187.512	7.480
3400	22.570	33.450	69.999	-268.561	-187.464	6.956
3500	22.570	33.203	72.246	-267.781	-187.520	6.464
3600	22.570	32.932	74.493	-267.006	-187.683	6.000
3700	22.570	32.633	76.740	-266.238	-187.952	5.562
3800	22.570	32.304	78.987	-265.476	-188.325	5.149
3900	22.570	31.953	81.234	-264.722	-188.801	4.758
4000	22.570	31.580	83.481	-263.975	-189.379	4.388

T, °K.	C <sub>p</sub>	S°	-(H°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	8.842	50.659	2.878	-172.772	-172.772	-172.772	INFINITE
200	10.688	57.319	2.059	-172.802	-173.571	-173.571	379.340
298	11.621	61.734	1.089	-173.094	-173.512	-173.512	198.512
300	11.638	61.806	1.022	-173.203	-174.842	-174.842	128.155
400	12.564	65.262	1.425	-173.384	-175.361	-175.361	177.372
500	12.815	68.073	2.485	-173.573	-176.815	-176.815	95.815
600	13.103	70.837	3.782	-173.777	-178.267	-178.267	64.205
700	13.297	72.472	5.182	-174.000	-179.719	-179.719	48.352
800	13.427	73.856	6.436	-174.243	-181.171	-181.171	38.382
900	13.522	75.020	7.787	-174.503	-182.623	-182.623	32.568
1000	13.592	77.272	9.443	-174.992	-184.075	-184.075	28.786
1100	13.644	78.570	10.500	-175.324	-185.527	-185.527	25.267
1200	13.685	79.750	11.871	-175.682	-186.979	-186.979	22.128
1300	13.717	80.856	13.242	-176.067	-188.431	-188.431	19.266
1400	13.743	81.876	14.615	-176.476	-189.883	-189.883	16.655
1500	13.764	82.822	15.990	-176.908	-191.335	-191.335	14.272
1600	13.782	83.711	17.367	-177.373	-192.787	-192.787	12.100
1700	13.796	84.547	18.746	-177.866	-194.239	-194.239	10.178
1800	13.808	85.336	20.126	-178.386	-195.691	-195.691	8.465
1900	13.818	86.083	21.508	-178.933	-197.143	-197.143	6.915
2000	13.827	86.792	22.890	-179.508	-198.595	-198.595	5.500
2100	13.835	87.467	24.273	-180.112	-199.999	-199.999	4.200
2200	13.841	88.111	25.657	-180.746	-201.353	-201.353	3.000
2300	13.847	88.726	27.041	-181.409	-202.657	-202.657	2.000
2400	13.852	89.315	28.426	-182.101	-203.911	-203.911	1.200
2500	13.857	89.881	29.812	-182.822	-205.115	-205.115	0.600
2600	13.861	90.425	31.198	-183.583	-206.269	-206.269	0.300
2700	13.864	90.948	32.584	-184.384	-207.383	-207.383	0.150
2800	13.868	91.452	33.971	-185.225	-208.457	-208.457	0.075
2900	13.870	91.939	35.357	-186.106	-209.491	-209.491	0.037
3000	13.873	92.409	36.745	-187.026	-210.485	-210.485	0.019
3100	13.875	92.864	38.132	-187.987	-211.439	-211.439	0.009
3200	13.877	93.300	39.520	-188.990	-212.353	-212.353	0.004
3300	13.879	93.732	40.908	-189.993	-213.227	-213.227	0.002
3400	13.881	94.146	42.296	-190.996	-214.061	-214.061	0.001
3500	13.883	94.548	43.684	-192.000	-214.855	-214.855	0.000
3600	13.884	94.939	45.072	-193.004	-215.609	-215.609	0.000
3700	13.886	95.320	46.461	-194.008	-216.323	-216.323	0.000
3800	13.887	95.690	47.849	-195.012	-217.000	-217.000	0.000
3900	13.888	96.051	49.238	-196.016	-217.637	-217.637	0.000
4000	13.889	96.403	50.627	-197.020	-218.231	-218.231	0.000
4100	13.890	96.746	52.016	-198.024	-218.785	-218.785	0.000
4200	13.891	97.080	53.405	-199.028	-219.300	-219.300	0.000
4300	13.892	97.407	54.794	-200.032	-219.775	-219.775	0.000
4400	13.893	97.727	56.183	-201.036	-220.210	-220.210	0.000
4500	13.894	98.039	57.573	-202.040	-220.604	-220.604	0.000
4600	13.894	98.344	58.962	-203.044	-221.000	-221.000	0.000
4700	13.895	98.643	60.352	-204.048	-221.406	-221.406	0.000
4800	13.896	98.935	61.741	-205.052	-221.812	-221.812	0.000
4900	13.896	99.222	63.131	-206.056	-222.218	-222.218	0.000
5000	13.897	99.503	64.520	-207.060	-222.624	-222.624	0.000
5100	13.897	99.778	65.910	-208.064	-223.030	-223.030	0.000
5200	13.898	100.048	67.300	-209.068	-223.436	-223.436	0.000
5300	13.898	100.313	68.690	-210.072	-223.842	-223.842	0.000
5400	13.899	100.572	70.079	-211.076	-224.248	-224.248	0.000
5500	13.899	100.827	71.469	-212.080	-224.654	-224.654	0.000
5600	13.899	101.078	72.859	-213.084	-225.060	-225.060	0.000
5700	13.900	101.324	74.249	-214.088	-225.466	-225.466	0.000
5800	13.900	101.566	75.639	-215.092	-225.872	-225.872	0.000
5900	13.901	101.803	77.029	-216.096	-226.278	-226.278	0.000
6000	13.901	102.037	78.419	-217.100	-226.684	-226.684	0.000

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

MAGNESIUM DIFLUORIDE (MgF<sub>2</sub>) (IDEAL GAS) MOL. WT. = 62.3088

Point Group C<sub>2v</sub> ΔF<sub>f</sub><sup>0</sup> = -172.8 ± 1.5 kcal. mole<sup>-1</sup>  
 S<sub>298.15</sub> = 61.734 cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>0</sup> 298.15 = -173.2 ± 1.5 kcal. mole<sup>-1</sup>  
 Ground State Quantum weight = (1)

Vibrational Frequencies and Degeneracies

ω, cm. <sup>-1</sup>	478 (1)
	241 (1)
	834 (1)

Bond Distances: Mg-F = 1.77 ± 0.02 Å  
 Bond Angle: F-Mg-F = 150 ± 5°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 1.80632 X 10<sup>-115</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The vapor pressure of MgF<sub>2</sub>(g) over MgF<sub>2</sub>(c) and MgF<sub>2</sub>(l) has been measured by many investigators using different methods. Based on the reported vapor pressure data, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	Method*	ΔH <sub>f</sub> <sup>0</sup> 298.15 <sup>b</sup> , kcal. mole <sup>-1</sup>	Third Law Value	Drift
Ruff and Boucher <sup>1</sup>	1934 - 2129	a	99.48 ± 2.56	96.19	-1.86 ± 1.33
Guenther <sup>2</sup>	1284 - 1530	b	95.06 ± 0.50	95.64	0.45 ± 0.33
Hamer <sup>3</sup>	1451 - 1533	b	93.88 ± 2.67	92.21	1.96 ± 1.78
	1568 - 1613	b	94.17 ± 6.60	96.21	1.96 ± 1.78
	1413 - 1518	c	96.73 ± 2.59	96.19	0.22 ± 2.09
	1533 - 1614	c	96.87 ± 4.35	96.09	-0.51 ± 2.74
Berkowitz and Marquart <sup>4</sup>	1450	c	1450	94.68	94.68
Parber, et al. <sup>5</sup>	1275 - 1513	c	80.72 ± 1.11	91.58	7.75 ± 0.80
Hildenbrand, et al. <sup>6</sup>	1328 - 1527	c	91.80 ± 1.11	93.40	-0.32 ± 0.76
	1544 - 1604	c	94.39 ± 5.00	93.95	-0.13 ± 3.17
	1425 - 1533	c	104.79 ± 1.53	95.75	-6.14 ± 4.65
	1540 - 1606	c	102.61	95.48	—
Margrave, et al. <sup>7</sup>	1241 - 1492	b	94.0	—	—
		b	95.77 ± 2.5	93.07	1.69 ± 0.08

\* a = Monometric method; b = Knudsen effusion method; and c = Torston effusion method

<sup>b</sup> = 298.15°K.

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- K. G. Guenther, Glasstech. Ber. **31**, 9 (1958).
- R. R. Hamer, Ph.D. Thesis, University of California, 1961. Also see R. R. Hamer and J. A. Pask, J. Am. Chem. Soc. **83**, 256 (1961).
- Berkowitz and Marquart, J. Chem. Phys. **37**, 1053 (1962). The value, 94.36 kcal. mole<sup>-1</sup>, was converted from the reported value 86 kcal. mole<sup>-1</sup> at 1300°K.
- M. A. Greenbaum, H. C. Ko, M. Wong and M. Parber, J. Phys. Chem. **68**, 965 (1964), whose reported ΔH<sub>f</sub><sup>0</sup> 298.15 value was derived using different values of free energy functions for MgF<sub>2</sub>(c) and MgF<sub>2</sub>(g) from those used here.
- The first two sets of data were obtained from D. L. Hildenbrand, et al., Philco, Ford Motor Company, U-1187, Experimental Program for Obtaining the Thermodynamic Properties of Propellant Combustion Products, U-1187, Third Quarterly Report, Mar. 15, 1961. The last ΔH<sub>f</sub><sup>0</sup> 298.15 value was given by D. L. Hildenbrand, private communication, Sept. 1, 1964. The heat of formation was reported by D. L. Hildenbrand, loc. cit., U-228, Fifth Quarterly Technical Report, Sept. 15, 1963. These values were summarized by D. L. Hildenbrand, et al., J. Chem. Phys. **40**, 2882 (1964).
- J. W. Green, G. D. Blue, T. C. Ehlers and J. L. Margrave, J. Chem. Phys. **41**, 2245 (1964).

When vapor pressure data were determined above melting point, 1536°K., the heat of sublimation was derived from the heat of vaporization obtained incorporating heat of melting. All data were carefully examined and some inconsistent vapor pressure points were discarded. The best value of ΔH<sub>f</sub><sup>0</sup> 298.15 for MgF<sub>2</sub>(c) was selected as 95.5 ± 1.5 kcal. mole<sup>-1</sup>. The heat of formation for MgF<sub>2</sub>(g) was calculated from the heats of formation and sublimation for MgF<sub>2</sub>(c).

Heat Capacity and Entropy.

The molecular structure of MgF<sub>2</sub>(g) has been reported to be linear by A. Buchler, J. L. Stauffer and W. Klemperer, Inertia Technical Report No. 7, June 30, 1964, A. D. Little, Inc., and bent by M. J. Linevsky, First Quarterly Report, Nov. 1, 1963 - Jan. 31, 1964, General Electric Company. An intensive investigation of the matrix spectrum of MgF<sub>2</sub>(g) has been made recently by D. E. Mann and G. V. Calder, National Bureau of Standards Report 8919, July 1, 1965. The final results were presented by D. E. Mann at the ICRP Working Group on Thermochemistry meeting on Mar. 17, 1966. The vibrational frequencies, bent structure and bond angle were confirmed by use of isotopic substitution, and were adopted here. The Mg-F bond distance was reported by P. A. Akshin, V. F. Spiridonov, G. A. Sobolev and V. A. Naumov, Zh. Fiz. Khim. **31**, 431 (1957). The three principal moments of inertia are: I<sub>A</sub> = 5.1660 X 10<sup>-10</sup>, I<sub>B</sub> = 1.6142 X 10<sup>-36</sup> and I<sub>C</sub> = 1.6959 X 10<sup>-36</sup> g. cm.<sup>2</sup>

MOL. WT. = 66.0102

(IDEAL GAS)

$\Delta H_f^{\circ} O = 17.9 \pm 1.2 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{\circ} S_{298.15} = 16.4 \pm 1.2 \text{ kcal. mole}^{-1}$

Point Group C<sub>2v</sub>  
 $S_{298.15} = 62.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
896 (1)	962 (1)
1524 (1)	573 (1)
552 (1)	737 (1)

Bond Distances: N-F = 1.364 Å N-N = 1.214 Å

Bond Angle: F-N-F = 114.5 ± 0.5°

Product of the Moments of Inertia:  $I_A I_B I_C = 6.543621 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

$\sigma = 2$

Heat of Formation

The heat of formation was derived from the heat of reaction  $N_2F_2(g) + 6/5 NH_3(g) = 2NH_4F(c) + 4/5 N_2(g)$  which was measured calorimetrically by O. T. Armstrong and S. Marantz<sup>1</sup>. There are two isomers, the trans and the active form of difluorodiazine. The heats of formation were determined to be 19.4 and 16.4 kcal. mole<sup>-1</sup> for the trans and the active isomers respectively. The active form of  $N_2F_2$  has been interpreted here as the cis isomer which will be discussed later. The heat of isomerization has also been reported as 3.0 kcal. mole<sup>-1</sup> by Armstrong and Marantz. The value,  $\Delta H_f^{\circ} 298$  (cis  $N_2F_2, g$ ) = 16.4 kcal. mole<sup>-1</sup>, is adopted in the tabulation.

A. V. Pankratov et al.<sup>2</sup> have measured the enthalpy of reaction  $N_2F_2(g) + 5KI = 2KF + N_2 + KI_3$  in acidic solution (pH = 3), and reported  $\Delta H_f^{\circ} 298$  (active  $N_2F_2, g$ ) = 25.3 ± 2.0 kcal. mole<sup>-1</sup>.

The "heat of isomerization" has been reported as 27.5 ± 5.0 kcal. mole<sup>-1</sup> by C. B. Colburn et al.<sup>9</sup>. The derivation of this value is unknown. The authors observed three values of the equilibrium constant for the isomerization reaction. Third law analysis of their data gives  $\Delta H_f^{\circ} 298 = 2.52 \pm 0.05 \text{ kcal. mole}^{-1}$  for the reaction cis  $N_2F_2(g) \rightarrow$  trans  $N_2F_2(g)$  which is in good agreement with Armstrong and Sidney's data.

Heat Capacity and Entropy

Although the infrared spectrum<sup>7,8</sup> of the active form of  $N_2F_2(g)$  has been interpreted as favoring the 1,1-difluorodiazine over the cis-configuration<sup>3,4</sup>, n.m.r.<sup>5</sup> and microwave studies definitely indicate the latter. The vibrational frequencies previously assigned to the 1,1-difluorodiazine have been adopted here for the cis isomer. The selected bond distances and angle were taken from the isotopic nitrogen microwave studies<sup>6</sup>. The principal moments of inertia were:  $I_A = 4.2438 \times 10^{-39}$ ,  $I_B = 10.5129 \times 10^{-39}$  and  $I_C = 14.7567 \times 10^{-39} \text{ g. cm.}^2$

See the trans  $N_2F_2(g)$  table for the comparison of the different physical properties between trans and cis isomers.

References:

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T, °K.	C <sub>v</sub>	S°	-(F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0	0.000	INFINITE	-	2.725	17.857	17.857	INFINITE
100	8.036	51.829	-	1.829	17.971	17.971	43.644
200	9.644	57.787	63.000	1.080	18.887	18.887	25.009
298	11.941	62.071	62.071	0.000	25.884	25.884	19.046
300	11.982	62.145	62.071	0.022	26.043	19.972	18.976
400	13.500	65.867	62.566	1.271	29.290	16.003	16.003
500	15.306	69.129	63.559	2.785	32.562	14.232	14.232
600	16.318	72.014	64.732	4.269	35.837	13.053	13.053
700	17.023	74.588	65.946	6.039	39.100	12.207	12.207
800	17.595	76.902	67.188	7.773	42.345	11.568	11.568
900	18.002	78.989	68.462	9.552	45.576	11.067	11.067
1000	18.313	80.912	69.892	11.370	48.788	10.662	10.662
1100	18.525	82.669	70.577	13.214	51.985	10.328	10.328
1200	18.746	84.292	71.726	15.080	55.168	10.047	10.047
1300	18.900	85.799	72.751	16.962	58.336	9.807	9.807
1400	19.025	87.205	73.734	18.859	61.489	9.598	9.598
1500	19.127	88.521	74.676	20.766	64.633	9.417	9.417
1600	19.213	89.758	75.581	22.684	67.765	9.256	9.256
1700	19.284	90.925	76.449	24.608	70.887	9.113	9.113
1800	19.345	92.029	77.285	26.540	73.997	8.984	8.984
1900	19.397	93.076	78.088	28.477	77.103	8.868	8.868
2000	19.442	94.072	78.843	30.419	80.198	8.763	8.763
2100	19.481	95.022	79.610	32.365	83.281	8.667	8.667
2200	19.514	95.929	80.331	34.315	86.361	8.579	8.579
2300	19.544	96.797	81.028	36.268	89.434	8.498	8.498
2400	19.570	97.630	81.703	38.224	92.499	8.423	8.423
2500	19.593	98.429	82.356	40.182	95.560	8.353	8.353
2600	19.614	99.198	82.989	42.143	98.614	8.289	8.289
2700	19.632	99.938	83.603	44.105	101.667	8.229	8.229
2800	19.649	100.653	84.199	46.069	104.707	8.172	8.172
2900	19.664	101.342	84.779	48.035	107.732	8.120	8.120
3000	19.677	102.009	85.342	50.002	110.743	8.070	8.070
3100	19.690	102.655	85.890	51.970	113.741	8.023	8.023
3200	19.711	103.286	86.424	53.940	116.728	7.978	7.978
3300	19.711	103.886	86.944	55.910	119.708	7.938	7.938
3400	19.720	104.475	87.451	57.882	122.681	7.898	7.898
3500	19.729	105.047	87.946	59.854	125.646	7.861	7.861
3600	19.736	105.603	88.428	61.827	128.608	7.825	7.825
3700	19.744	106.143	88.900	63.791	131.570	7.792	7.792
3800	19.750	106.670	89.361	65.756	134.526	7.760	7.760
3900	19.756	107.183	89.811	67.721	137.478	7.729	7.729
4000	19.762	107.683	90.252	69.677	140.429	7.700	7.700
4100	19.767	108.171	90.683	71.604	143.376	7.672	7.672
4200	19.772	108.648	91.105	73.481	146.320	7.645	7.645
4300	19.777	109.113	91.518	75.458	149.261	7.619	7.619
4400	19.781	109.568	91.923	77.436	152.201	7.594	7.594
4500	19.785	110.012	92.320	79.414	155.145	7.571	7.571
4600	19.789	110.447	92.710	81.393	158.084	7.548	7.548
4700	19.792	110.873	93.092	83.372	161.026	7.526	7.526
4800	19.796	111.290	93.456	85.352	163.961	7.505	7.505
4900	19.799	111.698	93.812	87.336	166.890	7.485	7.485
5000	19.802	112.098	94.166	89.310	169.812	7.466	7.466
5100	19.804	112.490	94.551	91.492	172.734	7.447	7.447
5200	19.807	112.875	94.909	93.472	175.657	7.429	7.429
5300	19.809	113.252	95.242	95.453	178.574	7.411	7.411
5400	19.812	113.622	95.979	97.434	181.484	7.394	7.394
5500	19.814	113.986	96.910	99.415	184.389	7.378	7.378
5600	19.816	114.343	96.236	101.397	187.288	7.363	7.363
5700	19.818	114.694	96.557	103.378	190.181	7.347	7.347
5800	19.820	115.038	96.873	105.360	193.068	7.333	7.333
5900	19.822	115.372	97.183	107.342	195.951	7.318	7.318
6000	19.823	115.710	97.489	109.325	198.824	7.304	7.304

Dec. 31, 1965

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	.000	INFINITE	-	2.923	20.659	20.659	INFINITE
100	8.453	51.506	72.695	- 2.119	22.813	22.813	49.856
200	10.774	63.062	63.860	- 1.160	19.639	25.733	28.118
298	12.779	62.752	62.752	.000	19.400	28.781	21.096
300	12.812	62.832	62.753	.024	19.397	28.839	21.008
400	14.592	66.744	63.275	1.387	19.293	32.006	17.486
500	15.583	70.090	64.312	2.989	19.285	35.186	15.379
600	16.473	73.014	65.523	4.494	19.346	38.362	13.973
700	17.139	75.605	66.782	6.176	19.449	41.524	12.964
800	17.641	77.928	68.033	7.916	19.580	44.668	12.202
900	18.026	80.029	69.251	9.701	19.730	47.795	11.606
1000	18.323	81.945	70.426	11.519	19.889	50.904	11.124
1100	18.558	83.702	71.554	13.363	20.053	53.998	10.728
1200	18.744	85.325	72.635	15.229	20.221	57.077	10.395
1300	18.895	86.832	73.670	17.111	20.389	60.142	10.110
1400	19.019	88.237	74.661	19.007	20.557	63.192	9.864
1500	19.121	89.553	75.610	20.914	20.724	66.232	9.650
1600	19.206	90.789	76.520	22.830	20.889	69.262	9.460
1700	19.277	91.956	77.394	24.755	21.053	72.280	9.292
1800	19.338	93.060	78.234	26.685	21.212	75.286	9.141
1900	19.390	94.107	79.042	28.622	21.372	78.268	9.005
2000	19.433	95.102	79.821	30.563	21.528	81.222	8.882
2100	19.474	96.052	80.571	32.509	21.682	84.156	8.769
2200	19.509	96.958	81.296	34.458	21.832	87.070	8.666
2300	19.538	97.826	81.996	36.410	21.980	90.010	8.571
2400	19.565	98.658	82.673	38.366	22.127	92.917	8.484
2500	19.588	99.457	83.328	40.323	22.268	95.811	8.403
2600	19.609	100.226	83.963	42.283	22.408	98.682	8.328
2700	19.628	100.967	84.580	44.245	22.546	101.529	8.258
2800	19.645	101.681	85.178	46.209	22.682	104.348	8.193
2900	19.660	102.370	85.759	48.174	22.815	107.130	8.132
3000	19.673	103.037	86.324	50.141	22.944	110.838	8.074
3100	19.686	103.682	86.873	52.109	23.072	113.465	8.020
3200	19.697	104.308	87.408	54.078	23.199	116.017	7.969
3300	19.707	104.914	87.930	56.048	23.317	118.508	7.921
3400	19.717	105.502	88.438	58.019	23.437	120.927	7.876
3500	19.726	106.074	88.934	59.991	23.553	123.278	7.832
3600	19.733	106.630	89.417	61.964	23.667	125.558	7.791
3700	19.741	107.171	89.890	63.938	23.779	127.770	7.752
3800	19.748	107.697	90.352	65.912	23.887	129.916	7.716
3900	19.754	108.210	90.803	67.887	23.993	131.998	7.680
4000	19.760	108.710	91.245	69.863	24.097	134.017	7.647
4100	19.765	109.198	91.676	71.839	24.197	135.974	7.614
4200	19.770	109.675	92.099	73.816	24.295	137.870	7.583
4300	19.775	110.140	92.514	75.793	24.392	139.706	7.554
4400	19.779	110.595	92.919	77.771	24.484	141.484	7.526
4500	19.783	111.039	93.317	79.749	24.574	143.206	7.499
4600	19.787	111.474	93.707	81.728	24.663	144.874	7.473
4700	19.791	111.900	94.090	83.707	24.748	146.488	7.448
4800	19.794	112.316	94.465	85.686	24.830	148.048	7.424
4900	19.797	112.724	94.833	87.665	24.909	149.556	7.401
5000	19.800	113.124	95.195	89.645	24.986	151.014	7.379
5100	19.803	113.516	95.551	91.625	25.060	152.422	7.357
5200	19.808	113.900	95.900	93.606	25.133	153.781	7.336
5300	19.810	114.278	96.243	95.586	25.201	155.094	7.316
5400	19.813	114.651	96.581	97.567	25.267	156.361	7.297
5500	19.815	115.012	96.912	99.548	25.330	157.586	7.279
5600	19.815	115.369	97.239	101.530	25.391	158.769	7.261
5700	19.817	115.720	97.560	103.511	25.448	159.910	7.244
5800	19.819	116.069	97.876	105.493	25.502	161.010	7.226
5900	19.820	116.403	98.187	107.475	25.556	162.070	7.210
6000	19.822	116.736	98.494	109.457	25.605	163.091	7.194

DIFLUORODIAZINE, Trans-(N<sub>2</sub>F<sub>2</sub>)

(IDEAL GAS)

MOL. WT. = 66.0102

Point group C<sub>2h</sub>

ΔH<sub>f</sub>° = 20.7 ± 1.2 kcal. mole<sup>-1</sup>

S<sub>298.15</sub>° = 62.75 cal. mole<sup>-1</sup> deg.<sup>-1</sup>

ΔH<sub>f</sub>° 298.15 = 19.4 ± 1.2 kcal. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_j$ , cm. <sup>-1</sup>	$g_j$ , cm. <sup>-1</sup>
1010 (1)	989 (1)
1636 (1)	421 (1)
592 (1)	360 (1)

Bond Distance: N-F = 1.44 Å N-N = 1.25 Å

Bond Angle: F-N-N = 115°

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 432.6784 X 10<sup>-117</sup> g.<sup>3</sup> cm.<sup>6</sup>

C = 2

Heat of Formation.

G. T. Armstrong and S. Marantz, J. Chem. Phys. 35, 169 (1963) have measured calorimetrically the enthalpy of reaction N<sub>2</sub>F<sub>2</sub>(g) + 8/3 NH<sub>3</sub>(g) = 2NH<sub>4</sub>F(c) + 4/3 N<sub>2</sub>(g), and reported ΔH<sub>f</sub>° 298 (trans N<sub>2</sub>F<sub>2</sub>, g) = 19.4 ± 1.2 kcal. mole<sup>-1</sup> which is adopted in this tabulation.

Heat Capacity and Entropy.

The bond distances and bond angle were obtained from S. H. Bauer, J. Am. Chem. Soc. 69, 3104 (1947), by electron diffraction. The fundamental vibrational frequencies were obtained from R. H. Sanborn, J. Chem. Phys. 33, 1855 (1960) by infrared spectroscopy. The three principal moments of inertia are I<sub>A</sub> = 0.919 X 10<sup>-39</sup>, I<sub>B</sub> = 21.2433 X 10<sup>-39</sup> and I<sub>C</sub> = 22.1623 X 10<sup>-39</sup> g. cm.<sup>2</sup>

As pointed out by R. Ettlinger, F. A. Johnson and C. B. Colburn, J. Chem. Phys. 34, 2187 (1961), the trans N<sub>2</sub>F<sub>2</sub> is the less active isomer which is different from the active isomer by its (1) vapor pressure (2) boiling point (3) heat of vaporization (4) critical temperature (5) melting point (6) mass spectral cracking pattern (7) NMR spectrum (8) infrared spectrum (9) heat of isomerization (10) reactivity with mercury and glass.

THIONYL DIFLUORIDE (SOF<sub>2</sub>) (IDEAL GAS)

Point Group C<sub>2v</sub>  
 $\Delta H_f^\circ 0 = [-134 \pm 10] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^\circ 298.15 = [-135 \pm 10] \text{ kcal. mole}^{-1}$   
 $S_{298.15}^\circ = 66.965 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm.}^{-1}$	$\omega, \text{ cm.}^{-1}$
1308 (1)	393 (1)
801 (1)	721 (1)
526 (1)	326 (1)

Bond Distance: O-S = 1.412 Å S-F = 1.565 Å

Bond Angle: O-S-F = 106° 49' F-S-F = 92° 49'

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 1.65545 X 10<sup>-114</sup> g.<sup>3</sup> cm.<sup>6</sup>

$\sigma = 1$

Heat of Formation.

From the enthalpy change,  $\Delta H_f^\circ 298.15 = 131.03 \text{ kcal. mole}^{-1}$ , for the reaction  $\text{SO}_2\text{F}_2(\text{g}) = 3\text{OP}_2(\text{g}) + \text{O}(\text{g})$ , the value of  $\Delta H_f^\circ 298.15$  for  $\text{SOP}_2(\text{g})$  was calculated to be -133.5 kcal. mole<sup>-1</sup>, using  $\Delta H_f^\circ 298.15 = -205.0$  and 59.56 kcal. mole<sup>-1</sup> for  $\text{SO}_2(\text{g})$  and  $\text{O}(\text{g})$ , respectively. The value of  $\Delta H_f^\circ 298.15$  was assumed to be the same as that for the reaction  $\text{SO}_2(\text{g}) = \text{SO}(\text{g}) + \text{O}(\text{g})$  which was calculated based on  $\Delta H_f^\circ 298.15 = -70.95$ , 0.52 and 59.56 kcal. mole<sup>-1</sup> for  $\text{SO}_2(\text{g})$ ,  $\text{SO}(\text{g})$  and  $\text{O}(\text{g})$ , respectively. Using  $\Delta H_f^\circ 298.15 = 127.86 \text{ kcal. mole}^{-1}$  for the reaction  $\text{SO}_2\text{F}_2(\text{g}) = \text{SOP}_2(\text{g}) + \text{O}(\text{g})$ , the value of  $\Delta H_f^\circ 298.15$  ( $\text{SOP}_2, \text{g}$ ) was evaluated as -136.7 kcal. mole<sup>-1</sup> where the  $\Delta H_f^\circ 298.15$  value was assumed to be the same as the S-O bond energy in  $\text{SO}_2(\text{g})$ . The value of  $\Delta H_f^\circ 298.15$  ( $\text{SOP}_2, \text{g}$ ) adopted is -135 ± 10 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The bond distances and angles were obtained from R. C. Ferguson, J. Am. Chem. Soc. 76, 850 (1954). The vibrational frequencies were taken from R. J. Gillespie and E. A. Robinson, Can. J. Chem. 39, 2171 (1961). The assignment of these vibrational frequencies was based on the previous measurements of the infrared and Raman spectra reported by J. K. O'Loane and M. K. Wilson, J. Chem. Phys. 25, 1313 (1955), P. Bender and J. M. Wood, J. Chem. Phys., 25, 1316 (1955) and D. M. Yost, Proc. Indian Acad. Sci. B, 533 (1938). The fundamental assignment reported by J. K. O'Loane and M. K. Wilson, loc. cit., was 1333, 808, 530, (410), 748 and 390 cm.<sup>-1</sup>. The three principal moments of inertia are: I<sub>A</sub> = 1.0034 X 10<sup>-38</sup>, I<sub>B</sub> = 9.7421 X 10<sup>-39</sup> and I<sub>C</sub> = 1.6935 X 10<sup>-38</sup> g. cm.<sup>2</sup>

The heat capacities of thionyl fluoride ( $\text{SOF}_2$ ) have been measured, from 12° to 230°K., by E. I. Pace and E. F. Turnbull, J. Chem. Phys. 43, 1953 (1965), for a sample of 99.976 mole % purity. Incorporating them with the measured  $\Delta H_f^\circ 1.506 \text{ kcal. mole}^{-1}$  at T<sub>m</sub> = 143.25°K. and  $\Delta H_v^\circ 5.091 \text{ kcal. mole}^{-1}$  at T<sub>b</sub> = 228.84°K., which was derived from the measured vapor pressure of  $\text{SOF}_2(1)$ , the entropy of  $\text{SOF}_2(\text{g})$  at 228.84°K. was evaluated as 63.56 e.u. This value is in excellent agreement with the corresponding value, 63.522 e.u., calculated using the adopted molecular constants. This indicates the fact that the molecular constants used for the calculation of the tabulated thermodynamic functions are adequate. Hence the new vibrational frequencies suggested by Pace and Turnbull, loc. cit., were not used.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	8.650	55.063	3.063	-133.862	-133.862	-133.862	INFINITE
200	11.495	61.914	2.254	-134.269	-133.334	-133.334	291.386
298	13.833	66.965	1.249	-134.697	-132.224	-132.224	144.480
300	13.873	66.965	+0.00	-135.040	-130.941	-130.941	95.978
400	15.508	67.051	+0.26	-135.065	-130.916	-130.916	95.367
500	16.622	74.868	1.500	-135.755	-129.497	-129.497	70.750
600	17.389	77.971	3.110	-136.256	-127.873	-127.873	55.890
700	17.928	80.694	4.813	-136.619	-126.160	-126.160	45.951
800	18.317	83.115	6.580	-136.892	-124.359	-124.359	38.828
900	18.605	85.290	8.393	-137.109	-123.835	-123.835	33.828
1000	18.821	87.262	10.240	-137.284	-123.433	-123.433	29.272
1100	18.989	89.064	12.112	-137.423	-123.150	-123.150	25.630
1200	19.120	90.722	14.003	-137.530	-122.974	-122.974	22.654
1300	19.224	92.257	15.908	-137.614	-122.892	-122.892	20.175
1400	19.309	93.684	17.826	-137.678	-122.883	-122.883	18.079
1500	19.378	95.019	19.753	-137.725	-122.932	-122.932	16.285
1600	19.435	96.271	21.687	-137.757	-122.941	-122.941	14.732
1700	19.483	97.451	23.628	-137.774	-122.925	-122.925	13.373
1800	19.524	98.566	25.574	-137.780	-122.895	-122.895	12.176
1900	19.559	99.623	27.524	-137.778	-122.851	-122.851	11.113
2000	19.588	100.627	29.478	-137.768	-122.800	-122.800	10.163
2100	19.614	101.583	31.436	-137.752	-122.745	-122.745	9.308
2200	19.637	102.496	33.396	-137.731	-122.687	-122.687	8.536
2300	19.656	103.369	35.358	-137.706	-122.627	-122.627	7.834
2400	19.671	104.206	37.323	-137.678	-122.565	-122.565	7.194
2500	19.683	104.999	39.290	-137.648	-122.501	-122.501	6.607
2600	19.692	105.751	41.259	-137.616	-122.435	-122.435	6.068
2700	19.700	106.464	43.227	-137.582	-122.367	-122.367	5.571
2800	19.715	107.136	45.198	-137.546	-122.298	-122.298	5.111
2900	19.728	107.773	47.170	-137.509	-122.228	-122.228	4.686
3000	19.735	108.385	49.143	-137.473	-122.158	-122.158	4.296
3100	19.744	108.965	51.117	-137.438	-122.088	-122.088	3.930
3200	19.752	109.522	53.092	-137.403	-122.018	-122.018	3.570
3300	19.760	109.979	55.068	-137.370	-121.948	-121.948	3.245
3400	19.767	110.448	57.044	-137.337	-121.878	-121.878	2.941
3500	19.772	110.928	59.021	-137.306	-121.808	-121.808	2.654
3600	19.778	111.417	60.998	-137.277	-121.738	-121.738	2.384
3700	19.783	111.915	62.977	-137.250	-121.668	-121.668	2.128
3800	19.788	112.420	64.955	-137.225	-121.598	-121.598	1.887
3900	19.792	112.932	66.934	-137.202	-121.528	-121.528	1.659
4000	19.796	113.451	68.914	-137.181	-121.458	-121.458	1.443
4100	19.800	113.976	70.893	-137.162	-121.388	-121.388	1.237
4200	19.804	114.507	72.874	-137.145	-121.318	-121.318	1.041
4300	19.810	115.044	74.854	-137.130	-121.248	-121.248	0.855
4400	19.813	115.587	76.835	-137.116	-121.178	-121.178	0.678
4500	19.815	116.136	78.816	-137.104	-121.108	-121.108	0.508
4600	19.818	116.691	80.797	-137.094	-121.038	-121.038	0.347
4700	19.820	117.252	82.779	-137.086	-120.968	-120.968	0.192
4800	19.822	117.819	84.761	-137.080	-120.898	-120.898	0.044
4900	19.824	118.392	86.743	-137.076	-120.828	-120.828	-0.098
5000	19.826	118.970	88.725	-137.074	-120.758	-120.758	-0.235
5100	19.828	119.553	90.708	-137.073	-120.688	-120.688	-0.365
5200	19.830	119.493	92.691	-137.073	-120.618	-120.618	-0.490
5300	19.831	119.493	94.673	-137.073	-120.548	-120.548	-0.611
5400	19.833	119.493	96.656	-137.073	-120.478	-120.478	-0.728
5500	19.834	119.493	98.640	-137.073	-120.408	-120.408	-0.839
5600	19.834	120.605	100.623	-137.073	-120.338	-120.338	-0.947
5700	19.835	121.962	102.606	-137.073	-120.268	-120.268	-1.051
5800	19.837	123.313	104.590	-137.073	-120.198	-120.198	-1.151
5900	19.838	124.658	106.574	-137.073	-120.128	-120.128	-1.248
6000	19.839	125.998	108.558	-137.073	-120.058	-120.058	-1.341
6100	19.840	127.331	110.542	-137.073	-119.988	-119.988	-1.432



LEAD DIFLUORIDE (PbF<sub>2</sub>) (CRYSTAL) MOL. WT. = 245.1668

$\Delta H_f^0 =$  Unknown  
 $\Delta H_f^0$  298.15 = -161.8 ± 1.2 kcal. mole<sup>-1</sup>  
 $\Delta H_f^0$  2 = [0.61] kcal. mole<sup>-1</sup>  
 $\Delta H_f^0$  1 = 0.65 kcal. mole<sup>-1</sup>  
 $\Delta H_m^0$  = 4.16 kcal. mole<sup>-1</sup>  
 $\Delta H_s^0$  298.15 = 55.0 kcal. mole<sup>-1</sup>

$\Delta C_p^0 =$  Unknown  
 $\Delta C_p^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
 $T_1 = 725^\circ\text{K.}$   
 $T_m = 1091^\circ\text{K.}$

$\Delta G_f^0 =$  Unknown  
 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
 $T_1 = 725^\circ\text{K.}$   
 $T_m = 1091^\circ\text{K.}$

$\Delta G_f^0 =$  Unknown  
 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
 $T_1 = 725^\circ\text{K.}$   
 $T_m = 1091^\circ\text{K.}$

$\Delta G_f^0 =$  Unknown  
 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
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 $T_m = 1091^\circ\text{K.}$

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 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
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$\Delta G_f^0 =$  Unknown  
 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
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 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
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$\Delta G_f^0 =$  Unknown  
 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
 $T_1 = 725^\circ\text{K.}$   
 $T_m = 1091^\circ\text{K.}$

$\Delta G_f^0 =$  Unknown  
 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
 $T_1 = 725^\circ\text{K.}$   
 $T_m = 1091^\circ\text{K.}$

$\Delta G_f^0 =$  Unknown  
 $\Delta G_f^0$  298.15 = [27 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_2 = 613^\circ\text{K.}$   
 $T_1 = 725^\circ\text{K.}$   
 $T_m = 1091^\circ\text{K.}$

Heat of Formation.

The heats of reaction involving PbF<sub>2</sub>(c) have been determined by many investigators. From the reported data the corresponding values of  $\Delta H_f^0$  298.15 for PbF<sub>2</sub>(c) were evaluated. The results obtained are presented as follows.

$\Delta H_f^0$  298.15 kcal. mole<sup>-1</sup> Reference

2.2 ± 1.0	-156.0 ± 1.0	1
32.05 ± 0.6*	-160.6 ± 1.7	2
29.24 ± 2.1*	-153.5 ± 3.1	3
-159.1 ± 0.5	-159.1 ± 0.5	4
-22.9 ± 0.3	-158.3 ± 0.5	5
-112.23 ± 0.2	-161.4 ± 0.4	6
-118.53 ± 0.08	-161.5 ± 1.1	7
-117.7 ± 0.6	-162.1 ± 1.2	8

Chemical Reaction

PbF<sub>2</sub>(c) + 2HNO<sub>3</sub>(aq.) = Pb(NO<sub>3</sub>)<sub>2</sub>(aq.) + 2HF(aq.)  
 PbF<sub>2</sub>(c) + H<sub>2</sub>O(g) = PbO(c) + 2HF(g)  
 PbF<sub>2</sub>(c) + H<sub>2</sub>O(l) = PbO(c) + 2HF(l)  
 Pb(c) + F<sub>2</sub>(g) = PbF<sub>2</sub>(c)  
 PbO(c) + 2HF(aq) = PbF<sub>2</sub>(c) + H<sub>2</sub>O(l)  
 2Hc(c) + PbF<sub>2</sub>(c) = 2HcF(c) + Pb(c)  
 1.5 PbF<sub>2</sub>(c) + Al(c) = AlF<sub>3</sub>(c) + 1.5 Pb(c)  
 1.5 PbF<sub>2</sub>(c) + Al(c) = AlF<sub>3</sub>(c) + 1.5 Pb(c)

\*The third law value.

- H. V. Wartenberg, Z. anorg. allgem. Chem. 151, 326 (1926).
- K. Jellinek and A. Rudat, Z. anorg. Chem. 175, 281 (1926). Second law  $\Delta H_f^0$  298.15 = 32.2 ± 1.0 kcal. mole<sup>-1</sup>.
- M. L. Donaghe, Compt. rend. 200, 2100 (1935). Second law  $\Delta H_f^0$  298.15 = 35.7 ± 0.6 kcal. mole<sup>-1</sup>.
- W. Jahn-Held and K. Jellinek, Z. Elektrochem. 52, 401 (1956). Based on  $\Delta H_f^0$  298.15 = -146.04 kcal. mole<sup>-1</sup>.
- H. V. Wartenberg, Z. anorg. allgem. Chem. 244, 337 (1940).
- R. W. Ivet and T. D. Vries, J. Am. Chem. Soc. 63, 2821 (1941).
- P. Gross, C. Heyman and D. L. Levi, "Physical Chemistry of Process Metallurgy," Part 2, Interscience Publishers, Inc., New York, 1961. Assuming PbF<sub>2</sub>(c) is  $\infty$ -form.
- V. P. Kolegov, A. M. Martynov and S. M. Skuratov, Russ. J. Inorg. Chem. 5, 1326 (1961). Assuming PbF<sub>2</sub>(c) is  $\infty$ -form.

The value of  $\Delta H_f^0$  298.15 (PbF<sub>2</sub>, c) adopted is the average of the last two  $\Delta H_f^0$  298.15 values listed above.

Heat Capacity and Entropy.

E. I. Benashek, K. M. Patsukova and I. F. Rassonkaya, Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshch. i Neorg. Khim., Acad. USSR 27, 223 (1956) measured the heat content (H°-H°<sub>298.15</sub>) for PbF<sub>2</sub>(c) at temperatures 670-1180°K. and found that there is a  $\beta$  -  $\gamma$  transition at 725°K. Based on their heat content measurements, the  $C_p$  (725-1099°K.) values were derived as 24.3 ± 0.2 cal. deg.<sup>-1</sup> mole<sup>-1</sup> by the least square method. The  $C_p$  values, 298.15-725°K., were estimated to be 17.72 + 0.0154 (T - 298.15) cal. deg.<sup>-1</sup> mole<sup>-1</sup>, using their heat content measurements, 670-725°K., which were based on a mixture of  $\beta$  and  $\gamma$  as a guide.  $\Delta H_f^0$  298.15 (PbF<sub>2</sub>, c) was estimated so that the  $\Delta H_f^0$  values derived from vapor pressure data by use of the second and third law methods agree.

Transition Data.

$T_1$  adopted was determined by Benashek, Patsukova and Rassonkaya, loc. cit. They also found that there is a slow or irreversible  $T_2$  ( $\beta$  -  $\alpha$ ) transition at 613°K. which is also adopted here. The polymorphism of PbF<sub>2</sub>(c) has been reported by many investigators. However, the results were not in agreement. The enthalpy difference at 725°K. for PbF<sub>2</sub>( $\beta$ , c) and PbF<sub>2</sub>( $\beta$ , c) is  $\Delta H_f^0$ . The value of  $\Delta H_f^0$  was estimated such that it generated free energy functions which yielded better agreement between the second and third law values of  $\Delta H_f^0$  for PbF<sub>2</sub>(c) and PbF<sub>2</sub>( $\beta$ , c), see PbF<sub>2</sub>( $\beta$ ) table for details.

Feeling Data.

See PbF<sub>2</sub>( $\beta$ ) table for details.

Heat of Sublimation.

The difference between  $\Delta H_f^0$  298.15 for PbF<sub>2</sub>( $\beta$ ) and PbF<sub>2</sub>(c) is  $\Delta H_s^0$  298.15.

Log K<sub>P</sub>

T, °K.	C <sub>p</sub>	S°	-(H°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	$\Delta H_f^0$	$\Delta F_f^0$
100	0					
200	17.720	27.000	27.000	0.000	-161.800	-150.789
300	17.750	27.110	27.000	0.833	-161.793	-150.721
400	17.790	27.247	27.115	1.885	-161.863	-149.492
500	17.830	27.407	27.299	3.091	-161.937	-148.258
600	17.870	27.583	27.500	4.451	-162.019	-147.022
700	17.910	27.773	27.715	5.978	-162.103	-145.787
800	17.950	27.977	27.943	7.673	-162.193	-144.553
900	17.990	28.195	28.183	9.537	-162.293	-143.323
1000	18.030	28.427	28.432	11.581	-162.403	-142.103
1100	18.070	28.673	28.693	13.915	-162.523	-140.888
1200	18.110	28.933	28.923	16.449	-162.653	-139.688
1300	18.150	29.207	29.207	19.183	-162.793	-138.503
1400	18.190	29.495	29.495	22.117	-162.943	-137.333
1500	18.230	29.797	29.797	25.261	-163.103	-136.183
1600	18.270	30.113	30.113	28.625	-163.273	-135.053
1700	18.310	30.443	30.443	32.219	-163.453	-133.943
1800	18.350	30.787	30.787	36.043	-163.643	-132.853
1900	18.390	31.145	31.145	40.107	-163.843	-131.783
2000	18.430	31.517	31.517	44.421	-164.053	-130.733

LEAD DIFLUORIDE (PbF<sub>2</sub>) (LIQUID)

$S_{298.15}^{\circ} = 29.74$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -157.543$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^{\circ} = 4.16$  kcal. mole<sup>-1</sup>  
 $\Delta H_v^{\circ} = 37.49$  kcal. mole<sup>-1</sup>  
 $T_m = 1091^{\circ}\text{K.}$   
 $T_b = 1576^{\circ}\text{K.}$

Heat of Formation.

$\Delta H_f^{298.15}(l)$  was obtained from  $\Delta H_f^{298.15}(c)$  by adding  $\Delta H_m^{\circ}$  and the difference between  $H_m^{\circ}$  and  $H_l^{\circ}$  for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity for PbF<sub>2</sub>(l) was derived to be  $24 \pm 2$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> from the heat content measurements (1099-1160°K.) reported by E. I. Banašek, N. N. Pataukova and I. S. Rassonskaya, Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk SSSR 27, 223 (1956), by least square method. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

$T_m$  adopted was reported by H. V. Martenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922), and later confirmed by M. Blank and G. Petit, Compt. rend. 249, 1305 (1959). The value of  $\Delta H_m^{\circ}$  was taken from the latter which was determined by freezing point lowering in the PbF<sub>2</sub>-NaF system.  $T_m = 1099^{\circ}\text{K.}$  was reported by Banašek, Pataukova and Rassonskaya, loc. cit. The enthalpy difference for PbF<sub>2</sub>(l) and PbF<sub>2</sub>(c) at 1099°K. was derived to be 2.98 kcal. mole<sup>-1</sup> which was not adopted.

Vaporization Data.

$T_b$  was calculated as the temperature at which the free energy change of the reaction PbF<sub>2</sub>(l) → PbF<sub>2</sub>(g) approaches zero. The difference between  $\Delta H_f^{\circ}$  for PbF<sub>2</sub>(g) and PbF<sub>2</sub>(l) is  $\Delta H_v^{\circ}$ . Martenberg and Bosse, loc. cit. reported  $T_b = 1565^{\circ}\text{K.}$  for PbF<sub>2</sub>(l).

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0						
100	24.000	29.742	0.000	-157.543	-147.950	108.005
200	24.000	29.742	0.044	-157.525	-147.286	107.293
300	24.000	29.742	0.084	-156.547	-144.022	78.686
400	24.000	29.742	0.124	-155.627	-141.000	61.628
500	24.000	29.742	0.164	-154.749	-138.157	50.321
600	24.000	29.742	0.204	-153.907	-135.268	42.231
700	24.000	29.742	0.244	-153.095	-132.495	36.194
800	24.000	29.742	0.284	-152.313	-129.823	31.524
900	24.000	29.742	0.324	-151.561	-127.243	27.808
1000	24.000	29.742	0.364	-150.839	-124.742	24.783
1100	24.000	29.742	0.404	-150.147	-122.315	22.276
1200	24.000	29.742	0.444	-149.485	-119.956	20.165
1300	24.000	29.742	0.484	-148.853	-117.660	18.367
1400	24.000	29.742	0.524	-148.251	-115.419	16.816
1500	24.000	29.742	0.564	-147.679	-113.235	15.466
1600	24.000	29.742	0.604	-147.137	-111.098	14.282
1700	24.000	29.742	0.644	-146.625	-109.012	13.235
1800	24.000	29.742	0.684	-146.143	-106.965	12.305
1900	24.000	29.742	0.724	-145.691	-104.958	11.469
2000	24.000	29.742	0.764	-145.269	-102.980	10.718
2100	24.000	29.742	0.804	-144.877	-101.032	10.032
2200	24.000	29.742	0.844	-144.515	-99.114	9.402
2300	24.000	29.742	0.884	-144.183	-97.226	8.826
2400	24.000	29.742	0.924	-143.881	-95.368	8.304
2500	24.000	29.742	0.964	-143.609	-93.540	7.836

LEAD DIFLUORIDE (PbF<sub>2</sub>) (IDEAL GAS) MOL. WT. = 245.1868

Point Group C<sub>2v</sub>  
 $\Delta H_f^0 = [-106.2 \pm 1.3] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = [71.0] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{298.15} = [-106.8 \pm 1.3] \text{ kcal. mole}^{-1}$   
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	Deg.
[450] (1)	1
[120] (1)	1
[450] (1)	1

Bond Distance: Pb-F = 2.15 ± 0.02 Å  
 Bond Angle: F-Pb-F = [95]°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [4.56617 X 10<sup>-11</sup>] g.<sup>3</sup> cm.<sup>6</sup>

σ = 2

Heat of Formation.

The vapor pressures of PbF<sub>2</sub>(l) and PbF<sub>2</sub>(c) were determined by (1) H. V. Wartenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922) and (2) A. N. Nemesyanov and B. Z. Iofa, Zh. Neorg. Khim. 4, 486 (1959), respectively. Using these data the corresponding heats of vaporization were evaluated by both the second and third law methods. The results obtained are presented as follows.

Equilibrium Reaction	Second Law Value	Third Law Value	Drift, e.u.	Reference
PbF <sub>2</sub> (l) = PbF <sub>2</sub> (g)	51.74 ± 0.35	50.58 ± 0.2	-0.80 ± 0.30	(1)
PbF <sub>2</sub> (c) = PbF <sub>2</sub> (g)	54.29 ± 2.5	55.78 ± 2.8	+1.18 ± 2.85	(2)

The value of ΔH<sub>f</sub><sup>298.15</sup> for PbF<sub>2</sub>(g) adopted is -106.8 ± 1.3 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The bond distance was determined by P. A. Aikshin, V. P. Spiridonov and A. N. Khodchenkov, Zh. Fiz. Khim. 32, 1679 (1958). The bond angle was assumed to be the same as that in PbX<sub>2</sub>(g) where X = Cl, Br or I. The vibrational frequencies were calculated from force constants, K = 2.07 X 10<sup>5</sup> and K<sub>1/2</sub> = 6.90 X 10<sup>5</sup> dynes/cm., by use of Valence Force method. The values of force constants were estimated by comparison with those for PbF(g), CaF(g), MgF(g), CaF<sub>2</sub>(g) and MgF<sub>2</sub>(g). The three principal moments of inertia are: I<sub>A</sub> = 1.55584 X 10<sup>-36</sup>, I<sub>B</sub> = 1.10382 X 10<sup>-38</sup> and I<sub>C</sub> = 2.65976 X 10<sup>-36</sup> g.<sup>2</sup> cm.<sup>2</sup>

T, °K.	C <sub>v</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	9.766	58.831	3.438	-106.184	-106.184	-106.184	INFINITE
200	11.589	66.189	2.465	-107.429	-107.429	-107.429	234.630
298	12.603	71.029	1.493	-106.660	-106.660	-106.660	118.224
300	12.616	71.107	1.493	-106.660	-106.660	-106.660	79.834
400	13.115	74.513	0.623	-106.803	-106.803	-106.803	79.351
500	13.379	77.771	1.313	-106.935	-106.935	-106.935	48.890
600	13.533	80.225	2.639	-107.089	-107.089	-107.089	48.198
700	13.628	82.310	3.985	-107.265	-107.265	-107.265	40.391
800	13.693	84.143	5.343	-107.458	-107.458	-107.458	34.745
900	13.738	85.756	6.710	-107.668	-107.668	-107.668	30.502
1000	13.770	87.208	8.081	-107.895	-107.895	-107.895	27.195
1100	13.794	88.522	9.457	-108.138	-108.138	-108.138	24.544
1200	13.812	89.723	10.835	-108.395	-108.395	-108.395	22.371
1300	13.827	90.829	12.215	-108.668	-108.668	-108.668	20.556
1400	13.838	91.854	13.597	-108.958	-108.958	-108.958	19.018
1500	13.847	92.809	14.981	-109.265	-109.265	-109.265	17.697
1600	13.855	93.703	16.365	-109.589	-109.589	-109.589	16.550
1700	13.861	94.543	17.750	-109.930	-109.930	-109.930	15.544
1800	13.867	95.336	19.136	-110.288	-110.288	-110.288	14.655
1900	13.871	96.085	20.522	-110.663	-110.663	-110.663	13.864
2000	13.875	96.797	21.909	-111.055	-111.055	-111.055	13.153
2100	13.878	97.474	23.297	-111.464	-111.464	-111.464	12.513
2200	13.881	98.120	24.684	-111.889	-111.889	-111.889	11.971
2300	13.884	98.737	26.072	-112.330	-112.330	-112.330	11.524
2400	13.886	99.307	27.461	-112.788	-112.788	-112.788	11.074
2500	13.888	99.835	28.849	-113.264	-113.264	-113.264	10.723
2600	13.890	100.339	30.238	-113.757	-113.757	-113.757	6.930
2700	13.891	100.824	31.627	-114.266	-114.266	-114.266	8.677
2800	13.893	101.296	33.016	-114.791	-114.791	-114.791	8.193
2900	13.894	101.754	34.405	-115.332	-115.332	-115.332	7.743
3000	13.895	102.207	35.794	-115.889	-115.889	-115.889	7.323
3100	13.896	102.656	37.184	-116.463	-116.463	-116.463	6.930
3200	13.897	103.101	38.573	-117.054	-117.054	-117.054	6.562
3300	13.898	103.534	39.963	-117.662	-117.662	-117.662	6.216
3400	13.899	103.954	41.352	-118.287	-118.287	-118.287	5.890
3500	13.899	104.361	42.742	-118.930	-118.930	-118.930	5.583
3600	13.900	104.754	44.132	-119.591	-119.591	-119.591	5.292
3700	13.900	105.133	45.522	-120.269	-120.269	-120.269	5.017
3800	13.901	105.507	46.912	-120.964	-120.964	-120.964	4.756
3900	13.901	105.876	48.302	-121.675	-121.675	-121.675	4.508
4000	13.902	106.240	49.692	-122.402	-122.402	-122.402	4.272
4100	13.902	106.600	51.082	-123.145	-123.145	-123.145	4.047
4200	13.903	106.956	52.473	-123.904	-123.904	-123.904	3.833
4300	13.903	107.308	53.863	-124.679	-124.679	-124.679	3.628
4400	13.903	107.656	55.253	-125.470	-125.470	-125.470	3.432
4500	13.904	108.000	56.644	-126.277	-126.277	-126.277	3.244
4600	13.904	108.340	58.034	-127.099	-127.099	-127.099	3.065
4700	13.904	108.676	59.424	-127.937	-127.937	-127.937	2.892
4800	13.905	109.009	60.815	-128.791	-128.791	-128.791	2.727
4900	13.905	109.339	62.205	-129.661	-129.661	-129.661	2.568
5000	13.905	109.665	63.596	-130.547	-130.547	-130.547	2.414
5100	13.905	109.988	64.986	-131.449	-131.449	-131.449	2.267
5200	13.906	110.308	66.377	-132.367	-132.367	-132.367	2.126
5300	13.906	110.625	67.767	-133.301	-133.301	-133.301	1.988
5400	13.906	110.939	69.158	-134.250	-134.250	-134.250	1.856
5500	13.906	111.250	70.548	-135.215	-135.215	-135.215	1.729
5600	13.906	111.558	71.939	-136.196	-136.196	-136.196	1.605
5700	13.906	111.864	73.330	-137.193	-137.193	-137.193	1.486
5800	13.907	112.167	74.720	-138.206	-138.206	-138.206	1.371
5900	13.907	112.467	76.111	-139.235	-139.235	-139.235	1.260
6000	13.907	112.764	77.501	-140.280	-140.280	-140.280	1.152
6100	13.907	113.058	78.892	-141.341	-141.341	-141.341	1.047

IRON TRIFLUORIDE (FeF<sub>3</sub>) (CRYSTAL)

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100						
200						
298	21.750	23.500	0.000	-249.000	-232.393	170.341
300	21.800	23.500	0.000	-248.992	-232.290	169.215
400	23.633	30.477	2.423	-248.390	-226.812	162.918
500	27.865	35.584	4.711	-247.988	-221.467	96.799
600	23.140	39.778	7.011	-247.665	-216.194	78.745
700	23.440	43.367	9.340	-247.402	-210.969	65.864
800	23.740	46.517	11.699	-247.210	-205.781	54.211
900	24.040	49.330	14.088	-247.111	-200.608	48.712
1000	24.340	51.879	16.507	-247.176	-195.442	42.712
1100	24.640	54.212	18.956	-247.440	-190.249	37.797
1200	24.940	56.369	21.435	-247.470	-185.054	33.701
1300	25.240	58.377	23.944	-247.138	-179.865	30.237
1400	25.540	60.259	26.483	-246.799	-174.704	27.271
1500	25.840	62.031	29.052	-246.449	-169.565	24.704
1600	26.140	63.708	31.651	-246.092	-164.452	22.462
1700	26.440	65.302	34.280	-246.015	-159.355	20.485
1800	26.740	66.822	36.939	-245.730	-154.267	18.730
1900	27.040	68.276	39.628	-245.104	-149.009	17.139
2000	27.340	69.670	42.347	-248.631	-143.746	15.707

ΔH<sub>f,0</sub> = Unknown

ΔH<sub>f</sub><sup>o</sup> 298.15 = -249 ± 3 kcal. mole<sup>-1</sup>

ΔH<sub>s</sub><sup>o</sup> 298.15 = [52.8] kcal. mole<sup>-1</sup>

S<sub>298.15</sub> = [23.5 ± 2] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>s</sub> = [1200]°K.

Heat of Formation.

The equilibrium pressures for the reaction 2FeF<sub>3</sub>(c) + H<sub>2</sub>(g) = 2FeF<sub>2</sub>(c) + 2HF(g) have been measured at temperatures 623, 723 and 823°K. by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 1/5, 281 (1928). Using the reported data, the enthalpy change of the reaction was evaluated as 37.9 and 31.3 kcal. mole<sup>-1</sup> by the third and second law methods, respectively. The corresponding ΔH<sub>f</sub><sup>o</sup> 298.15 (FeF<sub>3</sub>, c) values are calculated to be -252.4 and -249.2 kcal. mole<sup>-1</sup>. The equilibrium constants for the reaction 2FeF<sub>3</sub>(c) + 3H<sub>2</sub>O(g) = Fe<sub>2</sub>O<sub>3</sub>(c) + 6HF(g) were determined by L. Domange, Ann. Chim., 7, 225 (1937). Based on the third law value of ΔH<sub>f</sub><sup>o</sup> 298.15, 62.0 kcal. mole<sup>-1</sup>, the ΔH<sub>f</sub><sup>o</sup> 298.15 (FeF<sub>3</sub>, c) was calculated as -237.4 kcal. mole<sup>-1</sup>. The value of ΔH<sub>f</sub><sup>o</sup> 298.15 for FeF<sub>3</sub>(c) is selected to be -249 ± 3 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The heat capacities of FeF<sub>3</sub>(c) at temperatures 100-450°K. were determined by H. Bizette, R. Mainard and J. Picard, Comp. rend. 5508 (1965). The results were presented graphically by plotting C<sub>p</sub> vs. T. The C<sub>p</sub> curve shows a peak at 367°K. An antiferromagnetic transition at about 394°K. was reported by E. O. Wollan, H. R. Child, W. C. Koehler and M. K. Wilkinson, Phys. Rev. 112, 1132 (1958). The heat capacities above 450°K. and S<sub>298.15</sub> were estimated by comparison with those for FeCl<sub>3</sub>(c) and AlF<sub>3</sub>(c).

Sublimation Data.

The phenomenon that FeF<sub>3</sub>(c) sublimes without fusion at temperatures near 1000°C has been observed and reported by Poulenc, Ann. Chim. phys. (7), 2, 1 (1894). Based on this data the value of T<sub>s</sub> was estimated. The value of heat of sublimation (ΔH<sub>s</sub><sup>o</sup> 298.15) was calculated using an estimated entropy of sublimation, ΔS<sub>s</sub><sup>o</sup> = 40 e.u. in order to have ΔF<sub>r</sub><sup>o</sup> = 0 for the reaction FeF<sub>3</sub>(c) = FeF<sub>3</sub>(g) at 1200°K.

Point Group [D<sub>3h</sub>]  
 $\Delta H_f^0 = [-195.5 \pm 5] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = [72.7] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{298.15} = [-196.2 \pm 5] \text{ kcal. mole}^{-1}$   
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
[600] (1)	[600] (2)
[250] (1)	[220] (2)

Bond Distance: Fe-F = [1.9] cm.<sup>-1</sup>  
 Bond Angle: F-Fe-F = [120]<sup>o</sup>  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [9.96723 X 10<sup>-114</sup>] g.<sup>3</sup> cm.<sup>6</sup>  
 $\sigma^r = [6]$

Heat of Formation

The value of  $\Delta H_f^{298.15} (\text{FeF}_3, \text{g})$  was calculated from  $\Delta H_f^{298.15}$  and  $\Delta H_f^{298.15}$  for FeF<sub>3</sub>(c). The value  $\Delta H_g^{298.15} = 65.5 \text{ kcal. mole}^{-1}$  was derived from  $\Delta H_g^{1200}$  (see FeF<sub>3</sub>(c) table for details).

Heat Capacity and Entropy

The molecular structure, bond distance and angle were estimated by comparison with those for AlF<sub>3</sub>(g). The vibrational frequencies were estimated by comparison with those for AlF<sub>3</sub>(g), TiF<sub>4</sub>(g) and ZrF<sub>4</sub>(g). The three principal moments of inertia are: I<sub>A</sub> = I<sub>B</sub> = 1.7081 X 10<sup>-38</sup> and I<sub>C</sub> = 3.4182 X 10<sup>-38</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	$-(F^o - H_{298}^o)/T$	H <sup>o</sup> - H <sub>298</sub> <sup>o</sup>	$\Delta H_f^o$	$\Delta F_f^o$	Log K <sub>p</sub>
0	6.00	INFINITE	-	3.539	- 195.499	- 195.499	INFINITE
100	10.577	58.479	85.163	2.668	- 195.774	- 195.371	426.963
200	13.644	76.640	74.043	1.445	- 196.022	- 194.867	212.030
298	15.656	72.690	72.690	.000	- 196.200	- 194.259	142.389
300	15.697	72.787	72.690	.029	- 196.203	- 194.247	141.002
400	17.027	77.500	73.423	1.670	- 196.343	- 193.578	105.758
500	17.856	81.396	74.560	3.418	- 196.481	- 192.866	84.298
600	18.389	84.702	75.982	5.232	- 196.644	- 192.128	69.979
700	18.742	87.565	77.436	7.090	- 196.852	- 191.358	59.742
800	18.986	89.954	78.863	8.977	- 197.132	- 190.557	52.055
900	19.150	92.331	80.237	10.885	- 197.514	- 189.713	46.066
1000	19.288	94.357	81.549	12.807	- 198.076	- 188.820	41.264
1100	19.395	96.200	82.799	14.741	- 198.855	- 187.895	37.321
1200	19.460	97.890	84.987	16.684	- 199.821	- 186.831	34.025
1300	19.491	99.450	87.117	18.633	- 200.960	- 185.772	31.230
1400	19.506	100.898	89.193	20.587	- 202.258	- 184.694	28.831
1500	19.505	102.250	91.117	22.546	- 203.716	- 183.600	26.749
1600	19.497	103.516	92.811	24.508	- 205.335	- 182.488	24.925
1700	19.485	104.707	94.335	26.473	- 207.122	- 181.350	23.313
1800	19.468	105.852	95.682	28.443	- 209.079	- 180.184	21.876
1900	19.446	106.957	96.891	30.419	- 211.206	- 179.007	20.567
2000	19.420	108.008	97.971	32.381	- 213.501	- 177.886	19.383
2100	19.394	109.070	98.911	34.356	- 216.060	- 176.946	18.310
2200	19.371	110.167	99.776	36.338	- 218.883	- 176.148	17.332
2300	19.357	111.267	100.583	38.333	- 221.974	- 175.482	16.437
2400	19.352	112.315	101.346	40.336	- 225.336	- 174.945	15.615
2500	19.354	113.315	102.071	42.357	- 228.967	- 174.528	14.857
2600	19.362	114.261	102.751	44.394	- 232.876	- 174.224	14.155
2700	19.378	115.157	103.381	46.443	- 237.063	- 174.024	13.503
2800	19.403	116.000	103.966	48.500	- 241.526	- 173.924	12.897
2900	19.430	116.793	104.500	50.572	- 246.263	- 173.924	12.331
3000	19.464	117.533	105.000	52.652	- 251.272	- 174.024	11.801
3100	19.500	118.223	105.471	54.733	- 256.553	- 174.224	11.300
3200	19.538	118.863	105.911	56.813	- 262.106	- 174.528	10.839
3300	19.578	119.453	106.311	58.900	- 267.933	- 174.924	10.417
3400	19.619	120.000	106.671	61.000	- 274.046	- 175.424	10.025
3500	19.662	120.516	107.000	63.113	- 280.443	- 176.024	9.651
3600	19.708	121.000	107.311	65.233	- 287.126	- 176.724	9.293
3700	19.756	121.453	107.581	67.363	- 294.093	- 177.524	8.951
3800	19.806	121.871	107.811	69.500	- 301.346	- 178.424	8.623
3900	19.858	122.253	108.000	71.750	- 308.883	- 179.424	8.307
4000	19.912	122.600	108.153	74.113	- 316.716	- 180.524	8.001
4100	19.968	122.916	108.271	76.583	- 324.853	- 181.724	7.703
4200	20.026	123.193	108.353	79.163	- 333.293	- 183.024	7.413
4300	20.086	123.433	108.393	81.753	- 342.043	- 184.424	7.129
4400	20.148	123.633	108.393	84.353	- 351.103	- 185.924	6.851
4500	20.212	123.793	108.353	86.963	- 360.473	- 187.524	6.583
4600	20.278	123.913	108.271	89.583	- 370.153	- 189.224	6.325
4700	20.346	124.000	108.153	92.213	- 380.153	- 191.024	6.077
4800	20.416	124.053	108.000	94.853	- 390.383	- 192.924	5.839
4900	20.488	124.071	107.811	97.500	- 400.843	- 194.924	5.611
5000	20.562	124.053	107.581	100.163	- 411.533	- 197.024	5.393
5100	20.638	124.000	107.311	102.843	- 422.453	- 199.224	5.185
5200	20.716	123.913	107.000	105.543	- 433.603	- 201.524	4.987
5300	20.796	123.793	106.671	108.263	- 445.083	- 203.924	4.799
5400	20.878	123.633	106.311	111.000	- 456.893	- 206.424	4.621
5500	20.962	123.433	105.911	113.753	- 468.933	- 209.024	4.453
5600	21.048	123.193	105.471	116.523	- 481.203	- 211.724	4.295
5700	21.136	122.913	105.000	119.300	- 493.703	- 214.524	4.147
5800	21.226	122.600	104.500	122.093	- 506.433	- 217.424	4.009
5900	21.318	122.253	104.000	124.900	- 519.393	- 220.424	3.881
6000	21.412	121.871	103.516	127.723	- 532.583	- 223.524	3.763

MAGNESIUM DIFLUORIDE, DIMERIC (MgF<sub>2</sub>)<sub>2</sub> (IDEAL GAS)

$\Delta H_f^0 = -609.5 \pm 3.4 \text{ kcal. mole}^{-1}$

$\Delta H_f^0 = -411.9 \pm 3.4 \text{ kcal. mole}^{-1}$

Point Group [D<sub>2h</sub>]

S<sub>298.15</sub> = [74.63] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
[430] (1)	[390] (1)
[280] (1)	[660] (1)
[330] (1)	[930] (1)
[250] (1)	[700] (1)
[720] (1)	[500] (1)

Bond Distance: Mg-F = [1.77] Å

Bond Angle: F-Mg-F' = [135]° Mg-F'-Mg = [90]° F'-Mg-F' = [90]°

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [5.5711 × 10<sup>-11</sup>] g.<sup>3</sup> cm.<sup>6</sup>

σ = 4

Heat of Formation.

The enthalpy change, ΔH<sub>f</sub><sup>0</sup> = 30 kcal. mole<sup>-1</sup>, for the reaction MgF<sub>2</sub>(c) + MgF<sub>2</sub>(g) = (MgF<sub>2</sub>)<sub>2</sub>(g) was determined by J. Berkowitz and J. R. Marquart, J. Chem. Phys. **32**, 1853 (1962). Hence the heat of formation for (MgF<sub>2</sub>)<sub>2</sub>(g) was calculated.

Heat Capacity and Entropy.

The molecular structure was assumed to be planar. The two Mg atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two F atoms. The bond distance between Mg and F atom was estimated to be the same as that in the MgF<sub>2</sub>(g) molecule. The vibrational frequencies were estimated by comparison with those for MgF(g) and (NaF)<sub>2</sub>. The vibrational frequencies for (NaF)<sub>2</sub> were calculated by J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960). The three principal moments are 9.8896 × 10<sup>-39</sup>, 7.02735 × 10<sup>-38</sup>, and 8.01631 × 10<sup>-38</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>v</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	10.361	57.433	4.190	-409.478	-409.478	INFINITE
200	17.222	66.733	90.824	-410.325	-407.475	890.535
298	22.287	74.629	1.957	-411.667	-404.363	441.889
			.000	-411.900	-400.602	293.649
300	22.361	74.767	.041	-411.909	-400.532	291.788
400	25.489	81.667	2.447	-412.271	-396.682	216.737
500	27.376	87.574	5.098	-412.518	-392.753	171.672
600	28.559	92.678	7.899	-412.719	-388.782	141.614
700	29.337	97.142	10.797	-412.909	-384.775	120.132
800	29.671	101.097	13.759	-413.129	-380.745	104.015
900	30.251	104.638	16.766	-413.396	-376.680	91.470
1000	30.530	107.841	19.805	-413.665	-372.588	81.349
1100	30.741	110.761	22.869	-413.939	-368.455	73.042
1200	30.903	113.443	25.952	-414.214	-364.284	66.114
1300	31.031	115.922	29.049	-414.491	-360.076	60.288
1400	31.134	118.225	32.157	-414.769	-355.831	55.001
1500	31.217	120.376	35.275	-415.048	-351.551	50.084
1600	31.286	122.393	38.400	-415.326	-347.235	45.695
1700	31.343	124.282	41.532	-415.604	-342.884	41.822
1800	31.391	126.045	44.670	-415.882	-338.497	38.440
1900	31.432	127.683	47.813	-416.160	-334.074	35.529
2000	31.467	129.200	50.959	-416.438	-329.615	32.960
2100	31.497	130.612	54.109	-416.716	-325.120	30.718
2200	31.523	131.923	57.264	-416.994	-320.591	28.856
2300	31.546	133.138	60.423	-417.272	-316.028	27.303
2400	31.566	134.261	63.585	-417.550	-311.433	26.003
2500	31.584	135.303	66.751	-417.828	-306.807	24.915
2600	31.600	136.271	69.920	-418.106	-302.150	24.011
2700	31.614	137.171	73.091	-418.384	-297.463	23.278
2800	31.626	138.004	76.263	-418.662	-292.745	22.691
2900	31.638	138.775	79.436	-418.940	-288.000	22.148
3000	31.648	139.490	82.610	-419.218	-283.231	21.644
3100	31.657	140.154	85.785	-419.496	-278.438	21.174
3200	31.666	140.773	88.961	-419.774	-273.622	20.734
3300	31.673	141.352	92.137	-420.052	-268.783	20.321
3400	31.680	141.896	95.313	-420.330	-263.921	19.931
3500	31.687	142.410	98.489	-420.608	-259.036	19.561
3600	31.693	142.899	101.665	-420.886	-254.128	19.218
3700	31.698	143.368	104.841	-421.164	-249.197	18.898
3800	31.703	143.813	108.017	-421.442	-244.243	18.600
3900	31.708	144.231	111.193	-421.720	-239.265	18.324
4000	31.712	144.629	114.369	-422.000	-234.263	18.069
4100	31.716	145.004	117.545	-422.280	-229.237	17.834
4200	31.720	145.358	120.721	-422.560	-224.187	17.614
4300	31.723	145.695	123.897	-422.840	-219.113	17.407
4400	31.726	146.014	127.073	-423.120	-214.016	17.212
4500	31.729	146.317	130.249	-423.400	-208.900	17.028
4600	31.732	146.604	133.425	-423.680	-203.765	16.854
4700	31.735	146.877	136.601	-423.960	-198.611	16.690
4800	31.737	147.137	139.777	-424.240	-193.437	16.535
4900	31.739	147.385	142.953	-424.520	-188.244	16.389
5000	31.742	147.622	146.129	-424.800	-183.033	16.251
5100	31.744	147.848	149.305	-425.080	-177.805	16.120
5200	31.746	148.064	152.481	-425.360	-172.560	16.000
5300	31.747	148.271	155.657	-425.640	-167.299	15.889
5400	31.749	148.469	158.833	-425.920	-162.023	15.787
5500	31.751	148.658	162.009	-426.200	-156.733	15.693
5600	31.752	148.839	165.185	-426.480	-151.429	15.607
5700	31.754	149.012	168.361	-426.760	-146.111	15.528
5800	31.755	149.178	171.537	-427.040	-140.780	15.455
5900	31.757	149.336	174.713	-427.320	-135.435	15.387
6000	31.758	149.487	177.889	-427.600	-130.077	15.324

(IDEAL GAS)

SULFUR TETRAFLUORIDE (SF<sub>4</sub>)

Point Group C<sub>2v</sub>

S<sup>0</sup><sub>298.15</sub> = 69.236 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Ground State Quantum Weight = 1

ΔH<sub>f</sub><sup>0</sup> = -172.2 ± 2.5 kcal. mole<sup>-1</sup>

ΔH<sub>f</sub><sup>0</sup> 298.15 = -174.1 ± 2.5 kcal. mole<sup>-1</sup>

Vibrational Frequencies and Degeneracies

ν, cm. <sup>-1</sup>	ω, cm. <sup>-1</sup>
889 (1)	867 (1)
715 (1)	532 (1)
557 (1)	728 (1)
235 (1)	463 (1)
645 (1)	

Bond Distances: Equatorial S-P = 1.545 Å

Polar S-P = 1.646 Å

Bond Angles: Equatorial F-S-F = 101° 33'

Polar F-S-F = 186° 56'

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 6720 X 10<sup>-117</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

J. D. Vaughn and E. L. Muettterties, J. Phys. Chem. 64, 1787 (1960) measured the enthalpy of reaction of SF<sub>4</sub> and H<sub>2</sub>, both with SF<sub>4</sub> in excess to form HF and S and with H<sub>2</sub> in excess to form HF and H<sub>2</sub>S. Their results are not of highest accuracy due to difficulties in characterization of the SF<sub>4</sub> sample, corrections for non-ideality of HF vapor, solubility of H<sub>2</sub>, H<sub>2</sub>S, and SF<sub>4</sub> in condensed HF, and analysis for unreacted SF<sub>4</sub>. Corrected to the current JANAP heat of formation of HF monomer, their work yields ΔH<sub>f</sub><sup>0</sup> 298(g) = -174.4 ± 2.5 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

Raman and infrared spectra were obtained by R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc. 52, 1052 (1956). Their vibrational assignment is adopted except for one frequency for which they left a choice of 401 cm.<sup>-1</sup> or 645 cm.<sup>-1</sup>. K. Venkateswari and M. G. Krishna Pillai, Optics and Spectroscopy 11, 26 (1961) found 645 cm.<sup>-1</sup> more satisfactory in deriving force constants for SF<sub>4</sub> and the choice of 645 cm.<sup>-1</sup> is made on this basis. W. M. Tolles and W. D. Gwinn, J. Chem. Phys. 35, 1119 (1962) investigated the microwave spectrum and derived moments of inertia and structure given above. Electron diffraction data by K. Kimura and S. H. Bauer, J. Chem. Phys. 39, 3172 (1963) are in excellent agreement and less precise electron diffraction work by V. C. Ewing and L. E. Sutton, Trans. Faraday Soc. 59, 1241 (1963) is in agreement within experimental error. Nuclear magnetic resonance studies by F. A. Cotton, J. W. George, and J. S. Waugh, J. Chem. Phys. 28, 994 (1958) and by E. L. Muettterties and W. D. Phillips, J. Am. Chem. Soc. 81, 1084 (1959) indicate the presence of non-equivalent fluorine atoms, confirming the C<sub>2v</sub> structure indicated by the Raman and infrared spectrum, microwave spectrum, and electron diffraction. The three principal moments of inertia are I<sub>A</sub> = 1.2553 X 10<sup>-38</sup>, I<sub>B</sub> = 2.0539 X 10<sup>-38</sup> and I<sub>C</sub> = 2.6065 X 10<sup>-38</sup> g. cm.<sup>2</sup>

Log K<sub>P</sub>

ΔF<sup>0</sup>

ΔH<sub>f</sub><sup>0</sup>

H<sup>0</sup> - H<sup>298</sup>

S<sup>0</sup> - (F<sup>0</sup> - H<sup>298</sup>)/T

C<sub>p</sub>

T, K.

T, K.	C <sub>p</sub>	S <sup>0</sup> - (F <sup>0</sup> - H <sup>298</sup> )/T	H <sup>0</sup> - H <sup>298</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sup>0</sup>	Log K <sub>P</sub>
0	∞	∞	∞	∞	∞	∞
100	9.019	55.937	81.525	-172.208	-172.208	INFINITE
200	12.948	63.284	70.665	-170.998	-170.998	371.731
298	16.949	69.236	60.000	-166.965	-166.965	182.442
300	17.013	69.236	60.000	-163.514	-163.514	119.940
400	19.786	74.644	3.955	-159.918	-159.918	119.114
500	21.539	79.263	3.955	-156.117	-156.117	87.371
600	22.666	83.297	6.169	-152.233	-152.233	68.235
700	23.417	86.851	8.475	-148.284	-148.284	55.448
800	23.936	90.014	10.845	-145.603	-145.603	46.294
900	24.308	92.856	13.258	-143.183	-143.183	39.775
1000	24.582	95.431	15.703	-140.981	-140.981	34.039
1100	24.790	97.785	18.172	-138.867	-138.867	29.456
1200	24.950	99.949	20.659	-136.865	-136.865	25.712
1300	25.077	101.851	23.161	-134.970	-134.970	22.595
1400	25.178	103.613	25.674	-133.183	-133.183	19.961
1500	25.260	105.253	28.196	-131.504	-131.504	17.802
1600	25.328	107.186	30.725	-130.873	-130.873	16.051
1700	25.385	108.723	33.261	-130.340	-130.340	14.640
1800	25.433	110.175	35.802	-130.012	-130.012	13.415
1900	25.473	111.552	38.348	-129.844	-129.844	12.346
2000	25.508	112.859	40.897	-129.826	-129.826	11.419
2100	25.538	114.104	43.449	-129.920	-129.920	10.619
2200	25.564	115.293	46.004	-130.121	-130.121	9.921
2300	25.587	116.436	48.562	-130.426	-130.426	9.316
2400	25.607	117.534	51.121	-130.834	-130.834	8.781
2500	25.624	118.585	53.683	-131.344	-131.344	8.301
2600	25.638	119.597	56.246	-131.956	-131.956	7.871
2700	25.649	120.570	58.811	-132.670	-132.670	7.491
2800	25.657	121.471	61.377	-133.486	-133.486	7.161
2900	25.663	122.372	63.944	-134.404	-134.404	6.881
3000	25.668	123.243	66.513	-135.424	-135.424	6.651
3100	25.672	124.085	69.082	-136.546	-136.546	6.471
3200	25.676	124.901	71.652	-137.770	-137.770	6.341
3300	25.679	125.693	74.223	-139.096	-139.096	6.261
3400	25.681	126.460	76.795	-140.524	-140.524	6.226
3500	25.682	127.206	79.367	-142.054	-142.054	6.206
3600	25.683	127.931	81.940	-143.686	-143.686	6.196
3700	25.684	128.636	84.514	-145.420	-145.420	6.196
3800	25.685	129.322	87.088	-147.256	-147.256	6.196
3900	25.686	129.991	89.662	-149.194	-149.194	6.196
4000	25.687	130.643	92.237	-151.232	-151.232	6.196
4100	25.688	131.279	94.812	-153.370	-153.370	6.196
4200	25.689	131.900	97.386	-155.608	-155.608	6.196
4300	25.690	132.506	99.964	-157.946	-157.946	6.196
4400	25.691	133.098	102.541	-160.384	-160.384	6.196
4500	25.692	133.677	105.118	-162.922	-162.922	6.196
4600	25.693	134.244	107.695	-165.560	-165.560	6.196
4700	25.694	134.798	110.272	-168.298	-168.298	6.196
4800	25.695	135.341	112.850	-171.136	-171.136	6.196
4900	25.696	135.871	115.427	-174.074	-174.074	6.196
5000	25.697	136.393	118.005	-177.112	-177.112	6.196
5100	25.698	136.904	120.584	-180.250	-180.250	6.196
5200	25.699	137.404	123.161	-183.488	-183.488	6.196
5300	25.700	137.893	125.738	-186.826	-186.826	6.196
5400	25.701	138.371	128.315	-190.264	-190.264	6.196
5500	25.702	138.838	130.892	-193.802	-193.802	6.196
5600	25.703	139.294	133.469	-197.440	-197.440	6.196
5700	25.704	139.739	136.046	-201.178	-201.178	6.196
5800	25.705	140.173	138.623	-205.016	-205.016	6.196
5900	25.706	140.597	141.200	-208.954	-208.954	6.196
6000	25.707	141.011	143.777	-212.992	-212.992	6.196

$\Delta H_f^{\circ} 0 = -194.31 \pm 1.0 \text{ kcal. mole}^{-1}$

$\Delta H_f^{\circ} 298.15 = -196.35 \pm 1.0 \text{ kcal. mole}^{-1}$

Point Group C<sub>4v</sub>

$S_{298.15}^{\circ} = 80.06 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies	
$\omega_j, \text{cm.}^{-1}$	$\omega_j, \text{cm.}^{-1}$
710 (1)	575 (1)
593 (1)	[257](1)
318 (1)	273 (1)
	640 (2)
	372 (2)
	189 (2)

Bond Distance: I-P(equatorial) = [1.86] Å I-P(axial) = [1.75] Å

Bond Angle: P(equatorial)-I-P(equatorial) = [90°] and P(axial)-I-P(equatorial) = [90°]

Product of the Moment of Inertia:  $I_A I_B I_C = [4.103831 \times 10^{-113}] \text{g.}^3 \text{cm.}^6$

Heat of Formation.

A. A. Woolf, J. Chem. Soc., 231 (1951)(Source 1) measured the heat of hydrolysis of IP<sub>5</sub>(l) at 291°K. (reaction (1)) and also the alkaline heat of hydrolysis of IP<sub>5</sub>(l) at 291°K. (reaction (2)). The  $\Delta H_f^{\circ} 298.15 = 10.25 \text{ kcal. mole}^{-1}$  was obtained from the vapor pressure data over the liquid (288-345°K.) measured by O. Ruff and A. Braide, Z. anorg. allgem. Chem. 220, 43 (1934) (Source 2, reaction (3)). Second law analysis was used assuming  $\Delta C_p = -12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  for IP<sub>5</sub>(l) → IP<sub>5</sub>(g). The auxiliary heats of formation were obtained from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties" Part 1, NBS Technical Note 270-1 October 1965 and V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes" NBSRS - NBS 2, April 1965.

Source	Reaction	$\Delta H_f^{\circ} 291 \text{ kcal. mole}^{-1}$	$\Delta H_f^{\circ} 298.15 \text{ kcal. mole}^{-1}$	$\Delta H_f^{\circ} 298.15 \text{ kcal. mole}^{-1}$
1	(1) IP <sub>5</sub> (l) + 3H <sub>2</sub> O(l) =			
	5HF(250 H <sub>2</sub> O) + HIO <sub>3</sub> (1250 H <sub>2</sub> O)	-22.05	-22.64	(10.25)
1	(2) IP <sub>5</sub> (l) + 6KOH(220 H <sub>2</sub> O) =			
	5KF(250 H <sub>2</sub> O) + KIO <sub>3</sub> (1250 H <sub>2</sub> O) + 3H <sub>2</sub> O(l)	-118.9	-118.7	(10.25)
2	(3) IP <sub>5</sub> (l) → IP <sub>5</sub> (g)			10.25±0.14

Heat Capacity and Entropy.

G. M. Begun, W. H. Fletcher and D. P. Smith, J. Chem. Phys. 42, 2236 (1965) report the infrared (gas phase) and Raman (liquid phase) spectra and correlate the observations by means of normal coordinate calculations for similar molecules BrF<sub>5</sub>, IP<sub>5</sub>, ClF<sub>5</sub>, and XeOF<sub>4</sub>. The fundamental frequencies are taken from Begun, et al. Raman values from the liquid were used for the infrared inactive fundamentals  $\nu_4$  and  $\nu_6$  and for  $\nu_5$  which has yet to be observed in the infrared spectra of the gas. One Raman active frequency, presumably  $\nu_5$ , is not observed in any of the four molecules. The value  $\nu_5 = 257 \text{ cm.}^{-1}$  was obtained from the normal coordinate calculation. A tetragonal pyramidal structure (C<sub>4v</sub> symmetry) with the above parameters was assumed by Begun, et al., in the analysis of the spectra. The normal coordinate calculation gave close agreement with the observed spectra, suggesting that the actual structure is close to that assumed. The three principal moments of inertia are:  $I_A = 3.06607 \times 10^{-38}$ ,  $I_B = 3.06607 \times 10^{-38}$ , and  $I_C = 4.36541 \times 10^{-38} \text{ g. cm.}^2$

T, °K.	C <sub>p</sub>	S°	-(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	12.542	54.873	4.809	-194.309	-194.309	-194.309	INFINITE
200	20.153	71.666	3.883	-195.685	-195.685	-195.685	416.488
298	24.670	80.061	2.221	-196.162	-196.162	-196.162	202.527
			0.500	-196.352	-196.352	-196.352	131.824
300	24.732	80.214	0.546	-196.353	-196.353	-196.353	131.037
400	27.248	87.709	2.657	-198.253	-198.253	-198.253	95.238
500	28.679	93.957	5.460	-203.229	-203.229	-203.229	73.370
600	29.545	99.268	8.531	-202.843	-202.843	-202.843	58.578
700	30.101	103.867	11.358	-202.436	-202.436	-202.436	48.032
800	30.477	107.913	14.389	-202.021	-202.021	-202.021	40.140
900	30.742	111.519	17.450	-201.602	-201.602	-201.602	34.014
1000	30.935	114.768	20.535	-201.182	-201.182	-201.182	29.124
1100	31.080	117.724	23.636	-200.765	-200.765	-200.765	25.131
1200	31.192	120.433	26.750	-200.348	-200.348	-200.348	21.810
1300	31.279	122.933	29.873	-199.936	-199.936	-199.936	19.005
1400	31.349	125.254	33.005	-199.528	-199.528	-199.528	16.607
1500	31.405	127.419	36.143	-199.124	-199.124	-199.124	14.532
1600	31.452	129.447	39.285	-198.726	-198.726	-198.726	12.721
1700	31.490	131.355	42.433	-198.332	-198.332	-198.332	11.126
1800	31.523	133.156	45.583	-197.945	-197.945	-197.945	9.711
1900	31.551	134.861	48.737	-197.560	-197.560	-197.560	8.447
2000	31.574	136.480	51.893	-197.182	-197.182	-197.182	7.312
2100	31.594	138.021	55.052	-196.809	-196.809	-196.809	6.287
2200	31.612	139.491	58.212	-196.442	-196.442	-196.442	5.357
2300	31.628	140.897	61.374	-196.080	-196.080	-196.080	4.509
2400	31.641	142.243	64.538	-195.724	-195.724	-195.724	3.733
2500	31.653	143.535	67.702	-195.375	-195.375	-195.375	3.021
2600	31.664	144.777	70.868	-195.031	-195.031	-195.031	2.365
2700	31.673	145.972	74.035	-194.691	-194.691	-194.691	1.758
2800	31.682	147.124	77.203	-194.357	-194.357	-194.357	1.196
2900	31.689	148.236	80.371	-194.029	-194.029	-194.029	0.673
3000	31.696	149.310	83.541	-193.709	-193.709	-193.709	0.186
3100	31.702	150.350	86.711	-193.392	-193.392	-193.392	-0.268
3200	31.707	151.357	89.882	-193.082	-193.082	-193.082	-0.684
3300	31.713	152.329	93.052	-192.777	-192.777	-192.777	-1.084
3400	31.718	153.270	96.224	-192.476	-192.476	-192.476	-1.469
3500	31.722	154.178	99.390	-192.178	-192.178	-192.178	-1.823
3600	31.726	155.049	102.568	-191.897	-191.897	-191.897	-2.156
3700	31.730	155.891	105.747	-191.616	-191.616	-191.616	-2.470
3800	31.733	156.698	108.914	-191.339	-191.339	-191.339	-2.768
3900	31.736	157.473	112.088	-191.071	-191.071	-191.071	-3.049
4000	31.739	158.216	115.261	-190.806	-190.806	-190.806	-3.317
4100	31.742	158.929	118.435	-190.549	-190.549	-190.549	-3.571
4200	31.744	159.614	121.610	-190.297	-190.297	-190.297	-3.813
4300	31.747	160.271	124.784	-190.048	-190.048	-190.048	-4.043
4400	31.749	160.911	127.959	-189.810	-189.810	-189.810	-4.262
4500	31.751	162.175	131.134	-189.574	-189.574	-189.574	-4.472
4600	31.753	162.872	134.309	-189.344	-189.344	-189.344	-4.672
4700	31.754	163.555	137.485	-189.121	-189.121	-189.121	-4.863
4800	31.756	164.224	140.660	-188.902	-188.902	-188.902	-5.046
4900	31.758	164.879	143.836	-188.691	-188.691	-188.691	-5.222
5000	31.759	165.520	147.012	-188.486	-188.486	-188.486	-5.390
5100	31.760	166.141	150.188	-188.285	-188.285	-188.285	-5.551
5200	31.762	166.766	153.364	-188.091	-188.091	-188.091	-5.707
5300	31.763	167.375	156.540	-187.902	-187.902	-187.902	-5.856
5400	31.764	167.961	159.716	-187.721	-187.721	-187.721	-5.999
5500	31.765	168.548	162.893	-187.543	-187.543	-187.543	-6.137
5600	31.766	169.120	166.069	-187.374	-187.374	-187.374	-6.270
5700	31.767	169.682	169.246	-187.210	-187.210	-187.210	-6.398
5800	31.768	170.235	172.423	-187.048	-187.048	-187.048	-6.522
5900	31.769	170.778	175.600	-186.895	-186.895	-186.895	-6.641
6000	31.770	171.312	178.777	-186.747	-186.747	-186.747	-6.757

Mar. 31, 1962; Dec. 31, 1963; Mar. 31, 1965



Point Group O<sub>h</sub>  
 $\Delta H_f^0 = -288.46 \pm 0.24$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = 69.713$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $S_{298.15}^0 = 291.79 \pm 0.24$  kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
770 (1)	345 (3)
640 (2)	615 (3)
522 (3)	947 (3)

Bond Length = 1.564 Å  
 Bond Angle: F-S-F = 90°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 29,400 X 10<sup>-117</sup> g. cm.<sup>2</sup>

Heat of Formation

P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard, Preprint of Paper XIV on Fluorine Bomb Calorimetry, July, 1965, measured the enthalpy of combustion of rhombic sulfur in fluorine. Their result yields  $\Delta H_f^0 = -291.79 \pm 0.24$  kcal. mole<sup>-1</sup>. P. Gross, C. Haymen, and D. L. Levi, XVIII Intern. Congr. Pure and Appl. Chem., Abstr. 1, 90 (1959), reported -289.5 kcal. mole<sup>-1</sup> also based on direct combination of the elements. O'Hare, Settle, and Hubbard mentioned a private communication from Dr. Gross indicating -289.5 kcal. mole<sup>-1</sup> may be in error due to oxygen in the fluorine used and preliminary results of a redetermination are in better agreement with -291.79 kcal. mole<sup>-1</sup>. D. M. Yost and W. H. Claussen, J. Am. Chem. Soc. 55, 887 (1933) determined -262 kcal. mole<sup>-1</sup>, again by direct reaction of the elements, which now appears too low. The work of O'Hare et al., loc. cit., is adopted.

Heat Capacity and Entropy

V. C. Ewing and L. E. Sutton, Trans. Faraday Soc. 59, 124 (1963) measured the bond length adopted here by the electron diffraction technique. Earlier less accurate work by the same method by H. Braune and S. Knoke, Z. physik. Chem. B21, 297 (1935) and L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. USA 19, 68 (1933) is in agreement within experimental error. T. E. Morsy, Ber. Bunsenges Physik. Chem. 68, 277 (1964) reviewed the literature on Raman and infrared spectra. Frequencies given here differ slightly from his selection because more weight was given to the Raman frequencies of C. W. Gullikson, J. R. Nielsen, and A. T. Stair, Jr., J. Mol. Spectroscopy 1, 151 (1957). Calculated functions by Morsy loc. cit. are in reasonable agreement with the present work.

A. Eucken and E. Schröder, Z. physik. Chem. 41B, 307 (1936) measured low temperature thermal data from which K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961) calculated  $S_{298}^0 = 70.3 \pm 0.7$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> which agrees within experimental error with the spectroscopic result.

The three principal moments of inertia are I<sub>A</sub> = I<sub>B</sub> = I<sub>C</sub> = 3.0863 X 10<sup>-38</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	9.020	53.312	4.053	-288.460	-288.460	-288.460	INFINITE
200	16.505	61.796	3.234	-289.890	-282.716	-282.716	617.846
298	23.224	69.713	0.000	-291.790	-275.026	-266.966	300.520
300	23.329	69.857	0.043	-291.799	-266.813	-266.813	194.364
400	30.475	77.237	2.619	-292.632	-258.408	-258.408	141.181
500	34.807	83.763	5.358	-293.052	-249.802	-249.802	109.183
600	38.254	89.595	8.727	-293.236	-241.130	-241.130	87.627
700	41.000	94.670	12.047	-293.269	-232.446	-232.446	72.500
800	43.224	99.239	15.469	-293.170	-224.997	-224.997	61.563
900	45.067	103.354	18.984	-293.004	-218.862	-218.862	52.173
1000	46.587	107.091	22.511	-292.788	-213.900	-213.900	44.752
1100	47.829	110.509	26.097	-292.532	-209.188	-209.188	38.690
1200	48.834	113.656	29.744	-292.244	-204.774	-204.774	33.645
1300	49.649	116.569	33.434	-291.932	-200.618	-200.618	29.583
1400	50.314	119.281	37.161	-291.604	-196.670	-196.670	26.453
1500	50.867	121.816	40.927	-291.260	-192.988	-192.988	23.880
1600	51.334	124.192	44.734	-290.900	-189.518	-189.518	21.680
1700	51.734	126.436	48.574	-290.524	-186.318	-186.318	19.795
1800	52.082	128.554	52.446	-290.132	-183.334	-183.334	18.173
1900	52.394	130.561	56.346	-289.724	-180.518	-180.518	16.767
2000	52.674	132.469	60.269	-289.300	-177.838	-177.838	15.536
2100	52.934	134.286	64.211	-288.860	-175.352	-175.352	14.441
2200	53.174	136.020	68.169	-288.404	-173.018	-173.018	13.460
2300	53.394	137.680	72.139	-287.932	-170.798	-170.798	12.573
2400	53.594	139.270	76.116	-287.444	-168.670	-168.670	11.760
2500	53.774	140.797	80.196	-286.940	-166.618	-166.618	11.000
2600	53.934	142.264	84.274	-286.420	-164.618	-164.618	10.290
2700	54.074	143.678	88.346	-285.884	-162.744	-162.744	9.630
2800	54.194	145.040	92.406	-285.332	-160.978	-160.978	9.010
2900	54.294	146.356	96.446	-284.764	-159.300	-159.300	8.430
3000	54.374	147.627	100.466	-284.180	-157.698	-157.698	7.890
3100	54.434	148.858	104.466	-283.584	-156.158	-156.158	7.390
3200	54.474	150.049	108.446	-282.976	-154.670	-154.670	6.930
3300	54.494	151.201	112.396	-282.356	-153.230	-153.230	6.510
3400	54.494	152.316	116.316	-281.724	-151.838	-151.838	6.130
3500	54.474	153.396	120.196	-281.080	-150.478	-150.478	5.790
3600	54.434	154.441	124.036	-280.424	-149.148	-149.148	5.490
3700	54.374	155.454	127.836	-279.756	-147.838	-147.838	5.230
3800	54.294	156.427	131.596	-279.076	-146.538	-146.538	5.010
3900	54.194	157.361	135.316	-278.384	-145.248	-145.248	4.830
4000	54.074	158.256	138.996	-277.680	-143.958	-143.958	4.690
4100	53.934	159.111	142.636	-276.964	-142.668	-142.668	4.590
4200	53.774	160.027	146.236	-276.236	-141.368	-141.368	4.530
4300	53.594	161.004	149.796	-275.496	-140.058	-140.058	4.510
4400	53.394	162.041	153.316	-274.744	-138.738	-138.738	4.530
4500	53.174	163.136	156.796	-273.980	-137.408	-137.408	4.590
4600	52.934	164.289	160.236	-273.204	-136.068	-136.068	4.690
4700	52.674	165.494	163.636	-272.416	-134.708	-134.708	4.830
4800	52.394	166.751	166.986	-271.616	-133.328	-133.328	5.010
4900	52.094	168.061	170.296	-270.804	-131.928	-131.928	5.230
5000	51.774	171.421	173.566	-270.000	-130.508	-130.508	5.490
5100	51.434	174.731	176.796	-269.204	-129.068	-129.068	5.790
5200	51.074	178.001	180.000	-268.424	-127.608	-127.608	6.130
5300	50.694	181.231	183.176	-267.648	-126.128	-126.128	6.510
5400	50.294	184.421	186.316	-266.876	-124.628	-124.628	6.930
5500	49.874	187.571	189.416	-266.108	-123.108	-123.108	7.390
5600	49.434	190.681	192.476	-265.344	-121.568	-121.568	7.890
5700	48.974	193.751	195.500	-264.584	-120.008	-120.008	8.430
5800	48.494	196.781	198.496	-263.828	-118.428	-118.428	9.010
5900	47.994	199.771	201.456	-263.076	-116.828	-116.828	9.630
6000	47.474	202.721	204.380	-262.328	-115.208	-115.208	10.290

MOL. WT. = 68.88651

(CRYSTAL)

WÜSTITE (Fe<sub>0.947</sub>O)

$\Delta H_f^0 = -63.85 \pm 0.20$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -63.64 \pm 0.20$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^0 = 7.49$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 13.764 \pm 0.10$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_m = 1650^\circ\text{K.}$

Heat of Formation.

The chemical equilibria in the Fe-C-O and Fe-K-O systems have been studied by many investigators. Using the reported equilibrium constants for the following two reactions (1)  $\text{Fe}_{0.947}\text{O}(c) + \text{CO}(g) = 0.947\text{Fe}(c) + \text{CO}_2(g)$  and (2)  $\text{Fe}_{0.947}\text{O}(c,1) + \text{H}_2(g) = 0.947\text{Fe}(c) + \text{H}_2\text{O}(g)$ , the corresponding enthalpy changes ( $\Delta H_f^0$ ) were evaluated by both the second and third law methods. Based on the third law values for  $\Delta H_f^0$ , the  $\Delta H_f^{298.15}$  (Wüstite, c) values were also calculated. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	Second Law Value	Third Law Value	$\Delta H_f^{298.15}$ kcal. mole <sup>-1</sup>
Eastman <sup>1</sup>	(1)	873.2-1273.2	-3.80 ± 0.01	-4.01	-63.63
Eastman - Evans <sup>2</sup>	(1)	973.2-1273.2	-4.02 ± 0.01	-4.03	-63.61
Eastman <sup>1</sup>	(2)	873.2-1273.2	6.50 ± 0.12	5.90	-63.70
Eastman - Evans <sup>2</sup>	(2)	973.2-1273.2	5.81 ± 0.01	5.07	-62.86
Emmett - Schultz <sup>3</sup>	(2)	873.2-1273.2	5.95 ± 0.07	5.82	-63.62
Britzke et al. <sup>4</sup>	(2)	1123.2-1498.2	-2.25 ± 0.03	4.26	-62.06
Joinly - Murphy <sup>5</sup>	(2)	1360.0-1846.0	5.01 ± 0.61	6.01	-63.81
Chipman - Marshall <sup>6</sup>	(2)	1438.2-1633.2	5.03 ± 0.34	5.85	-62.83
Joinly - Murphy <sup>5</sup>	(2)	1653.2-1787.2	-2.61 ± 0.77	-0.02	-61.87
Joinly - Murphy <sup>5</sup>	(2)	1698.0-1700.0	—	0.67	-62.72
Britzke et al. <sup>4</sup>	(3)	1123.0-1473.0	-129.08 ± 0.18	-126.28	-63.14

- 1 E. D. Eastman, *J. Am. Chem. Soc.* **44**, 975 (1922).
- 2 E. D. Eastman and R. M. Evans, *J. Am. Chem. Soc.* **45**, 888 (1924). The  $K_p$  value at 1273.2°K. for reaction (1) is rejected by a statistical criterion.
- 3 P. H. Emmett and J. P. Schultz, *J. Am. Chem. Soc.* **52**, 4268 (1930).
- 4 E. V. Britzke, A. P. Kapustin, and T. I. Schaschkina, *Z. anorg. allgem. Chem.* **219**, 287 (1954). The  $K_p$  value at 1123°K. for reaction (3) is rejected by a statistical criterion.
- 5 W. E. Joinly and D. W. Murphy, *Ind. Eng. Chem.* **23**, 384 (1931). The  $K_p$  values at 1590 and 1645°K. are rejected by a statistical criterion.
- 6 J. Chipman and S. Marshall, *J. Am. Chem. Soc.* **52**, 299 (1940).

Britzke et al. also determined the equilibrium pressures for the reaction (3)  $1.894 \text{ Fe}(c) + \text{O}_2(g) = 2\text{Fe}_{0.947}\text{O}(c)$ . The corresponding  $\Delta H_f^{298.15}$  for Wüstite was evaluated based on the third law value for  $\Delta H_f^{298.15}$ . The adopted value of  $\Delta H_f^{298.15}$  (Wüstite, c) is the weighted average of the  $\Delta H_f^{298.15}$  listed in the above table.

Heat Capacity and Entropy.

The low temperature (54.37-298.16°K.) heat capacities ( $C_p$ ) were measured by S. S. Todd and K. R. Bonnickson, *J. Am. Chem. Soc.* **73**, 3894 (1951). The high temperature (298-1650°K.) heat capacities were determined by J. P. Coughlin, E. O. King and K. R. Bonnickson, *J. Am. Chem. Soc.* **73**, 3891 (1951). The two sets of  $C_p$  data were plotted and joined smoothly at 298°K. The  $C_p$  values above 1650°K. were obtained by graphical extrapolation. The low temperature (70.7-279.8°K.)<sup>a</sup> were also reported by R. W. Millar, *J. Am. Chem. Soc.* **51**, 215 (1929).  $S_{298.15}^0$  was derived from the low temperature heat capacities, based on  $S_{52}^0 = 0.696$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>. S. S. Todd and K. R. Bonnickson, loc. cit. added 0.41 e.u., the amount calculated for completely random distribution of the vacant Fe spaces in the Wüstite lattice. However, the free energy functions derived from  $S_{52}^0 = 0.696$  e.u. give better agreement between second and third law values for  $\Delta H_f^0$  than those derived from  $S_{52}^0 = 1.11$  e.u. Therefore the value 0.41 e.u. was not added here.

Melting Data.

$T_m$  and  $\Delta H_m^0$  were taken from J. P. Coughlin, E. O. King and K. R. Bonnickson, et al.  $T_m$  was reported as 1372°C. (1645°K.) by L. S. Darken and R. W. Querry, *J. Am. Chem. Soc.* **58**, 798 (1946) and as 1569°C. (1642°K.) by J. Chipman and S. Marshall, loc. cit.

T, °K.	$C_p^0$	$S^0$	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log $K_p$
0	.000	INFINITE	2.262	-	63.846	-	INFINITE
100	5.577	2.938	21.548	2.061	64.100	62.178	135.884
200	10.886	9.319	14.793	1.095	63.873	60.299	65.888
298	11.500	13.764	1.000	.000	63.640	58.595	42.949
300	11.516	13.835	13.764	.021	63.636	58.564	42.662
400	12.041	17.224	14.723	1.201	63.405	56.908	31.092
500	12.392	19.950	15.104	2.423	63.187	55.309	24.174
600	12.674	22.235	16.107	3.676	63.002	53.752	19.578
700	12.923	24.207	17.127	4.956	62.859	52.222	16.304
800	13.155	25.948	18.123	6.260	62.776	50.710	13.653
900	13.377	27.510	19.080	7.587	62.800	49.201	11.197
1000	13.593	28.931	19.996	8.946	62.941	47.686	10.4421
1100	13.805	30.237	20.868	10.305	63.293	46.140	9.167
1200	14.013	31.447	21.700	11.696	63.627	44.580	8.119
1300	14.220	32.577	22.493	13.108	63.923	43.017	7.232
1400	14.426	33.638	23.252	14.540	64.187	41.470	6.473
1500	14.630	34.640	23.978	15.993	64.408	39.938	5.819
1600	14.834	35.591	24.674	17.466	64.596	38.421	5.248
1700	15.006	36.496	25.345	18.959	64.757	36.911	4.745
1800	15.130	37.355	25.987	20.466	64.894	35.409	4.298
1900	15.220	38.178	26.597	21.986	65.012	34.921	3.879
2000	15.300	38.961	27.206	23.510	65.115	34.452	3.500
2100	15.353	39.709	27.783	25.043	65.209	34.003	3.158
2200	15.400	40.424	28.342	26.581	65.285	33.578	2.847
2300	15.440	41.109	28.882	28.123	65.342	33.178	2.563
2400	15.473	41.767	29.405	29.669	65.383	32.801	2.303
2500	15.500	42.399	29.912	31.217	65.457	32.425	2.065

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S° -(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> kcal. mole <sup>-1</sup>	ΔH <sub>f</sub> <sup>o</sup> kcal. mole <sup>-1</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100	11.930	14.520	0.000	- 65.020	- 60.097	44.050
200	11.950	14.570	0.022	- 65.015	- 60.067	43.757
300	12.990	14.604	1.240	- 64.770	- 58.854	31.936
400	12.760	20.898	2.497	- 64.562	- 56.897	24.868
500	13.120	23.257	3.792	- 64.375	- 55.382	20.172
600	13.620	25.503	5.119	- 64.209	- 53.896	16.826
700	13.700	27.113	6.475	- 64.157	- 52.627	14.322
800	13.930	28.740	7.857	- 64.138	- 51.964	12.375
900	14.190	30.222	9.259	- 64.103	- 48.495	10.817
1000	14.396	31.584	10.492	- 64.068	- 47.991	9.535
1100	14.600	32.757	12.162	- 64.805	- 46.474	8.464
1200	14.813	34.551	13.613	- 64.586	- 44.955	7.557
1300	15.000	36.122	15.104	- 64.366	- 43.453	6.783
1400	15.131	36.167	16.611	- 64.147	- 41.968	6.114
1500	15.300	37.150	18.134	- 63.932	- 40.496	5.531
1600	15.435	38.082	19.671	- 64.010	- 39.033	5.016
1700	15.590	38.969	21.223	- 63.894	- 37.566	4.561
1800	15.724	39.815	22.789	- 67.452	- 35.921	4.132
1900	15.850	40.625	24.368	- 67.380	- 34.266	3.744

ΔH<sub>f</sub><sup>o</sup> O = Unknown

ΔH<sub>f</sub><sup>o</sup> 298.15 = [-65.02] kcal. mole<sup>-1</sup>

ΔH<sub>f</sub><sup>o</sup> = [5.75] kcal. mole<sup>-1</sup>

ΔH<sub>f</sub><sup>o</sup> 298.15 = [121.62] kcal. mole<sup>-1</sup>

S<sub>298.15</sub><sup>o</sup> = [14.52] cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = [1650]°K.

Heat of Formation.

The value of ΔH<sub>f</sub><sup>o</sup> 298.15 for FeO(c) was derived based on an assumption that at 1650°K., ΔH<sub>f</sub><sup>o</sup> (FeO, c) = ΔH<sub>f</sub><sup>o</sup> (FeO, l). From the value ΔH<sub>f</sub><sup>o</sup> 1650 (FeO, c) = -39.77 kcal. mole<sup>-1</sup>, ΔH<sub>f</sub><sup>o</sup> 1650 (FeO, c) was calculated to be -65.97 kcal. mole<sup>-1</sup>, yielding ΔH<sub>f</sub><sup>o</sup> 298.15 (FeO, c) = -65.02 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The C<sub>p</sub> values were estimated assuming C<sub>p</sub> (FeO, c) = C<sub>p</sub> (Wüstite, c) + 0.053 C<sub>p</sub> (Fe, c). The C<sub>p</sub> values obtained were plotted. The adopted C<sub>p</sub> points were taken from the smoothed C<sub>p</sub> curve. S<sub>298.15</sub><sup>o</sup> for FeO(c) was calculated as S° (FeO, c) = S° (Wüstite, c) + 0.053 S° (Fe, c) + ΔS° (mixing) where ΔS° is the entropy of mixing (0.41 cal. deg.<sup>-1</sup> mole<sup>-1</sup>).

Melting Data.

T<sub>m</sub> is assumed to be the same as that for Wüstite. The difference between ΔH<sub>f</sub><sup>o</sup> 1650 for FeO(l) and FeO(c) is ΔH<sub>m</sub><sup>o</sup>.

Heat of Sublimation.

ΔH<sub>g</sub><sup>o</sup> 298.15 is calculated as the difference between ΔH<sub>f</sub><sup>o</sup> 298.15 for FeO(g) and FeO(c).

(LIQUID)

IRON OXIDE (FeO)

$$\Delta H_f^{298.15} = 18.029 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^{1650} = [5.75] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{\circ} = 18.029 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = [1650]^{\circ}\text{K.}$$

$$T_d = [3687]^{\circ}\text{K.}$$

Heat of Formation

The heat of formation ( $\Delta H_f^{298.15}$ ) was evaluated based on an assumption that the heat of melting of wüstite,  $\Delta H_m^{1650} = 7.49 \text{ kcal. mole}^{-1}$ , represents the enthalpy change of the reaction  $\text{Fe}_{0.947}\text{O}(c) = 0.947 \text{ FeO}(l) + 0.053 \text{ O}_2(g)$ . In other words, during melting the wüstite releases  $\text{O}_2(g)$  and converts to  $\text{FeO}(l)$ .

Heat Capacity and Entropy

The enthalpy changes ( $H_m^{\circ} - H_{298.15}^{\circ}$ , 1650-1800°K.) of liquid iron oxide were determined by J. P. Coughlin, E. G. King and K. R. Bonnickson, *J. Am. Chem. Soc.* **73**, 3891 (1951). The  $C_p$  (FeO, l) was derived as 16.3 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. This value was adopted as the heat capacity for FeO(l) up to 4000°K. A glass transition temperature was assumed at 1100°K.  $S_{298.15}^{\circ}$  (FeO, l) was calculated based on an assumption that the entropy of melting of wüstite represents also the entropy change of the reaction,  $\text{Fe}_{0.947}\text{O}(c) = 0.947 \text{ FeO}(l) + 0.053 \text{ O}_2(g)$ . From the entropy of melting,  $\Delta S_m^{1650} = 4.539 \text{ e.u.}$ , the value  $S_{298.15}^{\circ}$  (FeO, l) = 18.029 e.u. was derived.

Melting Data

The melting point ( $T_m$ ) for wüstite (Fe<sub>0.947</sub>O, c) has been reported by many investigators. However, the composition of the liquid state of wüstite was not identified. An assumption was made that during melting the reaction  $\text{Fe}_{0.947}\text{O}(c) = 0.947 \text{ FeO}(l) + 0.053 \text{ O}_2(g)$  occurs. Hence the related thermodynamic properties were derived.

Decomposition Temperature

$T_d$  is the temperature at which  $\Delta F_f^{\circ}$  equals zero.

T, °K.	$C_p^{\circ}$	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>F</sub>
0						
100						
200						
298	11.500	18.029	0.000	- 59.642	- 55.765	40.875
300	11.516	18.029	0.021	- 59.638	- 55.741	40.606
400	12.041	18.489	1.021	- 59.440	- 54.673	29.761
500	12.392	19.370	2.423	- 59.259	- 53.252	23.275
600	12.674	20.373	3.676	- 59.113	- 52.065	18.064
700	12.923	21.302	4.946	- 59.011	- 50.899	15.891
800	13.155	22.144	6.260	- 58.974	- 49.745	13.589
900	13.377	23.036	7.587	- 59.030	- 48.588	11.798
1000	13.593	23.916	8.936	- 59.252	- 47.418	10.363
1100	16.300	25.133	10.306	- 50.676	- 46.210	9.181
1200	16.300	25.974	11.946	- 50.633	- 44.993	8.194
1300	16.300	26.725	13.566	- 59.255	- 43.788	7.361
1400	16.300	27.431	15.196	- 58.896	- 42.612	6.652
1500	16.300	28.098	16.826	- 58.554	- 41.462	6.041
1600	16.300	28.730	18.456	- 58.232	- 40.333	5.509
1700	16.300	29.333	20.086	- 58.218	- 39.218	5.052
1800	16.300	29.913	21.716	- 58.023	- 38.104	4.626
1900	16.300	30.465	23.346	- 61.518	- 36.819	4.235
2000	16.300	31.097	24.976	- 61.394	- 35.524	3.882
2100	16.300	31.773	26.606	- 61.276	- 34.231	3.562
2200	16.300	32.496	28.236	- 61.166	- 32.945	3.273
2300	16.300	33.269	29.866	- 61.062	- 31.667	3.009
2400	16.300	34.095	31.496	- 60.965	- 30.392	2.767
2500	16.300	34.884	33.126	- 60.875	- 29.118	2.545
2600	16.300	35.636	34.756	- 60.791	- 27.849	2.341
2700	16.300	36.362	36.386	- 60.714	- 26.586	2.152
2800	16.300	37.064	38.016	- 60.644	- 25.321	1.976
2900	16.300	37.744	39.646	- 60.580	- 24.060	1.813
3000	16.300	38.405	41.276	- 60.522	- 22.802	1.661
3100	16.300	39.046	42.906	- 60.471	- 21.543	1.519
3200	16.300	39.668	44.536	- 60.421	- 20.287	1.387
3300	16.300	40.273	46.166	- 60.371	- 19.036	1.263
3400	16.300	40.861	47.796	- 60.321	- 17.791	1.146
3500	16.300	41.434	49.426	- 60.271	- 16.551	1.034
3600	16.300	42.000	51.056	- 60.221	- 15.316	0.926
3700	16.300	42.559	52.686	- 60.171	- 14.086	0.822
3800	16.300	43.113	54.316	- 60.121	- 12.861	0.722
3900	16.300	43.663	55.946	- 60.071	- 11.641	0.626
4000	16.300	44.209	57.576	- 60.021	- 10.426	0.534
4100	16.300	44.751	59.206	- 59.971	- 9.216	0.446
4200	16.300	45.289	60.836	- 59.921	- 8.011	0.362
4300	16.300	45.823	62.466	- 59.871	- 6.811	0.282
4400	16.300	46.353	64.096	- 59.821	- 5.616	0.206
4500	16.300	46.879	65.726	- 59.771	- 4.426	0.134
4600	16.300	47.401	67.356	- 59.721	- 3.241	0.066
4700	16.300	47.919	68.986	- 59.671	- 2.061	0.002
4800	16.300	48.433	70.616	- 59.621	- 0.886	- 0.066
4900	16.300	48.943	72.246	- 59.571	- 0.211	- 0.134
5000	16.300	49.449	73.876	- 59.521	- 0.466	- 0.202

IRON OXIDE (FeO) (IDEAL GAS) MOL. WT. = 71.8464

Ground State Configuration [ $5\Sigma$ ]  $\Delta H_f^0 = 56.6 \pm 10$  kcal. mole $^{-1}$

$S_{298.15}^0 = [56.42]$  cal. deg. $^{-1}$  mole $^{-1}$   $\Delta H_f^0 298.15 = 56.6 \pm 10$  kcal. mole $^{-1}$

Electronic Levels and Quantum Weight

$\epsilon$	$\frac{\epsilon_1}{0}$	$\frac{\epsilon_1}{[5]}$
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$\omega_e X_e = 5.0$  cm. $^{-1}$   $\sigma = 1$   
 $B_e = [0.4184]$  cm. $^{-1}$   $\alpha_e = [0.00293]$  cm. $^{-1}$   
 $r_e = [1.8]$  Å

Heat of Formation.

The dissociation energy ( $D_0$ ) for FeO (g) was reported as 4.8 e.v. (110.7 kcal. mole $^{-1}$ ) and 4 + 1 e.v. (92 + 23 kcal. mole $^{-1}$ ) by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950 and A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd. London, 1953, respectively. The corresponding values of  $\Delta H_f^0 298.15$  for FeO (g) were evaluated to be 47.4 and 65.8 + 23 kcal. mole $^{-1}$ . The  $\Delta H_f^0 298.15$  (FeO, g) adopted is the average of these two.

Heat Capacity and Entropy.

The values of  $\omega_e$  and  $\omega_e X_e$  were taken from G. Herzberg, loc. cit. The bond distance ( $r_e$ ) was calculated according to the method suggested by K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946), assuming FeO (g) as a polar molecule. Hence the constants,  $B_e$  and  $\alpha_e$  were estimated. The ground state configuration was estimated by comparison with that for CrO (g) obtained from R. A. Berg and O. Sinanoglu, J. Chem. Phys. 32, 1082 (1960). The entropy values may be in error by a few entropy units due to the uncertainties in the following electronic levels. The principal moment of inertia is  $6.6899 \times 10^{-39}$  g. cm. $^2$

T, °K.	C <sub>p</sub>	S <sup>0</sup>	-(F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	56.600	56.600	INFINITE
100	6.958	48.660	2.412	1.417	56.836	56.193	- 118.432
200	7.108	53.510	4.702	7.16	56.775	51.556	- 156.335
298	7.505	56.410	6.449	10.00	56.600	49.031	- 35.939
300	7.513	56.465	6.479	10.14	56.596	48.984	- 35.683
400	7.899	58.682	7.859	15.50	56.386	46.477	- 25.393
500	8.181	60.476	8.726	21.50	56.151	44.027	- 19.243
600	8.376	61.986	9.585	28.19	55.872	41.628	- 12.628
700	8.513	63.288	10.352	35.26	55.538	39.279	- 6.263
800	8.612	64.432	11.032	42.70	55.128	36.982	- 0.103
900	8.684	65.451	11.622	50.42	54.610	34.744	8.437
1000	8.739	66.369	12.122	58.36	53.911	32.572	17.118
1100	8.782	67.204	12.542	66.42	52.992	30.487	26.057
1200	8.817	67.969	12.882	74.61	52.285	28.467	35.184
1300	8.845	68.676	13.141	82.95	51.917	26.497	44.454
1400	8.868	69.333	13.312	91.44	51.532	24.556	53.833
1500	8.888	69.945	13.399	100.00	51.131	22.643	63.299
1600	8.904	70.519	13.405	108.63	50.713	20.758	72.835
1700	8.919	71.060	13.332	117.32	49.988	18.903	82.430
1800	8.932	71.570	13.172	126.06	49.445	17.091	92.075
1900	8.944	72.053	12.927	134.84	49.215	15.494	101.782
2000	8.954	72.512	12.592	143.66	44.604	13.944	111.524
2100	8.964	72.949	12.166	152.52	43.987	12.428	121.293
2200	8.971	73.366	11.650	161.42	43.364	10.940	131.087
2300	8.976	73.766	11.044	170.35	42.736	9.479	140.901
2400	8.980	74.148	10.350	179.32	42.101	8.045	150.733
2500	8.986	74.515	9.577	188.31	41.460	6.640	160.580
2600	8.993	74.868	8.723	197.32	40.814	5.259	170.442
2700	9.000	75.208	7.800	206.35	40.167	3.900	180.316
2800	9.015	75.535	6.817	215.40	39.513	2.563	190.192
2900	9.027	75.852	5.772	224.47	38.859	1.247	200.067
3000	9.027	76.158	4.675	233.56	38.189	0.000	210.000
3100	9.033	76.454	3.527	242.67	37.504	- 1.276	220.000
3200	9.038	76.741	2.332	251.80	36.813	- 2.563	230.000
3300	9.043	77.019	1.090	260.94	36.117	- 3.850	240.000
3400	9.049	77.289	- 0.207	270.10	35.416	- 5.137	250.000
3500	9.054	77.551	- 1.522	279.27	34.711	- 6.424	260.000
3600	9.059	77.807	- 2.846	288.44	34.004	- 7.711	270.000
3700	9.063	78.055	- 4.170	297.61	33.296	- 9.000	280.000
3800	9.068	78.297	- 5.494	306.78	32.587	- 10.287	290.000
3900	9.073	78.532	- 6.818	315.94	31.871	- 11.574	300.000
4000	9.077	78.762	- 8.142	325.10	31.156	- 12.861	310.000
4100	9.082	78.986	- 9.466	334.26	30.441	- 14.148	320.000
4200	9.086	79.205	- 10.790	343.41	29.726	- 15.435	330.000
4300	9.091	79.419	- 12.114	352.56	29.011	- 16.722	340.000
4400	9.095	79.628	- 13.438	361.71	28.296	- 18.009	350.000
4500	9.100	79.837	- 14.762	370.86	27.581	- 19.296	360.000
4600	9.104	80.032	- 16.086	380.01	26.866	- 20.583	370.000
4700	9.108	80.228	- 17.410	389.16	26.151	- 21.870	380.000
4800	9.112	80.420	- 18.734	398.31	25.436	- 23.157	390.000
4900	9.117	80.608	- 20.058	407.46	24.721	- 24.444	400.000
5000	9.121	80.792	- 21.382	416.61	24.006	- 25.731	410.000
5100	9.125	80.973	- 22.706	425.76	23.291	- 27.018	420.000
5200	9.129	81.150	- 24.030	434.91	22.576	- 28.305	430.000
5300	9.133	81.324	- 25.354	444.06	21.861	- 29.592	440.000
5400	9.137	81.495	- 26.678	453.21	21.146	- 30.879	450.000
5500	9.142	81.661	- 27.992	462.36	20.431	- 32.166	460.000
5600	9.146	81.827	- 29.306	471.51	19.716	- 33.453	470.000
5700	9.150	81.989	- 30.620	480.66	19.001	- 34.740	480.000
5800	9.154	82.148	- 31.934	489.81	18.286	- 36.027	490.000
5900	9.158	82.305	- 33.248	498.96	17.571	- 37.314	500.000
6000	9.162	82.459	- 34.562	508.11	16.856	- 38.601	510.000

$\Delta H_f^0 = -195.8 \pm 0.3 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -197.3 \pm 0.3 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 20.889 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_d = 1735^\circ\text{K.}$

Heat of Formation.

The chemical equilibria for the reaction  $4\text{Fe}_3\text{O}_4(c) + \text{O}_2(g) = 6\text{Fe}_2\text{O}_3(c)$  have been studied by several investigators from the reported data the corresponding values of  $\Delta H_f^{298.15}$  and  $\Delta H_f^{298.15}$  (Fe<sub>2</sub>O<sub>3</sub>, c) were evaluated. The results obtained are given as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	$\Delta H_f^{298.15}$ , kcal. mole <sup>-1</sup>	$\Delta H_f^{298.15}$ , kcal. mole <sup>-1</sup>
Tret'yakov and Khomyakov <sup>1</sup>	1373-1728	-106.32 ± 0.19	-111.05	-197.11	-197.11
Schmahl <sup>2</sup>	1583-1663	-123.96 ± 1.37	-112.94	-197.42	-197.42
Smiltens <sup>3</sup>	1373-1673	-117.88 ± 0.38	-114.25	-197.64	-197.64
Darken and Gurry <sup>4</sup>	1723	-110.29	---	-196.98	-196.98

<sup>1</sup> Y. D. Tret'yakov and K. G. Khomyakov, Russ. J. Inorg. Chem. **7**, 628 (1962).

<sup>2</sup> N. G. Schmahl, Z. Elektrochem. **47**, 821 (1941).

<sup>3</sup> J. Smiltens, J. Am. Chem. Soc. **79**, 4877 (1957).

<sup>4</sup> L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. **69**, 798 (1946).  $\Delta H_f^{298.15}$  was calculated based on  $\Delta H_f^{1723} = -54.5 \text{ kcal. mole}^{-1}$ .

The value of  $\Delta H_f^{298.15}$  adopted for Fe<sub>2</sub>O<sub>3</sub>(c) is the weighted average of the  $\Delta H_f^{298.15}$  values listed in the above table.

Heat Capacity and Entropy.

The low temperature (5.59-345.42°K.) heat capacities were determined by F. Gronvold and E. F. Westrum, Jr., J. Am. Chem. Soc. **81**, 1780 (1959). The high temperature (298-1750°K.)  $C_p$  values were obtained from J. P. Coughlin, E. G. King and K. R. Bonnicksen, J. Am. Chem. Soc. **73**, 3891 (1951). The two sets of data were plotted and joined smoothly at 298°K. The  $C_p$  values above 1750°K. were obtained by graphical extrapolation. The heat capacities of Fe<sub>2</sub>O<sub>3</sub>(c) have also been reported by G. G. Brown and C. C. Furness, Trans. Am. Inst. Chem. Eng. **13**, 309 (1926), from the smoothed  $C_p$  data, based on  $S_{298.15}^0 = 20.889 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ . J. P. Coughlin, E. G. King and K. R. Bonnicksen, loc. cit. measured the heat-content for hematite and found two anomalies, presumably of magnetic nature, at about 950 and 1050°K., respectively. Both appear to involve maxima in the heat-capacity curves rather than isothermal heats of transformation. The complex magnetic properties at low temperatures were discussed by F. Gronvold and E. F. Westrum, Jr., loc. cit. No heat capacity anomaly was observed at the magnetic transition about 250°K. The Curie points of the antiferromagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were reported by A. Aharoni, E. H. Frei and M. Schieber, Phys. Rev. **121**, 439 (1962) and J. Lielemez and A. C. D. Chaklader, Phys. Rev. Letters, **13**, 866 (1965).

Temperature of Decomposition.

$T_d$  is the temperature at which  $\Delta F_r^0 = 0$  for the reaction  $6\text{Fe}_2\text{O}_3(c) = 4\text{Fe}_3\text{O}_4(c) + \text{O}_2(g)$ . In other words, Fe<sub>2</sub>O<sub>3</sub>(c) decomposes into Fe<sub>3</sub>O<sub>4</sub>(c) and O<sub>2</sub>(g) at 1735°K.

T, °K.	$C_p$	$S^0 - (F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_r^0$	Log K <sub>r</sub>
0	∞	INFINITE	3.719	-195.757	-195.757	INFINITE
100	7.528	38.192	3.470	-196.783	-190.611	416.560
200	18.300	12.256	2.144	-197.321	-184.182	201.295
298	24.800	20.889	∞	-197.300	-177.719	130.265
300	24.900	21.043	∞	-197.296	-177.598	129.374
400	28.710	28.752	2.735	-196.925	-171.081	93.470
500	31.500	35.469	5.750	-196.356	-164.681	71.979
600	33.740	41.413	9.4014	-195.685	-158.409	57.697
700	35.786	46.768	12.490	-194.954	-152.253	47.533
800	37.815	51.679	16.171	-194.206	-146.206	38.940
900	39.792	56.248	20.051	-193.499	-140.248	34.055
1000	41.714	60.440	24.025	-192.824	-134.363	29.364
1100	43.646	63.760	27.505	-192.132	-128.461	25.322
1200	45.622	66.695	30.879	-191.432	-122.540	22.316
1300	47.648	69.409	34.270	-190.732	-116.616	19.684
1400	49.726	71.935	37.678	-190.032	-110.678	17.259
1500	51.850	74.299	41.105	-189.324	-104.672	15.279
1600	54.026	76.522	44.550	-188.612	-98.600	13.528
1700	56.252	78.622	48.005	-187.900	-92.422	11.984
1800	58.528	80.601	51.470	-187.188	-86.188	10.611
1900	60.854	82.467	54.942	-186.476	-80.000	9.341
2000	63.230	84.291	58.424	-185.764	-73.864	8.195
2100	65.656	86.079	61.908	-185.052	-67.772	7.157
2200	68.132	87.828	65.400	-184.340	-61.720	6.214
2300	70.658	89.538	68.900	-183.628	-55.712	5.354
2400	73.234	91.209	72.408	-182.916	-49.744	4.565
2500	75.860	92.841	75.924	-182.204	-43.816	3.839
2600	78.536	94.435	79.448	-181.492	-37.928	3.165
2700	81.262	96.000	82.972	-180.780	-32.080	2.541
2800	84.038	97.535	86.500	-180.068	-26.272	1.967
2900	86.864	99.040	90.024	-179.356	-20.504	1.443
3000	89.740	100.510	93.552	-178.644	-14.776	0.969

MAGNETITE (Fe<sub>3</sub>O<sub>4</sub>) (CRYSTAL) MOL. WT. = 231.5396

$\Delta H_f^0 = -266.4 \pm 0.2$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -267.9 \pm 0.2$  kcal. mole<sup>-1</sup>  
 $\Delta H_m^0 = 33.0 \pm 2.0$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 34.72$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_m = 1870 \pm 2^\circ K.$

Heat of Formation.

The equilibrium constants for the following four reactions, i.e. (1)  $3Fe(c) + 4H_2O(g) = Fe_3O_4(c) + 4H_2(g)$ ; (2)  $Fe_3O_4(c) + H_2(g) = 3FeO(c) + CO(g)$ ; (3)  $Fe_3O_4(c) + CO(g) = 3FeO(c) + CO_2(g)$ ; and (4)  $2Fe_3O_4(c) = 6FeO(c) + O_2(g)$ , have been studied by several investigators. Using their reported equilibrium data, the corresponding enthalpy changes ( $\Delta H_f^{298.15}$ ) were evaluated by both the second and third law methods. Based on the third law value for  $\Delta H_f^{298.15}$ , the respective  $\Delta H_f^{298.15}$  values for  $Fe_3O_4(c)$  were also derived. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	Second Law Value	Third Law Value	$\Delta H_f^{298.15}$ kcal. mole <sup>-1</sup>
Fricke, et al. <sup>1</sup>	(1)	653.2-823.2	-29.68 ± 1.30	-36.91	-268.10
Eastman <sup>2</sup>	(2)	873.2-1273.2	22.41 ± 0.09	19.29	-268.01
Eastman and Evans <sup>3</sup>	(2)	973.2-1273.2	21.56 ± 0.07	18.54	-267.26
Eastman <sup>2</sup>	(3)	873.2-1273.2	11.87 ± 0.03	9.38	-267.93
Eastman and Evans <sup>3</sup>	(3)	973.2-1273.2	11.63 ± 0.03	9.38	-267.94
Salmon <sup>5</sup>	(4)	1473.2-1673.2	183.73	183.73	-267.79

1. R. Fricke, K. Walter and W. Leher, Z. Elektrochem. 47, 487 (1941). The two  $\Delta H_f^{298.15}$  values listed are the average values of three separate results derived from three sets of experimental data.  
 2. E. D. Eastman, J. Am. Chem. Soc. 44, 975 (1922).  
 3. E. D. Eastman and R. M. Evans, J. Am. Chem. Soc. 45, 888 (1924).  
 4. P. H. Emmett and J. P. Schultz, J. Am. Chem. Soc. 52, 4268 (1930).  
 5. O. N. Salmon, J. Phys. Chem. 65, 550 (1961).

The enthalpy change of the reaction  $Fe_{0.947}O(c) + 0.0525 Fe(c) + 0.6787 O_2(g) = 0.5685 Fe_3O_4(c)$  has been determined by G. L. Humphrey, E. G. King and K. K. Kelley, U. S. Bur. Mines RI 4870 (1952). Based on  $\Delta H_f^{298.15} = -93.46$  kcal. mole<sup>-1</sup> (average of two separate values derived from two experimental determinations) and  $\Delta H_f^{298.15} = -93.46$  kcal. mole<sup>-1</sup>, the value of  $\Delta H_f^{298.15}$  ( $Fe_3O_4, c$ ) was calculated as  $-266.5$  kcal. mole<sup>-1</sup>. The enthalpy change,  $\Delta H_f^{298.15} = 4.33$  kcal. mole<sup>-1</sup>, for the reaction  $3Fe(c) + 4CO_2(g) = Fe_3O_4(c) + 4CO(g)$  was reported by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946). The corresponding  $\Delta H_f^{298.15}$  ( $Fe_3O_4, c$ ) was evaluated as  $-266.22$  kcal. mole<sup>-1</sup>. The adopted value of  $\Delta H_f^{298.15}$  for  $Fe_3O_4(c)$  is selected as  $-267.9 \pm 0.2$  kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The low temperature (60.5-299.7°K.) heat capacities were reported by R. W. Miller, J. Am. Chem. Soc. 51, 215 (1929). The high temperature (298-1800°K.) heat capacities were obtained from J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3891 (1951). These two sets of data were plotted and joined smoothly at 298°K. The  $C_p$  values above 1800°K. were obtained by graphical extrapolation. Heat capacities (90-295°K.) for  $Fe_3O_4(c)$  were also reported by G. S. Parks and K. K. Kelley, J. Phys. Chem. 30, 47 (1926).  $S_{298.15}^0$  ( $Fe_3O_4, c$ ) was derived from the smoothed  $C_p$  data mentioned previously, using  $S_{44.7}^0 = 0.969$  e.u. J. P. Coughlin, E. G. King and K. R. Bonnickson, loc. cit. measured the heat-content for magnetite and found a magnetic anomaly around 880°K., corresponding to a maximum in heat capacity. A maximum heat capacity of 37.1 cal. deg.<sup>-1</sup> mole<sup>-1</sup> at 114.15°K. was also reported by R. W. Miller, loc. cit.

Melting Data.

$T_m$  and  $\Delta H_m^0$  were obtained from L. S. Darken and R. W. Gurry, loc. cit.

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298</sub> )/T	H <sup>o</sup> -H <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	+0.00	INFINITE	-	5.873	-266.398	-266.398	INFINITE
100	13.464	6.599	60.756	5.416	-267.676	-259.592	567.310
200	27.950	12.076	37.732	3.131	-268.017	-251.358	274.658
298	35.190	34.720	34.720	+0.00	-267.900	-243.191	178.255
300	35.300	34.938	34.720	+0.65	-267.894	-243.038	177.044
400	40.900	45.878	36.174	3.881	-267.378	-234.820	128.294
500	45.980	55.555	39.100	8.228	-266.518	-226.772	98.117
600	50.800	64.364	42.586	13.067	-265.379	-218.926	78.740
700	55.620	72.557	46.289	18.388	-263.981	-211.290	65.965
800	60.440	80.299	50.060	24.191	-262.378	-203.874	55.693
900	68.000	87.696	53.834	30.476	-260.649	-196.661	47.754
1000	88.000	92.753	57.477	35.276	-260.974	-189.541	41.422
1100	48.000	97.328	60.895	40.076	-261.977	-182.336	36.225
1200	48.000	101.504	64.108	44.876	-262.962	-175.096	31.888
1300	48.000	105.347	67.134	49.676	-261.745	-167.849	28.217
1400	48.000	108.994	69.982	54.476	-261.190	-160.646	25.077
1500	48.000	112.423	72.688	59.276	-260.691	-153.483	22.361
1600	48.000	115.313	75.266	64.076	-260.252	-146.350	19.989
1700	48.000	118.426	77.708	68.876	-260.741	-139.227	17.898
1800	48.000	121.567	80.036	73.676	-260.959	-132.079	16.036
1900	48.000	124.552	82.259	78.476	-261.713	-124.980	14.306
2000	48.000	126.634	84.386	83.276	-271.881	-116.827	12.744
2100	48.000	128.366	86.425	88.076	-272.071	-108.853	11.328
2200	48.000	130.599	88.383	92.876	-272.287	-101.077	10.041
2300	48.000	132.731	90.265	97.676	-272.523	-93.296	8.865
2400	48.000	134.776	92.077	102.476	-272.783	-85.497	7.785
2500	48.000	136.735	93.825	107.276	-273.067	-77.685	6.791
2600	48.000	138.618	95.512	112.076	-273.371	-69.867	5.873
2700	48.000	140.429	97.142	116.876	-273.699	-62.033	5.021
2800	48.000	142.175	98.719	121.676	-274.049	-54.185	4.229
2900	48.000	143.859	100.247	126.476	-274.421	-46.325	3.491
3000	48.000	145.486	101.728	131.276	-274.815	-38.448	2.801

HYDROGEN, MONATOMIC (H) (IDEAL GAS)

Ground State Configuration  $2s^2 1/2$   
 $\Delta H_f^0 = 51.631 \pm 0.001$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 298.15 = 52.100 \pm 0.001$  kcal. mole<sup>-1</sup>

$S_{298.15}^0 = 27.392$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

Electronic Levels and Quantum Weight

$E_2$ , cm. <sup>-1</sup>	$E_1$
0.000	2
82256.907	2
82256.942	2
82259.272	4
97492.198	2
97492.208	2
97492.305	4
97492.342	6

Heat of Formation.

The heat of formation was calculated from  $D_0^0(H_2) = 36113.0 \pm 0.3$  cm.<sup>-1</sup>, reported by G. Herzberg and A. Monfils, J. of Molecular Spectroscopy 5, 482 (1960). This value was measured more precisely than the value  $D_0^0(H_2) = 36116 \pm 6$  cm.<sup>-1</sup> by H. Beutler, Z. Phys. Chem. B23, 315 (1935).

Heat Capacity and Entropy.

Electronic levels taken from C. E. Moore, Nati. Bur. Standards (U. S.) Circ. 467 (1949).

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	$-(F^o - H_{298}^o)/T$	H <sup>o</sup> - H <sub>298}^o</sub>	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	∞	∞	∞	∞	51.631	∞	∞
100	4.968	25.498	27.897	4.984	51.748	110.954	5.332
200	4.968	27.392	27.392	0.000	51.948	110.954	5.332
298	4.968	27.392	27.392	0.000	52.100	110.954	5.332
300	4.968	27.423	27.392	0.009	52.103	110.954	5.332
400	4.968	28.852	27.587	5.56	52.253	110.954	5.332
500	4.968	29.961	27.955	1.003	52.400	110.954	5.332
600	4.968	30.867	28.367	1.500	52.547	110.954	5.332
700	4.968	31.632	28.780	1.996	52.692	110.954	5.332
800	4.968	32.296	29.179	2.493	52.836	110.954	5.332
900	4.968	32.881	29.559	2.990	52.977	110.954	5.332
1000	4.968	33.404	29.917	3.487	53.115	110.954	5.332
1100	4.968	33.878	30.256	3.984	53.249	110.954	5.332
1200	4.968	34.310	30.576	4.481	53.379	110.954	5.332
1300	4.968	34.708	30.879	4.977	53.503	110.954	5.332
1400	4.968	35.076	31.166	5.474	53.623	110.954	5.332
1500	4.968	35.419	31.438	5.971	53.737	110.954	5.332
1600	4.968	35.739	31.697	6.468	53.845	110.954	5.332
1700	4.968	36.041	31.944	6.965	53.948	110.954	5.332
1800	4.968	36.325	32.179	7.461	54.046	110.954	5.332
1900	4.968	36.598	32.405	7.958	54.140	110.954	5.332
2000	4.968	36.848	32.621	8.455	54.230	110.954	5.332
2100	4.968	37.090	32.826	8.952	54.314	110.954	5.332
2200	4.968	37.322	33.027	9.449	54.395	110.954	5.332
2300	4.968	37.542	33.216	9.945	54.471	110.954	5.332
2400	4.968	37.754	33.403	10.442	54.546	110.954	5.332
2500	4.968	37.957	33.581	10.939	54.615	110.954	5.332
2600	4.968	38.152	33.753	11.436	54.682	110.954	5.332
2700	4.968	38.339	33.919	11.933	54.745	110.954	5.332
2800	4.968	38.520	34.081	12.430	54.806	110.954	5.332
2900	4.968	38.694	34.237	12.926	54.863	110.954	5.332
3000	4.968	38.862	34.388	13.423	54.918	110.954	5.332
3100	4.968	39.025	34.535	13.920	54.971	110.954	5.332
3200	4.968	39.183	34.678	14.417	55.021	110.954	5.332
3300	4.968	39.336	34.817	14.914	55.068	110.954	5.332
3400	4.968	39.484	34.952	15.410	55.113	110.954	5.332
3500	4.968	39.628	35.083	15.907	55.156	110.954	5.332
3600	4.968	39.768	35.212	16.404	55.196	110.954	5.332
3700	4.968	39.904	35.337	16.901	55.233	110.954	5.332
3800	4.968	40.037	35.459	17.398	55.269	110.954	5.332
3900	4.968	40.166	35.578	17.895	55.302	110.954	5.332
4000	4.968	40.292	35.694	18.391	55.333	110.954	5.332
4100	4.968	40.414	35.806	18.888	55.362	110.954	5.332
4200	4.968	40.534	35.919	19.385	55.388	110.954	5.332
4300	4.968	40.651	36.027	19.882	55.412	110.954	5.332
4400	4.968	40.765	36.134	20.379	55.435	110.954	5.332
4500	4.968	40.877	36.238	20.875	55.454	110.954	5.332
4600	4.968	40.986	36.340	21.372	55.473	110.954	5.332
4700	4.968	41.093	36.440	21.869	55.489	110.954	5.332
4800	4.968	41.198	36.536	22.366	55.503	110.954	5.332
4900	4.968	41.300	36.634	22.863	55.515	110.954	5.332
5000	4.968	41.400	36.728	23.359	55.525	110.954	5.332
5100	4.968	41.499	36.821	23.856	55.534	110.954	5.332
5200	4.968	41.595	36.912	24.353	55.541	110.954	5.332
5300	4.968	41.690	37.001	24.850	55.545	110.954	5.332
5400	4.968	41.783	37.089	25.347	55.548	110.954	5.332
5500	4.968	41.874	37.175	25.844	55.550	110.954	5.332
5600	4.968	41.963	37.260	26.340	55.549	110.954	5.332
5700	4.968	42.051	37.343	26.837	55.547	110.954	5.332
5800	4.968	42.138	37.425	27.334	55.543	110.954	5.332
5900	4.968	42.223	37.506	27.831	55.537	110.954	5.332
6000	4.968	42.306	37.585	28.328	55.530	110.954	5.332

Dec. 31, 1960; Sept. 30, 1965



Ground State Configuration 1S<sub>0</sub>  
 $\Delta H_{f,0}^{\circ} = 34.2 \pm 0.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_{f,298.15}^{\circ} = 26.015 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_{f,298.15}^{\circ} = 33.2 \pm 0.5 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight  
 $\frac{\epsilon_{l \text{ cm.}^{-1}}}{g_l}$

Heat of Formation.

The heat of formation was calculated from the equation:  $H(\epsilon) + e^{-} \rightarrow H^{-}(\epsilon)$  with the JANAF auxiliary value for  $H(\epsilon)$  (this supplement); using an I.P. =  $6.085096 \times 10^5 \text{ cm.}^{-1}$  ( $.754 \text{ e.v.} \approx 17.39 \text{ kcal/mole}$ ) for  $H^{-}(\epsilon)$  obtained from C. L. Pekeris, Phys. Rev. **125**, 1470 (1962). The I.P. value for  $H^{-}(\epsilon)$  reported by C. W. Scherr and R. E. Knight, Rev. Mod. Phys. **35**, 436 (1963) is in agreement with the value of Pekeris.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Helium. The electronic levels above  $1 \times 10^5 \text{ cm.}^{-1}$  were omitted because their contribution is negligible below 6000°K. The  $H_{298}^{\circ}$  value at 0°K. is  $-1.481 \text{ kcal/mole}$ .

T, °K.	C <sub>p</sub>	S°	$-\ln(F^{-}H_{298}^{\circ})/T$	H <sup>-</sup> -H <sub>298</sub> <sup>°</sup>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	Log K <sub>p</sub>
100	4.968	26.015	26.015	0.00	33.200	31.583	-23.150
200	4.968	26.045	26.045	0.009	33.104	31.574	-23.000
298	4.968	27.475	26.210	2.06	32.687	31.085	-16.985
300	4.968	28.583	26.576	1.093	32.447	30.685	-13.412
400	4.968	29.489	26.900	1.500	32.147	30.356	-11.057
500	4.968	30.254	27.403	1.996	31.796	30.066	-9.593
600	4.968	30.918	28.002	2.493	31.443	29.866	-8.158
700	4.968	31.503	28.181	2.960	31.087	29.683	-7.209
800	4.968	32.027	28.540	3.487	30.728	29.553	-6.458
900	4.968	32.500	28.879	3.984	30.365	29.453	-5.851
1000	4.968	32.933	29.199	4.481	29.998	29.385	-5.351
1200	4.968	33.330	29.502	4.977	29.626	29.351	-4.934
1300	4.968	33.699	29.788	5.474	29.249	29.342	-4.580
1400	4.968	34.041	30.061	5.971	28.866	29.364	-4.278
1500	4.968	34.362	30.320	6.468	28.477	29.409	-4.017
1600	4.968	34.663	30.566	6.965	28.083	29.480	-3.790
1700	4.968	34.947	30.802	7.461	27.685	29.574	-3.591
1800	4.968	35.216	31.027	7.958	27.282	29.688	-3.415
1900	4.968	35.471	31.243	8.455	26.875	29.825	-3.259
2000	4.968	35.713	31.450	8.952	26.462	29.984	-3.120
2100	4.968	35.944	31.649	9.449	26.046	30.161	-2.996
2200	4.968	36.165	31.841	9.945	25.627	30.359	-2.885
2300	4.968	36.376	32.025	10.442	25.204	30.574	-2.784
2400	4.968	36.579	32.204	10.939	24.776	30.805	-2.693
2500	4.968	36.774	32.376	11.436	24.346	31.055	-2.610
2600	4.968	36.962	32.542	11.933	23.912	31.318	-2.535
2700	4.968	37.142	32.703	12.430	23.476	31.603	-2.467
2800	4.968	37.317	32.859	12.926	23.037	31.900	-2.404
2900	4.968	37.486	33.011	13.423	22.595	32.215	-2.347
3000	4.968	37.649	33.158	13.920	22.151	32.542	-2.294
3100	4.968	37.809	33.300	14.417	21.704	32.881	-2.246
3200	4.968	37.965	33.439	14.914	21.254	33.238	-2.201
3300	4.968	38.117	33.574	15.410	20.803	33.608	-2.160
3400	4.968	38.265	33.706	15.907	20.349	33.992	-2.122
3500	4.968	38.409	33.834	16.404	19.892	34.387	-2.088
3600	4.968	38.552	33.959	16.901	19.432	34.800	-2.055
3700	4.968	38.690	34.081	17.398	18.971	35.222	-2.026
3800	4.968	38.828	34.200	17.895	18.507	35.655	-1.998
3900	4.968	38.964	34.316	18.391	18.042	36.102	-1.972
4000	4.968	39.097	34.430	18.888	17.574	36.559	-1.949
4100	4.968	39.227	34.541	19.388	17.105	37.024	-1.926
4200	4.968	39.354	34.650	19.882	16.630	37.502	-1.906
4300	4.968	39.478	34.756	20.376	16.156	37.993	-1.887
4400	4.968	39.599	34.860	20.875	15.679	38.499	-1.870
4500	4.968	39.715	34.962	21.372	15.201	39.008	-1.853
4600	4.968	39.828	35.062	21.869	14.720	39.530	-1.838
4700	4.968	39.938	35.159	22.366	14.237	40.069	-1.823
4800	4.968	40.045	35.254	22.863	13.752	40.612	-1.807
4900	4.968	40.149	35.347	23.359	13.266	41.159	-1.791
5000	4.968	40.251	35.444	23.856	12.778	41.728	-1.778
5100	4.968	40.351	35.534	24.353	12.288	42.294	-1.777
5200	4.968	40.448	35.624	24.850	11.795	42.883	-1.768
5300	4.968	40.543	35.711	25.347	11.301	43.472	-1.759
5400	4.968	40.636	35.798	25.844	10.806	44.072	-1.751
5500	4.968	40.727	35.882	26.340	10.309	44.682	-1.744
5600	4.968	40.816	35.966	26.837	9.810	45.295	-1.737
5700	4.968	40.903	36.047	27.334	9.309	45.927	-1.730
5800	4.968	41.000	36.128	27.831	8.806	46.563	-1.725
5900	4.968	41.095	36.207	28.328	8.302	47.200	-1.719
6000	4.968	41.190	36.284	28.825	7.797	47.842	-1.714

MOL. WT. = 56.10357

(CRYSTAL)

POTASSIUM HYDROXIDE (KOH)

$\Delta H_f^0 = -100.7 \pm 0.1$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -101.5 \pm 0.1$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = -153.5$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = 2.240$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = 298.15$  (to monomer) = (46.1) kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = 298.15$  (to dimer) = (45.6) kcal. mole<sup>-1</sup>

$S^0_{298.15} = 18.95$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $T_f = 522^\circ K$   
 $T_m = 675^\circ K$

Heat of Formation.

The standard enthalpy of formation,  $\Delta H_f^0$  (KOH, c) =  $-101.5 \pm 0.1$  kcal. mole<sup>-1</sup>, was calculated from the heat of solution of KOH(c), the heat of hydrolysis of potassium metal and the appropriate auxiliary data.

M. A. Peshetnikov<sup>1</sup> has measured the heat of solution KOH(c)  $\rightarrow$  KOH(650 H<sub>2</sub>O) as  $-13.865 \pm 0.005$  kcal. mole<sup>-1</sup> at 298.15°K. in the solution calorimeter. Using the auxiliary heat of dilution reported by V. E. Parker<sup>2</sup>, the selected heat of solution of KOH(c) at infinite dilution is  $-13.770$  kcal. mole<sup>-1</sup>. The heat of solution  $\Delta H(c) \rightarrow$  KOH(650 H<sub>2</sub>O) has also been measured as  $-13.80 \pm 0.10$  kcal. mole<sup>-1</sup> in the solution calorimeter by A. E. Hatton, D. L. Hildebrand, G. C. Sinks and D. R. Stull<sup>3</sup>. Both results are in good agreement.

The heat of hydrolysis of potassium metal,  $\Delta H_f^0$  298, has been measured in the solution calorimeter by the following investigators.

Source	Number of Moles of H <sub>2</sub> O	$\Delta H_f^0$ 298 (KOH(c)) kcal. mole <sup>-1</sup>	$\Delta H_f^0$ 298 (KOH(c)) kcal. mole <sup>-1</sup>
Gunn et al. <sup>4</sup>	1000	-46.877 ± 0.01	-101.531
Messer et al. <sup>5</sup>	OO	-17.02 ± 0.15	-101.555
Ketchen et al. <sup>6</sup>	OO	-46.894 ± 0.24	-101.439

The values of  $\Delta H_f^0$  298 (KOH(c)) were calculated from the heats of reaction,  $\Delta H_f^0$  298, using  $\Delta H_f^0$  298(H<sub>2</sub>O, l) =  $-68.315$  kcal. mole<sup>-1</sup>. Combination of the selected heat of solution of KOH(c) at infinite dilution with the heat of formation of KOH(650 H<sub>2</sub>O) gives the heat of formation of KOH(c) in the last column of the table. A weighted average of these three measurements was taken for the selected heat of formation of KOH(c).

The earlier investigations have been reviewed by P. R. Bitchowsky and P. D. Rossini<sup>8</sup> and C. E. Messer et al.<sup>5</sup>, and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of KOH(c) from 15° to 340°K. have been measured by A. E. Hatton et al.<sup>7</sup> who have also observed a sharp peak in the heat capacity curve in the temperature range from 210° to 230°K. These values of  $C_p$  were adopted in the calculation. W. L. Powers and G. C. Blalock<sup>9</sup> have measured the high temperature enthalpy changes of the solid KOH in the  $\alpha$  and  $\beta$  phases by the drop method. Their enthalpy data are scattered and not precise enough to accurately define the heat capacities in the  $\alpha$  phase. Therefore, the selected heat capacities between 310° and 522°K. were estimated from a graphical extrapolation of the low temperature heat capacity curve, and the tabulated  $H^0 - H^0_{298}$  functions are in agreement with their enthalpy measurements within the experimental uncertainty. The heat capacities of KOH(c) in the  $\beta$  phase were obtained from Powers and Blalock<sup>9</sup>.

The entropy ( $S^0_{298} = 18.95$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>) was taken from Hatton et al.<sup>7</sup>, based on an extrapolation of  $S^0_{15} = 0.054$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Transition and Melting Data.

Hatton et al.<sup>7</sup> have found a lambda transition at 227.4°K. in the heat capacity measurement. The adopted heat of  $\alpha$ - $\beta$  transition at 522°K. and heat of melting at 675°K. were obtained from Powers and Blalock<sup>9</sup>. P. S. Seward and K. E. Martin<sup>10</sup> found  $\Delta H_m^0 = 1.83$  kcal. mole<sup>-1</sup> at 693°K. in phase diagram studies of the system KOH-K<sub>2</sub>CO<sub>3</sub>.

Heat of Sublimation.

See KOH(g) table for details.

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- P. S. Seward and K. E. Martin, J. Am. Chem. Soc., **71**, 3564 (1949).

T, °K.	C <sub>p</sub>	S <sup>0</sup>	$-(F^0 - H^0_{298})/T$	$H^0 - H^0_{298}$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>f</sub>
0	0.000	0.000	INFINITE	2.226	-100.694	-100.694	INFINITE
100	8.164	5.705	31.103	2.560	-101.477	-97.901	213.963
200	12.978	12.857	20.368	1.502	-101.681	-94.220	102.059
298	15.746	18.949	18.949	0.000	-101.510	-90.594	66.407
300	15.769	19.046	18.949	0.029	-101.507	-90.526	65.948
400	17.400	23.798	19.586	1.685	-101.868	-86.786	47.418
500	19.020	27.853	20.843	3.505	-101.505	-83.055	36.303
600	18.800	31.200	22.685	6.209	-99.455	-79.652	29.000
700	18.800	37.098	24.543	8.789	-99.131	-76.345	23.836
800	18.800	39.609	26.272	10.669	-98.715	-73.120	19.975
900	18.800	41.823	27.880	12.349	-98.310	-69.944	16.995
1000	18.800	43.804	29.375	14.829	-97.923	-66.813	14.602
1100	18.800	45.596	30.749	16.309	-116.443	-62.497	12.457
1200	18.800	47.232	32.074	18.189	-115.871	-57.834	10.533
1300	18.800	48.736	33.299	20.069	-115.288	-53.022	8.804
1400	18.800	50.136	34.442	21.949	-114.711	-48.154	7.343
1500	18.800	51.427	35.441	23.829	-114.150	-43.225	6.042

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100	19.860	23.518	23.518	0.000	- 88.879	65.150
200						
298						
300	19.860	23.641	23.519	0.037	- 88.820	64.705
400	19.860	29.355	24.298	2.023	- 85.994	46.767
500	19.860	33.786	25.769	4.009	- 82.441	36.035
600	19.860	37.407	27.416	5.995	- 79.393	28.919
700	19.860	40.469	29.068	7.981	- 76.436	23.864
800	19.860	43.121	30.662	9.967	- 73.555	20.094
900	19.860	45.460	32.179	11.953	- 70.736	17.177
1000	19.860	47.552	33.613	13.939	- 67.975	14.856
1100	19.860	49.445	34.968	15.925	- 64.238	12.763
1200	19.860	51.173	36.247	17.911	- 59.765	10.885
1300	19.860	52.763	37.458	19.997	- 55.352	9.306
1400	19.860	54.234	38.604	21.983	- 51.704	7.960
1500	19.860	55.605	39.692	23.969	- 46.676	6.801
1600	19.860	56.886	40.727	25.955	- 42.406	5.792
1700	19.860	58.090	41.714	27.841	- 38.179	4.908
1800	19.860	59.226	42.655	29.627	- 33.991	4.127
1900	19.860	60.299	43.556	31.313	- 29.836	3.432
2000	19.860	61.318	44.419	33.799	- 25.715	2.810
2100	19.860	62.287	45.247	35.785	- 21.625	2.251
2200	19.860	63.211	46.042	37.771	- 17.565	1.745
2300	19.860	64.094	46.806	39.757	- 13.534	1.286
2400	19.860	64.936	47.546	41.743	- 9.520	0.867
2500	19.860	65.750	48.258	43.729	- 5.547	0.485

S°<sub>298.15</sub> = 23.518 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

S°<sub>298.15</sub> = 23.518 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

ΔH<sub>f</sub><sup>o</sup><sub>298.15</sub> = -98.433 kcal. mole<sup>-1</sup>

T<sub>m</sub> = 673°K.

ΔH<sub>f</sub><sup>o</sup> = 2.240 kcal. mole<sup>-1</sup>

T<sub>b</sub> (monomeric gas) = 1600°K.

ΔH<sub>v</sub><sup>o</sup> (to monomer) = 32.0 kcal. mole<sup>-1</sup>

Heat of Formation.

The heat of formation of KOH(l) at 298°K. was obtained from that of the crystal by adding ΔH<sub>m</sub><sup>o</sup> and the difference between H°<sub>73</sub>-H°<sub>298</sub> for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase, C<sub>p</sub> = 19.86 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, was obtained from the enthalpy measurements in the drop calorimeter by W. D. Powers and G. C. Blalock, ORNL-1653, Oak Ridge Nat'l. Lab., Jan. 1954. The constant C<sub>p</sub> was extrapolated below the melting point and up to 2500°K.

The entropy, S°<sub>298.15</sub> = 23.51 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See KOH(c) table for details.

Vaporization Data.

The boiling point 1600°K. was calculated as the temperature at which the free energies of formation (ΔF<sub>f</sub><sup>o</sup>) for both KOH(l) and KOH(g) are equal. The difference in the heats of formation (ΔH<sub>f</sub><sup>o</sup>) of KOH(l) and KOH(g) at the boiling point is the heat of vaporization. If ½(OH)<sub>2</sub>(g) is also considered as a minor component in the vapor mixture (approximately 2% of total vapor pressure at the boiling point) the calculated boiling point is unchanged as 1600°K. (see KOH(g) table for details).

H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), have studied the vapor pressures of liquid KOH and reported the boiling point as 1597°K.

Point Group  $C_s$   
 $\Delta H_f^0 = -54.3 \pm 5$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = [59.4]$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^0 = -55.4 \pm 5$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = 298.15$  = -55.4  $\pm$  5 kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm.<sup>-1</sup>  
 408 (1)  
 [1300](1)  
 [3700](1)

Bond Distance: K-O = [2.21] Å O-H = [0.96] Å  
 Bond Angle: K-O-H = [110]°

Product of the Moments of Inertia:  $I_A I_B I_C = [1.22325] \times 10^{-116}$  g.<sup>3</sup> cm.<sup>3</sup>

Heat of Formation.

R. P. Porter and R. C. Schoonmaker, J. Phys. Chem. 62, 254 and 466 (1958), have investigated the potassium hydroxide vapor by the mass-spectrometric method and found that the KOH vaporizes mainly as gaseous dimer in the temperature range from 573° to 723°K. Later, Schoonmaker and Porter, J. Chem. Phys. 31, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of H<sub>2</sub>O in their sample container. Using the reported partial pressures of KOH(g) and K<sub>2</sub>(OH)<sub>2</sub>(g) at 641° and 686°K. and JANAF free energy functions, the third law calculations give  $\Delta H_f^0 = -45.4 \pm 5$  kcal. mole<sup>-1</sup> for 2KOH(g)  $\rightarrow$  K<sub>2</sub>(OH)<sub>2</sub>(g), and  $\Delta H_f^0 = 45.1 \pm 3.5$  kcal. mole<sup>-1</sup> for KOH(c)  $\rightarrow$  KOH(g), and  $\Delta H_f^0 = 45.6 \pm 5$  kcal. mole<sup>-1</sup> for 2KOH(c)  $\rightarrow$  K<sub>2</sub>(OH)<sub>2</sub>(g). The uncertainties given were derived by assuming  $K_p$  to be good to a factor of 5 as stated by the authors and including an extra factor of 2 as possible error in activity. To this was added an estimate of the uncertainty due to functions used. In order to have good agreement between the calculated total pressures of monomeric and dimeric KOH(g) and the observed vapor pressures measured by H. von Wartenberg and F. Albrecht, Z. Elektrochem. 27, 162 (1921), the heat of sublimation to monomeric gas was adjusted to  $\Delta H_s^0 = 46.08$  kcal. mole<sup>-1</sup>. (The heat of sublimation to dimeric gas was unchanged as  $\Delta H_s^0 = 45.64$  kcal. mole<sup>-1</sup>). The calculated boiling point is 1600°K. which is in good agreement with 1597  $\pm$  10°K. reported by Wartenberg and Albrecht. The heats of formation were calculated from the selected heats of sublimation as  $\Delta H_f^0$  298 (KOH,g) = -55.4 and  $\Delta H_f^0$  298 (K<sub>2</sub>(OH)<sub>2</sub>,g) = -157.4 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The bond distance K-O was estimated by adding the bond length difference (0.04 Å) between H-O(g) and H-F(g) to the bond distance K-F(g) (2.17146 Å) which has been accurately measured by R. K. Hicnie and H. Lew, Can. J. Phys. 42, 43 (1964). The bond distance O-H was estimated from that in H<sub>2</sub>O(g). The bent molecular configuration with the bond angle of 110° has been proposed by S. H. Bauer, R. M. Diner and R. F. Porter, J. Chem. Phys. 25, 991 (1958), but a linear model has also been suggested by R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. 31, 830 (1959). The bent model has been adopted in the tabulation. The three principal moments of inertia are:  $I_A = [0.1256] \times 10^{-39}$ ,  $I_B = [9.8070] \times 10^{-39}$  and  $I_C = [9.9326] \times 10^{-39}$  g. cm.<sup>2</sup>

The K-O stretching frequency (408 cm.<sup>-1</sup>) was obtained from L. H. Spinar and J. L. Matzgrave, Spectrochim. Acta 12, 244 (1957) in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

L. Brewer and D. F. Mastick, J. Am. Chem. Soc. 73, 2045 (1951), have calculated theoretically the bond distances of gaseous alkali oxides (Li-O = 1.52 Å, Na-O = 1.94 Å and K-O = 2.27 Å) which have been quoted by Bauer, Diner and Porter, loc. cit., and many other authors.

T. °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	8.143	48.78	66.467	1.768	54.256	120.950
200	8.578	50.245	71.1	55.014	55.920	61.107
298	9.550	58.392	88.302	55.434	56.277	41.252
300	9.559	58.451	88.303	55.442	56.283	41.002
400	10.028	61.267	98.773	56.475	56.385	35.4807
500	10.420	63.549	99.507	56.914	56.311	24.614
600	10.743	65.478	60.346	57.359	56.152	20.4454
700	11.012	67.155	61.201	57.677	55.930	17.462
800	11.247	68.641	62.040	58.027	55.658	15.205
900	11.459	69.978	62.846	58.416	55.340	13.438
1000	11.654	71.194	63.624	58.752	55.086	12.017
1100	11.834	72.315	64.364	59.046	54.874	10.644
1200	12.000	73.352	65.070	59.298	54.696	9.353
1300	12.153	74.318	65.744	59.516	54.546	8.250
1400	12.294	75.224	66.380	59.698	54.420	7.220
1500	12.422	76.077	67.007	59.844	54.314	6.255
1600	12.539	76.882	67.600	59.956	54.222	5.792
1700	12.645	77.646	68.166	60.034	54.140	5.162
1800	12.741	78.371	68.715	60.081	54.068	4.602
1900	12.827	79.062	69.242	60.100	54.000	4.099
2000	12.906	79.722	69.745	60.100	53.937	3.640
2100	12.978	80.354	70.239	60.081	53.878	3.238
2200	13.043	80.954	70.713	60.046	53.824	2.865
2300	13.101	81.520	71.161	60.000	53.774	2.525
2400	13.151	82.059	71.612	59.944	53.728	2.212
2500	13.204	82.567	72.045	59.880	53.686	1.925
2600	13.258	83.046	72.450	59.808	53.648	1.658
2700	13.309	83.495	72.828	59.729	53.614	1.412
2800	13.356	83.920	73.180	59.644	53.584	1.183
2900	13.401	84.324	73.520	59.554	53.556	0.969
3000	13.443	84.709	73.845	59.460	53.530	0.769
3100	13.481	85.072	74.150	59.362	53.506	0.582
3200	13.516	85.416	74.438	59.260	53.484	0.406
3300	13.547	85.742	74.709	59.154	53.464	0.240
3400	13.575	86.052	74.964	59.044	53.446	0.085
3500	13.601	86.347	75.204	58.930	53.430	0.000
3600	13.624	86.627	75.429	58.812	53.416	-0.063
3700	13.644	86.892	75.640	58.690	53.404	-0.125
3800	13.661	87.142	75.836	58.564	53.394	-0.186
3900	13.675	87.377	76.018	58.434	53.386	-0.245
4000	13.686	87.598	76.186	58.300	53.380	-0.302
4100	13.694	87.804	76.340	58.162	53.376	-0.357
4200	13.700	87.995	76.481	58.020	53.374	-0.410
4300	13.704	88.171	76.609	57.874	53.374	-0.461
4400	13.706	88.333	76.724	57.724	53.376	-0.510
4500	13.706	88.481	76.826	57.570	53.380	-0.557
4600	13.704	88.615	76.915	57.412	53.386	-0.602
4700	13.699	88.736	76.991	57.250	53.394	-0.645
4800	13.691	88.843	77.054	57.084	53.404	-0.686
4900	13.679	88.936	77.104	56.914	53.416	-0.725
5000	13.670	89.015	77.141	56.740	53.430	-0.761
5100	13.654	89.080	77.164	56.562	53.446	-0.794
5200	13.628	89.131	77.174	56.380	53.464	-0.824
5300	13.601	89.169	77.171	56.194	53.484	-0.850
5400	13.574	89.204	77.156	56.004	53.506	-0.872
5500	13.547	89.235	77.129	55.810	53.530	-0.890
5600	13.519	89.262	77.091	55.612	53.556	-0.904
5700	13.491	89.285	77.041	55.410	53.584	-0.914
5800	13.462	89.304	76.979	55.204	53.614	-0.920
5900	13.433	89.319	76.906	55.000	53.646	-0.922
6000	13.404	89.330	76.822	54.798	53.680	-0.920

Mar. 31, 1962; June 30, 1962; Mar. 31, 1966

$\Delta H_f^0 = -114.16 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -115.84 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $\Delta H_m = 5.010 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15}(\text{to monomer}) = [57.0] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15}(\text{to dimer}) = [50.2] \text{ kcal. mole}^{-1}$

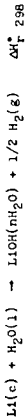
$S_{298.15}^0 = 10.225 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 74.3^\circ\text{K.}$

Heat of Formation.

The standard enthalpy of formation,  $\Delta H_f^{298}(\text{LiOH, c}) = -115.84 \pm 0.1 \text{ kcal. mole}^{-1}$ , was calculated from the heat of solution of lithium hydroxide (c), the heat of hydrolysis of lithium metal and the appropriate auxiliary data.

N. A. Peshetnikov<sup>1</sup> has measured the heat of solution  $\text{LiOH(c)} \rightarrow \text{LiOH(400 H}_2\text{O)}$  as  $-5.479 \pm 0.007 \text{ kcal. mole}^{-1}$  at  $298.15^\circ\text{K.}$  by solution calorimetry. Using the auxiliary heat of dilution reported by V. E. Parker<sup>2</sup>, the selected heat of solution of lithium hydroxide (c) at infinite dilution is  $-5.532 \text{ kcal. mole}^{-1}$ .

The heat of hydrolysis of lithium metal,  $\Delta H_f^{298}$ , has been measured in the solution calorimeter by the following investigators.



Source	Number of moles of H <sub>2</sub> O	$\Delta H_f^{298}$ kcal. mole <sup>-1</sup>	$\Delta H_f^{298}(\text{LiOH, c})$ kcal. mole <sup>-1</sup>
Gunn et al. <sup>3</sup>	1000	$-53.115 \pm 0.019$	$-121.532$
Messer et al. <sup>4</sup>	OO	$-53.075 \pm 0.20$	$-121.390$
			$-115.900$
			$-115.758$

The values of  $\Delta H_f^{298}(\text{LiOH(aq)})$  were calculated from the heats of reaction  $\Delta H_r^{298}$  using the  $\Delta H_f^{298}(\text{H}_2\text{O, l}) = -68.315 \text{ kcal. mole}^{-1}$ . Combination of the selected heat of solution of  $\text{LiOH(c)}$  at infinite dilution with the heat of formation of  $\text{LiOH(aq)}$  gives the heat of formation of  $\text{LiOH(c)}$  in the last column of the table. A weighted average of these measurements was taken for the adopted heat of formation of lithium hydroxide (c).

The earlier calorimetric investigations have been reviewed by P. R. Bichowsky and F. D. Rossini<sup>5</sup>, and C. E. Messer et al.<sup>6</sup>, and these data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of lithium hydroxide (c) from  $15.91^\circ$  to  $302.85^\circ\text{K.}$  have been measured by T. W. Bauer, H. L. Johnston and E. C. Kerr<sup>7</sup>. The high temperature heat capacities which were determined from the enthalpy measurements in the temperature range from  $418^\circ$  to  $876^\circ\text{K.}$  by the drop method have been reported by C. H. Shomate and A. J. Cohen<sup>8</sup>. The low temperature and the high temperature heat capacities have been joined smoothly by the Shomate method<sup>9</sup>. The smooth values of heat capacity of  $\text{LiOH(c)}$  were adopted in the tabulation.

W. D. Powers and G. C. Blalock<sup>10</sup> have also measured the high temperature enthalpy changes of  $\text{LiOH(c)}$  by the drop method. Their results are in agreement with the tabulated  $H_f^{298}$  values within the experimental uncertainty.

The entropy ( $S_{298}^0 = 10.225 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ ) was obtained from Bauer et al.<sup>7</sup>, based on an extrapolation of  $S_{15}^0 = 0.028 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Melting Data.

The adopted heat of melting and the melting point were obtained from the enthalpy measurements by Shomate and Cohen<sup>8</sup>. Powers and Blalock<sup>10</sup> also found the heat of melting  $\Delta H_m^0 = 5.029 \text{ kcal. mole}^{-1}$  at  $74.6^\circ\text{K.}$  which is in good agreement with the adopted value.

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T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	0.000	0.000	INFINITE	1.770	-114.456	-114.456	INFINITE
100	3.492	2.044	18.416	1.637	-115.178	-111.911	244.581
200	8.600	6.124	11.218	1.019	-115.641	-108.442	118.500
298	11.850	10.225	10.225	0.000	-115.840	-104.858	76.863
300	11.900	10.299	10.225	0.022	-115.842	-104.790	76.339
400	13.900	14.020	10.719	1.320	-115.867	-101.098	55.237
500	15.230	17.272	11.712	2.780	-116.540	-97.337	42.546
600	16.300	20.143	12.682	4.357	-116.404	-93.507	34.060
700	17.370	22.737	13.430	6.040	-116.161	-89.709	28.008
800	18.165	25.117	15.357	7.824	-115.821	-85.953	23.481
900	18.800	27.294	16.546	9.673	-115.426	-82.242	19.971
1000	19.336	29.303	17.723	11.590	-114.981	-78.578	17.173
1100	19.807	31.168	18.661	13.538	-114.494	-74.961	14.893
1200	20.234	32.910	19.460	15.540	-113.971	-71.390	13.002
1300	20.630	34.546	21.020	17.593	-113.414	-67.865	11.409
1400	21.004	36.088	22.042	19.665	-112.826	-64.382	10.050
1500	21.360	37.550	23.027	21.783	-112.210	-60.944	8.880
1600	21.704	38.939	23.979	23.937	-111.565	-57.546	7.860
1700	22.038	40.265	24.896	26.124	-145.939	-52.862	6.796
1800	22.364	41.534	25.778	28.344	-143.059	-47.412	5.757
1900	22.685	42.752	26.648	30.597	-143.824	-42.121	4.832
2000	23.000	43.923	27.483	32.881	-143.325	-36.059	4.006

$\Delta H_f^{298.15} = 11.574 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{298.15} = -113.263 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^0 = 5.010 \text{ kcal. mole}^{-1}$   
 $\Delta H_v^0(\text{to monomer}) = 40.1 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 11.574 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 744.3^\circ\text{K.}$   
 $T_b(\text{monomeric gas}) = 1803^\circ\text{K.}$

Heat of Formation.

The heat of formation of LiOH(l) at 298.15°K. was obtained from that of the crystal by adding  $\Delta H_m^0$  and the difference between  $H_{744.3}^0 - H_{298.15}^0$  for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacity of the liquid phase,  $C_p = 20.74 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ , was obtained from the enthalpy measurements in the drop calorimeter by C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc. **77**, 285 (1955).

W. D. Powers and G. C. Bialock, ORNL-1653, Oak Ridge Nat'l. Lab., have also determined the heat capacity of lithium hydroxide (l),  $C_p = 22.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ , from the enthalpy measurements by the drop method.

The entropy ( $S_{298.15}^0 = 11.574 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ ) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiOH(c) table for details.

Vaporization Data.

The boiling point was calculated as the temperature at which the free energies of formation ( $\Delta F_f^0$ ) for both LiOH(l) and LiOH(g) are equal. The difference in the heats of formation ( $\Delta H_f^0$ ) of LiOH(l) and LiOH(g) at the boiling point is the heat of vaporization ( $\Delta H_v^0$ ).

T, °K.	C <sub>p</sub>	S <sup>0</sup> - (F <sup>0</sup> - H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> - H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0						
100	20.740	11.574	0.000	-113.263	-102.683	75.269
200	20.740	11.575	0.38	-113.249	-102.618	74.757
300	20.740	11.576	1.17	-113.234	-102.585	74.419
400	20.740	11.577	2.41	-113.220	-102.570	74.194
500	20.740	11.578	4.18	-113.207	-102.563	74.030
600	20.740	11.579	6.44	-113.195	-102.561	73.925
700	20.740	11.580	9.17	-113.184	-102.562	73.866
800	20.740	11.581	12.34	-113.174	-102.564	73.841
900	20.740	11.582	15.92	-113.165	-102.566	73.849
1000	20.740	11.583	19.87	-113.157	-102.568	73.877
1100	20.740	11.584	24.16	-113.150	-102.570	73.921
1200	20.740	11.585	28.76	-113.144	-102.572	73.979
1300	20.740	11.586	33.64	-113.139	-102.574	74.049
1400	20.740	11.587	38.78	-113.135	-102.575	74.129
1500	20.740	11.588	44.16	-113.132	-102.576	74.207
1600	20.740	11.589	49.76	-113.130	-102.576	74.281
1700	20.740	11.590	55.56	-113.128	-102.576	74.349
1800	20.740	11.591	61.54	-113.127	-102.575	74.411
1900	20.740	11.592	67.68	-113.126	-102.574	74.466
2000	20.740	11.593	73.96	-113.126	-102.572	74.514
2100	20.740	11.594	80.36	-113.126	-102.569	74.555
2200	20.740	11.595	86.86	-113.126	-102.565	74.589
2300	20.740	11.596	93.44	-113.126	-102.560	74.616
2400	20.740	11.597	100.08	-113.126	-102.554	74.635
2500	20.740	11.598	106.76	-113.126	-102.547	74.646
2600	20.740	11.599	113.46	-113.126	-102.539	74.649
2700	20.740	11.600	120.16	-113.126	-102.530	74.644
2800	20.740	11.601	126.84	-113.126	-102.520	74.631
2900	20.740	11.602	133.48	-113.126	-102.509	74.610
3000	20.740	11.603	140.06	-113.126	-102.497	74.581
3100	20.740	11.604	146.56	-113.126	-102.484	74.544
3200	20.740	11.605	152.96	-113.126	-102.470	74.499
3300	20.740	11.606	159.24	-113.126	-102.455	74.446
3400	20.740	11.607	165.38	-113.126	-102.439	74.384
3500	20.740	11.608	171.36	-113.126	-102.422	74.313

$\Delta H_f^0 = -58.1 \pm 4 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -58.8 \pm 4 \text{ kcal. mole}^{-1}$

Point Group  $C_s$   
 $S_{298.15} = [52.0] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm.}^{-1}$   
 [1000](1)  
 [1300](1)  
 [3700](1)

Bond Distance: Li-O = [1.60] Å O-H = [0.96] Å

$\sigma = 1$

Bond Angle: Li-O-H = [110]°  
 Product of the Moments of Inertia:  $I_A I_B I_C = [0.6156 \times 10^{-117}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. **33**, 533 (1960), have studied the equilibrium of  $\text{Li}_2\text{O}(c) + \text{H}_2\text{O}(g) \rightleftharpoons 2\text{LiOH}(g)$  by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K, the heat of reaction  $\text{Li}_2\text{O}(c) + \text{H}_2\text{O}(g) \rightarrow 2\text{LiOH}(g)$  at 298.15°K. has been calculated by both the second and the third law methods as 86.1 and 83.2 kcal. mole<sup>-1</sup>, respectively. (The third law drift is  $-2.2 \pm 2.6 \text{ e.u.}$ ) The third law value was taken for the calculation of the heat of formation of LiOH(g) at 298.15°K.

Heat Capacity and Entropy.

Since the bond distance Li-F(g) ( $r_e = 1.56399 \text{ Å}$ ) was accurately measured from the microwave studies by L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagh and V. E. Derr, J. Chem. Phys. **38**, 1203 (1963), the bond distance Li-O in LiOH(g) was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance Li-F(g). Also the bond distance Li-O(g) was estimated as 1.62 Å from the matrix-isolated infrared spectrum by D. White, K. S. Seshadri, D. P. Dever, D. E. Mann, M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963). These two are in good agreement. The bond distance O-H was estimated from that in  $\text{H}_2\text{O}(g)$ . The adopted bent molecular configuration with bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. F. Porter, J. Chem. Phys. **29**, 991 (1958). The three principal moments of inertia are  $I_A = [0.1237] \times 10^{-39}$ ,  $I_B = [2.1699] \times 10^{-39}$  and  $I_C = [2.2936] \times 10^{-39} \text{ g. cm.}^2$

The Li-O stretching frequency was estimated to be the same as that in  $\text{Li}_2\text{O}(g)$  ( $\nu = 987 \text{ cm.}^{-1}$ , see  $\text{Li}_2\text{O}(g)$  table). The bending and the O-H stretching frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

T. °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S° -(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub> kcal. mole <sup>-1</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞
100	7.949	43.240	2.400	58.089	58.089	INFINITE
200	8.041	48.764	1.605	58.149	59.001	128.947
298	8.474	52.044	1.000	58.433	59.762	65.305
				58.843	60.329	44.222
300	8.485	52.097	0.16	58.851	60.339	43.957
400	9.107	54.622	0.895	59.296	60.767	33.202
500	9.686	56.718	1.835	60.488	61.008	26.666
600	10.163	58.528	2.829	60.935	61.068	22.244
700	10.551	60.124	3.865	61.339	61.058	19.024
800	10.875	61.555	4.937	61.711	60.994	16.663
900	11.154	62.852	6.039	62.063	60.882	14.784
1000	11.400	64.041	7.166	62.398	60.733	13.273
1100	11.620	65.138	8.318	62.717	60.551	12.030
1200	11.818	66.157	9.490	63.024	60.340	10.989
1300	11.996	67.110	10.681	63.320	60.104	10.104
1400	12.157	68.005	11.888	63.606	59.846	9.342
1500	12.302	68.849	13.111	63.885	59.568	8.679
1600	12.432	69.647	14.348	64.156	59.271	8.096
1700	12.550	70.405	15.597	64.419	58.960	7.509
1800	12.658	71.125	16.858	64.675	58.636	6.921
1900	12.751	71.812	18.128	64.925	58.300	6.334
2000	12.837	72.468	19.408	65.171	57.955	5.748
2100	12.915	73.096	20.695	65.413	57.600	5.162
2200	12.986	73.699	21.990	65.651	57.235	4.576
2300	13.049	74.277	23.292	65.884	56.860	4.000
2400	13.106	74.834	24.600	66.113	56.475	3.434
2500	13.159	75.370	25.913	66.337	56.086	2.878
2600	13.207	75.887	27.231	66.556	55.693	2.332
2700	13.251	76.386	28.554	66.770	55.296	1.796
2800	13.291	76.869	29.881	66.979	54.895	1.270
2900	13.327	77.337	31.212	67.183	54.490	0.754
3000	13.361	77.788	32.547	67.382	54.081	0.248
3100	13.392	78.227	33.884	67.576	53.668	-0.258
3200	13.420	78.653	35.225	67.765	53.251	-0.766
3300	13.446	79.068	36.568	67.949	52.830	-1.274
3400	13.471	79.468	37.914	68.128	52.405	-1.782
3500	13.493	79.859	39.262	68.302	51.976	-2.290
3600	13.513	80.239	40.613	68.471	51.543	-2.798
3700	13.533	80.611	41.965	68.636	51.106	-3.306
3800	13.552	80.971	43.319	68.796	50.665	-3.814
3900	13.568	81.323	44.675	68.951	50.220	-4.322
4000	13.584	81.667	46.033	69.101	49.771	-4.830
4100	13.599	82.002	47.392	69.246	49.318	-5.338
4200	13.612	82.330	48.773	69.386	48.861	-5.846
4300	13.625	82.651	50.115	69.521	48.400	-6.354
4400	13.637	82.964	51.417	69.651	47.935	-6.862
4500	13.649	83.271	52.682	69.776	47.466	-7.370
4600	13.659	83.571	54.027	69.896	46.993	-7.878
4700	13.669	83.864	55.374	69.999	46.516	-8.386
4800	13.679	84.152	56.720	70.096	46.035	-8.894
4900	13.688	84.434	58.067	70.188	45.550	-9.402
5000	13.696	84.711	59.419	70.275	45.061	-9.910
5100	13.704	84.982	60.772	70.357	44.568	-10.418
5200	13.711	85.249	62.128	70.434	44.071	-10.926
5300	13.719	85.510	63.484	70.506	43.570	-11.434
5400	13.727	85.766	64.841	70.573	43.065	-11.942
5500	13.732	86.018	66.199	70.636	42.557	-12.450
5600	13.738	86.266	67.557	70.695	42.045	-12.958
5700	13.744	86.510	68.916	70.749	41.529	-13.466
5800	13.749	86.750	70.276	70.799	41.009	-13.974
5900	13.754	86.986	71.634	70.845	40.484	-14.482
6000	13.759	87.214	72.993	70.887	39.955	-14.989

Ground State Configuration  $3 \Sigma^-$   
 $S_{298.15}^{\circ} = 43.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{\circ} = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{\circ} 298.15 = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$

## Electronic Level and Quantum Weight

$$\frac{\epsilon_1, \text{ cm.}^{-1}}{0} \frac{g_1}{3}$$

$$\omega_e x_e = 3315 \text{ cm.}^{-1}$$

$$\omega_e = 16,6684 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$r_e = 1.038 \text{ \AA}$$

## Heat of Formation.

The value,  $\Delta H_f^{\circ} 298_1$  (NH, g) =  $81.0 \pm 2.5 \text{ kcal. mole}^{-1}$ , was calculated from the selected dissociation energy,  $D_0 = 85 \pm 2 \text{ kcal. mole}^{-1}$ , based on the following investigations. J. L. Franklin, V. H. Dibeler, R. M. Reese and M. Krause, *J. Am. Chem. Soc.* **80**, 298 (1958) and R. I. Reed and W. Snedden, *J. Chem. Soc.* 4132 (1959) have determined the dissociation energy of NH(g) by electron impact as  $85 \pm 2 \text{ kcal. mole}^{-1}$  and  $85.3 \pm 6 \text{ kcal. mole}^{-1}$ , respectively. A. L. Companion and F. O. Ellison, *J. Chem. Phys.* **32**, 1132 (1960), and P. C. H. Jordan and H. C. Lonquet-Higgins, *Mol. Phys.* **5**, 121 (1962) have calculated theoretically the dissociation energy by a semi-empirical method and obtained  $83.3 \text{ kcal. mole}^{-1}$  and  $81.2 \text{ kcal. mole}^{-1}$ , respectively. These results are in good agreement. G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, 1950, has estimated the dissociation energy  $D_0(\text{NH}, g) = 5.8 \text{ e.v.}$  ( $87.6 \text{ kcal. mole}^{-1}$ ) based on the average of two earlier theoretical calculations by R. S. Mulliken, ( $D_0 = 4.2 \text{ e.v.}$ ), *Rev. Mod. Phys.* **4**, 1 (1932) and G. King ( $D_0 = 3.4 \text{ e.v.}$ ), *J. Chem. Phys.* **5**, 378 (1936). A. G. Gaydon, "Dissociation Energies", 2nd Ed., Chapman & Hall Ltd., London, 1953, favored G. Glockler's estimation  $D_0 = 86.3 \text{ kcal. mole}^{-1}$  which was based upon the comparison of force constants and D values of related hydrides (i.e. CH, OH and FH).

## Heat Capacity &amp; Entropy.

The rotational constants  $B_e$  and  $C_e$  were obtained from R. N. Dixon, *Can. J. Phys.* **37**, 1171 (1959). The vibrational constants  $\omega_e$  and  $\omega_e x_e$  were calculated from Dixon's data:  $B_e = 16.6684 \text{ cm.}^{-1}$ ,  $D_e = 16.85 \times 10^{-4} \text{ cm.}^{-1}$  and  $\omega_e = 3125.6 \text{ cm.}^{-1}$  by the relation  $D_e = 4 B_e^3 / \omega_e^2$  and  $\omega_e = \omega_e - 2 \omega_e x_e$ .

D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **41**, 2838 (1964) have observed from the spectrum of NH the vibrational fundamental  $\omega = 3133 \pm 2 \text{ cm.}^{-1}$  in Ar and  $N_2$  matrices. K. Rosengren and G. C. Pimentel, *J. Chem. Phys.* **43**, 507 (1965) also reported  $\omega = 3122.2 \pm 0.6 \text{ cm.}^{-1}$  in  $N_2$  matrix and  $\omega = 3131.6 \pm 0.4 \text{ cm.}^{-1}$  in Ar matrix.

T, °K.	C <sub>p</sub> <sup>‡</sup>	S <sup>‡</sup> - (S <sup>‡0</sup> - H <sup>‡0</sup> )/T	H <sup>‡</sup> - H <sup>‡0</sup>	ΔH <sub>f</sub> <sup>‡</sup>	ΔF <sup>‡</sup>	Log K <sub>p</sub>
0	6.000	INFINITE	2.066	80.988	80.985	INFINITE
100	6.261	35.966	1.386	80.986	80.983	-17.9229
200	6.503	40.514	0.884	80.989	80.986	-8.7456
298	6.706	43.295	0.000	81.000	79.527	-58.321
300	6.966	43.338	0.13	81.000	79.558	-57.955
400	6.973	45.331	7.13	81.001	79.077	-43.204
500	6.994	46.991	14.08	80.998	78.596	-34.353
600	7.041	48.179	21.10	80.994	78.117	-28.453
700	7.119	49.270	28.17	80.987	77.638	-24.238
800	7.223	50.228	35.34	80.979	77.159	-21.078
900	7.343	51.085	42.62	80.972	76.682	-18.620
1000	7.471	51.885	50.03	80.967	76.206	-16.654
1100	7.601	52.593	57.57	80.963	75.730	-15.046
1200	7.727	53.250	65.23	80.962	75.255	-13.705
1300	7.847	53.874	73.02	80.963	74.778	-12.571
1400	7.960	54.459	80.92	80.966	74.303	-11.599
1500	8.064	55.012	88.94	80.970	73.827	-10.756
1600	8.161	55.536	97.07	80.974	73.350	-10.019
1700	8.250	56.033	105.26	80.980	72.874	-9.368
1800	8.331	56.507	113.55	80.986	72.397	-8.790
1900	8.406	56.959	121.92	80.994	71.921	-8.272
2000	8.474	57.392	130.36	81.001	71.443	-7.807
2100	8.538	57.807	138.86	81.009	70.964	-7.385
2200	8.596	58.206	147.43	81.016	70.485	-7.002
2300	8.650	58.590	156.05	81.025	70.007	-6.652
2400	8.701	58.953	164.73	81.033	69.527	-6.331
2500	8.747	59.315	173.45	81.041	69.046	-6.036
2600	8.791	59.659	182.22	81.049	68.567	-5.763
2700	8.832	59.991	191.03	81.057	68.088	-5.511
2800	8.870	60.313	199.89	81.066	67.606	-5.277
2900	8.907	60.625	208.78	81.075	67.127	-5.059
3000	8.941	60.928	217.70	81.082	66.643	-4.855
3100	8.973	61.221	226.66	81.091	66.163	-4.664
3200	9.004	61.507	235.65	81.099	65.680	-4.486
3300	9.034	61.784	244.66	81.106	65.200	-4.318
3400	9.062	62.054	253.71	81.115	64.718	-4.160
3500	9.089	62.317	262.79	81.122	64.236	-4.011
3600	9.114	62.574	271.89	81.128	63.751	-3.870
3700	9.139	62.824	281.02	81.135	63.269	-3.737
3800	9.163	63.068	290.17	81.141	62.787	-3.611
3900	9.186	63.306	299.34	81.146	62.305	-3.491
4000	9.209	63.539	308.54	81.151	61.821	-3.378
4100	9.230	63.767	317.76	81.155	61.336	-3.269
4200	9.251	63.989	327.00	81.159	60.856	-3.167
4300	9.272	64.207	336.26	81.163	60.372	-3.068
4400	9.292	64.421	345.54	81.165	59.885	-2.974
4500	9.311	64.630	354.84	81.167	59.400	-2.885
4600	9.330	64.835	364.17	81.169	58.919	-2.799
4700	9.349	65.035	373.51	81.170	58.438	-2.717
4800	9.367	65.232	382.86	81.170	57.955	-2.639
4900	9.385	65.426	392.24	81.170	57.467	-2.563
5000	9.403	65.616	401.63	81.170	56.982	-2.491
5100	9.420	65.802	411.04	81.168	56.500	-2.421
5200	9.437	65.985	420.47	81.167	56.018	-2.354
5300	9.454	66.165	429.92	81.165	55.534	-2.290
5400	9.470	66.342	439.36	81.162	55.048	-2.228
5500	9.486	66.516	448.86	81.156	54.566	-2.168
5600	9.502	66.687	458.35	81.154	54.081	-2.111
5700	9.518	66.855	467.86	81.150	53.602	-2.055
5800	9.534	67.021	477.39	81.144	53.116	-2.001
5900	9.549	67.184	486.93	81.139	52.633	-1.950
6000	9.563	67.344	496.49	81.132	52.152	-1.900



MOL. WT. = 39.95717

(CRYSTAL)

SODIUM HYDROXIDE (NaOH)

$\Delta H_f^0 = -100.82 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -101.90 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 = -1.519 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 = -1.519 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15}(\text{to monomer}) = [51.5] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15}(\text{to dimer}) = [49.0] \text{ kcal. mole}^{-1}$

$\Delta H_f^0 = -100.82 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -101.90 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $T_m = 585.55^\circ\text{K.}$   
 $T_m = 582.25^\circ\text{K.}$

Heat of Formation.

The standard enthalpy of formation,  $\Delta H_f^{298}(\text{NaOH}, c) = -101.90 \pm 0.1 \text{ kcal. mole}^{-1}$ , was calculated from the heat of solution of sodium hydroxide (c) and the heat of sodium metal hydrolysis and the appropriate auxiliary data. K. F. Fehsenkov<sup>1</sup> has measured the heat of solution  $\Delta H_{sol}(c) \rightarrow \text{NaOH}(400 \text{ H}_2\text{O})$  as  $-10.145 \pm 0.015 \text{ kcal. mole}^{-1}$  at  $298.15^\circ\text{K.}$  by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Farmer<sup>2</sup>, the selected heat of solution of sodium hydroxide (c) at infinite dilution is  $-10.555 \text{ kcal. mole}^{-1}$ . Also L. E. Murch and K. F. Glaque<sup>3</sup> measured calorimetrically the heat of solution of solid samples of NaOH-mH<sub>2</sub>O in the range from  $n = 0.1$  to  $1.0$ . when extrapolated to  $n = 0$  and infinite dilution, this result yields the heat of solution of NaOH(c) at infinite dilution,  $\Delta H_f^{298} = -10.635 \text{ kcal. mole}^{-1}$ , which is in good agreement with the value selected.

The heat of sodium metal hydrolysis,  $\Delta H_f^{298}$ , has been measured in the solution calorimeter by the following investigators.  $\text{Na}(c) + \text{H}_2\text{O}(l) \rightarrow \text{NaOH}(m\text{H}_2\text{O}) + 1/2 \text{H}_2(g)$   $\Delta H_f^{298}$

Source	Number of Moles of H <sub>2</sub> O	$\Delta H_f^{298}$ (NaOH(mH <sub>2</sub> O)) kcal. mole <sup>-1</sup>	$\Delta H_f^{298}$ (NaOH, c) kcal. mole <sup>-1</sup>
Sum et al. <sup>4</sup>	1000	$-44.047 \pm 0.008$	$-112.445$
Messer et al. <sup>5</sup>	OO	$-44.215 \pm 0.20$	$-112.550$
Ketchen et al. <sup>5</sup>	OO	$-44.054 \pm 0.20$	$-112.359$
			$-101.814$

The values of  $\Delta H_f^{298}(\text{NaOH}(m\text{H}_2\text{O}))$  were calculated from the heat of reaction  $\Delta H_r^{298}$  using the  $\Delta H_f^{298}(\text{H}_2\text{O}, l) = -68.315 \text{ kcal. mole}^{-1}$ . Combination of the selected heat of solution of NaOH(c) at infinite dilution with the heat of formation of NaOH(mH<sub>2</sub>O) gives the heat of formation of NaOH(c) in the last column of the table. A weighted average of these three measurements has been taken for the selected heat of formation of sodium hydroxide (c).

The earlier investigations have been reviewed by P. R. Bichowsky and F. D. Rossini<sup>6</sup> and C. E. Messer et al.<sup>4</sup>, and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

L. E. Murch and K. F. Glaque<sup>3</sup> have measured low temperature heat capacities of NaOH·0.05014 H<sub>2</sub>O and NaOH·0.37776 H<sub>2</sub>O from  $15^\circ$  to  $350^\circ\text{K.}$  and calculated the values of  $C_p$  for the pure phase of NaOH(c). T. E. Douglas and J. L. Dever<sup>7</sup> have measured the enthalpy changes from  $273^\circ$  to  $973^\circ\text{K.}$  in the drop calorimeter and derived the heat capacities. The low temperature and the high temperature heat capacities were joined smoothly by Murch and Glaque, and the smooth values were adopted in the tabulation. Low temperature heat capacities from  $50^\circ$  to  $300^\circ\text{K.}$  have also been measured by J. L. Kelly and P. E. Snyver<sup>8</sup>, whose data are in good agreement with those reported by Murch and Glaque. M. K. Popov and D. M. Ginzburg<sup>9</sup> have determined the heat capacities of NaOH(c) in the temperature range from  $298^\circ$  to  $577^\circ\text{K.}$  from the enthalpy measurements by drop calorimetry. The reported  $^{500}C_p^{298} = 3.112 \text{ kcal. mole}^{-1}$  is in good agreement with the tabulated value.

Transition and Melting Data.

The adopted heat of transition and the transition temperature, and the adopted heat of melting and the melting point were obtained from Douglas and Dever.<sup>7</sup> Popov and Ginzburg<sup>9</sup> reported the heat of transition  $\Delta H_{tr} = 1.930 \text{ kcal. mole}^{-1}$  at  $576.8^\circ\text{K.}$  and the heat of melting  $\Delta H_m = 1.625 \text{ kcal. mole}^{-1}$  at  $555.16^\circ\text{K.}$

Heat of Sublimation.

See NaOH(g) table for details.

References:

1. V. B. Farmer, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RES 2, April, 1965.
2. S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958).
3. S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958).
4. K. F. Fehsenkov, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RES 2, April, 1965.
5. E. E. Ketchen and W. E. Wallace, J. Am. Chem. Soc. 76, 4735 (1954).
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9. M. K. Popov and D. M. Ginzburg, Zhur. Obshch. Khim. 26, 97 (1956).
10. L. E. Murch and K. F. Glaque, J. Phys. Chem. 67, 2552 (1963).
11. L. E. Murch and K. F. Glaque, J. Phys. Chem. 67, 2552 (1963).

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	0.000	INFINITE	-	2.506	-100.815	-100.815	INFINITE
100	6.631	3.713	-	2.254	-101.620	-98.127	214.456
200	11.850	10.176	-	1.292	-101.886	-94.501	103.266
298	14.228	15.440	-	0.000	-101.900	-90.867	66.607
300	14.260	15.488	0.026	-	-101.899	-90.798	66.147
400	15.520	19.772	1.518	-	-102.453	-87.060	47.567
500	17.963	23.461	17.109	-	-102.252	-83.230	36.360
600	20.560	29.710	18.618	6.655	-100.221	-79.559	28.079
700	20.560	32.879	20.435	8.711	-99.611	-76.164	23.760
800	20.560	35.624	22.166	10.767	-99.002	-72.856	19.903
900	20.560	38.046	23.798	12.823	-98.399	-69.624	16.907
1000	20.560	40.212	25.333	14.879	-97.805	-66.458	14.524
1100	20.560	42.172	26.776	16.935	-97.228	-63.354	12.587
1200	20.560	43.961	28.135	18.991	-119.903	-59.842	10.899
1300	20.560	45.606	29.416	21.047	-119.144	-54.867	9.224
1400	20.560	47.130	30.628	23.103	-118.394	-49.951	7.788
1500	20.560	48.549	31.776	25.159	-117.654	-45.088	6.569
1600	20.560	49.875	32.866	27.215	-116.922	-40.274	5.501
1700	20.560	51.122	33.904	29.271	-116.197	-35.505	4.564
1800	20.560	52.287	34.893	31.327	-115.481	-30.779	3.737
1900	20.560	53.409	35.839	33.383	-114.772	-26.093	3.001
2000	20.560	54.463	36.744	35.439	-114.072	-21.444	2.383

$\Delta H_f^\circ 298.15 = -99.998 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^\circ = 1.519 \text{ kcal. mole}^{-1}$   
 $\Delta H_v^\circ(\text{to monomer}) = 37.9 \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = 17.727 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 592.25^\circ\text{K.}$   
 $T_b(\text{monomeric gas}) = 1662.7^\circ\text{K.}$

Heat of Formation.

The heat of formation of NaOH(l) at 298°K. was obtained from that of the crystal by adding  $\Delta H_m^\circ$  and the difference between  $H_{592.25}^\circ - H_{298.15}^\circ$  for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacities in the temperature range from 592.3° to 1000°K. were obtained from the enthalpy measurements of sodium hydroxide (l) in the drop calorimeter by T. B. Douglas and J. L. Dever<sup>1</sup>. The heat capacities below the melting point and above 1000°K. were extrapolated from the selected heat capacity curve.

Douglas and Dever<sup>1</sup> have also compared their heat capacity values with those from W. D. Fowers and G. C. Blalock<sup>2</sup> who have applied the same drop method to determine the heat capacities of NaOH(l). Both results are in reasonable agreement. M. M. Popov and G. M. Ginzburg<sup>3</sup> applying the same technique obtained different values of heat capacity. The smoothed enthalpy data reported by Ginzburg<sup>4</sup> are 200 to 500 cal. mole<sup>-1</sup> smaller than the tabulated values at the temperature range from 700° to 1000°K.

The entropy ( $S_{298}^\circ = 17.65 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ ) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See NaOH(c) table for details.

Vaporization Data.

The boiling point 1662.7°K. was calculated as the temperature at which the free energies of formation ( $\Delta F_f^\circ$ ) for both NaOH(l) and NaOH(g) are equal. The difference in the heats of formation ( $\Delta H_f^\circ$ ) of NaOH(l) and NaOH(g) at the boiling point is the heat of vaporization. If  $\text{Na}_2(\text{OH})_2(\text{g})$  is also considered as a minor component in the vapor mixture (approximately 6% of total vapor pressure at the boiling point) the calculated boiling point is 1653°K. (see NaOH(g) table for details).

H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), have studied the vapor pressures of liquid NaOH and reported the boiling point as 1661°K.

Reference:

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- 2 W. D. Fowers and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Earth Hydroxides at High Temperatures", ORNL-1653, Oak Ridge Nat'l. Lab. Jan. 1954.
- 3 M. M. Popov and G. M. Ginzburg, Zhur. Obshchei Khim. 26, 971 (1956).
- 4 G. M. Ginzburg, ibid. 26, 968 (1956).

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S <sup>o</sup> -(F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup> kcal. mole <sup>-1</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0						
100						
200						
298	20.690	17.727	0.000	-99.998	-89.659	65.722
300	20.988	17.857	0.030	-99.984	-89.595	65.270
400	20.844	21.871	2.130	-99.830	-84.187	47.000
500	20.716	26.511	4.208	-99.317	-82.820	34.201
600	20.570	32.275	6.272	-98.702	-79.579	28.987
700	20.430	38.143	8.322	-98.096	-76.441	23.866
800	20.290	44.015	10.358	-97.509	-73.387	20.049
900	20.150	50.536	12.380	-96.940	-70.406	17.097
1000	20.010	57.651	14.388	-96.395	-67.487	14.749
1100	19.870	64.552	16.382	-95.879	-64.623	12.839
1200	19.730	71.245	18.362	-95.390	-61.816	11.173
1300	19.590	77.728	20.328	-94.932	-59.060	9.515
1400	19.450	84.001	22.280	-94.500	-56.350	8.102
1500	19.310	90.064	24.218	-94.093	-53.685	6.885
1600	19.170	95.917	26.142	-93.710	-51.063	5.825
1700	19.030	101.560	28.052	-93.350	-48.484	4.871
1800	18.890	107.001	29.949	-93.010	-45.945	4.071
1900	18.750	112.248	31.834	-92.690	-43.445	3.338
2000	18.610	117.301	33.708	-92.390	-40.984	2.682
2100	18.470	122.160	35.572	-92.110	-38.561	2.090
2200	18.330	126.825	37.428	-91.850	-36.175	1.555
2300	18.190	131.301	39.276	-91.610	-33.824	1.068
2400	18.050	135.588	41.118	-91.390	-31.506	0.624
2500	17.910	139.696	42.955	-91.190	-29.221	0.217
2600	17.770	143.635	44.787	-91.010	-26.969	-0.157
2700	17.630	147.405	46.617	-90.850	-24.750	-0.503
2800	17.490	151.006	48.445	-90.710	-22.562	-0.822
2900	17.350	154.438	50.270	-90.590	-20.404	-1.116
3000	17.210	157.701	52.095	-90.490	-18.275	-1.384

(IDEAL GAS)

SODIUM HYDROXIDE (NaOH)

Point Group  $C_2$   
 $S_{298.15} = [56.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 Ground State Quantum Weight = 1

$\Delta H_f^0 = -49.4 \pm 5 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = -50.4 \pm 5 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies  
 $\frac{\omega}{\text{cm.}^{-1}}$   
 [1300](1)  
 [3700](1)  
 Bond Distance: Na-O = [1.97] Å O-H = [0.96] Å

$\sigma = 1$

Bond Angle: Na-O-H = [110°]  
 Product of the Moments of Inertia:  $I_A I_B I_C = [5.3062] \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. 28, 454 (1958), have found in their mass-spectrometric studies that the NaOH(l) vaporizes mainly as gaseous dimer in the temperature range from 573° to 753°K. They have also calculated by the slope method the heat of dimerization,  $\Delta H_{298}^0 = -54 \pm 5 \text{ kcal. mole}^{-1}$ , for  $2\text{NaOH}(g) = \text{Na}_2(\text{OH})_2(g)$  and the heat of sublimation,  $\Delta H_{298}^0 = 46.3 \pm 3 \text{ kcal. mole}^{-1}$ , for  $\text{NaOH}(c) = \text{NaOH}(g)$ . The single law values were determined using ion intensity ratios, however, a third law calculation using a single data point converted by the authors to absolute pressure (J. Phys. Chem. 62, 488 (1958)) yields  $\Delta H_{298}^0 = -51.8 \text{ kcal. mole}^{-1}$ ,  $\Delta H_{298}^0(\text{to monomer}) = 49.5 \text{ kcal. mole}^{-1}$  and  $\Delta H_{298}^0(\text{to dimer}) = 41.1 \text{ kcal. mole}^{-1}$  which are in agreement within the limit of uncertainty. Later, Porter and Schoonmaker, J. Chem. Phys. 31, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container, and the uncertainty in the heat of sublimation might be  $\pm 5 \text{ kcal. mole}^{-1}$ , but the heat of dimerization should not be seriously affected because it was calculated from slopes of both species. In order to have good agreement between the calculated total pressures of monomer and dimer of sodium hydroxide (g) and the observed vapor pressures by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), the heat of dimerization and the heat of sublimation have been so chosen as  $\Delta H_{298}^0 = -54 \text{ kcal. mole}^{-1}$  and  $\Delta H_{298}^0(\text{to monomer}) = 51.5 \text{ kcal. mole}^{-1}$ , respectively, which are still within the limit of Porter and Schoonmaker's data. The calculated boiling point is 1653°K. which is in good agreement with 1661  $\pm 20^\circ\text{K}$ . reported by Wartenberg and Albrecht, loc. cit. The heats of formation were calculated from the selected heat of dimerization and heat of sublimation as  $\Delta H_f^{298}(\text{NaOH}, g) = -50.4 \text{ kcal. mole}^{-1}$  and  $\Delta H_f^{298}(\text{Na}_2(\text{OH})_2, g) = -154.8 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

The bent molecular configuration with the bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. F. Porter, J. Chem. Phys. 29, 991 (1958). The bond distance O-H was estimated from that in  $\text{H}_2\text{O}(g)$ . The bond distance Na-O is estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-P(g) to the bond distance Na-F(g) (1.92595 Å) which has been accurately measured by R. K. Bauer and H. Lew, Can. J. Phys. 41, 1461 (1963). The Na-O stretching frequency was obtained from L. H. Spiner and J. L. Margrave, Spectrochim. Acta 12, 244 (1958), in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rigid convergence to a constant as a heavier atom is attached. The three principal moments of inertia are  $I_A = [0.1252] \times 10^{-59}$ ,  $I_B = [6.449] \times 10^{-39}$  and  $I_C = [6.5742] \times 10^{-39} \text{ g. cm.}^2$ .

T. °K.	$C_p$	$S^0$	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>f</sub>
0	∞	∞	∞	2.550	-49.359	-49.359	INFINITE
100	8.095	46.936	1.752	49.618	50.447	50.447	110.252
200	8.889	52.700	1.903	49.997	51.135	51.135	55.878
298	9.486	56.456	2.000	50.400	51.608	51.608	37.830
300	9.496	56.515	2.018	50.407	51.615	51.615	37.800
400	9.986	59.316	2.192	51.479	51.904	51.904	28.359
500	10.391	61.589	2.402	51.916	51.958	51.958	22.711
600	10.722	63.514	2.608	52.308	51.929	51.929	18.915
700	10.996	65.188	2.815	52.668	51.837	51.837	16.184
800	11.235	66.672	3.026	53.003	51.696	51.696	14.123
900	11.449	68.008	3.240	53.322	51.513	51.513	12.500
1000	11.646	69.224	3.469	53.629	51.294	51.294	11.210
1100	11.827	70.343	3.707	53.934	51.048	51.048	10.142
1200	11.995	71.370	3.952	54.234	50.774	50.774	9.163
1300	12.149	72.345	4.204	54.528	50.477	50.477	8.277
1400	12.290	73.251	4.461	54.816	50.158	50.158	7.466
1500	12.418	74.103	4.724	55.098	49.822	49.822	6.733
1600	12.535	74.909	4.992	55.376	49.474	49.474	6.069
1700	12.642	75.672	5.264	55.651	49.112	49.112	5.479
1800	12.738	76.397	5.541	55.924	48.737	48.737	4.954
1900	12.825	77.088	5.821	56.196	48.358	48.358	3.948
2000	12.904	77.748	6.104	56.466	47.974	47.974	3.500
2100	12.976	78.380	6.390	56.734	47.586	47.586	3.023
2200	13.041	78.986	6.678	57.000	47.194	47.194	2.524
2300	13.100	79.566	6.968	57.264	46.798	46.798	2.006
2400	13.154	80.124	7.259	57.526	46.398	46.398	1.476
2500	13.203	80.662	7.551	57.786	45.994	45.994	0.933
2600	13.247	81.181	7.844	58.044	45.586	45.586	0.378
2700	13.286	81.682	8.138	58.299	45.174	45.174	-0.198
2800	13.320	82.166	8.432	58.551	44.758	44.758	-0.682
2900	13.350	82.634	8.726	58.800	44.338	44.338	-1.170
3000	13.379	83.087	9.020	59.046	43.914	43.914	-1.661
3100	13.407	83.527	9.314	59.289	43.486	43.486	-2.156
3200	13.434	83.954	9.608	59.529	43.054	43.054	-2.654
3300	13.472	84.368	9.902	59.766	42.618	42.618	-3.154
3400	13.494	84.770	10.196	59.999	42.178	42.178	-3.656
3500	13.516	85.162	10.490	60.229	41.734	41.734	-4.160
3600	13.535	85.543	10.784	60.456	41.286	41.286	-4.666
3700	13.554	85.914	11.078	60.679	40.834	40.834	-5.174
3800	13.571	86.275	11.372	60.899	40.378	40.378	-5.682
3900	13.586	86.628	11.666	61.116	39.918	39.918	-6.192
4000	13.601	86.972	11.954	61.330	39.454	39.454	-6.704
4100	13.615	87.308	12.242	61.541	38.986	38.986	-7.218
4200	13.628	87.637	12.530	61.749	38.514	38.514	-7.734
4300	13.640	87.957	12.818	61.954	38.038	38.038	-8.250
4400	13.651	88.271	13.106	62.156	37.558	37.558	-8.766
4500	13.662	88.578	13.394	62.355	37.074	37.074	-9.282
4600	13.672	88.878	13.682	62.551	36.586	36.586	-9.798
4700	13.682	89.173	13.970	62.744	36.094	36.094	-10.314
4800	13.691	89.461	14.258	62.934	35.598	35.598	-10.830
4900	13.699	89.743	14.546	63.121	35.098	35.098	-11.346
5000	13.707	90.020	14.834	63.306	34.594	34.594	-11.862
5100	13.715	90.291	15.122	63.489	34.086	34.086	-12.378
5200	13.723	90.558	15.410	63.669	33.574	33.574	-12.894
5300	13.728	90.819	15.698	63.846	33.058	33.058	-13.410
5400	13.735	91.076	15.986	64.020	32.538	32.538	-13.926
5500	13.741	91.328	16.274	64.191	32.014	32.014	-14.442
5600	13.747	91.576	16.562	64.359	31.486	31.486	-14.958
5700	13.752	91.819	16.850	64.524	30.954	30.954	-15.474
5800	13.757	92.058	17.138	64.686	30.418	30.418	-15.990
5900	13.762	92.293	17.426	64.846	29.878	29.878	-16.506
6000	13.767	92.525	17.714	65.003	29.334	29.334	-17.022

MOL. WT. = 17.0074

(IDEAL GAS)

HYDROXYL (OH)

$$\Delta H_f^0 = 9.290 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 43.880 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$S_{298.15}^0 = 43.880 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 9.290 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 43.880 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$S_{298.15}^0 = 43.880 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Electronic Levels and Multiplicities

$\epsilon_1, \text{ cm.}^{-1}$	$g_1$
0	2
139.7	2

$$\omega_e^x e = 82.81 \text{ cm.}^{-1}$$

$$\omega_e = 3755.21 \text{ cm.}^{-1}$$

$$\alpha_e = 0.714 \text{ cm.}^{-1}$$

$$B_e = 18.871 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$r_e = 0.9706 \text{ \AA}$$

Heat of Formation.

P. Gray, Trans. Farad. Soc. 55, 408 (1959) has summarized the determinations of the heat of formation of OH and concludes that the short extrapolation by Barrow, Arkiv. Fysik, 11, 281 (1956) of the  $B(2\Sigma^+)$   $\rightarrow A(2\Sigma^+)$  system gives the most reliable result. The value of  $D_0 = 101.33 \text{ kcal. mole}^{-1}$  was adopted and leads to a heat of formation of  $9.432 \text{ kcal. mole}^{-1}$ . A recent determination of the dissociation energy from measurements of the concentration of the radicals in water oxygen mixtures by A. P. Purmal and A. V. Prost, Vestn. Mosk. Univ., Ser. II Khim. 15, 25 (1961) gives  $\Delta E_D(\text{OH}) = 102.8 \pm 0.8 \text{ kcal. mole}^{-1}$  in good agreement with the adopted value. Also V. A. Medvedev, V. V. Korobov and V. P. Babuz, Zhur. Fiz. Khim. 33, 58 (1959) reported a heat of dissociation of  $102.2 \pm 1 \text{ kcal. mole}^{-1}$  from dissociation of water in a spherical bomb.

Heat Capacity and Entropy.

The molecular constants were all given by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. This calculation gives values in excellent agreement with L. Haar, A. S. Friedman and C. W. Beckett, National Bureau of Standards Monograph No. 20, May 1961. The agreement with the higher order correction calculations of H. L. Johnston, J. Belzer and L. Savedoff, IR 316-5, Ohio State University, available as ATI 139 967, is good between 298 and 4000°K. This earlier work uses different constants and also a different value of the ground state splitting constant, but at 6000°K. the entropy difference is still less than 0.25%.

T, °K.	$C_p$	$S^0$	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	6.000	0.000	INFINITE	-2.192	9.289	9.289	INFINITE
100	7.798	35.726	50.398	-1.467	9.001	9.001	-9.672
200	7.526	40.885	44.541	-0.711	8.393	8.393	-9.475
298	7.167	43.880	43.880	0.000	8.307	8.307	-6.089
300	7.165	43.925	43.881	0.013	8.299	8.299	-6.046
400	7.087	45.974	44.160	0.725	8.442	8.442	-5.327
500	7.055	47.531	44.687	1.432	8.434	7.540	-3.296
600	7.057	48.837	45.275	2.137	8.411	7.163	-2.609
700	7.050	49.897	45.892	2.842	8.379	6.720	-2.120
800	7.040	50.817	46.523	3.550	8.338	6.284	-1.735
900	7.032	51.724	47.174	4.273	8.288	5.852	-1.472
1000	7.032	52.641	47.848	5.003	8.250	5.706	-1.247
1100	7.039	53.595	47.975	5.742	8.206	5.353	-1.064
1200	7.049	53.847	48.437	6.491	8.164	5.005	-0.912
1300	7.059	54.455	48.877	7.252	8.124	4.661	-0.784
1400	7.066	55.027	49.296	8.023	8.086	4.318	-0.674
1500	7.067	55.566	49.696	8.805	8.050	3.980	-0.580
1600	7.063	56.077	50.079	9.596	8.014	3.642	-0.497
1700	7.053	56.563	50.447	10.397	8.980	3.307	-0.425
1800	7.037	57.025	50.789	11.207	8.947	2.975	-0.361
1900	7.024	57.467	51.139	12.024	8.914	2.645	-0.304
2000	7.026	57.891	51.466	12.849	8.881	2.313	-0.253
2100	7.033	58.296	51.782	13.681	8.849	1.988	-0.207
2200	7.045	58.686	52.087	14.520	8.815	1.662	-0.165
2300	7.062	59.062	52.382	15.364	8.782	1.336	-0.127
2400	7.086	59.424	52.668	16.214	8.748	1.014	-0.092
2500	7.116	59.773	52.945	17.069	8.711	0.690	-0.060
2600	7.152	60.110	53.214	17.929	8.675	0.372	-0.031
2700	7.194	60.436	53.476	18.794	8.637	0.054	-0.004
2800	7.240	60.752	53.730	19.662	8.598	0.264	0.021
2900	7.288	61.058	53.977	20.535	8.557	0.478	0.044
3000	7.338	61.355	54.218	21.411	8.515	0.693	0.065
3100	7.384	61.644	54.453	22.291	8.472	0.918	0.085
3200	7.426	61.924	54.682	23.174	8.427	1.151	0.104
3300	7.464	62.197	54.906	24.060	8.381	1.389	0.121
3400	7.500	62.462	55.124	24.949	8.333	1.637	0.137
3500	7.533	62.721	55.338	25.841	8.283	1.886	0.153
3600	7.562	62.973	55.546	26.735	8.232	2.135	0.167
3700	7.588	63.218	55.750	27.632	8.179	2.384	0.180
3800	7.611	63.458	55.950	28.532	8.125	2.633	0.193
3900	7.631	63.692	56.145	29.434	8.069	2.882	0.205
4000	7.648	63.922	56.337	30.338	8.011	3.131	0.216
4100	7.662	64.145	56.525	31.245	7.952	3.380	0.227
4200	7.673	64.364	56.709	32.153	7.892	3.629	0.237
4300	7.681	64.579	56.889	33.064	7.830	3.878	0.247
4400	7.686	64.788	57.066	33.976	7.768	4.127	0.255
4500	7.689	64.994	57.240	34.889	7.701	4.376	0.264
4600	7.690	65.195	57.411	35.802	7.635	4.625	0.272
4700	7.689	65.393	57.579	36.715	7.567	4.874	0.280
4800	7.686	65.586	57.744	37.628	7.499	5.123	0.287
4900	7.681	65.776	57.906	38.541	7.429	5.372	0.294
5000	7.673	65.963	58.065	39.459	7.358	5.621	0.301
5100	7.662	66.146	58.222	40.374	7.286	5.870	0.307
5200	7.648	66.326	58.376	41.288	7.213	6.119	0.313
5300	7.631	66.502	58.527	42.208	7.140	6.368	0.318
5400	7.611	66.676	58.677	43.127	7.065	6.617	0.324
5500	7.588	66.847	58.824	44.048	6.989	6.866	0.329
5600	7.562	67.015	58.968	45.060	6.912	7.115	0.334
5700	7.534	67.180	59.111	45.994	6.835	7.364	0.339
5800	7.503	67.343	59.252	46.929	6.757	7.613	0.343
5900	7.472	67.503	59.400	47.866	6.678	7.862	0.348
6000	7.436	67.661	59.527	48.803	6.598	8.111	0.352

Dec. 31, 1960; Mar. 31, 1966

HYDROXYL UNIPROTONATED ION (OH<sup>+</sup>) (IDEAL GAS)

Ground State Configuration  $3 \sum^-$   
 $\Delta H_f^\circ O = 313.3 \pm 2.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^\circ 298.15 = 43.657 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^\circ 298.15 = 314.8 \pm 2.5 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$$\frac{\epsilon_j, \text{ cm.}^{-1}}{g_j}$$

$\omega_e = [2955] \text{ cm.}^{-1}$   
 $\nu_e = 16.793 \text{ cm.}^{-1}$   
 $\nu_e = 0.732 \text{ cm.}^{-1}$   
 $r_e = 1.0289 \text{ \AA}$   
 $\sigma^- = 1$

Heat of Formation.

The ionization potential of hydroxyl has been determined by M. M. Mann, A. Hustrulid and J. T. Tate, Phys. Rev. 58, 340 (1940) from electron impact data on water vapor, as 13.6 e.v. S. N. Foner and R. L. Hudson, J. Chem. Phys. 25, 602 (1956) have measured the appearance potential of OH<sup>+</sup> from OH as  $13.18 \pm 0.1 \text{ e.v.}$  (303.96 kcal.). This value was the one adopted to obtain the heat of formation of OH<sup>+</sup>(g) from that of OH(g) at 0°K.

Heat Capacity and Entropy.

The molecular constants, with the exception of  $\omega_e x_e$ , were all given by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. The value of  $\omega_e x_e$  was estimated by analogy with OH(g) and other diatomic hydrides.

The value of  $H_T - H_{298}$  at 0°K. is -2.06 kcal. mole<sup>-1</sup>.

T. °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (F <sup>o</sup> - H <sub>298}^o)/T</sub>	H <sup>o</sup> - H <sub>298}^o</sub>	ΔH <sub>f}^o</sub>	ΔF <sub>f}^o</sub>	Log K <sub>p</sub>
0						
100	6.969	43.657	43.657	314.800	312.254	- 228.888
200	6.969	43.700	43.657	314.800	312.238	- 227.465
300	6.982	43.731	43.657	314.800	311.306	- 170.090
400	7.020	43.768	43.657	314.800	310.252	- 135.611
500	7.095	43.812	43.657	314.800	309.101	- 112.590
600	7.204	43.855	43.657	314.800	307.871	- 96.122
700	7.337	43.898	43.657	314.800	306.573	- 83.752
800	7.485	43.941	43.657	314.800	305.217	- 74.117
900	7.625	43.984	43.657	314.800	303.807	- 66.397
1000	7.765	44.027	43.657	314.800	302.349	- 60.071
1100	7.897	44.070	43.657	314.800	300.847	- 54.792
1200	8.019	44.113	43.657	314.800	299.304	- 50.517
1300	8.131	44.156	43.657	314.800	297.722	- 46.476
1400	8.233	44.200	43.657	314.800	296.106	- 42.643
1500	8.326	44.243	43.657	314.800	294.454	- 39.021
1600	8.417	44.287	43.657	314.800	292.765	- 35.500
1700	8.507	44.331	43.657	314.800	291.038	- 32.079
1800	8.597	44.375	43.657	314.800	289.272	- 28.658
1900	8.687	44.419	43.657	314.800	287.466	- 25.237
2000	8.777	44.463	43.657	314.800	285.620	- 21.816
2100	8.867	44.507	43.657	314.800	283.734	- 18.395
2200	8.957	44.551	43.657	314.800	281.808	- 14.974
2300	9.047	44.595	43.657	314.800	279.842	- 11.553
2400	9.137	44.639	43.657	314.800	277.836	- 8.132
2500	9.227	44.683	43.657	314.800	275.790	- 4.711
2600	9.317	44.727	43.657	314.800	273.704	- 1.290
2700	9.407	44.771	43.657	314.800	271.578	2.131
2800	9.497	44.815	43.657	314.800	269.412	5.312
2900	9.587	44.859	43.657	314.800	267.206	8.493
3000	9.677	44.903	43.657	314.800	264.960	11.674
3100	9.767	44.947	43.657	314.800	262.674	14.855
3200	9.857	44.991	43.657	314.800	260.348	18.036
3300	9.947	45.035	43.657	314.800	257.982	21.217
3400	10.037	45.079	43.657	314.800	255.576	24.398
3500	10.127	45.123	43.657	314.800	253.130	27.579
3600	10.217	45.167	43.657	314.800	250.644	30.760
3700	10.307	45.211	43.657	314.800	248.118	33.941
3800	10.397	45.255	43.657	314.800	245.552	37.122
3900	10.487	45.299	43.657	314.800	242.946	40.303
4000	10.577	45.343	43.657	314.800	240.300	43.484
4100	10.667	45.387	43.657	314.800	237.614	46.665
4200	10.757	45.431	43.657	314.800	234.888	49.846
4300	10.847	45.475	43.657	314.800	232.122	53.027
4400	10.937	45.519	43.657	314.800	229.316	56.208
4500	11.027	45.563	43.657	314.800	226.470	59.389
4600	11.117	45.607	43.657	314.800	223.584	62.570
4700	11.207	45.651	43.657	314.800	220.658	65.751
4800	11.297	45.695	43.657	314.800	217.692	68.932
4900	11.387	45.739	43.657	314.800	214.686	72.113
5000	11.477	45.783	43.657	314.800	211.640	75.294
5100	11.567	45.827	43.657	314.800	208.554	78.475
5200	11.657	45.871	43.657	314.800	205.428	81.656
5300	11.747	45.915	43.657	314.800	202.262	84.837
5400	11.837	45.959	43.657	314.800	199.056	88.018
5500	11.927	46.003	43.657	314.800	195.810	91.199
5600	12.017	46.047	43.657	314.800	192.524	94.380
5700	12.107	46.091	43.657	314.800	189.198	97.561
5800	12.197	46.135	43.657	314.800	185.832	100.742
5900	12.287	46.179	43.657	314.800	182.426	103.923
6000	12.377	46.223	43.657	314.800	178.980	107.104

Ground State Configuration  $1 \Sigma^+$   
 $\Delta H_f^0 = 41.229 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^0 = -32.9 \pm 1.0 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 = 298.15 = -34.4 \pm 1.0 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$\epsilon_i, \text{ cm.}^{-1}$	$g_i$	$\sigma$	$r_e$
0	1	$\sigma = 1$	$r_e = 1.834 \text{ \AA}$
$\omega_e x_e = [74.7] \text{ cm.}^{-1}$			
$\alpha_e = [0.65] \text{ cm.}^{-1}$			
$B_e = 18.87 \text{ cm.}^{-1}$			

Heat of Formation.

L. M. Branscomb, Joint Institute for Laboratory Astrophysics Report No. 62, Feb. 1st, 1966 has deduced an electron affinity of OH of  $1.83 \pm 0.04 \text{ e.v. (} 42.2 \pm 0.9 \text{ kcal.)}$  from the photodetachment spectrum of OH<sup>-</sup>(g). The vibrational state was deduced to be the ground state since no other absorption sequences could be detected by a thorough search. P. M. Page, Faraday Soc. Discussions 19, 87 (1955) has reviewed the methods and results of earlier determinations of the electron affinity of OH(g) and concludes that it is  $85 \pm 1 \text{ kcal.}$  However he does state that it is not generally known whether the flame systems chiefly investigated are in thermodynamic equilibrium. In a later paper P. M. Page and T. M. Sugden, Trans. Faraday Soc. 53, 1092 (1957) conclude that much higher concentrations of radicals are obtained in flames than predicted thermodynamically. However for certain systems at lower temperatures they estimate only a factor of 3 increase in concentration and thus calculate the electron affinity as  $61 \text{ kcal. mole}^{-1}$ . The value reported by Branscomb, loc. cit. is adopted here.

Heat Capacity and Entropy.

Branscomb loc. cit. has used his photodetachment spectra to obtain values of  $\omega_e$ ,  $B_e$  and  $r_e$  for OH<sup>-</sup>(g) which are remarkably similar to those for OH(g). The values of  $\omega_e x_e$  and  $\alpha_e$  were estimated by comparison with OH(g) and other hydrides. The ground state configuration was assumed to be that of HF(g) with which it is isoelectronic. The value of  $H_{298}^0$  at 0°K. is  $-2.057 \text{ kcal. mole}^{-1}$ .

T, °K.	C <sub>v</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0						
100	6.965	41.229	0.000	-34.400	-33.248	24.371
200						
298						
300	6.965	41.272	0.013	-34.409	-33.240	24.216
400	6.969	43.276	0.110	-34.912	-32.776	17.908
500	6.978	44.832	0.407	-35.427	-32.182	14.067
600	7.002	46.106	1.066	-35.952	-31.468	11.468
700	7.047	47.188	2.008	-36.486	-30.696	9.584
800	7.116	48.133	3.516	-37.027	-29.833	8.150
900	7.204	48.977	4.232	-37.571	-28.902	7.018
1000	7.306	49.741	4.874	-38.115	-27.908	6.099
1100	7.415	50.462	5.683	-38.659	-26.862	5.337
1200	7.527	51.092	6.460	-39.202	-25.793	4.691
1300	7.638	51.699	7.198	-39.745	-24.723	4.140
1400	7.746	52.269	7.908	-40.287	-23.653	3.650
1500	7.848	52.807	8.748	-40.830	-22.619	3.237
1600	7.944	53.317	9.537	-41.345	-21.664	2.864
1700	8.018	53.801	10.236	-41.878	-20.672	2.520
1800	8.106	54.261	11.144	-42.409	-19.731	2.228
1900	8.196	54.705	11.960	-42.941	-18.841	1.956
2000	8.267	55.126	12.783	-43.472	-18.022	1.707
2100	8.334	55.513	13.613	-44.004	-17.276	1.479
2200	8.436	55.920	14.449	-44.536	-16.601	1.270
2300	8.453	56.294	15.292	-45.067	-16.007	1.076
2400	8.506	56.655	16.140	-45.601	-15.499	0.897
2500	8.556	57.004	16.993	-46.136	-15.072	0.730
2600	8.602	57.340	17.851	-46.671	-14.727	0.574
2700	8.645	57.666	18.713	-47.208	-14.461	0.428
2800	8.685	57.981	19.580	-47.747	-14.271	0.291
2900	8.723	58.286	20.450	-48.285	-14.151	0.161
3000	8.758	58.582	21.324	-48.827	-14.099	0.039
3100	8.792	58.870	22.202	-49.369	-14.079	-0.076
3200	8.823	59.150	23.082	-49.913	-14.110	-0.185
3300	8.853	59.422	23.966	-50.459	-14.204	-0.289
3400	8.881	59.686	24.853	-51.005	-14.358	-0.388
3500	8.908	59.944	25.742	-51.554	-14.572	-0.482
3600	8.934	60.196	26.635	-52.104	-14.847	-0.572
3700	8.958	60.441	27.529	-52.657	-15.182	-0.658
3800	8.982	60.680	28.426	-53.211	-15.577	-0.740
3900	9.004	60.913	29.326	-53.766	-16.032	-0.819
4000	9.026	61.142	30.227	-54.323	-16.547	-0.895
4100	9.047	61.365	31.131	-54.882	-17.124	-0.968
4200	9.067	61.583	32.036	-55.442	-17.763	-1.038
4300	9.086	61.797	32.944	-56.004	-18.464	-1.105
4400	9.105	62.006	33.854	-56.567	-19.228	-1.170
4500	9.123	62.211	34.765	-57.132	-20.056	-1.233
4600	9.141	62.411	35.678	-57.697	-20.949	-1.294
4700	9.158	62.608	36.593	-58.265	-21.907	-1.352
4800	9.174	62.801	37.510	-58.834	-22.931	-1.409
4900	9.190	62.990	38.428	-59.404	-24.021	-1.464
5000	9.206	63.176	39.348	-59.974	-25.177	-1.517
5100	9.222	63.359	40.269	-60.546	-26.399	-1.569
5200	9.237	63.538	41.192	-61.120	-27.687	-1.619
5300	9.251	63.714	42.116	-61.694	-29.043	-1.667
5400	9.266	63.887	43.042	-62.269	-30.477	-1.715
5500	9.280	64.057	43.970	-62.845	-31.991	-1.761
5600	9.294	64.224	44.898	-63.422	-33.585	-1.806
5700	9.307	64.389	45.828	-64.000	-35.259	-1.849
5800	9.321	64.551	46.760	-64.579	-36.923	-1.893
5900	9.334	64.711	47.692	-65.159	-38.677	-1.935
6000	9.347	64.868	48.626	-65.739	-40.521	-1.975

Point Group C<sub>2h</sub> ΔH<sub>f</sub><sup>0</sup> = -154.3 ± 5 kcal. mole<sup>-1</sup>

S<sub>298.15</sub> = [78.4] cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>0</sup> 298.15 = -157.4 ± 5 kcal. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm. <sup>-1</sup>	ω, cm. <sup>-1</sup>
[273](1)	[3700](1)
[150](1)	[3700](1)
[235](1)	[1250](1)
[150](1)	[1250](1)
[255](1)	[1250](1)
[256](1)	[1250](1)

Bond Distances: K-O = [2.43] Å O-H = [0.96] Å

Bond Angle: K-O-K = [90°] K-O-H = [110°]

Products of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [3.7587] X 10<sup>-113</sup> g. cm.<sup>6</sup>

σ = 2

Heat Capacity and Entropy.

See KOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. F. Porter, J. Chem. Phys. 29, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 850 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 553 (1960), have also postulated a model for Li<sub>2</sub>(OH)<sub>2</sub>(g) which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100°. The last one was adopted for the molecular configuration of K<sub>2</sub>(OH)<sub>2</sub>, but the bond angle O-K-O was modified to 90° (i.e. a square planar configuration for potassium and oxygen atoms). The bond angle K-O-H in K<sub>2</sub>(OH)<sub>2</sub>(g) was assumed to be 110°. The bond distance K-O in K<sub>2</sub>(OH)<sub>2</sub>(g) was estimated 10% longer than that in KOH(g). The bond distance O-H was estimated to be the same in H<sub>2</sub>O(g). The three principal moments of inertia are I<sub>A</sub> = [17.5602] X 10<sup>-39</sup>, I<sub>B</sub> = [38.5534] X 10<sup>-39</sup> and I<sub>C</sub> = [55.6452] X 10<sup>-39</sup> g. cm.<sup>2</sup>

The first six selected vibrational frequencies were taken to be equal to those for K<sub>2</sub>F<sub>2</sub>(g) (see K<sub>2</sub>F<sub>2</sub>(g) table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	0.000	INFINITE	4.415	-154.317	-154.317	INFINITE
100	13.560	60.051	3.451	-153.261	-153.261	3.9512
200	17.684	70.956	1.827	-150.679	-150.679	1.64554
298	19.445	78.366	0.000	-157.387	-147.620	1.087208
300	19.4456	78.487	0.036	-157.403	-147.559	1.07497
400	21.4073	84.315	2.066	-159.406	-143.932	78.641
500	22.4452	89.110	4.244	-160.144	-139.975	61.183
600	23.578	93.464	6.568	-160.747	-135.881	49.495
700	24.888	97.072	8.952	-161.255	-131.695	41.117
800	26.299	100.392	11.440	-161.695	-127.444	34.816
900	27.819	103.433	13.947	-162.088	-123.137	29.902
1000	29.445	106.159	16.613	-162.459	-118.790	25.962
1100	26.925	108.702	19.281	-200.630	-112.358	22.323
1200	27.362	111.063	21.966	-200.491	-104.336	19.002
1300	27.751	113.269	24.752	-200.330	-96.333	16.195
1400	28.100	115.339	27.545	-200.149	-88.338	13.790
1500	28.412	117.288	30.371	-199.954	-80.356	11.708
1600	28.692	119.131	33.226	-199.748	-72.391	9.888
1700	28.943	120.878	36.108	-199.531	-64.439	8.284
1800	29.168	122.539	39.014	-199.307	-56.499	6.860
1900	29.370	124.122	41.941	-199.081	-48.573	5.587
2000	29.552	125.633	44.887	-198.850	-40.656	4.443
2100	29.716	127.079	47.851	-198.619	-32.751	3.408
2200	29.864	128.464	50.830	-198.394	-24.856	2.469
2300	29.998	129.798	53.823	-198.170	-16.976	1.613
2400	30.119	131.074	56.829	-197.953	-9.099	0.829
2500	30.220	132.306	59.847	-197.748	-1.241	0.108
2600	30.300	133.494	62.875	-197.548	6.622	0.557
2700	30.422	134.640	65.912	-197.354	14.467	1.171
2800	30.505	135.748	68.959	-197.165	22.306	1.741
2900	30.582	136.820	72.013	-196.981	30.151	2.272
3000	30.652	137.858	75.075	-196.804	37.978	2.767
3100	30.717	138.864	78.143	-196.789	45.808	3.229
3200	30.776	139.840	81.218	-196.696	53.634	3.663
3300	30.831	140.788	84.298	-196.629	61.423	4.053
3400	30.881	141.704	87.384	-196.591	69.278	4.414
3500	30.928	142.605	90.474	-196.584	77.198	4.751
3600	30.972	143.477	93.569	-196.612	84.912	5.155
3700	31.012	144.326	96.669	-196.678	92.731	5.477
3800	31.049	145.154	99.772	-196.784	100.553	5.783
3900	31.085	145.961	102.876	-196.946	108.377	6.073
4000	31.117	146.748	105.989	-197.158	116.212	6.350
4100	31.148	147.517	109.102	-197.424	124.049	6.612
4200	31.176	148.268	112.218	-197.756	131.894	6.863
4300	31.203	149.002	115.337	-198.154	139.749	7.103
4400	31.228	149.719	118.459	-198.630	147.610	7.332
4500	31.252	150.421	121.583	-199.187	155.489	7.552
4600	31.274	151.108	124.709	-199.831	163.380	7.762
4700	31.295	151.781	127.838	-200.570	171.284	7.965
4800	31.314	152.440	130.968	-201.408	179.200	8.160
4900	31.333	153.086	134.100	-202.354	187.142	8.347
5000	31.350	153.719	137.234	-203.410	195.095	8.528
5100	31.367	154.340	140.370	-204.584	203.090	8.703
5200	31.382	154.950	143.508	-205.878	211.084	8.872
5300	31.397	155.547	146.647	-207.296	219.126	9.036
5400	31.411	156.134	149.787	-208.843	227.175	9.194
5500	31.424	156.711	152.929	-210.517	235.264	9.349
5600	31.437	157.277	156.070	-212.321	243.389	9.499
5700	31.449	157.834	159.216	-214.251	251.536	9.644
5800	31.460	158.381	162.362	-216.308	259.727	9.787
5900	31.471	158.919	165.508	-218.487	267.957	9.926
6000	31.482	159.448	168.656	-220.784	276.226	10.062

LITHIUM HYDROXIDE, DIMERIC (Li<sub>2</sub>O<sub>2</sub>H<sub>2</sub>) (IDEAL GAS)

Point Group C<sub>2h</sub>  
 $\Delta H_f^\circ O = -178.6 \pm 4$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^\circ 298.15 = -181.4 \pm 4$  kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies	
$\omega_j$ , cm. <sup>-1</sup>	$\omega_j$ , cm. <sup>-1</sup>
[465](1)	[3700](1)
[305](1)	[3700](1)
[407](1)	[1250](1)
[385](1)	[1250](1)
[640](1)	[1250](1)
[460](1)	[1250](1)

Bond Distance: Li-O = [1.76] Å O-H = [0.96] Å  
 Bond Angle: Li-O-Li = [90]° Li-O-H = [110]°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [4.56956] X 10<sup>-115</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have studied the Li<sub>2</sub>O(c)-H<sub>2</sub>O(g) equilibrium by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K. the heat of reaction Li<sub>2</sub>O(g) + H<sub>2</sub>O(g) → 2LiOH(g) at 298° has been calculated by the second law and the third law methods as 63.2 and 63.7 kcal. mole<sup>-1</sup>, respectively. (The third law drift is 0.5 ± 1.5 e.u.)  
 Combination of the third law value ( $\Delta H_f^\circ 298 = 63.7$  kcal. mole<sup>-1</sup>) with the heat of formation of lithium hydroxide(g) ( $\Delta H_f^\circ 298 = -58.8$  kcal. mole<sup>-1</sup>) gives the heat of formation of dimeric lithium hydroxide (g) ( $\Delta H_f^\circ 298 = -181.4$  kcal. mole<sup>-1</sup>) which has been adopted in the tabulation.

J. B. Berkowitz-Mattuck and A. Buchler, J. Phys. Chem. 67, 1386 (1963), have also studied the Li<sub>2</sub>O(c)-H<sub>2</sub>O(g) equilibrium by the transpiration method, and reported two equilibrium constants ( $K_{1095}^\circ = 0.105$  and  $K_{1145}^\circ = 0.357$ ) for the reaction Li<sub>2</sub>O(c) + H<sub>2</sub>O(g) → Li<sub>2</sub>(OH)<sub>2</sub>(g). Using the third law method, the heat of reaction has been calculated from the equilibrium constants as 12.7 kcal. mole<sup>-1</sup> at 298.15°K. The heat of formation of Li<sub>2</sub>(OH)<sub>2</sub>(g) can be derived as  $\Delta H_f^\circ 298 = -188.2 \pm 3.5$  kcal. mole<sup>-1</sup> which is different from the adopted value of Berkowitz, Meschi and Chupka, loc. cit. Berkowitz-Mattuck and Buchler attempted to explain the difference by inferring that the solid-gas equilibrium was not properly established in the measurement of Berkowitz, Meschi and Chupka, however, the absence of drift in the third law analysis does not support this conclusion.

Heat Capacity and Entropy.

S. H. Bauer, R. M. Diner and R. F. Porter, J. Chem. Phys. 29, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for Li<sub>2</sub>(OH)<sub>2</sub>(g) which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100°. The last one was adopted for the molecular configuration of Li<sub>2</sub>(OH)<sub>2</sub>(g), but the bond angle O-Li-O was modified to 90° (i.e. a square planar configuration for lithium and oxygen atoms). The bond angle Li-O-H in Li<sub>2</sub>(OH)<sub>2</sub>(g) was assumed to be 110°. The bond distance Li-O in Li<sub>2</sub>(OH)<sub>2</sub>(g) was estimated 10% longer than that in LiOH(g). The bond distance O-H was estimated to be the same in H<sub>2</sub>O(g). The three principal moments of inertia are: I<sub>A</sub> = [9.445] X 10<sup>-39</sup>, I<sub>B</sub> = [3.7789] X 10<sup>-39</sup> and I<sub>C</sub> = [12.8035] X 10<sup>-39</sup> g.<sup>2</sup> cm.<sup>2</sup>

The first six selected vibrational frequencies were taken to be equal to those for Li<sub>2</sub>F<sub>2</sub>(g) (see Li<sub>2</sub>F<sub>2</sub>(g) table) and the rest were O-H stretching and bending frequencies.

T. °K.	C <sub>v</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	Log K <sub>p</sub>
0	0.000	INFINITE	0	-178.587	INFINITE
100	9.118	57.762	3.463	-179.480	388.175
200	13.613	58.482	1.505	-180.502	196.531
298	16.882	64.563	0.000	-181.433	126.534
300	16.935	64.568	0.31	-181.450	125.715
400	19.420	65.895	1.854	-182.274	92.598
500	21.319	66.651	3.856	-184.478	72.576
600	22.761	68.421	6.103	-185.172	59.111
700	23.873	69.843	8.437	-185.718	49.462
800	24.762	70.719	10.870	-186.173	42.206
900	25.497	71.995	13.384	-186.567	36.549
1000	26.123	73.502	15.966	-186.910	32.014
1100	26.656	75.288	18.606	-187.211	28.298
1200	27.143	77.343	21.297	-187.478	25.196
1300	27.585	79.633	24.033	-187.715	22.568
1400	27.937	82.191	26.809	-187.927	20.312
1500	28.271	85.029	29.619	-188.120	18.356
1600	28.588	88.1575	32.462	-188.294	16.642
1700	28.833	91.603	35.332	-188.447	15.136
1800	29.069	95.458	38.227	-188.578	13.794
1900	29.282	100.835	41.145	-188.682	12.590
2000	29.472	107.842	44.083	-188.762	11.500
2100	29.644	115.485	47.039	-188.823	10.512
2200	29.798	123.875	50.111	-188.868	9.622
2300	29.938	133.045	53.298	-188.900	8.822
2400	30.064	143.049	56.598	-188.921	8.118
2500	30.178	153.937	59.999	-188.934	7.502
2600	30.283	165.662	63.503	-188.940	6.969
2700	30.378	178.288	67.114	-188.940	6.502
2800	30.464	191.867	70.831	-188.934	6.092
2900	30.544	206.452	74.657	-188.921	5.732
3000	30.616	222.095	78.592	-188.900	5.422
3100	30.683	238.845	82.636	-188.875	5.162
3200	30.745	256.652	86.790	-188.848	4.952
3300	30.801	275.562	91.054	-188.819	4.782
3400	30.852	295.522	95.428	-188.789	4.652
3500	30.902	316.588	100.812	-188.758	4.562
3600	30.947	338.815	107.206	-188.726	4.502
3700	30.989	362.252	114.620	-188.694	4.462
3800	31.028	386.952	123.064	-188.662	4.432
3900	31.064	412.962	132.548	-188.630	4.412
4000	31.097	440.342	143.082	-188.600	4.402
4100	31.129	469.142	154.676	-188.570	4.402
4200	31.158	500.422	167.340	-188.540	4.402
4300	31.186	534.242	181.084	-188.510	4.402
4400	31.212	570.662	195.918	-188.480	4.402
4500	31.236	609.742	211.852	-188.450	4.402
4600	31.259	651.522	228.886	-188.420	4.402
4700	31.280	696.042	247.030	-188.390	4.402
4800	31.300	743.362	266.284	-188.360	4.402
4900	31.319	793.542	286.658	-188.330	4.402
5000	31.337	846.642	308.152	-188.300	4.402
5100	31.354	902.722	330.776	-188.270	4.402
5200	31.370	961.842	354.540	-188.240	4.402
5300	31.384	1024.062	379.454	-188.210	4.402
5400	31.400	1089.462	405.528	-188.180	4.402
5500	31.414	1158.002	432.772	-188.150	4.402
5600	31.427	1229.662	461.196	-188.120	4.402
5700	31.439	1304.422	490.810	-188.090	4.402
5800	31.451	1382.262	521.524	-188.060	4.402
5900	31.462	1463.172	553.348	-188.030	4.402
6000	31.473	1547.142	586.282	-188.000	4.402



T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	+0.00	∞	∞	∞	40.757	40.757	∞
100	7.5949	37.7897	53.5774	40.750	41.015	89.635	-89.635
200	7.5934	43.3303	47.2119	4.783	41.633	45.092	-45.092
298	8.1024	46.4488	46.4488	+0.00	40.070	42.337	-31.033
300	8.0277	46.4738	46.4688	0.015	42.351	30.851	-30.851
400	8.2250	48.8711	46.4005	8.20	39.834	23.478	-23.478
500	8.4492	50.8733	47.410	1.661	39.619	19.232	-19.232
600	8.6846	52.308	48.099	2.522	39.427	16.953	-16.953
700	9.1242	53.691	48.801	3.423	39.259	14.306	-14.306
800	9.491	54.936	49.491	4.355	39.113	12.776	-12.776
900	9.841	56.072	50.160	5.321	38.988	11.591	-11.591
1000	10.180	57.127	50.804	6.323	38.884	10.646	-10.646
1100	10.501	58.112	51.424	7.357	38.798	9.874	-9.874
1200	10.799	59.039	52.021	8.422	38.729	9.232	-9.232
1300	11.071	59.914	52.595	9.516	38.673	8.690	-8.690
1400	11.319	60.744	53.147	10.635	38.628	8.226	-8.226
1500	11.542	61.533	53.680	11.779	38.591	7.824	-7.824
1600	11.743	62.284	54.195	12.943	38.559	7.473	-7.473
1700	11.923	63.001	54.692	14.126	38.534	7.163	-7.163
1800	12.084	63.688	55.173	15.327	38.513	6.888	-6.888
1900	12.229	64.345	55.638	16.543	38.497	6.642	-6.642
2000	12.359	64.975	56.089	17.772	38.482	6.421	-6.421
2100	12.475	65.581	56.527	19.014	38.469	6.221	-6.221
2200	12.580	66.164	56.952	20.267	38.457	6.039	-6.039
2300	12.675	66.725	57.365	21.530	38.446	5.873	-5.873
2400	12.760	67.267	57.766	22.807	38.436	5.720	-5.720
2500	12.838	67.788	58.157	24.082	38.423	5.580	-5.580
2600	12.908	68.284	58.537	25.369	38.412	5.451	-5.451
2700	12.972	68.753	58.907	26.663	38.400	5.321	-5.321
2800	13.031	69.205	59.269	27.963	38.386	5.211	-5.211
2900	13.084	69.641	59.621	29.269	38.373	5.117	-5.117
3000	13.133	70.058	59.965	30.580	38.357	5.021	-5.021
3100	13.177	70.458	60.301	31.895	38.342	4.931	-4.931
3200	13.218	70.840	60.629	33.215	38.324	4.846	-4.846
3300	13.256	71.216	60.949	34.539	38.305	4.767	-4.767
3400	13.291	71.587	61.265	35.866	38.283	4.693	-4.693
3500	13.323	71.948	61.570	37.197	38.259	4.622	-4.622
3600	13.353	72.313	61.870	38.531	38.233	4.556	-4.556
3700	13.381	72.670	62.165	39.868	38.203	4.493	-4.493
3800	13.407	73.027	62.451	41.207	38.172	4.434	-4.434
3900	13.431	73.375	62.735	42.549	38.138	4.378	-4.378
4000	13.453	73.715	63.013	43.893	38.102	4.324	-4.324
4100	13.474	74.048	63.284	45.239	38.062	4.274	-4.274
4200	13.493	74.374	63.551	46.588	38.020	4.225	-4.225
4300	13.511	74.691	63.812	47.938	37.975	4.179	-4.179
4400	13.529	75.000	64.069	49.290	37.927	4.135	-4.135
4500	13.545	75.307	64.322	50.644	37.875	4.093	-4.093
4600	13.560	75.613	64.570	51.999	37.822	4.054	-4.054
4700	13.574	75.916	64.813	53.356	37.765	4.015	-4.015
4800	13.587	76.215	65.053	54.714	37.705	3.979	-3.979
4900	13.600	76.512	65.288	56.073	37.642	3.944	-3.944
5000	13.612	76.807	65.520	57.434	37.576	3.910	-3.910
5100	13.623	77.126	65.748	58.795	37.507	3.878	-3.878
5200	13.633	77.441	65.972	60.158	37.436	3.847	-3.847
5300	13.643	77.751	66.193	61.522	37.360	3.818	-3.818
5400	13.653	78.056	66.410	62.887	37.282	3.789	-3.789
5500	13.662	78.356	66.624	64.252	37.201	3.762	-3.762
5600	13.670	78.653	66.835	65.619	37.117	3.735	-3.735
5700	13.678	78.949	67.043	66.986	37.029	3.710	-3.710
5800	13.685	79.243	67.247	68.355	36.939	3.685	-3.685
5900	13.694	79.537	67.447	69.724	36.845	3.662	-3.662
6000	13.701	79.831	67.648	71.093	36.749	3.639	-3.639

Dec. 31, 1960; Dec. 31, 1965

AMIDOGEN (NH<sub>2</sub>)

(IDEAL GAS)

MOL. WT. = 16.02264

Point Group C<sub>2v</sub>

$$\Delta H_f^0 = 40.8 \pm 3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 40.1 \pm 3 \text{ kcal. mole}^{-1}$$

$$S_{298}^{0.15} = 46.5 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
3175 (1)
1499 (1)
3220 (1)

Bond Distances: N-H = 1.024 Å

Bond Angle: H-N-H = 103°

Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 8.5 X 10<sup>-120</sup> g.<sup>3</sup> cm.<sup>6</sup>

σ<sup>-</sup> = 2

Heat of Formation.

The heat of formation of amidogen at 298.15°K., ΔH<sub>f</sub><sup>0</sup> (NH<sub>2</sub>, g) = 39.8 kcal. mole<sup>-1</sup>, was obtained from the pyrolysis of N<sub>2</sub>H<sub>4</sub> by J. A. Kerr, R. C. Sekhar and A. F. Trotman-Dickenson, J. Chem. Soc. 3217 (1965). They have reinvestigated the rate constants of the thermal decomposition N<sub>2</sub>H<sub>4</sub> → 2NH<sub>2</sub> at different temperatures using the same techniques as M. Swarc, J. Chem. Phys. 17, 505 (1949), and revised the activation energy to 57.1 kcal. mole<sup>-1</sup> for the reaction at 874°K. (instead of 60 kcal. mole<sup>-1</sup> at 1000°K. reported by Swarc). The activation energy was assumed to be the same as the dissociation energy of the N-H bond in hydrazine. Using all JANAF auxiliary data, one obtains D<sub>0</sub> (H<sub>2</sub>N-NH<sub>2</sub>) = 55.4 ± 3 kcal. mole<sup>-1</sup> and ΔH<sub>f</sub><sup>0</sup> 298 (NH<sub>2</sub>, g) = 40.1 ± 3 kcal. mole<sup>-1</sup>.

P. M. Page, Trans Faraday Soc. 57, 1254 (1961), has measured the electron affinity of NH<sub>2</sub> and has applied the results to calculate the dissociation energy, D<sub>0</sub> (H-NH<sub>2</sub>) = 102 ± 3 kcal. mole<sup>-1</sup>. This value leads to the heat of formation ΔH<sub>f</sub><sup>0</sup> 298 (NH<sub>2</sub>, g) = 40.4 ± 3 kcal. mole<sup>-1</sup> which is in good agreement with the value selected. E. R. Lippincott and M. O. Dayhoff, Spectrochim. Acta, 16, 807 (1960) calculated theoretically the dissociation energy D<sub>0</sub> (H<sub>2</sub>N-NH<sub>2</sub>) = 59 kcal. mole<sup>-1</sup> which gives ΔH<sub>f</sub><sup>0</sup> 298 (NH<sub>2</sub>, g) = 41.9 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The bond distance and angle were measured from the electronic absorption spectra of NH<sub>2</sub> by K. Dressler and D. A. Ramsay, Phil. Trans. Roy. Soc. London Ser. A 251, 553 (1959). The three principal moments of inertia are I<sub>A</sub> = 0.1189 X 10<sup>-39</sup> g. cm.<sup>2</sup>, I<sub>B</sub> = 0.2149 X 10<sup>-39</sup> g. cm.<sup>2</sup> and I<sub>C</sub> = 0.3338 X 10<sup>-39</sup> g. cm.<sup>2</sup>

The selected vibrational frequencies were obtained from the infrared spectrum of NH<sub>2</sub> by matrix isolation by D. E. Milligan and M. E. Jacox, J. Chem. Phys. 43, 4487 (1965). K. N. Tanner and R. L. King, Nature 181, 963 (1958) have also determined the vibrational frequencies ω<sub>1</sub> = 3500 cm.<sup>-1</sup> and ω<sub>3</sub> = 3280 cm.<sup>-1</sup> by flash photolysis and calculated ω<sub>2</sub> = 1060 cm.<sup>-1</sup>. The symmetric and the antisymmetric stretching frequencies are in good agreement. M. Tsuboi, Spectrochim. Acta 16, 505 (1960), has observed NH<sub>2</sub> bending frequencies, 1572 cm.<sup>-1</sup>, 1619 cm.<sup>-1</sup> and 1623 cm.<sup>-1</sup>, in HCONH<sub>2</sub>(g), C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>(g) and CH<sub>3</sub>NH<sub>2</sub>(g), respectively. In light of these observations and the adopted ω<sub>2</sub> Tanner and King's bending frequency seems to be in error.

(IDEAL GAS)

DIIMIDE, CIS-(N<sub>2</sub>H<sub>2</sub>)

Point Group C<sub>2v</sub> ΔH<sub>f</sub><sup>0</sup> = 52.6 ± 5 kcal. mole<sup>-1</sup>

S<sup>0</sup><sub>298.15</sub> = [52.2] cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>0</sup><sub>298.15</sub> = 50.9 ± 5 kcal. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_j$ , cm. <sup>-1</sup>	$\omega_j$ , cm. <sup>-1</sup>
[3095](1)	[3205](1)
[1406](1)	[1495](1)
[1360](1)	[910](1)

Bond Distance: N-H = [1.014] Å N-N = [1.25] Å

Bond Angle: H-N-N = [100]°

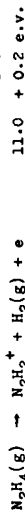
Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [1.3968] X 10<sup>-117</sup> g.<sup>3</sup> cm.<sup>6</sup>

σ<sup>-</sup> = 2

Heat of Formation.

The standard enthalpy of formation, ΔH<sub>f</sub><sup>0</sup><sub>298</sub> (N<sub>2</sub>H<sub>2</sub>f g) = 50.9 kcal. mole<sup>-1</sup>, was calculated from the appearance and ionization potentials of di-imide reported by S. N. Poner and R. L. Hudson, J. Chem. Phys. **29**, 442 (1958), using the JANAF ΔH<sub>f</sub><sup>0</sup> (N<sub>2</sub>H<sub>2</sub>f g) = 26.1 kcal. mole<sup>-1</sup> in calculation. For example:

ΔH<sub>f</sub><sup>0</sup> O



From the above heat of formation and that for NH(g) in the JANAF Tables 12-31-65, one can calculate a N-N bond energy of 109.4 ± 5 kcal. mole<sup>-1</sup> at 0°K. This is in agreement with the N-N bond in molecules such as N<sub>2</sub>F<sub>2</sub>.

Heat Capacity and Entropy.

The bond distances and angle were obtained from a quantum-mechanical calculation by W. Wheeland and P. S. K. Chen, J. Chem. Phys. **24**, 67 (1956). The three principal moments of inertia are I<sub>A</sub> = [0.3116] X 10<sup>-39</sup>, I<sub>B</sub> = [1.9686] X 10<sup>-39</sup> and I<sub>C</sub> = [2.2802] X 10<sup>-39</sup> g. cm.<sup>2</sup>

Since there are 12 valency electrons in N<sub>2</sub>H<sub>2</sub>, A. D. Walsh, J. Chem. Soc. 2288 (1953), has predicted a bent ground state, existing in either a cis or a trans configuration for diimide. E. J. Blau and B. F. Hochhelmer, J. Chem. Phys. **41**, 1174 (1964), have measured the infrared spectrum of diimide which was frozen in a cold trap as one of the decomposition products of N<sub>2</sub>H<sub>4</sub>. The spectrum of the solid N<sub>2</sub>H<sub>2</sub> at liquid nitrogen temperature agrees with the predicted non-linear planar structure, and the molecule N<sub>2</sub>H<sub>2</sub> appears mainly in cis form. They have also assigned six fundamental vibrational frequencies for cis N<sub>2</sub>H<sub>2</sub>(s) which have been adopted here for gaseous cis N<sub>2</sub>H<sub>2</sub>. Blau and Hochhelmer also observed two gas phase bands (1277 - 1314 and 3050 - 3190 cm.<sup>-1</sup>). K. Rosengren and G. C. Pimentel, J. Chem. Phys. **43**, 507 (1965), have observed these bands in matrix isolation studies. They assigned ω<sub>1</sub> or ω<sub>4</sub> = 3074 cm.<sup>-1</sup> and ω<sub>3</sub> = 1279 cm.<sup>-1</sup> which are in satisfactory agreement with the selected frequencies.

T, °K.	C <sub>p</sub>	S <sup>0</sup> - (F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> - H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞	∞	∞	52.580	52.580	INFINITE
100	7.950	43.355	2.416	52.580	52.580	INFINITE
200	8.095	48.689	1.621	53.846	53.846	- 117.674
298	8.737	52.223	0.022	51.424	55.948	- 61.134
300	8.753	52.277	0.016	50.890	58.281	- 62.719
400	9.784	54.932	0.41	50.424	58.326	- 62.489
500	10.677	57.234	1.975	50.056	63.535	- 37.270
600	11.682	59.307	3.114	49.783	66.259	- 24.134
700	12.769	61.207	4.347	49.586	69.021	- 12.548
800	13.948	62.964	5.664	49.454	71.807	- 19.616
900	14.231	64.600	7.054	49.373	74.607	- 18.116
1000	14.630	66.131	8.507	49.334	77.412	- 16.918
1100	15.356	67.570	10.017	49.330	80.220	- 15.938
1200	15.818	68.926	11.576	49.354	83.029	- 15.121
1300	16.222	70.209	13.179	49.402	85.832	- 14.429
1400	16.576	71.424	14.819	49.467	88.635	- 13.835
1500	16.887	72.578	16.493	49.546	91.429	- 13.321
1600	17.161	73.677	18.195	49.634	94.217	- 12.869
1700	17.402	74.725	19.922	49.729	97.000	- 12.470
1800	17.613	75.725	21.675	49.830	99.777	- 12.124
1900	17.803	76.683	23.450	49.936	102.551	- 11.826
2000	17.970	77.601	25.235	50.066	105.316	- 11.568
2100	18.119	78.481	27.039	50.184	108.075	- 11.347
2200	18.252	79.327	28.858	50.305	110.829	- 11.149
2300	18.372	80.141	30.689	50.428	113.577	- 10.972
2400	18.479	80.926	32.532	50.553	116.320	- 10.819
2500	18.575	81.682	34.385	50.676	119.056	- 10.687
2600	18.663	82.412	36.247	50.800	121.791	- 10.572
2700	18.742	83.118	38.117	50.925	124.524	- 10.479
2800	18.814	83.801	39.995	51.049	127.240	- 10.401
2900	18.879	84.462	41.880	51.174	129.964	- 10.334
3000	18.939	85.103	43.771	51.296	132.677	- 10.285
3100	18.993	85.725	45.667	51.418	135.385	- 10.254
3200	19.043	86.329	47.569	51.538	138.092	- 10.231
3300	19.089	86.916	49.476	51.656	140.795	- 10.214
3400	19.132	87.486	51.387	51.774	143.496	- 10.202
3500	19.171	88.041	53.302	51.888	146.192	- 10.192
3600	19.207	88.582	55.221	52.000	148.883	- 10.188
3700	19.241	89.109	57.143	52.109	151.573	- 10.189
3800	19.272	89.622	59.069	52.217	154.262	- 10.192
3900	19.301	90.123	60.998	52.322	156.947	- 10.195
4000	19.327	90.612	62.929	52.423	159.627	- 10.198
4100	19.352	91.090	64.863	52.522	162.304	- 10.201
4200	19.376	91.556	66.799	52.617	164.984	- 10.204
4300	19.398	92.013	68.738	52.711	167.654	- 10.207
4400	19.418	92.459	70.679	52.801	170.325	- 10.210
4500	19.437	92.895	72.622	52.887	172.996	- 10.213
4600	19.455	93.323	74.566	52.971	175.667	- 10.216
4700	19.472	93.741	76.513	53.052	178.338	- 10.219
4800	19.488	94.151	77.460	53.129	181.001	- 10.222
4900	19.503	94.553	78.413	53.203	183.661	- 10.225
5000	19.517	94.948	78.475	53.274	186.319	- 10.228
5100	19.531	95.334	78.402	53.342	188.981	- 10.231
5200	19.543	95.714	78.268	53.408	191.639	- 10.234
5300	19.554	96.086	78.073	53.469	194.300	- 10.237
5400	19.565	96.452	77.822	53.527	196.951	- 10.240
5500	19.577	96.811	77.522	53.581	199.611	- 10.243
5600	19.588	97.164	77.164	53.632	202.262	- 10.246
5700	19.597	97.510	76.753	53.680	204.922	- 10.249
5800	19.605	97.851	76.292	53.725	207.575	- 10.252
5900	19.615	98.187	75.782	53.766	210.222	- 10.255
6000	19.624	98.516	75.227	53.804	212.876	- 10.258

Point Group C<sub>2h</sub>  
 $\Delta H_f^0 = -151.8 \pm 5$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0 = -154.8 \pm 154.8$  kcal. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
[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]°

Products of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [8.156754] X 10<sup>-114</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

See NeOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. P. Porter, J. Chem. Phys. 29, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. 31, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for Li<sub>2</sub>(OH)<sub>2</sub>(g) which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the angle O-Li-O = 100°. The last one was adopted for the molecular configuration of Na<sub>2</sub>(OH)<sub>2</sub>, but the bond angle O-Na-O was modified to 90° (i.e. a square planar configuration for sodium and oxygen atoms). The bond angle Na-O-H in Na<sub>2</sub>(OH)<sub>2</sub>(g) was assumed to be 110°. The bond distance O-H was estimated to be the same in H<sub>2</sub>O(g). The three principal moments of inertia are I<sub>A</sub> = [14.0831] X 10<sup>-39</sup>, I<sub>B</sub> = [18.1678] X 10<sup>-39</sup> and I<sub>C</sub> = [31.8449] X 10<sup>-39</sup> g.<sup>2</sup> cm.<sup>2</sup>

The first six selected vibrational frequencies were taken to be equal to those for Na<sub>2</sub>F<sub>2</sub>(g) (see Na<sub>2</sub>F<sub>2</sub>(g) table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.

T. °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	0.000	0.000	INFINITE	4.135	-151.754	-151.754	INFINITE
100	11.929	56.308	88.609	3.230	-152.961	-152.961	329.711
200	16.752	66.319	75.110	1.758	-153.946	-148.369	162.130
298	18.949	73.442	0.000	0.000	-154.800	-145.448	106.616
300	18.985	73.559	73.642	0.035	-154.815	-145.389	105.916
400	20.765	79.272	74.705	2.025	-156.918	-142.023	77.598
500	22.248	84.070	75.714	4.178	-157.677	-138.207	60.410
600	23.434	88.236	77.661	6.465	-158.287	-134.254	48.902
700	24.381	91.925	79.269	8.957	-158.787	-130.209	40.653
800	25.157	95.230	81.061	11.335	-159.203	-126.097	34.448
900	25.813	98.232	82.804	13.484	-159.560	-121.936	29.610
1000	26.381	100.981	84.486	16.495	-159.874	-117.737	25.731
1100	26.881	103.520	86.103	19.158	-160.168	-113.513	22.553
1200	27.324	105.878	87.654	21.869	-160.419	-109.344	19.732
1300	27.720	108.081	89.141	24.622	-160.631	-105.135	16.834
1400	28.073	110.148	90.569	27.412	-160.803	-100.940	14.352
1500	28.388	112.096	91.939	30.235	-160.939	-96.757	12.203
1600	28.671	113.937	93.257	33.088	-161.047	-92.588	10.325
1700	28.924	115.683	94.526	35.968	-161.126	-88.430	8.669
1800	29.151	117.343	95.748	38.872	-161.174	-84.289	7.199
1900	29.355	118.925	96.926	41.798	-161.197	-80.157	5.884
2000	29.538	120.435	98.064	44.742	-161.197	-76.042	4.703
2100	29.704	121.881	99.164	47.705	-161.174	-71.938	3.636
2200	29.853	123.266	100.228	50.683	-161.126	-67.840	2.666
2300	29.988	124.596	101.259	53.675	-161.047	-63.746	1.933
2400	30.110	125.875	102.258	56.680	-160.939	-59.657	1.379
2500	30.221	127.106	103.228	59.696	-160.803	-55.582	0.975
2600	30.322	128.294	104.169	62.724	-160.631	-51.523	0.657
2700	30.414	129.440	105.084	65.761	-160.419	-47.478	0.401
2800	30.498	130.547	105.974	68.806	-160.174	-43.441	0.279
2900	30.575	131.619	106.840	71.860	-159.896	-39.410	0.197
3000	30.646	132.657	107.683	74.921	-159.582	-35.384	0.144
3100	30.711	133.663	108.505	77.989	-159.236	-31.363	0.109
3200	30.771	134.639	109.306	81.063	-158.857	-27.354	0.084
3300	30.826	135.586	110.088	84.142	-158.444	-23.356	0.064
3400	30.877	136.507	110.852	87.228	-157.997	-19.369	0.049
3500	30.924	137.403	111.598	90.318	-157.523	-15.392	0.034
3600	30.968	138.275	112.327	93.413	-157.019	-11.426	0.024
3700	31.008	139.125	113.040	96.512	-156.484	-7.469	0.016
3800	31.045	139.951	113.747	99.614	-155.919	-3.520	0.010
3900	31.079	140.758	114.440	102.721	-155.326	0.420	0.006
4000	31.114	141.546	115.118	105.831	-154.706	2.359	0.004
4100	31.145	142.314	115.783	108.943	-154.059	4.297	0.003
4200	31.173	143.065	116.434	112.059	-153.384	6.234	0.002
4300	31.200	143.799	117.013	115.178	-152.684	8.161	0.001
4400	31.225	144.516	117.630	118.299	-151.959	10.079	0.001
4500	31.249	145.218	118.236	121.423	-151.206	11.988	0.001
4600	31.271	145.906	118.830	124.549	-150.426	13.888	0.001
4700	31.292	146.578	119.413	127.677	-149.619	15.771	0.001
4800	31.312	147.237	119.986	130.808	-148.784	17.638	0.001
4900	31.331	147.883	120.548	133.940	-147.919	19.489	0.001
5000	31.348	148.516	121.102	137.074	-147.026	21.324	0.001
5100	31.365	149.137	121.645	140.209	-146.106	23.144	0.001
5200	31.380	149.746	122.180	143.347	-145.160	24.948	0.001
5300	31.395	150.344	122.706	146.485	-144.189	26.736	0.001
5400	31.409	150.931	123.223	149.626	-143.194	28.508	0.001
5500	31.423	151.508	123.732	152.767	-142.174	30.264	0.001
5600	31.435	152.074	124.233	155.910	-141.129	32.004	0.001
5700	31.447	152.631	124.726	159.054	-140.060	33.728	0.001
5800	31.459	153.178	125.212	162.200	-138.969	35.436	0.001
5900	31.470	153.715	125.691	165.346	-137.846	37.128	0.001
6000	31.480	154.244	126.162	168.493	-136.692	38.804	0.001

HYDROGEN SULFIDE (H<sub>2</sub>S) (IDEAL GAS)

Point Group C<sub>2v</sub> ΔH<sub>f</sub><sup>0</sup> = -4.18 ± 0.15 kcal. mole<sup>-1</sup>

S<sub>298.15</sub><sup>0</sup> = 49.15 cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>0</sup> 298.15 = -4.88 ± 0.15 kcal. mole<sup>-1</sup>

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.<sup>-1</sup>

- 2614.56 (1)
- 1102.68 (1)
- 2627.48 (1)

Bond Distance: S-H = 1.328 Å

Bond Angle: H-S-H = 92.2°

Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 4.69 X 10<sup>-11</sup> g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The heat of formation of hydrogen sulfide has been calorimetrically measured by H. Zeumer and W. A. Roth, Z. Elektrochem. 40, 777 (1934), and A. P. Kapustiniskii and R. T. Kankovskii, Zhur. Fiz. Khim. 32, 2810 (1958), as ΔH<sub>f</sub><sup>0</sup> 298 = -4.80 ± 0.15 kcal. mole<sup>-1</sup> and ΔH<sub>f</sub><sup>0</sup> 298 = -4.94 ± 0.08 kcal. mole<sup>-1</sup>, respectively. A weighted average of these two values was taken for the standard enthalpy of formation of hydrogen sulfide.

Heat Capacity and Entropy.

The bond distance, angle and vibrational frequencies were obtained from H. C. Allen, Jr. and E. K. Plyler, J. Chem. Phys. 25, 1132 (1956).

J. S. Gordon, private communication, Feb. 7, 1961, has calculated C<sub>p</sub> from 298 to 6000°K. by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes second order corrections for vibrational anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The correction constants were obtained from Allen and Plyler, loc. cit. Below 298°K. the rigid-rotator harmonic oscillator method was used to calculate the functions, but at 298°K. and above Gordon's thermodynamic functions were adopted in this tabulation.

T, °K.	C <sub>p</sub>	S <sup>0</sup>	-(F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	.000	INFINITE	INFINITE	2.281	4.184	4.184	INFINITE
100	7.949	40.359	56.219	1.586	4.212	5.813	12.266
200	7.678	45.872	49.927	.791	4.213	7.859	7.439
298	8.172	49.151	49.151	.000	4.880	7.955	5.891
300	8.176	49.202	49.151	.015	4.888	7.974	5.809
400	8.1504	51.597	49.476	.849	5.847	8.918	4.872
500	8.889	53.536	50.100	1.718	6.615	9.596	4.194
600	9.306	55.193	50.813	2.628	7.262	10.129	3.689
700	9.737	56.660	51.546	3.580	7.812	10.538	3.290
800	10.162	57.988	52.269	4.575	8.267	10.862	2.942
900	10.567	59.209	52.973	5.612	8.641	11.107	2.633
1000	10.943	60.342	53.654	6.687	8.941	11.271	2.351
1100	11.281	61.401	54.311	7.799	9.192	11.358	2.094
1200	11.584	62.396	54.944	8.943	9.406	11.364	1.861
1300	11.853	63.334	55.553	10.115	9.580	11.291	1.648
1400	12.092	64.221	56.141	11.312	9.724	11.139	1.454
1500	12.303	65.063	56.708	12.532	9.841	10.907	1.278
1600	12.491	65.863	57.255	13.772	9.928	10.698	1.121
1700	12.658	66.625	57.784	15.030	9.995	10.514	0.981
1800	12.808	67.353	58.296	16.303	10.043	10.351	0.854
1900	12.941	68.049	58.791	17.590	10.075	10.204	0.746
2000	13.063	68.716	59.271	18.891	10.093	10.071	0.654
2100	13.171	69.356	59.736	20.203	10.098	9.951	0.576
2200	13.270	69.971	60.187	21.525	10.091	9.844	0.510
2300	13.360	70.563	60.625	22.856	10.072	9.750	0.454
2400	13.444	71.133	61.051	24.197	10.041	9.669	0.406
2500	13.520	71.684	61.466	25.545	10.000	9.598	0.365
2600	13.590	72.215	61.869	26.900	9.949	9.536	0.328
2700	13.655	72.729	62.262	28.263	9.888	9.482	0.294
2800	13.715	73.227	62.645	29.631	9.818	9.435	0.262
2900	13.771	73.709	63.018	31.005	9.740	9.394	0.231
3000	13.824	74.177	63.382	32.385	9.655	9.358	0.201
3100	13.874	74.631	63.738	33.770	9.564	9.326	0.172
3200	13.921	75.071	64.085	35.160	9.458	9.298	0.144
3300	13.964	75.495	64.425	36.554	9.347	9.273	0.117
3400	14.007	75.902	64.756	37.953	9.231	9.250	0.091
3500	14.047	76.296	65.081	39.356	9.110	9.229	0.066
3600	14.085	76.672	65.399	40.762	8.984	9.209	0.042
3700	14.122	77.038	65.710	42.173	8.853	9.190	0.019
3800	14.156	77.385	66.015	43.586	8.718	9.171	0.000
3900	14.189	77.715	66.314	45.004	8.579	9.152	-0.019
4000	14.223	78.023	66.607	46.424	8.436	9.133	-0.038
4100	14.258	78.309	66.895	47.848	8.290	9.114	-0.057
4200	14.285	78.598	67.177	49.275	8.141	9.095	-0.076
4300	14.314	78.875	67.453	50.705	7.989	9.076	-0.095
4400	14.343	79.155	67.725	52.138	7.834	9.057	-0.114
4500	14.371	79.437	67.992	53.574	7.676	9.038	-0.133
4600	14.397	80.213	68.254	55.012	7.515	9.019	-0.152
4700	14.423	80.523	68.512	56.455	7.351	8.999	-0.171
4800	14.450	80.827	68.765	57.897	7.184	8.979	-0.190
4900	14.475	81.125	69.015	59.343	7.014	8.958	-0.209
5000	14.500	81.418	69.260	60.792	6.841	8.937	-0.228
5100	14.523	81.705	69.501	62.243	6.665	8.916	-0.247
5200	14.548	81.988	69.738	63.697	6.486	8.894	-0.266
5300	14.571	82.265	69.972	65.153	6.304	8.872	-0.285
5400	14.594	82.538	70.202	66.611	6.119	8.850	-0.304
5500	14.616	82.806	70.429	68.071	5.932	8.827	-0.323
5600	14.639	83.069	70.652	69.534	5.742	8.804	-0.342
5700	14.661	83.328	70.873	70.999	5.549	8.780	-0.361
5800	14.682	83.584	71.089	72.466	5.353	8.756	-0.380
5900	14.705	83.835	71.303	73.936	5.154	8.731	-0.399
6000	14.725	84.082	71.514	75.407	4.952	8.706	-0.418

AMMONIA (NH<sub>3</sub>) (IDEAL GAS) MOL. WT. = 17.03081

Point Group, C<sub>3v</sub> ΔH<sub>f</sub><sup>0</sup> = -9.30 kcal. mole<sup>-1</sup>  
 ΔH<sub>f</sub><sup>0</sup> 298.15 = -10.97 ± 0.1 kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies  
 Zero-order "Harmonic" Observed Wave Numbers  
 3508 (1) 3444 (2) 1627 (2)  
 1022 (1) 1691 (2) 1627 (2)

Bond Length: N-H = 1.024 Å Bond Angle: H-N-H = 106.67°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 3.4626 X 10<sup>-41</sup> g.<sup>3</sup> cm.<sup>6</sup>

HEAT OF FORMATION  
 A weighted average based on analysis using JANAF functions was selected. Haber, Tamaru and Oehmlig, Z. Elektrochem., 21, 206 (1915) obtained ΔH<sub>f</sub><sup>0</sup> = 11.10 for NH<sub>3</sub> = 0.5 H<sub>2</sub> + 1.5 H<sub>2</sub> by flow calorimetry. Estimated uncertainty is 1% and the formation value was corrected by 0.025 kcal. for non-ideality of NH<sub>3</sub>. Becker and Roth, Ibid., 49, 836 (1934) measured ΔH<sub>f</sub><sup>0</sup> (NH<sub>3</sub>(g) + H<sub>2</sub>O(l, aq.)) = 17.594 kcal. and (NH<sub>3</sub>(g) + H<sub>2</sub>O(l, aq.)) = 182.9 ± 0.24 for 3H<sub>2</sub>O(l) + N<sub>2</sub>(g) → 1.5 O<sub>2</sub>(g) + 2NH<sub>3</sub>(g). Equilibrium data from Larson and Dodge, J. Am. Chem. Soc., 45, 2318 (1923) and Haber, Tamaru and Ponnas, Z. Elektrochem., 21, 89 (1915) were analyzed as tabulated by Stephenson and McMahon, J. Am. Chem. Soc., 61, 437 (1939) from the non-ideality corrections of Gillespie and Beattie, Phys. Rev., 36, 743 (1930). Data (1000-5000 atm) from Winchester and Dodge, A.I.Ch.E. Journal, 2, 431-6 (1956) were omitted because of uncertainty in non-ideality while data (1 atm) of Haber and Maschke, Z. Elektrochem., 21, 128 (1915) were assumed ideal. High-temperature calorimetry of the direct decomposition includes Haber and Tamaru, Z. Elektrochem., 21, 191 (1915) and Wittig and Schatz, Ibid., 63, 470 (1959).

Source	Method	ΔH <sub>f</sub> <sup>0</sup> 298 (kcal. mole <sup>-1</sup> )	Drift (e.u.)
Haber, Tamaru, Oehmlig (1915)	Flow calorimetry at 298°K	-11.07	
Becker, Roth (1934)	Indirect calorimetry at 294°K	-11.05±0.12	
Larson, Dodge (1923)	K <sub>p</sub> from P <sub>1</sub> (10-1000 atm, 600-800°K)	-10.86(-10.92±0.03)*	-0.17±0.05
Haber, Tamaru, Ponnas (1915)	K <sub>p</sub> from P <sub>2</sub> (30 atm, 800-1200°K)	-10.89(-10.95±0.05)*	0.04±0.05
Haber, Maschke (1915)	K <sub>p</sub> (1 atm, 900-1400°K)	-10.87(-10.60±0.1)*	-0.22±0.08
Haber, Tamaru (1915)	Flow calorimetry (739-932°K)	-10.97	
Wittig, Schatz (1959)	Flow calorimetry at 823°K	-10.96	

\*Third law values for equilibrium data are followed by second law values in parentheses.  
 Heat Capacity and Entropy  
 The functions are an approximation of the non-rigid rotator anharmonic oscillator based on calculations of Harrison and Kobe, Chem. Eng. Progr., 49, No. 7, 545 (1953) and Yungman, Gurvich and Ritscher, Trudy Gosudarst. Inst. Priklad. Khim., 49, 20 (1952). In these calculations anharmonicity of v<sub>2</sub> associated with inversion doubling was treated by summation over anharmonicity and vibrational interaction of the other fundamentals. JANAF functions agree with the results to within 0.02 e.u. in the range 298-1500°K.

Two sets of rigid rotator harmonic oscillator functions were also tested for consistency with the ammonia data (see below). These were obtained from molecular dimensions and either calculated zero order frequencies (ω<sub>r</sub>) or observed wave numbers (ω<sub>r</sub>) obtained by Benedict and Plyler, Can. J. Phys., 35, 1235 (1957) from high resolution infrared studies. Herzberg, "Infrared and Raman Spectra", pp. 303-4, 1945 states that ω<sub>r</sub> should be used and the JANAF functions give better, but not perfect, agreement with the observed ω<sub>r</sub> for NH<sub>3</sub>. Principal moments of inertia are I<sub>A</sub> = 4.418 X 10<sup>-40</sup> and I<sub>B</sub> = I<sub>C</sub> = 2.803 X 10<sup>-40</sup> g. cm.<sup>2</sup>. Electron diffraction studies by Bartlmann and Beagley, Acta Chem. Scand., 19, 2077 (1964) give slightly different constants (bond distance 1.019 Å and angle = 109.1°).

T, °K	Heat Capacity, C <sub>p</sub>		Entropy, S <sup>0</sup>	
	Observed	JANAF	Observed	JANAF
253.15	8.221(4)	8.269	23.9.72	44.23(u.c)
423.15	9.422(4)	9.423	29.6.15	46.03
800.	12.07±0.2(f)	12.225	800.	{ 55.86(u.c) 56.02(f) 56.09(f) }

(a) N. S. Osborne, H. F. Stinson, T. S. Slight, Jr., and C. S. Cragoe, M.S. Sci. Papers, 20, 65 (1924-6) measured C<sub>p</sub> of gaseous NH<sub>3</sub> (258 to 423°K and 0.5 to 20 atm) within an estimated maximum error of 0.5% (about 0.03 cal. deg.<sup>-1</sup> mole<sup>-1</sup>) and obtained ω<sub>r</sub> by use of a suitable equation of state.  
 (b) R. Overstall and H. F. Glaueque, J. Am. Chem. Soc., 59, 254 (1937) determined the entropy of the real gas at the normal boiling point as S<sub>373.72</sub> = 44.06 ± 0.10 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.  
 (c) (S<sup>0</sup>)<sub>298.15</sub> = 0.17 cal. deg.<sup>-1</sup> mole<sup>-1</sup> from the initial coefficient equation derived by Hirschfelder, McClure and Hesse, J. Chem. Phys., 10, 201 (1942) from the PVT data of Meyers and Jessup, Refrig. Eng., 11, 345 (1925).  
 (d) Combination of ΔH<sub>f</sub><sup>0</sup> 800 = -12.83 kcal. mole<sup>-1</sup> from the calorimetric measurement of P. E. Wittig and H. Schatz, Z. Elektrochem., 63, 470 (1959) with ΔG<sub>800</sub> = 8.335 kcal. mole<sup>-1</sup> from equilibrium data (f).  
 (e) S<sup>0</sup> second law analysis of the equilibrium data (f).  
 (f) K<sub>p</sub> values based on the equilibrium data of Haber, Tamaru and Ponnas and of Larson and Dodge were analyzed by regression analysis to give ΔG<sub>800</sub> = 8.335 ± 0.004, ΔH<sub>800</sub> = -12.666 ± 0.017 and ΔH<sub>p</sub> 800 = -2.31 ± 0.20.

T, °K	C <sub>p</sub> <sup>0</sup>	S <sup>0</sup>	-(F <sup>0</sup> -H <sub>298</sub> <sup>0</sup> )/T	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup> /T	ΔH <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	7.920	37.210	1.609	2.404	9.302	INFINITE
200	8.054	42.740	0.811	1.609	8.146	17.801
298	8.151	46.033	0.000	0.000	6.708	6.139
300	8.152	46.033	0.016	0.016	6.708	2.869
400	8.210	48.633	0.503	10.980	3.871	2.820
500	8.267	50.780	1.067	11.482	1.867	0.778
600	8.323	52.679	1.630	12.282	3.790	1.380
700	8.379	54.400	2.193	12.824	6.494	2.027
800	8.435	55.986	2.756	12.824	9.235	2.523
900	8.491	57.464	3.319	13.016	12.005	2.915
1000	8.547	58.851	3.882	13.163	14.792	3.233
1100	8.603	60.161	4.445	13.271	17.594	3.495
1200	8.659	61.404	5.008	13.343	20.405	3.716
1300	8.715	62.588	5.571	13.385	23.218	3.903
1400	8.771	63.718	6.134	13.402	26.032	4.064
1500	8.827	64.798	6.697	13.399	28.845	4.204
1600	8.883	65.833	7.260	13.381	31.666	4.325
1700	8.939	66.823	7.823	13.347	34.483	4.433
1800	8.995	67.774	8.386	13.303	37.294	4.528
1900	9.051	68.688	8.949	13.250	40.104	4.613
2000	9.107	69.566	9.512	13.191	42.911	4.689
2100	9.163	70.411	10.075	13.125	45.717	4.757
2200	9.219	71.227	10.638	13.053	48.514	4.819
2300	9.275	72.015	11.201	12.973	51.310	4.875
2400	9.331	72.777	11.764	12.887	54.107	4.927
2500	9.387	73.516	12.327	12.797	56.893	4.973
2600	9.443	74.234	12.890	12.697	59.679	5.016
2700	9.499	74.930	13.453	12.592	62.461	5.056
2800	9.555	75.607	14.016	12.480	65.237	5.092
2900	9.611	76.266	14.579	12.360	68.015	5.125
3000	9.667	76.908	15.142	12.236	70.780	5.156
3100	9.723	77.532	15.705	12.105	73.546	5.185
3200	9.779	78.141	16.268	11.973	76.307	5.211
3300	9.835	78.734	16.831	11.838	79.067	5.236
3400	9.891	79.314	17.394	11.698	81.814	5.259
3500	9.947	79.879	17.957	11.557	84.565	5.280
3600	10.003	80.432	18.520	11.412	87.307	5.300
3700	10.059	80.972	19.083	11.265	90.051	5.319
3800	10.115	81.501	19.646	11.112	92.787	5.336
3900	10.171	82.019	20.209	10.958	95.520	5.353
4000	10.227	82.527	20.772	10.800	98.246	5.368
4100	10.283	83.024	21.335	10.639	100.972	5.382
4200	10.339	83.512	21.898	10.474	103.694	5.396
4300	10.395	84.000	22.461	10.306	106.409	5.408
4400	10.451	84.488	23.024	10.134	109.117	5.420
4500	10.507	84.974	23.587	9.961	111.823	5.431
4600	10.563	85.461	24.150	9.781	114.534	5.441
4700	10.619	85.948	24.713	9.600	117.236	5.451
4800	10.675	86.434	25.276	9.415	119.928	5.460
4900	10.731	86.920	25.839	9.228	122.617	5.469
5000	10.787	87.406	26.402	9.039	125.305	5.477
5100	10.843	87.892	26.965	8.848	127.993	5.485
5200	10.899	88.378	27.528	8.657	130.678	5.492
5300	10.955	88.864	28.091	8.466	133.355	5.499
5400	11.011	89.350	28.654	8.275	136.026	5.505
5500	11.067	89.836	29.217	8.084	138.697	5.511
5600	11.123	90.322	29.780	7.893	141.361	5.517
5700	11.179	90.808	30.343	7.702	144.028	5.522
5800	11.235	91.294	30.906	7.511	146.683	5.527
5900	11.291	91.780	31.469	7.320	149.337	5.532
6000	11.347	92.266	32.032	7.129	151.984	5.536

MOL. WT. = 32.04528

HYDRAZINE (N<sub>2</sub>H<sub>4</sub>) (LIQUID)

$S_{298.15} = 29.05 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^{\circ} 298.15 = 12.10 \pm 0.1 \text{ kcal. mole}^{-1}$   
 $\Delta H_m^{\circ} = 3.025 \text{ kcal. mole}^{-1}$   
 $T_m = 274.69^{\circ}\text{K.}$   
 $T_b = 386.9^{\circ}\text{K.}$

Heat of Formation.

A. M. Hughes, R. J. Corruccini and E. C. Gilbert, J. Am. Chem. Soc. 61, 2639 (1939), measured the heats of combustion of hydrazine and hydrazine monohydrate. The data, adjusted as suggested by L. G. Cole and E. C. Gilbert, J. Am. Chem. Soc. 73, 5423 (1951), are summarized below. Heats of solution determined by V. C. Bushnell, A. M. Hughes and E. C. Gilbert, J. Am. Chem. Soc. 59, 2142 (1937) interrelate N<sub>2</sub>H<sub>4</sub>(l) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O(l). An intermediate value was selected from the resulting heats of formation.

Source	Reaction	$\Delta H_f^{\circ} 298$	$\Delta H_f^{\circ} 298$
Hughes	N <sub>2</sub> H <sub>4</sub> (l) + O <sub>2</sub> (g) → N <sub>2</sub> (g) + 2H <sub>2</sub> O(l)	-148.68 ± 0.06	12.05
Hughes	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O(l) + O <sub>2</sub> (g) → N <sub>2</sub> (g) + 3H <sub>2</sub> O(l)	-147.00 ± 0.06	---
Bushnell	N <sub>2</sub> H <sub>4</sub> (l) + H <sub>2</sub> O(l) → N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O(l)	-1.80	12.17*

\*From combination of second and third reactions.

Heat Capacity and Entropy.

Heat capacities (12-340°K) of hydrazine crystal and liquid were determined by D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc. 71, 2293 (1949). Values beyond the experimental range for the liquid were extrapolated linearly. The entropy was obtained from the heat of melting and the smoothed heat capacities of the crystal using  $S_{12}^{\circ} = 0.023 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Melting Data.

Taken from Scott et al., loc. cit.

Vaporization Data.

The normal boiling point and heat of vaporization are those calculated for the ideal gas from these tables. The boiling point found for the real gas (387.3°K) by W. Hieber and A. Woerner, Z. Elektrochem. 40, 252 (1934) is in good agreement. The selected heat of vaporization,  $\Delta H_{298}^{\circ} = 10.69 \text{ kcal. mole}^{-1}$ , is based on the vapor pressure data of Scott et al., loc. cit., series III. Vapor pressure measurements of Hieber and Woerner, loc. cit., and E. T. Chang and N. A. Gokcen, AD-456288, Defense Documentation Center, January, 1964, are in satisfactory agreement as shown below.

Source	Temp. Range °K.	$\Delta H_{298}^{\circ}$ (kcal. mole <sup>-1</sup> ) 2nd Law	$\Delta H_{298}^{\circ}$ (kcal. mole <sup>-1</sup> ) 3rd Law	3rd Law Drift e.u.
Scott, et al. (1949)	275-343	10.683 ± 0.003	10.696	0.05 ± 0.01
Chang, Gokcen (1964)	276-325	10.40 ± 0.03	10.68	0.91 ± 0.09
Hieber, Woerner (1934)	293-387	10.82 ± 0.03	10.71	-0.33 ± 0.07

The second law-third law consistency of Scott et al. reflects the use of these data in selection of the gas phase functions (see H<sub>2</sub>N<sub>2</sub> gas).

Dec. 31, 1965

T. °K.	C <sub>p</sub>	S°	-(F°-H <sub>298</sub> °)/T	H°-H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0							
100	20.850	5.428	49.091	4.406	11.611	19.797	4.263
200	22.250	19.910	31.164	2.451	11.857	27.880	3.9484
298	23.623	26.730	26.050	1.800	12.100	35.094	2.9183
300	23.650	29.196	29.050	4.044	12.105	35.840	2.6108
400	25.660	36.236	29.999	2.503	12.476	33.701	2.3876
500	27.860	42.218	31.861	5.179	13.054	51.444	2.1485
600	30.060	47.492	34.034	8.075	13.838	59.052	21.509

MOL. WT. = 32.04528

(IDEAL GAS)

HYDRAZINE (N<sub>2</sub>H<sub>4</sub>)

Point Group C<sub>2</sub>  
 $\Delta H_f^0 = 57.03 \pm 0.4$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^0(298.15) = 22.79 \pm 0.2$  kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_e$ , cm. <sup>-1</sup>	$\omega_e$ , cm. <sup>-1</sup>	$\omega_e$ , cm. <sup>-1</sup>
3350	875	3280
3261	760	1275
1312	377	[933]
1098	3330	966

Bond Distances: N-H = 1.022 Å N-N = 1.449 Å  
 Bond Angle: H-N-H = 109.47° H-N-N = 112.0°  
 Torsional angle between two NH<sub>2</sub> groups > 90° from eclipsed position.  
 Product of the Moments of Inertia:  $I_A I_B I_C = 7.307 \times 10^{-117}$  g.<sup>3</sup> cm.<sup>6</sup>

$\sigma = 2$

Heat of Formation.

This was obtained from the heat of formation of the liquid and the selected heat of vaporization,  $\Delta H_{298}^0 = 10.69$  kcal. mole<sup>-1</sup>, derived from the vapor pressure data (Series III) of D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc. 71, 2293 (1949). Other vapor pressure data from W. Hieber and A. Woerner, Z. Elektrochem. 40, 252 (1934) and E. T. Chang and N. A. Gokcen, AD-458288, Defense Documentation Center, January, 1964, are in satisfactory agreement (see N<sub>2</sub>H<sub>4</sub> liquid table).

Heat Capacity and Entropy.

Functions were calculated from the constants given above using the rigid rotator harmonic oscillator method. The entropy was increased by R ln 2 because two rotameric forms are implied by use of the torsional frequency. Small but arbitrary adjustments were made in the assignment of the bending mode frequencies in order to reproduce the vapor pressure data of Scott et al., loc. cit., as closely as possible. Calculated values of  $S_{298}^0 = 57.03$  and  $S_{340}^0 = 58.70$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> may be compared with 56.99 and 58.69, respectively, derived from the data of Scott et al. Internal rotation calculations would require a complex potential function in order to fit the data. The barrier to inversion (990 cm.<sup>-1</sup> ~ 2.8 kcal.) is slightly less than the barrier to internal rotation at the trans position (1110 cm.<sup>-1</sup> ~ 3.2 kcal.) according to analyses of the microwave data by T. Kasuya, Sci. Papers, Inst. Phys. Chem. Res. (Tokyo) 56, No. 1, 1-39 (1962) and T. Kasuya and T. Kojima, J. Phys. Soc. Japan 18, 364-8 (1963).

From matrix isolation and gas phase infrared studies, E. Catalano, R. H. Sanborn and J. M. Prazer, J. Chem. Phys. 35, 2265 (1963), have suggested possible uncertainties in the assignment of the bending mode frequencies in the region from 1630 to 740 cm.<sup>-1</sup>. The question hinges on the uncertain existence of a gas phase fundamental at about 1600 cm.<sup>-1</sup> as observed by P. A. Giguere and I. D. Liu, J. Chem. Phys. 20, 136 (1952). No corresponding matrix band was found and the gas phase band appeared to be due to absorption on the cell windows. A vapor phase Raman frequency at 1564 cm.<sup>-1</sup> was observed, however, by Yu. I. Kotov and V. M. Tatevskii, Opt. i Spektroskopiya 15, 65 (1963). Catalano et al. suggest one assignment based on the uncertain fundamental and a tentative alternative assignment excluding it. The two assignments give entropies that are 0.26 cal. deg.<sup>-1</sup> mole<sup>-1</sup> lower and 0.12 higher than the third law value. The lower calculated entropy is probably more reasonable, but the higher value could be more easily modified to agree with the third law value. Thus the alternative assignment was adopted with  $\nu_{11}$  arbitrarily increased from ~810 to 933 cm.<sup>-1</sup>.

The structural constants are based primarily on the electron diffraction study of Y. Morino, T. Iijima and Y. Murata, Bull. Chem. Soc. Japan 33, 46 (1960). Related analyses of the infrared fine structure of the torsional frequency (377 cm.<sup>-1</sup>), A. Yamaguchi, I. Ichishima, T. Shimanouchi and S. Mizushima, Spectrochim. Acta 15, 1471 (1960), and of the microwave spectra, Kasuya and Kojima, loc. cit., are in close agreement. The microwave data give an H-N-H angle of 106° and a torsional angle of 90.2°. Principal moments of inertia of the adopted structure are  $I_A = 0.574 \times 10^{-39}$ ,  $I_B = 3.573 \times 10^{-39}$  and  $I_C = 3.563 \times 10^{-39}$  g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	0.000	INFINITE	- 2.755	26.155	26.155	INFINITE
100	8.214	46.625	61.180	24.751	62.891	- 62.891
200	9.718	52.717	57.030	23.730	33.192	- 36.268
298	12.145	57.030	0.000	22.790	38.042	- 27.884
300	12.194	57.031	0.023	22.774	38.136	- 27.781
400	14.747	60.971	1.872	22.038	43.375	- 23.698
500	16.861	64.498	2.957	21.522	48.772	- 21.517
600	18.538	67.126	4.740	21.183	54.257	- 19.762
700	19.100	70.690	6.654	20.975	59.787	- 18.666
800	21.081	73.427	8.705	20.871	65.339	- 17.849
900	22.111	75.970	10.866	20.849	70.901	- 17.216
1000	23.030	78.348	13.124	20.897	76.460	- 16.709
1100	23.854	80.583	15.469	21.002	82.011	- 16.293
1200	24.592	82.690	17.892	21.156	87.553	- 15.945
1300	25.252	84.685	20.384	21.349	93.077	- 15.647
1400	25.842	86.579	22.940	21.576	98.580	- 15.389
1500	26.367	88.380	25.551	21.826	104.060	- 15.164
1600	26.836	90.097	28.211	22.094	109.522	- 14.963
1700	27.254	91.737	30.916	22.382	114.972	- 14.785
1800	27.626	93.305	33.660	22.683	120.410	- 14.624
1900	27.960	94.808	36.440	22.998	125.835	- 14.478
2000	28.258	96.250	39.254	23.321	131.241	- 14.345
2100	28.525	97.635	42.091	23.651	136.671	- 14.223
2200	28.766	98.968	44.955	24.000	142.044	- 14.110
2300	28.982	100.251	47.843	24.326	147.404	- 14.006
2400	29.177	101.484	50.751	24.669	152.750	- 13.913
2500	29.354	102.684	53.678	25.011	158.073	- 13.818
2600	29.515	103.838	56.621	25.357	163.394	- 13.734
2700	29.660	104.955	59.580	25.703	168.695	- 13.654
2800	29.793	106.036	62.553	26.049	173.981	- 13.579
2900	29.915	107.084	65.539	26.397	179.254	- 13.509
3000	30.026	108.100	68.536	26.741	184.526	- 13.442
3100	30.128	109.086	71.543	27.086	189.777	- 13.379
3200	30.221	110.044	74.562	27.428	195.011	- 13.319
3300	30.307	110.975	77.587	27.766	200.227	- 13.262
3400	30.387	111.881	80.622	28.105	205.426	- 13.207
3500	30.460	112.763	83.664	28.437	210.689	- 13.155
3600	30.528	113.622	86.714	28.767	215.991	- 13.106
3700	30.591	114.459	89.770	29.091	221.268	- 13.058
3800	30.650	115.276	92.832	29.413	226.522	- 13.013
3900	30.704	116.073	95.900	29.729	231.748	- 12.969
4000	30.755	116.851	98.973	30.040	236.946	- 12.927
4100	30.802	117.611	102.051	30.347	242.115	- 12.887
4200	30.847	118.354	105.133	30.647	247.250	- 12.849
4300	30.888	119.080	108.220	30.944	252.354	- 12.811
4400	30.927	119.790	111.311	31.235	257.424	- 12.775
4500	30.963	120.486	114.405	31.518	262.461	- 12.740
4600	30.998	121.167	117.503	31.799	267.476	- 12.707
4700	31.030	121.834	120.605	32.073	272.465	- 12.675
4800	31.060	122.487	123.715	32.341	277.430	- 12.644
4900	31.089	123.128	126.827	32.604	282.371	- 12.614
5000	31.116	123.756	129.927	32.862	287.292	- 12.584
5100	31.141	124.371	133.040	33.113	292.193	- 12.556
5200	31.165	124.972	136.155	33.360	297.076	- 12.529
5300	31.188	125.578	139.273	33.600	301.945	- 12.502
5400	31.210	126.175	142.393	33.834	306.793	- 12.476
5500	31.230	126.728	145.514	34.061	311.626	- 12.451
5600	31.249	127.291	148.638	34.283	316.449	- 12.427
5700	31.268	127.844	151.764	34.500	321.259	- 12.404
5800	31.285	128.388	154.892	34.710	326.054	- 12.381
5900	31.302	128.923	158.021	34.914	330.834	- 12.359
6000	31.318	129.449	161.152	35.113	335.607	- 12.337

Dec. 31, 1960; Dec. 31, 1965

$$\Delta H_f^0 = -142.7 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -143.7 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [10.5 \pm 1.5] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298} = 144.7 \pm 20 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 6.44 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 3098 \pm 20 \text{ }^\circ\text{K.}$$

$$T_B = 3466 \text{ }^\circ\text{K.}$$

## Heat of Formation.

C. E. Holley and E. J. Huber, *J. Am. Chem. Soc.* **73**, 5577 (1951) reported  $\Delta H_f^{298}$  (MgO, c) = -143.7 kcal. mole<sup>-1</sup> by combustion calorimetry. Heat of solution measurements by C. H. Shomate and E. H. Ruffman, *J. Am. Chem. Soc.* **65**, 1625 (1943) yielded  $\Delta H_f^{298}$  (MgO, c) = -143.84 kcal. mole<sup>-1</sup>, well within the adopted  $\Delta H_f^{298}$  (MgO, c) = -143.7 ± 0.5 kcal. mole<sup>-1</sup>.

## Heat Capacity and Entropy.

Low temperature heat capacities have been reported by:

1. W. Lien and N. Phillips, *J. Chem. Phys.* **29**, 1415 (1958), 1.5-4°K.
2. W. F. Giaque and R. C. Archibald, *J. Am. Chem. Soc.* **59**, 561 (1937), 20-301°K.
3. G. S. Parks and K. K. Kelley, *J. Phys. Chem.* **30**, 47 (1926), 94-291°K.
4. T. H. K. Barron, W. T. Berg, and J. A. Morrison, *Proc. Roy. Soc. (London)* **A250**, 70 (1959), 10-270°K.
5. P. Gunther, *Ann. Physik* **51**, 828 (1916), 21-84°K.

High temperature heat contents have been reported by:

6. A. C. Victor and T. B. Douglas, *J. Res. N.B.S.* **67A**, 325 (1963), 373-1173°K.
7. L. B. Pankratz and K. K. Kelley, *U. S. Bur. Mines* **RI 6295**, (1963), 400-1800°K.

The samples of (1) and (2) were finely divided magnesia and the other samples were periclase. Periclase is taken to be the standard state. The high temperature heat content data of (6) and (7) were joined by a Shomate plot with the low temperature  $C_p$  data of (4). The heat capacity was extrapolated linearly above 1800°K to a value of 14 cal. mole<sup>-1</sup> deg.<sup>-1</sup> at 3100°K.  $S_{298.15}^0 = 6.44 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$  is from (4).

## Melting Data.

$T_m$  (MgO, c) = 3098 ± 20°K by R. N. McNally, P. I. Peters, and P. H. Ribbe, *J. Am. Ceram. Soc.* **44**, 491 (1961) was adopted. Their value is 41°K higher than the earlier measurements of C. W. Kanolt, *J. Wash. Acad. Sci.* **3**, 315 (1913). K. K. Kelley, *Bur. Mines Bull.* **393** (1936) calculated  $\Delta H_m^0$  (MgO, c) = 18.5 ± 1.5 kcal./mole from melting point measurements in the MgO - ZrO<sub>2</sub> system.

## Sublimation Data.

$T_B$  is the temperature at which the free energy change of the reaction MgO(c) = MgO(g) approaches zero. The difference between  $\Delta H_f^{298.15}$  for MgO(c) and MgO(g) is  $\Delta H_g^{298.15}$ .

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	1.866	6.00	12.445	1.235	-142.701	-142.701	INFINITE
200	6.370	3.369	7.177	1.186	-143.163	-143.163	307.966
298	8.882	6.440	4.000	1.186	-143.640	-143.640	151.431
300	8.915	6.495	3.967	1.186	-143.701	-143.701	99.675
400	10.169	9.251	6.807	1.186	-143.709	-143.709	99.025
500	10.848	11.598	7.557	2.038	-143.664	-130.746	72.854
600	11.285	13.616	8.386	3.138	-143.603	-128.185	57.152
700	11.604	15.381	9.262	4.283	-143.540	-125.620	46.689
800	11.856	16.947	10.176	5.457	-143.490	-123.064	39.218
900	12.077	18.335	10.964	6.652	-143.463	-120.512	33.618
1000	12.232	19.635	11.748	7.867	-143.463	-117.960	29.263
1100	12.382	20.808	12.537	9.098	-143.463	-115.403	25.740
1200	12.506	21.891	13.332	10.343	-143.463	-112.843	22.848
1300	12.586	22.895	14.037	11.597	-143.463	-110.283	20.438
1400	12.664	23.831	14.665	12.860	-143.463	-107.723	18.398
1500	12.743	24.707	15.287	14.130	-143.463	-105.163	16.575
1600	12.821	25.532	15.902	15.409	-143.463	-102.603	14.945
1700	12.890	26.312	16.492	16.695	-143.463	-100.043	13.417
1800	12.978	27.052	17.058	17.988	-143.463	-97.483	11.989
1900	13.057	27.755	17.603	19.290	-143.463	-94.923	10.661
2000	13.136	28.427	18.127	20.600	-143.463	-92.363	9.433
2100	13.214	29.070	18.633	21.917	-143.463	-89.803	8.305
2200	13.293	29.693	19.122	23.243	-143.463	-87.243	7.277
2300	13.371	30.297	19.594	24.576	-143.463	-84.683	6.350
2400	13.450	30.880	20.051	25.917	-143.463	-82.123	5.522
2500	13.529	31.440	20.494	27.266	-143.463	-79.563	4.795
2600	13.607	31.933	20.924	28.623	-143.463	-77.003	4.167
2700	13.686	32.448	21.341	29.987	-143.463	-74.443	3.640
2800	13.764	32.947	21.747	31.360	-143.463	-71.883	3.213
2900	13.843	33.431	22.141	32.740	-143.463	-69.323	2.886
3000	13.921	33.902	22.526	34.128	-143.463	-66.763	2.659
3100	14.000	34.359	22.900	35.525	-143.463	-64.203	2.532
3200	14.079	34.805	23.265	36.928	-143.463	-61.643	2.505
3300	14.157	35.240	23.621	38.340	-143.463	-59.083	2.578
3400	14.236	35.663	23.969	39.760	-143.463	-56.523	2.751
3500	14.314	36.077	24.309	41.187	-143.463	-53.963	3.024
3600	14.393	36.482	24.642	42.623	-143.463	-51.403	3.297
3700	14.472	36.877	24.967	44.066	-143.463	-48.843	3.570
3800	14.550	37.264	25.286	45.517	-143.463	-46.283	3.843
3900	14.629	37.643	25.598	46.976	-143.463	-43.723	4.116
4000	14.707	38.014	25.904	48.443	-143.463	-41.163	4.389



MAGNESIUM OXIDE (MgO) (LIQUID)

T. °K. C<sub>p</sub> S° - (F° - H<sub>f</sub><sup>298</sup>)/T H° - H<sub>f</sub><sup>298</sup> ΔH<sub>f</sub><sup>o</sup> ΔF<sub>f</sub> Log K<sub>p</sub>

T. °K.	C <sub>p</sub>	S° - (F° - H <sub>f</sub> <sup>298</sup> )/T	H° - H <sub>f</sub> <sup>298</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub>	Log K <sub>p</sub>
0						
100						
200						
298	8.882	12.033	12.033	0.000	-120.090	88.024
300						
300	8.915	12.088	12.033	0.16	-120.052	87.454
400	10.169	14.844	12.400	0.78	-118.021	64.480
500	10.848	17.191	13.130	2.030	-115.993	50.698
600	11.285	19.209	13.979	3.138	-113.978	41.514
700	11.604	20.974	14.855	4.283	-111.972	34.957
800	11.856	22.540	15.719	5.457	-109.975	30.042
900	12.057	23.948	16.557	6.652	-107.982	26.220
1000	12.232	25.228	17.361	7.867	-105.810	23.124
1100	12.382	26.491	18.130	9.098	-103.592	20.581
1200	12.507	27.648	18.865	10.343	-101.372	18.462
1300	12.586	28.688	19.567	11.597	-99.150	16.668
1400	12.664	29.624	20.238	12.860	-96.948	15.055
1500	12.743	30.300	20.880	14.130	-94.761	13.408
1600	12.821	31.125	21.495	15.408	-92.592	11.970
1700	12.900	31.905	22.085	16.695	-90.442	10.704
1800	12.978	32.645	22.651	17.988	-88.311	9.591
1900	13.057	33.348	23.196	19.290	-86.199	8.578
2000	13.136	34.020	23.720	20.600	-84.115	7.678
2100	14.500	34.684	24.226	21.922	-82.050	6.865
2200	14.500	35.359	24.717	23.242	-80.000	6.120
2300	14.500	36.034	25.194	24.562	-77.966	5.458
2400	14.500	36.708	25.657	25.872	-75.946	4.846
2500	14.500	37.382	26.108	27.167	-73.938	4.284
2600	14.500	37.781	26.546	28.412	-71.942	3.767
2700	14.500	38.338	26.972	29.642	-69.958	3.290
2800	14.500	38.856	27.387	30.852	-67.986	2.849
2900	14.500	39.334	27.791	32.045	-66.034	2.439
3000	14.500	39.786	28.185	33.212	-64.102	2.058
3100	14.500	40.331	28.570	34.462	-62.180	1.702
3200	14.500	40.742	28.944	35.692	-60.276	1.370
3300	14.500	41.238	29.310	36.912	-58.388	1.058
3400	14.500	41.671	29.667	38.122	-56.516	0.766
3500	14.500	42.091	30.016	39.312	-54.660	0.492
3600	14.500	42.500	30.357	40.482	-52.820	0.233
3700	14.500	42.897	30.691	41.632	-50.994	0.011
3800	14.500	43.284	31.017	42.762	-49.182	-0.241
3900	14.500	43.660	31.337	43.872	-47.384	-0.459
4000	14.500	44.027	31.649	44.962	-45.598	-0.665
4100	14.500	44.385	31.956	46.032	-43.826	-0.861
4200	14.500	44.735	32.256	47.082	-42.066	-1.047
4300	14.500	45.076	32.550	48.112	-40.318	-1.224
4400	14.500	45.409	32.838	49.122	-38.582	-1.392
4500	14.500	45.735	33.121	50.112	-36.850	-1.553
4600	14.500	46.054	33.399	51.082	-35.122	-1.706
4700	14.500	46.366	33.672	52.032	-33.400	-1.852
4800	14.500	46.671	33.939	52.962	-31.684	-1.992
4900	14.500	46.970	34.202	53.872	-29.974	-2.125
5000	14.500	47.263	34.461	54.762	-28.270	-2.253

ΔH<sub>f</sub><sup>o</sup> 298.15 = [12.033] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 ΔH<sub>m</sub><sup>o</sup> = [18.5 ± 1.5] kcal. mole<sup>-1</sup>  
 ΔH<sub>v</sub><sup>o</sup> = [113.4] kcal. mole<sup>-1</sup>

Heat of Formation.

ΔH<sub>f</sub><sup>o</sup> 298.15(1) was calculated from ΔH<sub>f</sub><sup>o</sup> 298.15(c) by adding ΔH<sub>m</sub><sup>o</sup> and the difference between H<sub>m</sub><sup>o</sup> - H<sub>l</sub><sup>o</sup> 298 for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2066°K. C<sub>p</sub>(1) below 2066°K. were assumed to be equal to those of MgO(c). At and above 2066°K. the heat capacities were assumed to be constant at 7.25 cal. deg.<sup>-1</sup> g. atom<sup>-1</sup>. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See MgO(c) table for details.

Vaporization Data.

W. R. Mott, Tran. Am. Electrochem. Soc. 34, 255 (1916) estimated the boiling point at 3873°K. by comparing crater distances of arc image deposits with reference compounds. T<sub>B</sub> = 3533°K. is the temperature at which the free energy change of the reaction MgO(l) = MgO(g) approaches zero. The difference between ΔH<sub>f</sub><sup>o</sup> 3533 for MgO(g) and MgO(l) is ΔH<sub>v</sub><sup>o</sup>.

MAGNESIUM OXIDE (MgO) (IDEAL GAS) MOL. WT. = 40.3114

Ground State Configuration  $3\Sigma$   $\Delta H_f^0 = 1.0 \pm 20 \text{ kcal mole}^{-1}$  $S_{298.15}^0 = 52.889 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   $\Delta H_f^0 298.15 = 1.0 \pm 20 \text{ kcal. mole}^{-1}$ 

## Electronic Levels and Quantum Weights

 $\epsilon_i \text{ cm.}^{-1}$   $g_i$ 

0 3

 $\omega_e = 902 \text{ cm.}^{-1}$   $\omega_e x_e = 13.0 \text{ cm.}^{-1}$   $\sigma = 1$  $B_e = [0.625] \text{ cm.}^{-1}$   $\kappa_e = [0.0094] \text{ cm.}^{-1}$   $r_e = [1.672] \text{ \AA}$ 

## Heat of Formation.

There is considerable discordance in the heat of formation results even though results were adjusted to a common  $3\Sigma$  ground state where necessary. A mean  $\Delta H_f^0 298 \text{ (MgO, g)} = 1.0 \pm 20 \text{ kcal. mole}^{-1}$  was selected.

R. L. Altman, J. Phys. Chem. **67**, 366 (1963) made a Knudsen effusion and oxygen transpiration study of the vaporization of MgO. The predominant vapor species over MgO(c) were shown to be Mg(g) and O<sub>2</sub>(g). MgO transpiration results with oxygen at 1 atm yielded a 3rd law heat of sublimation  $\Delta H_g^0 298 \text{ (MgO, g)} = 162.3 \text{ kcal. mole}^{-1}$  and  $\Delta H_f^0 298 \text{ (MgO, g)} = 18.6 \text{ kcal. mole}^{-1}$ .

J. Drowart, G. Eksteen and G. Verhaegen, Trans. Far. Soc. **50**, 1920 (1964) used the Knudsen effusion-mass spectrometer technique to determine relative ion intensities and enthalpies for the reaction  $\text{MgO(g)} + \text{O(g)} \rightarrow \text{Mg(g)} + \text{O}_2\text{(g)}$ . After adjusting their values for a  $3\Sigma$  ground state we calculated  $\Delta H_f^0 298 \text{ (MgO, g)} = 11.9 \text{ kcal. mole}^{-1}$ . Similar calculations for their data on  $\text{MgO(g)} + \text{WO}_2\text{(g)} \rightarrow \text{Mg(g)} + \text{WO}_3\text{(g)}$  yielded  $\Delta H_f^0 298 = 10.5 \text{ kcal. mole}^{-1}$ . The agreement is fortuitous, however, since uncertainties in the JANAF values for  $\text{WO}_2\text{(g)}$  and  $\text{WO}_3\text{(g)}$  are on the order of 7 kcal. each.

R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. **23**, 1347 (1955) mass spectrometrically determined an upper limit for the vapor pressure of MgO(c) at 1950°K. Their results reduce to a lower limit of 148.6 kcal. mole<sup>-1</sup> for  $\Delta H_g 298.15 \text{ (MgO, c)}$  or a lower limit of 4.9 kcal. mole<sup>-1</sup> for  $\Delta H_f 298 \text{ (MgO, g)}$ .

E. Bulewicz and T. Sugden, Trans. Far. Soc. **55**, 720 (1959), using a flame photometric technique, reported  $D_0^0 = 98 \pm 2 \text{ kcal. mole}^{-1}$  for MgO.  $\Delta H_f^0 298 \text{ (MgO, g)} = -4.1 \text{ kcal. mole}^{-1}$  was calculated.

I. Veits and L. Qurvich, Optika and Spektroskopiya **1**, 22 (1956) used a flame technique to obtain  $D_0^0 = 100 \text{ kcal. mole}^{-1}$ . A 4 kcal. mole<sup>-1</sup> adjustment for  $1\Sigma$  to  $3\Sigma$  yields  $\Delta H_f^0 298 \text{ (MgO, g)} = -2.1 \text{ kcal. mole}^{-1}$ .

The flame method data of L. Hultdt and A. Lagerquist, Arkiv Fysik **2**, 333 (1950) yielded a  $3\Sigma$  adjusted  $D_0^0 = 115 \text{ kcal. mole}^{-1}$ .  $\Delta H_f^0 298 \text{ (MgO, g)} = -21.1 \text{ kcal. mole}^{-1}$  was calculated.

L. Brewer and R. F. Porter, J. Chem. Phys. **22**, 1876 (1954) have shown by vapor pressure measurements on MgO(c) that the solid vaporizes mainly into molecular species. They gave spectroscopic evidence that the  $3\Sigma$  electronic state of MgO(g) is not the principal vaporizing species. Using their vapor pressures for the reaction  $\text{MgO(c)} = \text{MgO(g)}$  and a  $3\Sigma$  ground state we calculated 2nd and 3rd law heat of sublimation at 298°K. of 120.0 and 129.1 kcal. mole<sup>-1</sup>. The 3rd law value yields  $\Delta H_f^0 298 \text{ (MgO, g)} = -14.6 \text{ kcal. mole}^{-1}$ .

## Heat Capacity and Entropy.

The fundamental frequency and anharmonicity correction were reported by L. Brewer and R. Porter, J. Chem. Phys. **22**, 1876 (1954) and are based on a  $3\Sigma$  ground state. The rotational constants were estimated by H. L. Schick 35 al. AVCO Corp. RAD-SR-62-251, 15 Dec. 1962. Although the ground state and spectroscopic constants are in doubt, the free energies are probably within RT in 3 of true values.

T. °K.	C <sub>v</sub>	S°	-(F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.958	45.133	2.411	1.122	1.122	1.122	INFINITE
200	7.104	49.983	1.416	1.974	1.974	1.974	3.455
298	7.489	52.889	1.000	3.163	3.163	3.163	3.763
300	7.506	52.936	0.996	3.172	3.172	3.172	3.768
400	7.897	55.151	0.785	4.046	4.046	4.046	3.933
500	8.189	56.946	0.590	4.996	4.996	4.996	4.010
600	8.396	58.459	0.426	5.996	5.996	5.996	4.046
700	8.545	59.765	0.267	7.046	7.046	7.046	4.060
800	8.654	60.913	0.127	8.146	8.146	8.146	4.061
900	8.737	61.937	0.065	9.296	9.296	9.296	4.053
1000	8.802	62.861	0.087	10.496	10.496	10.496	3.999
1100	8.854	63.703	0.150	11.746	11.746	11.746	3.939
1200	8.897	64.475	0.215	13.046	13.046	13.046	3.883
1300	8.934	65.189	0.282	14.396	14.396	14.396	3.830
1400	8.966	65.852	0.351	15.796	15.796	15.796	3.780
1500	8.994	66.472	0.422	17.246	17.246	17.246	3.734
1600	9.019	67.053	0.494	18.746	18.746	18.746	3.692
1700	9.042	67.600	0.567	20.296	20.296	20.296	3.653
1800	9.063	68.118	0.641	21.896	21.896	21.896	3.617
1900	9.083	68.608	0.716	23.546	23.546	23.546	3.583
2000	9.101	69.075	0.791	25.246	25.246	25.246	3.550
2100	9.119	69.519	0.866	26.996	26.996	26.996	3.518
2200	9.135	69.944	0.941	28.796	28.796	28.796	3.487
2300	9.151	70.350	1.016	30.646	30.646	30.646	3.457
2400	9.167	70.746	1.091	32.546	32.546	32.546	3.428
2500	9.182	71.115	1.166	34.496	34.496	34.496	3.400
2600	9.196	71.462	1.241	36.496	36.496	36.496	3.373
2700	9.210	71.787	1.316	38.546	38.546	38.546	3.347
2800	9.224	72.101	1.391	40.646	40.646	40.646	3.322
2900	9.238	72.401	1.466	42.796	42.796	42.796	3.297
3000	9.251	72.795	1.541	44.996	44.996	44.996	3.273
3100	9.265	73.098	1.616	47.246	47.246	47.246	3.250
3200	9.278	73.393	1.691	49.546	49.546	49.546	3.228
3300	9.291	73.678	1.766	51.896	51.896	51.896	3.207
3400	9.303	73.956	1.841	54.296	54.296	54.296	3.187
3500	9.316	74.226	1.916	56.746	56.746	56.746	3.168
3600	9.329	74.488	1.991	59.246	59.246	59.246	3.150
3700	9.341	74.744	2.066	61.796	61.796	61.796	3.133
3800	9.353	74.993	2.141	64.396	64.396	64.396	3.117
3900	9.366	75.237	2.216	67.046	67.046	67.046	3.102
4000	9.378	75.474	2.291	69.746	69.746	69.746	3.087
4100	9.390	75.706	2.366	72.496	72.496	72.496	3.073
4200	9.402	75.932	2.441	75.296	75.296	75.296	3.060
4300	9.414	76.153	2.516	78.146	78.146	78.146	3.047
4400	9.426	76.370	2.591	81.046	81.046	81.046	3.035
4500	9.438	76.582	2.666	84.096	84.096	84.096	3.023
4600	9.450	76.789	2.741	87.296	87.296	87.296	3.012
4700	9.462	76.993	2.816	90.546	90.546	90.546	3.001
4800	9.474	77.192	2.891	93.946	93.946	93.946	2.991
4900	9.485	77.388	2.966	97.496	97.496	97.496	2.981
5000	9.497	77.579	3.041	101.196	101.196	101.196	2.972
5100	9.509	77.768	3.116	105.046	105.046	105.046	2.963
5200	9.521	77.952	3.191	109.046	109.046	109.046	2.955
5300	9.532	78.134	3.266	113.196	113.196	113.196	2.947
5400	9.544	78.312	3.341	117.496	117.496	117.496	2.940
5500	9.556	78.487	3.416	121.946	121.946	121.946	2.933
5600	9.567	78.660	3.491	126.546	126.546	126.546	2.927
5700	9.579	78.829	3.566	131.296	131.296	131.296	2.921
5800	9.591	78.996	3.641	136.196	136.196	136.196	2.915
5900	9.602	79.160	3.716	141.246	141.246	141.246	2.910
6000	9.614	79.321	3.791	146.446	146.446	146.446	2.905

Dec. 31, 1960; Dec. 31, 1965

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.679	4.775	38.112	3.354	-298.653	-298.653	INFINITE
200	17.521	13.751	23.789	2.008	-300.273	-283.268	637.995
298	23.000	21.844	21.844	0.000	-301.574	-274.261	309.540
300	23.050	21.887	21.845	0.043	-301.578	-274.092	201.038
400	26.290	29.085	22.790	2.518	-302.238	-266.885	199.675
500	28.540	35.199	24.675	5.462	-302.536	-255.506	144.726
600	30.500	40.581	26.886	8.217	-302.617	-246.090	111.682
700	32.100	45.404	29.193	11.348	-302.535	-236.648	99.638
800	33.580	49.788	31.497	14.653	-315.396	-228.219	75.865
900	34.950	53.823	33.757	18.060	-318.796	-217.953	62.448
1000	36.250	57.574	35.953	21.621	-316.249	-206.876	52.863
1100	37.450	61.086	38.080	25.306	-315.487	-195.848	45.187
1200	38.580	64.394	40.136	29.016	-314.451	-187.006	38.911
1300	39.650	67.420	42.124	32.616	-313.154	-179.237	33.694
1400	40.670	70.276	44.044	37.009	-311.683	-163.061	29.292
1500	41.650	72.982	45.901	41.072	-310.086	-150.244	25.455
1600	42.590	75.544	47.696	46.197	-340.380	-137.519	21.891
1700	43.400	77.976	49.332	49.376	-338.911	-124.884	18.784
1800	44.100	80.292	51.112	53.603	-337.409	-112.339	16.055
1900	44.700	82.502	52.742	57.873	-335.875	-99.874	13.640
2000	45.200	84.612	54.321	62.181	-334.315	-87.497	11.488
2100	45.611	86.531	55.852	66.525	-332.730	-75.194	9.4561
2200	45.931	88.267	57.339	70.903	-331.125	-62.965	7.826
2300	46.232	89.815	58.783	75.311	-329.499	-50.815	6.255
2400	46.517	91.185	60.187	79.748	-327.856	-38.730	4.829
2500	46.788	92.438	61.553	84.214	-326.197	-26.722	3.527
2600	47.048	93.593	62.888	88.714	-324.525	-14.875	2.336

MAGNESIUM SULFATE (MgSO<sub>4</sub>) (CRYSTAL)

MOL. WT. = 120.3736

ΔH<sub>f</sub><sup>o</sup> 0 = -298.8 ± 5 kcal. mole<sup>-1</sup>

ΔH<sub>f</sub><sup>o</sup> 298.15 = -301.6 ± 5 kcal. mole<sup>-1</sup>

ΔH<sub>m</sub><sup>o</sup> = 3.5 kcal. mole<sup>-1</sup>

S<sub>298.15</sub><sup>o</sup> = 21.844 ± 0.2 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = 1400°K.

Heat of Formation.

The adopted ΔH<sub>f</sub><sup>o</sup> 298.15 = -301.6 ± 5 kcal. mole<sup>-1</sup> was calculated from the ΔH<sub>f</sub><sup>o</sup> 298.15 = 63.3 ± 5 kcal. mole<sup>-1</sup> for the reaction MgO(c) + SO<sub>3</sub>(g) = MgSO<sub>4</sub>(c). The value of ΔH<sub>f</sub><sup>o</sup> 298.15 was calculated by the third law method using the equilibrium data obtained from a transpiration study by Knopf and Staude.<sup>1</sup> In addition Marchal<sup>2</sup> measured the total pressure of SO<sub>3</sub>(g), SO<sub>2</sub>(g) and O<sub>2</sub>(g) above MgSO<sub>4</sub>(c) and partial pressures were obtained by application of the SO<sub>3</sub>-SO<sub>2</sub> equilibrium data. Another value of ΔH<sub>f</sub><sup>o</sup> 298.15 (MgSO<sub>4</sub>, c) may be derived from the measured heat of solution of MgSO<sub>4</sub>(c) by Thomsen<sup>3a</sup> and the measured heats of mixing of MgCl<sub>2</sub>(200 H<sub>2</sub>O) with H<sub>2</sub>SO<sub>4</sub>(200 H<sub>2</sub>O) and MgSO<sub>4</sub>(200 H<sub>2</sub>O) with 2HCl(100 H<sub>2</sub>O) by Thomsen<sup>3b</sup>.

References

- 1 MgO(c) + SO<sub>3</sub>(g) = MgSO<sub>4</sub>(c) T, °K RANGE 1144-1313 ΔH<sub>f</sub><sup>o</sup> 298.15 kcal. mole<sup>-1</sup> 63.284 ΔH<sub>f</sub><sup>o</sup> 298.15 kcal. mole<sup>-1</sup> -301.574
- 2 MgO(c) + SO<sub>3</sub>(g) = MgSO<sub>4</sub>(c) 1223-1428 0.525 72.394 -310.667
- 3a MgSO<sub>4</sub>(c) → MgSO<sub>4</sub>(200 H<sub>2</sub>O) 298.15 -20.84
- 3b MgCl<sub>2</sub>(200 H<sub>2</sub>O) + H<sub>2</sub>SO<sub>4</sub>(200 H<sub>2</sub>O) → MgSO<sub>4</sub>(200 H<sub>2</sub>O) + 2HCl(100 H<sub>2</sub>O) 298.15 -305.1\*

\*Combination of the reactions 3a and 3b with the following ΔH<sub>f</sub><sup>o</sup> 298.15: H<sub>2</sub>SO<sub>4</sub>(200 H<sub>2</sub>O) = -212.387, HCl(100 H<sub>2</sub>O) = -39.74 and MgCl<sub>2</sub>(200 H<sub>2</sub>O) = -189.5 kcal. mole<sup>-1</sup>.

References

- 1 H. J. Knopf and H. Staude, Z. Physik. Chem. (Leipzig) **204**, 265-275 (1955).
- 2 G. Marchal, J. Chim. Phys. **22**, 493 (1925).
- 3a and 3b J. Thomsen, "Thermochemische Untersuchungen," vols I-IV, Barth, Leipzig (1882-1886).

Heat Capacity and Entropy.

The low temperature heat capacities 53.3-295.4°K. were measured by G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. **64**, 2949 (1942). The heat capacities in the temperature range 298-1400°K. were estimated from the equation MgSO<sub>4</sub>(c) = CaSO<sub>4</sub>(c) + MgO(c) - CaO(c). CaSO<sub>4</sub>(c) and CaO(c) C<sub>p</sub> were calculated using the equations C<sub>p</sub> = 16.78 + 23.80 X 10<sup>-3</sup>T and C<sub>p</sub> = 11.67 + 1.08 X 10<sup>-5</sup>T<sup>2</sup> - 1.56 X 10<sup>-8</sup>T<sup>3</sup> respectively, K. K. Kelley, U. S. Bur. Mines Bull. **584** (1960). The heat capacity of MgO(c) was calculated from the correlation of the low temperature heat capacities and high temperature heat content using the Shomate functions to back calculate the heat capacities. The values from the two sources join smoothly at 298°K. Above the melting point (1400°K.) the heat capacity was graphically extrapolated. The entropy was calculated at 50.12°K. using the Debye and Einstein function D( $\frac{242}{T}$ ) + 2E( $\frac{378}{T}$ ) + 2E( $\frac{866}{T}$ ) + E( $\frac{1583}{T}$ ) given by G. E. Moore and K. K. Kelley loc. cit. The value of S<sub>50.12</sub> = 1.08 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Data.

T<sub>m</sub> and ΔH<sub>m</sub><sup>o</sup> from K. K. Kelley, U. S. Bur. Mines Bull. **393** (1936).

(LIQUID)

MAGNESIUM SULFATE (MgSO<sub>4</sub>)

$$\Delta H_f^\circ 298.15 = -297.9 \pm 5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 3.5 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 24.464 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1400^\circ \text{K.}$$

Heat of Formation.

The  $\Delta H_f^\circ 298.15$  was obtained from  $\Delta H_f^\circ 298.15(c)$  by adding  $\Delta H_m^\circ$  and the difference between  $H_m^\circ - H_m^\circ 298.15$  for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 1000°K. The heat capacity below 1000°K. was obtained from the heat capacity of the crystal. Above 1000°K. the heat capacity was assumed constant and estimated as 39.0 cal. deg.<sup>-1</sup> mole<sup>-1</sup> by comparison with those for MgCl<sub>2</sub>(l), KCl(l) and K<sub>2</sub>SO<sub>4</sub>(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See MgSO<sub>4</sub>(c) table.

T, °K.	C <sub>p</sub>	S°	-(H° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0							
100							
200							
298	23.000	24.464	24.464	0.000	-297.864	-271.332	198.892
300	23.050	24.606	24.464	0.043	-297.868	-271.367	197.545
400	26.290	31.705	25.410	2.318	-298.528	-262.223	143.272
500	28.540	37.818	27.295	5.262	-298.826	-253.106	110.632
600	30.500	43.201	29.506	8.217	-298.907	-243.952	88.859
700	32.100	48.024	31.813	11.348	-298.825	-234.772	73.299
800	33.580	52.408	34.117	14.633	-311.686	-226.905	61.987
900	34.950	56.427	36.376	18.046	-311.100	-216.341	52.535
1000	38.000	60.248	38.573	21.676	-312.484	-205.665	44.948
1100	38.000	63.870	40.710	25.476	-311.607	-195.031	38.749
1200	38.000	67.176	42.780	29.276	-310.774	-184.468	33.596
1300	38.000	70.219	44.775	33.076	-309.986	-173.974	29.4249
1400	38.000	73.034	46.694	36.876	-339.605	-163.061	25.455
1500	38.000	75.656	48.539	40.676	-338.492	-150.491	21.927
1600	38.000	78.108	50.311	44.476	-337.391	-137.993	18.849
1700	38.000	80.412	52.015	48.276	-336.301	-125.563	16.142
1800	38.000	82.584	53.653	52.076	-335.226	-113.198	13.744
1900	38.000	84.639	55.230	55.876	-334.162	-100.892	11.605
2000	38.000	86.588	56.750	59.676	-333.110	-88.644	9.687
2100	38.000	88.442	58.215	63.476	-332.069	-76.447	7.956
2200	38.000	90.210	59.650	67.276	-331.027	-64.287	6.387
2300	38.000	91.890	61.076	71.076	-330.024	-52.136	4.960
2400	38.000	93.516	62.518	74.876	-329.028	-40.055	3.655
2500	38.000	95.067	63.957	78.676	-328.023	-28.123	2.459

Point Group C<sub>2v</sub>  
 $\Delta H_f^0 = -83.7 \pm 12$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = [56.5]$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -85.9 \pm 12$  kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies  
 $\omega$ , cm.<sup>-1</sup>  
 [1320] (1)  
 [750] (1)  
 [1220] (1)

Bond Distance: N-O = [1.23] Å  
 Bond Angle: O-N-O = [116]°  
 Product of the Moments of Inertia:  $I_A I_B I_C = [25.6905] \times 10^{-117}$  g.<sup>3</sup> cm.<sup>6</sup>  
 $\sigma = 2$

Heat of Formation.

The heat of formation of NO<sub>2</sub><sup>-</sup>(g) was calculated from the electron affinity of NO<sub>2</sub>(g) and the JANAF value of  $\Delta H_f^0$  for NO<sub>2</sub>(g), 4.0 ± 0.5 ev and 8.6 ± 0.2 kcal. mole<sup>-1</sup>, respectively. The former was obtained from the National Bureau of Standards Report 8628, "Preliminary Report on the Thermodynamic Properties of Selected Light Element and Some Related Compounds", January 1965.

Heat Capacity and Entropy.

The bond distance N-O and the angle O-N-O of NO<sub>2</sub><sup>-</sup>(g) were estimated to be the same as those in NaNO<sub>2</sub>(c) which have been determined by G. B. Carpenter, Acta Cryst. 5, 132(1952). The three individual moments of inertia are  $I_A = [0.6872] \times 10^{-59}$  g. cm.<sup>2</sup>,  $I_B = [5.7804] \times 10^{-59}$  g. cm.<sup>2</sup> and  $I_C = [6.4676] \times 10^{-59}$  g. cm.<sup>2</sup>. The vibrational frequencies of NO<sub>2</sub><sup>-</sup>(g) were assumed to be the same as those for nitrite ion in solution which have been measured by D. Williams, J. Am. Chem. Soc. 61, 2887(1939). These measured frequencies in nitrite solution are comparable to those in NO<sub>2</sub>(g) (1357.8, 756.8 and 1665.5 cm.<sup>-1</sup>), reported by G. R. Bird et al., J. Chem. Phys. 40, 5378 (1964).

T, K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0						
100						
200						
298	9.016	56.517	0.000	85.850	79.780	58.477
300	9.033	56.573	0.017	85.862	79.742	58.089
400	9.851	56.982	0.966	86.469	77.609	42.401
500	10.766	61.609	2.093	87.011	75.330	32.925
600	11.412	63.631	3.114	87.509	72.945	26.569
700	11.905	65.429	4.281	87.980	70.404	22.004
800	12.279	67.044	5.491	88.436	67.950	18.562
900	12.564	68.508	6.733	88.884	65.363	15.871
1000	12.785	69.844	8.001	89.327	62.725	13.708
1100	12.958	71.071	9.289	89.770	60.044	11.929
1200	13.095	72.204	10.592	90.212	57.322	10.439
1300	13.206	73.257	11.907	90.656	54.562	9.172
1400	13.296	74.239	13.232	91.102	51.770	8.081
1500	13.370	75.159	14.566	91.551	48.945	7.131
1600	13.432	76.024	15.906	92.003	46.089	6.295
1700	13.483	76.840	17.251	92.458	43.206	5.554
1800	13.528	77.612	18.602	92.916	40.295	4.892
1900	13.565	78.344	19.957	93.380	37.359	4.297
2000	13.598	79.041	21.315	93.848	34.400	3.759
2100	13.626	79.705	22.676	94.320	31.414	3.269
2200	13.650	80.339	24.040	94.798	28.408	2.822
2300	13.672	80.946	25.406	95.278	25.378	2.411
2400	13.691	81.529	26.774	95.765	22.330	2.033
2500	13.708	82.088	28.144	96.257	19.261	1.684
2600	13.723	82.626	29.516	96.753	16.170	1.359
2700	13.736	83.144	30.889	97.255	13.052	1.077
2800	13.748	83.644	32.263	97.761	9.916	0.831
2900	13.759	84.126	33.638	98.271	6.766	0.611
3000	13.769	84.593	35.015	98.787	3.622	0.426
3100	13.778	85.045	36.392	99.306	0.463	0.31
3200	13.786	85.482	37.770	99.831	2.753	1.188
3300	13.793	85.907	39.149	100.360	5.964	3.395
3400	13.800	86.318	40.529	100.893	9.198	5.971
3500	13.806	86.719	41.909	101.429	12.438	8.977
3600	13.812	87.108	43.290	101.971	15.701	12.313
3700	13.817	87.486	44.671	102.515	18.982	15.718
3800	13.822	87.855	46.053	103.063	22.270	19.181
3900	13.826	88.214	47.436	103.614	25.574	22.603
4000	13.830	88.564	48.819	104.168	28.894	26.000
4100	13.834	88.905	50.202	104.726	32.232	29.373
4200	13.838	89.239	51.585	105.287	35.573	32.725
4300	13.841	89.564	52.969	105.850	38.940	36.057
4400	13.844	89.884	54.354	106.416	42.336	39.370
4500	13.847	90.194	55.738	106.984	45.696	42.664
4600	13.850	90.498	57.123	107.555	49.100	45.933
4700	13.852	90.796	58.508	108.129	52.510	49.177
4800	13.855	91.088	59.893	108.705	55.935	52.400
4900	13.857	91.373	61.279	109.282	59.366	55.603
5000	13.859	91.653	62.665	109.861	62.814	58.787
5100	13.861	91.928	64.051	110.443	66.275	61.950
5200	13.863	92.197	65.437	111.025	69.742	65.093
5300	13.865	92.461	66.823	111.610	73.230	68.215
5400	13.866	92.720	68.209	112.197	76.720	71.318
5500	13.868	92.975	69.597	112.784	80.225	74.400
5600	13.870	93.225	70.984	113.373	83.739	77.473
5700	13.871	93.470	72.371	113.963	87.261	80.536
5800	13.872	93.711	73.758	114.555	90.805	83.589
5900	13.874	93.948	75.145	115.148	94.349	86.632
6000	13.875	94.182	76.533	115.743	97.899	89.665

NITROGEN, DIATOMIC (N<sub>2</sub>) (IDEAL GAS - REFERENCE STATE)

MCL. WT. = 28.0134

Ground State Configuration 1  $\Sigma^+ +$   
 $S_{298.15} = 45.77 \pm 0.01$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>       $\Delta H_f^\circ 0 = 0$   
 $\Delta H_f^\circ 298.15 = 0$

$\omega_e x_e = 14.059$  cm.<sup>-1</sup>       $\sigma^- = 2$   
 $B_e = 1.99825$  cm.<sup>-1</sup>       $r_e = 1.08758 \pm 0.0001$  Å

Heat of Formation.

The heat of formation ( $\Delta H_f^\circ$ ) for N<sub>2</sub>(g) is zero at all temperatures by definition.

Heat Capacity and Entropy.

The functions adopted here are based on the direct summation calculations of L. Glatt, J. Felzer and H. L. Johnston, Ohio State Univ. Res. Found. Proj. 316, Report No. 9, 1953. They calculated the functions for N<sub>2</sub><sup>14,14</sup> by a direct summation using spectroscopic data given by G. Herzberg, "Diatomic Molecules", D. Van Nostrand Co., New York, 1950. The entropies were changed by -Rln9 to remove the effects of nuclear spin included by Glatt, Beizer, and Johnston, and by 0.012 for the difference in spectroscopic constants. J. A. Goff and S. Gratch, Trans. Am. Soc. Mech. Engrs., 72, 741 (1950), calculated a set of functions by a direct summation over the ground state levels only. Agreement with the functions of Glatt, Beizer, and Johnston is within 0.1%.

B. P. Stoicheff, Can. J. Phys. 32, 630 (1954), determined the spectroscopic constants of N<sub>2</sub><sup>14,14</sup> by combining his measured rotational spectra with the results of band spectra given in the literature. The constants listed above have been corrected to apply to the naturally occurring isotopic composition listed by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys., 30, 565 (1958).

T, °K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	.000	INFINITE	2.072	.000	.000	.000
100	6.926	38.170	1.379	.000	.000	.000
200	6.957	42.992	.683	.000	.000	.000
298	6.961	45.770	.000	.000	.000	.000
300	6.961	45.813	.013	.000	.000	.000
400	6.990	47.818	.710	.000	.000	.000
500	7.069	49.386	1.413	.000	.000	.000
600	7.196	50.685	2.125	.000	.000	.000
700	7.350	51.806	2.853	.000	.000	.000
800	7.512	52.798	3.596	.000	.000	.000
900	7.670	53.692	4.355	.000	.000	.000
1000	7.815	54.507	5.129	.000	.000	.000
1100	7.945	55.258	5.917	.000	.000	.000
1200	8.061	55.955	6.718	.000	.000	.000
1300	8.162	56.604	7.529	.000	.000	.000
1400	8.252	57.212	8.350	.000	.000	.000
1500	8.330	57.784	9.179	.000	.000	.000
1600	8.398	58.324	10.015	.000	.000	.000
1700	8.458	58.835	10.858	.000	.000	.000
1800	8.512	59.320	11.707	.000	.000	.000
1900	8.559	59.782	12.560	.000	.000	.000
2000	8.601	60.222	13.418	.000	.000	.000
2100	8.638	60.642	14.280	.000	.000	.000
2200	8.672	61.045	15.146	.000	.000	.000
2300	8.703	61.431	16.016	.000	.000	.000
2400	8.731	61.802	16.882	.000	.000	.000
2500	8.756	62.159	17.761	.000	.000	.000
2600	8.779	62.503	18.638	.000	.000	.000
2700	8.800	62.835	19.517	.000	.000	.000
2800	8.820	63.155	20.398	.000	.000	.000
2900	8.838	63.465	21.280	.000	.000	.000
3000	8.855	63.765	22.165	.000	.000	.000
3100	8.871	64.055	23.051	.000	.000	.000
3200	8.886	64.337	23.939	.000	.000	.000
3300	8.900	64.611	24.829	.000	.000	.000
3400	8.914	64.877	25.719	.000	.000	.000
3500	8.927	65.135	26.611	.000	.000	.000
3600	8.939	65.387	27.505	.000	.000	.000
3700	8.950	65.632	28.399	.000	.000	.000
3800	8.962	65.871	29.295	.000	.000	.000
3900	8.972	66.104	30.191	.000	.000	.000
4000	8.983	66.331	31.089	.000	.000	.000
4100	8.993	66.553	31.988	.000	.000	.000
4200	9.002	66.770	32.888	.000	.000	.000
4300	9.012	66.982	33.788	.000	.000	.000
4400	9.021	67.189	34.690	.000	.000	.000
4500	9.030	67.392	35.593	.000	.000	.000
4600	9.039	67.591	36.496	.000	.000	.000
4700	9.048	67.785	37.400	.000	.000	.000
4800	9.057	67.976	38.306	.000	.000	.000
4900	9.066	68.162	39.212	.000	.000	.000
5000	9.074	68.346	40.119	.000	.000	.000
5100	9.083	68.525	41.027	.000	.000	.000
5200	9.091	68.702	41.935	.000	.000	.000
5300	9.100	68.875	42.845	.000	.000	.000
5400	9.109	69.045	43.755	.000	.000	.000
5500	9.118	69.213	44.667	.000	.000	.000
5600	9.127	69.377	45.579	.000	.000	.000
5700	9.136	69.539	46.492	.000	.000	.000
5800	9.145	69.698	47.406	.000	.000	.000
5900	9.155	69.854	48.321	.000	.000	.000
6000	9.165	70.008	49.237	.000	.000	.000

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298<sup>o</sup>)/T</sub>	H <sup>o</sup> -H <sub>298<sup>o</sup></sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	.000	.000	INFINITE	4.520	-369.657	-369.657	INFINITE
100	11.517	6.108	47.083	4.097	-371.007	-364.160	795.834
200	21.465	17.575	29.505	2.386	-371.771	-356.969	390.059
298	26.900	27.211	27.211	.000	-372.100	-349.623	256.268
300	27.000	27.378	27.212	.050	-372.103	-349.483	254.866
400	30.900	35.712	28.321	2.956	-373.459	-341.827	186.756
500	33.450	42.896	30.535	6.181	-373.363	-333.923	145.951
600	35.170	49.151	33.128	9.614	-373.077	-326.060	118.762
700	36.620	54.695	35.820	13.206	-372.654	-318.258	96.360
800	37.800	59.652	38.494	16.926	-372.123	-310.522	84.827
900	38.990	64.173	41.099	20.767	-371.497	-302.856	73.340
1000	40.100	68.339	43.618	24.721	-370.788	-295.266	64.527
1100	41.180	72.212	46.043	28.786	-370.006	-287.755	57.169
1200	42.210	75.959	48.377	32.958	-415.627	-279.400	50.883
1300	43.200	79.582	50.622	37.239	-415.622	-285.011	45.570
1400	44.150	82.978	52.784	41.529	-412.845	-286.911	40.104
1500	44.800	85.952	54.868	46.041	-411.548	-285.826	35.815
1600	45.327	88.470	56.878	50.547	-409.802	-284.839	32.076
1700	45.810	91.234	58.818	55.105	-420.316	-273.843	28.776
1800	46.250	93.864	60.693	59.708	-438.653	-212.333	25.780
1900	46.647	96.375	62.805	64.353	-416.957	-200.917	23.110
2000	47.000	98.777	64.259	69.036	-415.234	-189.594	20.717

SODIUM METASILICATE (Na<sub>2</sub>SiO<sub>3</sub>)

(CRYSTAL)

MOL. WT. = 122.0638

$$\Delta H_f^o = -369.7 \pm 0.6 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -372.1 \pm 0.6 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^o = 12.5 \text{ kcal. mole}^{-1}$$

$$S^{298.15} = 27.211 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1361^\circ \text{K.}$$

Heat of Formation.

The  $\Delta H_f^{298.15}$  was calculated from the  $\Delta H_f^{298.15}$  of its constituent oxides Na<sub>2</sub>O(c) + SiO<sub>2</sub>(c) = Na<sub>2</sub>SiO<sub>3</sub>(c) given by K. K. Kelley in the report of investigations 5301, U. S. Department of the Interior, Bureau of Mines, 1962, and from the  $\Delta H_f^{298.15}$  of Na<sub>2</sub>O(c) (June 30, 1962) and SiO<sub>2</sub>(c) (Dec. 31, 1962) in JANAF tables. The  $\Delta H_f^{298.15} = -55.2 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

At low temperatures C<sub>p</sub> was used from K. K. Kelley, J. Am. Chem. Soc., 61, 471 (1939). Above 298.15°K. C<sub>p</sub> was calculated by using the B. F. Naylor equation C<sub>p</sub> = 31.14 + 0.00960T - (647,000/T<sup>2</sup>) obtained from his enthalpy data in the range 298-1361°K. J. Am. Chem. Soc., 67, 466 (1945). The values from the two sources join smoothly at 298°. The entropy was calculated at 53.6 using the Debye and Planck-Einstein function D(53.6) + 2E(53.6) + 2E(518) given by K. K. Kelley, J. Am. Chem. Soc. 61, 471 (1939). The value of S<sub>53.6</sub><sup>o</sup> = 1.4457 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Data.

T<sub>m</sub> and ΔH<sub>m</sub><sup>o</sup> were taken from B. F. Naylor, J. Am. Chem. Soc., 67, 466 (1945).

$\Delta H_f^{298.15} = 30.260 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_m^{298.15} = -363.483 \pm 1.0 \text{ kcal. mole}^{-1}$

$T_m = 1361^\circ\text{K.}$

Heat of Formation.

The  $\Delta H_f^{298.15}$  was calculated from the  $\Delta H_f^{298.15}$  of its constituent oxides Na<sub>2</sub>O(c) + SiO<sub>2</sub>(c) = Na<sub>2</sub>SiO<sub>3</sub>(s) given by K. K. Kelley in the report of Investigation 5901, U. S. Department of the Interior, Bureau of Mines, 1962 and from the  $\Delta H_f^{298.15}$  of Na<sub>2</sub>O(c) (June 30, 1962) and SiO<sub>2</sub>(c) (Dec. 31, 1962) in JANAF tables. The  $\Delta H_m^{298.15} = -46.7 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

The heat capacity below  $T_m$  was estimated so that the enthalpy between 298°K. and  $T_m$  was consistent with the measured heat of formation at 426°K. below which the heat capacity was that of the solid. Above the glass transition the heat capacity was assumed constant at 42.6 cal. mole<sup>-1</sup> deg.<sup>-1</sup> as measured by B. F. Naylor, J. Am. Chem. Soc. 67, 466 (1945), from 1361 to 1747°K.

The entropy at 298° was obtained from that of the crystal by adding  $\Delta S_m$  plus the difference between  $S_{Tm}^{298}$  for crystal and liquid.

Melting Data.

See the crystal table.

T. °K.	C <sub>p</sub>	S° - (F° - H <sub>298</sub> °)/T	H° - H <sub>298</sub> °	ΔH <sub>f</sub> <sup>298</sup>	ΔF <sub>f</sub> <sup>298</sup>	Log K <sub>f</sub>
0						
100						
200						
298	26.724	30.260	0.000	-363.483	-341.915	250.619
300	26.831	30.426	0.050	-363.486	-341.781	248.975
400	30.956	31.755	1.295	-364.843	-334.428	182.714
500	42.800	47.963	6.936	-363.990	-326.894	142.878
600	42.800	55.386	16.602	-362.858	-310.581	116.402
700	42.800	61.846	29.456	-361.747	-312.459	97.549
800	42.800	67.599	47.078	-360.656	-305.493	83.453
900	42.800	72.740	68.011	-359.591	-298.660	72.521
1000	42.800	77.249	91.813	-358.536	-291.944	63.801
1100	42.800	81.320	117.477	-357.559	-285.336	56.688
1200	42.800	85.053	145.806	-356.696	-278.898	50.610
1300	42.800	88.474	176.710	-355.910	-272.572	45.071
1400	42.800	91.581	210.186	-355.166	-266.306	40.012
1500	42.800	94.363	246.246	-354.436	-260.152	35.497
1600	42.800	97.365	284.905	-353.716	-254.085	32.360
1700	42.800	99.960	326.068	-353.007	-248.070	29.165
1800	42.800	102.407	369.642	-352.316	-242.226	26.252
1900	42.800	104.721	415.533	-351.646	-236.554	23.654
2000	42.800	106.916	463.642	-351.000	-231.054	21.324
2100	42.800	109.004	513.877	-350.376	-225.726	19.223
2200	42.800	110.995	566.146	-349.771	-220.571	17.319
2300	42.800	112.898	620.356	-349.186	-215.586	15.586
2400	42.800	114.719	676.416	-348.626	-210.771	14.002
2500	42.800	116.467	734.346	-348.086	-206.126	12.551
2600	42.800	118.145	794.166	-347.566	-201.641	11.214
2700	42.800	119.760	855.896	-347.066	-197.311	9.981
2800	42.800	121.317	919.556	-346.586	-193.136	8.840
2900	42.800	122.819	985.156	-346.126	-189.116	7.780
3000	42.800	124.270	1052.706	-345.686	-185.251	6.794
3100	42.800	125.673	1122.216	-345.266	-181.541	5.875
3200	42.800	127.032	1193.696	-344.866	-177.986	5.015
3300	42.800	128.349	1267.156	-344.486	-174.586	4.211
3400	42.800	129.627	1342.606	-344.126	-171.341	3.456
3500	42.800	130.868	1420.056	-343.786	-168.251	2.747
3600	42.800	132.073	1500.506	-343.466	-165.311	2.081
3700	42.800	133.246	1583.956	-343.166	-162.526	1.451
3800	42.800	134.387	1670.406	-342.886	-159.896	0.851
3900	42.800	135.499	1760.856	-342.626	-157.426	0.281
4000	42.800	136.583	1855.306	-342.386	-155.111	-0.153



T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	+0.00	INFINITE	-	6.319	-586.761	-586.761	INFINITE
100	15.890	10.202	66.032	5.673	-588.666	-577.985	1263.124
200	29.575	25.957	42.514	3.321	-589.750	-566.820	619.363
298	37.500	39.366	30.136	.000	-590.250	-555.446	407.135
300	37.700	39.598	30.366	.070	-590.255	-555.229	404.485
400	44.300	51.397	40.070	4.487	-591.619	-543.431	296.903
500	48.850	61.798	44.085	8.856	-591.350	-531.405	232.266
600	51.940	70.989	47.919	13.202	-590.789	-519.463	189.205
700	54.270	79.174	51.724	19.215	-590.013	-507.637	158.484
800	56.300	86.555	55.624	24.745	-589.072	-495.932	135.476
900	58.200	93.297	59.441	30.470	-587.990	-484.350	117.611
1000	60.050	99.524	63.142	36.383	-586.775	-472.897	103.347
1100	61.900	105.342	66.716	42.488	-585.423	-461.579	91.703
1200	62.770	110.766	70.164	48.723	-630.466	-449.466	81.955
1300	63.519	115.821	73.684	55.038	-628.570	-434.461	73.016
1400	64.168	120.552	76.679	61.423	-626.630	-419.602	65.400
1500	64.720	124.999	79.753	67.868	-624.655	-404.885	58.989
1600	65.173	129.191	82.713	74.364	-622.648	-390.296	53.309
1700	65.528	133.151	85.545	80.900	-644.821	-375.616	48.286
1800	65.794	136.906	88.214	87.466	-642.697	-359.844	43.689
1900	65.974	140.468	90.686	94.053	-640.567	-344.189	39.589
2000	66.000	143.852	93.426	100.651	-638.442	-328.648	35.911

SODIUM DISILICATE (Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>)

(CRYSTAL)

MOL. WT. = 182.1486

ΔH<sub>f</sub>° = -586.76 ± 3.0 kcal. mole<sup>-1</sup>

ΔH<sub>f</sub>° 298.15 = -590.25 ± 3.0 kcal. mole<sup>-1</sup>

ΔH<sub>m</sub> = 8.5 kcal. mole<sup>-1</sup>

S°<sub>298.15</sub> = 39.366 ± 1.2 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = 1147°K.

Heat of Formation.

The ΔH<sub>f</sub>° 298.15 was calculated from the ΔH<sub>f</sub>° 298.15 of its constituent oxides Na<sub>2</sub>O(c) + 2SiO<sub>2</sub>(c) = Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(c) given by K. K. Kelley in the report of investigation 5501, U. S. Department of the Interior, Bureau of Mines 1962, and from the ΔH<sub>f</sub>° 298.15 of Na<sub>2</sub>O(c) (June 30, 1962) and SiO<sub>2</sub>(c) (Dec. 31, 1962) in JANAF tables. The ΔH<sub>f</sub>° 298.15(c) = -55.3 ± 2.0 kcal. mole<sup>-1</sup> was reported by Kelley. However in order to obtain consistency with the liquid phase this was adjusted to -54.75 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

At low temperatures C<sub>p</sub> were used from K. K. Kelley, J. Am. Chem. Soc., 61, 471 (1939). Above 298.15°K. C<sub>p</sub> was calculated by using the B. P. Naylor equation C<sub>p</sub> = 44.38 + 0.016687<sup>-1</sup>(1.067,000/T<sup>2</sup>) J. Am. Chem. Soc., 67, 466 (1945). The data from the two sources join smoothly at 298°K. The entropy was calculated at 54.3°K. using the Debye and Planck-Einstein function D(40/T) + 4E(328/T) + 2E(502/T) + 2E(1228/T) given by K. K. Kelley, J. Am. Chem. Soc., 61, 471 (1939). The S°<sub>54.3</sub> = 3.597 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Data.

T<sub>m</sub> was taken from B. Naylor, J. Am. Chem. Soc., 67, 466 (1945). ΔH<sub>m</sub> was taken from K. K. Kelley, U. S. Bureau of Mines Bulletin 393 (1936).

SODIUM DISILICATE (Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) (LIQUID)

S<sub>298.15</sub><sup>o</sup> = 45.465 ± 1.2 cal. deg.<sup>-1</sup> mole<sup>-1</sup> ΔH<sub>f</sub><sup>o</sup> 298.15 = -582.885 ± 3.0 kcal. mole<sup>-1</sup>  
 T<sub>m</sub> = 1147°K. ΔH<sub>m</sub> = 8.5 kcal. mole<sup>-1</sup>

Heat of Formation.

The ΔH<sub>f</sub><sup>o</sup> 298.15 was calculated from the ΔH<sub>f</sub><sup>o</sup> 298.15 of its constituent oxides Na<sub>2</sub>O(c) + 2SiO<sub>2</sub>(c) = Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(gl) given by K. K. Kelley in the report of investigation 5901, U. S. Department of the Interior, Bureau of Mines 1962, and from the ΔH<sub>f</sub><sup>o</sup> 298.15 of Na<sub>2</sub>O(c) (June 30, 1962) and SiO<sub>2</sub>(c) (Dec. 31, 1962) in JANAP tables. The ΔH<sub>f</sub><sup>o</sup> 298.15(gl) = -49.1 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The heat capacity below the melting point was estimated so that the enthalpy between 298°K. and the melting point was consistent with the measured heat of formation of the glass and the heat of formation of the liquid at the melting point. This entailed an assumed glass transition at 765°K. below which the heat capacity was that of the solid. Above the glass transition the heat capacity was assumed constant at 62.35 cal. mole<sup>-1</sup> deg.<sup>-1</sup> as measured by B. P. Naylor, J. Am. Chem. Soc. 67, 466 (1945), from 1147 to 1744°K.

The entropy at 298°K. was obtained from that of the crystal by adding ΔS<sub>m</sub> plus the difference between S<sub>m</sub><sup>o</sup> for crystal and liquid.

Melting Data.

See the crystal table.

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S <sup>o</sup> -(F <sup>o</sup> -H <sub>298</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup> kcal. mole <sup>-1</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0						
100						
200						
298	37.500	45.465	0.000	-582.885	-549.899	403.068
300	37.700	45.466	0.070	-582.890	-549.694	400.432
400	44.300	47.079	4.187	-584.254	-538.506	294.212
500	48.850	47.897	8.856	-583.994	-527.099	230.379
600	51.940	47.088	13.922	-583.424	-515.758	187.856
700	54.210	45.274	19.115	-582.648	-504.541	157.517
800	55.650	43.459	24.469	-581.493	-493.442	134.796
900	56.250	41.643	31.234	-579.891	-482.581	118.171
1000	56.250	39.827	37.439	-578.855	-471.856	103.106
1100	62.350	38.011	43.674	-576.872	-461.228	91.633
1200	62.350	36.195	49.900	-574.910	-450.604	81.928
1300	62.350	34.379	56.144	-572.968	-440.000	73.227
1400	62.350	32.563	62.379	-571.046	-429.415	65.592
1500	62.350	30.747	68.614	-569.144	-418.854	59.067
1600	62.350	28.931	74.849	-567.262	-408.316	53.760
1700	62.350	27.115	81.084	-565.400	-397.800	48.799
1800	62.350	25.300	87.319	-563.558	-387.304	44.254
1900	62.350	23.484	93.554	-561.736	-376.828	40.199
2000	62.350	21.669	99.789	-560.934	-366.372	36.560
2100	62.350	19.853	106.024	-560.152	-355.936	33.276
2200	62.350	18.038	112.259	-559.390	-345.520	30.299
2300	62.350	16.222	118.494	-558.648	-335.124	27.589
2400	62.350	14.407	124.729	-557.926	-324.748	25.111
2500	62.350	12.591	130.964	-557.224	-314.392	22.838
2600	62.350	10.776	137.199	-556.542	-304.056	20.744
2700	62.350	8.960	143.434	-555.880	-293.740	18.812
2800	62.350	7.145	149.669	-555.238	-283.444	17.022
2900	62.350	5.329	155.904	-554.616	-273.168	15.360
3000	62.350	3.514	162.139	-554.014	-262.912	13.813
3100	62.350	1.698	168.374	-553.432	-252.676	12.369
3200	62.350	0.883	174.609	-552.870	-242.460	11.019
3300	62.350	0.067	180.844	-552.328	-232.264	9.755
3400	62.350	0.252	187.079	-551.806	-222.088	8.567
3500	62.350	0.437	193.314	-551.304	-211.932	7.452
3600	62.350	0.622	199.549	-550.822	-201.796	6.414
3700	62.350	0.807	205.784	-550.360	-191.680	5.452
3800	62.350	0.992	212.019	-549.918	-181.584	4.566
3900	62.350	1.177	218.254	-549.496	-171.508	3.756
4000	62.350	1.362	224.489	-549.094	-161.452	3.022

Ground State Configuration 2s<sup>2</sup>2p<sup>4</sup>  
 $\Delta H_f^{\circ} = 25.2 \pm .5$  kcal/mole  
 $\Delta H_f^{\circ} = 37.712$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $S_{298.15}^{\circ} = 24.3 \pm .5$  kcal/mole

Electronic Levels and Quantum Weight

$\mathcal{E}_1'$ , cm. <sup>-1</sup>	$\frac{g_1}{g_0}$
0.0	4
[160.0]	2

Heat of Formation.

The heat of formation was calculated from the equation:  $O(g) + e^- \rightarrow O^-(g)$  with the JANAF auxiliary value for O(g); using the measured electron affinity = 1.465 e.v. (33.783 kcal/mole) obtained from L. M. Branscomb, D. S. Burch, S. J. Smith and S. Oelتمان, Phys. Rev. **111**, 504 (1958). Other calculated values for the electron affinity are: 1.22 e.v. E. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964); 1.16 e.v. E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964); and 1.47 e.v. B. Ealén, J. Chem. Phys. **33**, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were estimated by assuming that the extra electron would produce an electronic structure similar to the next higher atomic numbered element, in this case F(II). An analogy was then made between O<sup>-</sup> and F(I) with O(II) and F(III), and O(II) and F(III) in order to estimate the height of the first level above the ground state. The data for F(I), O(I), F(II), O(II) and F(III) were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949. It is possible that the entropy below 3000°K. could be in error by 0.5 e.v. due to the estimation of the low lying electronic level. The electronic levels above  $1 \times 10^5$  cm.<sup>-1</sup> were omitted because their contribution is negligible below 6000°K. The  $H^{\circ}-H_{298}^{\circ}$  value at 0°K. is -1.567 kcal/mole.

T, °K.	C <sub>p</sub>	S <sup>o</sup>	$-(F^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0							
100	5.149	37.712	37.712	.000	24.300	21.849	16.015
200	5.147	37.743	37.712	.010	24.294	21.834	15.905
300	5.081	39.214	37.913	.521	23.953	21.064	11.508
400	5.045	40.344	38.290	1.027	23.596	20.383	8.909
500	5.024	41.261	38.711	1.530	23.225	19.776	7.203
600	5.010	42.035	39.112	2.032	22.842	19.231	6.004
700	5.001	42.703	39.538	2.532	22.446	18.742	5.120
800	4.994	43.292	39.923	3.032	22.042	18.302	4.444
900	4.990	43.818	40.286	3.531	21.631	17.910	3.914
1000	4.986	44.293	40.629	4.030	21.213	17.557	3.488
1100	4.983	44.727	40.953	4.528	20.790	17.243	3.140
1200	4.981	45.125	41.259	5.027	20.364	16.966	2.852
1300	4.979	45.495	41.548	5.525	19.933	16.719	2.610
1400	4.978	45.839	41.823	6.022	19.498	16.506	2.405
1500	4.977	46.159	42.084	6.520	19.061	16.321	2.229
1600	4.976	46.461	42.333	7.018	18.620	16.163	2.078
1700	4.975	46.745	42.570	7.515	18.177	16.033	1.947
1800	4.974	47.014	42.797	8.013	17.730	15.924	1.832
1900	4.974	47.269	43.014	8.510	17.281	15.841	1.731
2000	4.974	47.512	43.223	9.008	16.829	15.781	1.642
2100	4.973	47.743	43.423	9.505	16.373	15.741	1.564
2200	4.972	47.965	43.616	10.002	15.916	15.722	1.494
2300	4.972	48.176	43.801	10.499	15.455	15.724	1.432
2400	4.972	48.370	43.980	10.997	14.992	15.744	1.376
2500	4.972	48.574	44.153	11.494	14.526	15.784	1.327
2600	4.971	48.762	44.321	11.991	14.057	15.839	1.282
2700	4.971	48.942	44.482	12.488	13.585	15.916	1.242
2800	4.971	49.117	44.639	12.985	13.113	16.007	1.206
2900	4.971	49.285	44.791	13.482	12.636	16.118	1.174
3000	4.971	49.448	44.939	13.970	12.158	16.242	1.145
3100	4.970	49.606	45.082	14.476	11.677	16.378	1.118
3200	4.970	49.759	45.222	14.973	11.194	16.532	1.095
3300	4.970	49.908	45.357	15.470	10.700	16.698	1.073
3400	4.970	50.052	45.490	15.967	10.222	16.881	1.054
3500	4.970	50.192	45.618	16.464	9.733	17.079	1.037
3600	4.970	50.328	45.744	16.961	9.242	17.293	1.021
3700	4.970	50.460	45.866	17.458	8.750	17.518	1.007
3800	4.970	50.589	45.986	17.955	8.256	17.754	.995
3900	4.970	50.715	46.102	18.452	7.761	18.005	.984
4000	4.970	50.838	46.216	18.949	7.263	18.268	.974
4100	4.969	50.958	46.328	19.446	6.765	18.537	.965
4200	4.969	51.075	46.437	19.943	6.265	18.825	.957
4300	4.969	51.189	46.543	20.440	5.763	19.121	.950
4400	4.969	51.301	46.648	20.937	5.261	19.432	.944
4500	4.969	51.410	46.750	21.434	4.758	19.754	.938
4600	4.969	51.517	46.851	21.931	4.254	20.092	.936
4700	4.969	51.621	46.949	22.428	3.751	20.438	.937
4800	4.969	51.724	47.045	22.925	3.247	20.778	.937
4900	4.969	51.824	47.140	23.421	2.744	21.141	.934
5000	4.969	51.923	47.233	23.918	2.225	21.516	.922
5100	4.969	52.019	47.324	24.415	1.716	21.898	.920
5200	4.969	52.114	47.413	24.912	1.207	22.293	.918
5300	4.969	52.207	47.501	25.409	.696	22.693	.919
5400	4.969	52.298	47.588	25.906	.185	23.107	.918
5500	4.969	52.387	47.672	26.403	-.326	23.533	.918
5600	4.969	52.475	47.756	26.900	-.838	23.957	.919
5700	4.969	52.562	47.838	27.397	-1.350	24.399	.920
5800	4.969	52.647	47.919	27.894	-1.863	24.846	.922
5900	4.969	52.730	47.998	28.390	-2.377	25.304	.922
6000	4.969	52.811	48.075	28.887	-2.891	25.774	.922

SULFUR MONOXIDE (SO)

(IDEAL GAS)

MOL. WT. = 48.0654

Ground State Configuration  $3 \sum^-$   
 $S_{298.15}^\circ = 53.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^\circ = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^\circ = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Height

$E_i$  (e.v.)  $E_i$  (cm.<sup>-1</sup>)  $g_i$

$\omega_e x_e = 6.116 \text{ cm.}^{-1}$   
 $\alpha_e = 0.00562 \text{ cm.}^{-1}$

$\sigma = 1$   
 $r_e = 1.481 \text{ \AA}$

Heat of Formation.

The dissociation energy of sulfur monoxide has been reported by following investigators:

Investigator	$D_0$ (SO) e.v. (kcal. mole <sup>-1</sup> )
E. V. Martin, Phys. Rev. 41, 167 (1932).	5.053 (116.5)
A. G. Gaydon, "Dissociation Energies", Chapman & Hall Ltd. London, 1953.	5.184 (119.5)
G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. 2nd Ed., 1950.	4.001 (92.3)
R. G. W. Norrish and G. A. Oldershaw, Proc. Roy. Soc. A249, 498 (1959).	5.357 (123.5)
J. J. McCarvey, W. D. McCreath, Proc. Roy. Soc. A278, 490 (1964).	5.510 (127.1)

E. V. Martin, loc. cit., has measured the spectrum of SO(g) in the region 2400-4000 Å, and both Herzberg's and Herzberg favored  $D_0$  (SO) = 92.3 kcal. mole<sup>-1</sup> but Gaydon  $D_0$  (SO) = 119.5 kcal. mole<sup>-1</sup>.

Norrish and Oldershaw, loc. cit., redetermined the absorption spectrum of SO by flash photolysis, and also corrected Martin's original vibrational numbering, and then obtained the dissociation energy,  $D_0$ (SO) = 123.5 kcal. mole<sup>-1</sup>, based on the assumption of predissociation into  $S(^1D)$  and  $O(^3P)$ . This value,  $D_0 = 123.5 \text{ kcal. mole}^{-1}$ , has been selected as the dissociation energy for SO(g) and combination with JANAF values of  $\Delta H_f^\circ$  (S; s) and  $\Delta H_f^\circ$  (O; g) gives the heat of formation of sulfur monoxide,  $\Delta H_f^\circ = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$ , which is adopted in this tabulation.

R. Colin, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. 50, 306 (1954), have confirmed the selected  $D_0$  (SO) = 123.5 kcal. mole<sup>-1</sup> in their mass spectrometric studies on the vaporization of CS, S<sub>2</sub>S and BS. J. J. McCarvey and W. D. McCreath, loc. cit., reported the dissociation energy to be 127.1 kcal. mole<sup>-1</sup> based on their ultraviolet spectroscopic studies. This value appears to be the  $D_e$  from the minimum of the potential curve which corresponds to  $D_0$  (SO) = 125 ± 1.5 kcal. mole<sup>-1</sup>.

Besides the spectroscopic information, G. St. Pierre and J. Chipman, J. Am. Chem. Soc. 76, 4787 (1954), have reported  $\Delta H_f^\circ = -19 \text{ kcal. mole}^{-1}$  for the reaction  $0.5 S_2(g) + 0.5 O_2(g) \rightarrow SO(g)$  in the equilibrium study of iron-iron oxide alloys with SO<sub>2</sub> or SO<sub>2</sub>-CO mixtures. Using  $\Delta H_f^\circ$  298 (S<sub>2</sub>; g) = 30.8 kcal. mole<sup>-1</sup>, the derived heat of formation,  $\Delta H_f^\circ$  298 (SO; g) = -3.6 kcal. mole<sup>-1</sup> was obtained. However, this value is doubtful because the reported  $\Delta H_f^\circ$  298 = -19 kcal. mole<sup>-1</sup> was dependent upon many assumptions and subsidiary data. E. W. Dewing and P. D. Richardson, Trans. Faraday Soc. 53, 679(1958) have measured the equilibrium constants for the reaction  $S_2(g) + 2SO(g) \rightarrow 4SO(g)$  at 1250°C. and  $SO_2(g) \rightarrow SO(g) + 1/2 O_2(g)$  at 1500°C. Using the JANAF auxiliary data, the former yields  $\Delta H_f^\circ$  298 (SO; g) = +0.15 kcal. mole<sup>-1</sup> and the latter -0.17 kcal. mole<sup>-1</sup>, respectively. The average of these two values is  $\Delta H_f^\circ$  298 = 0 kcal. mole<sup>-1</sup>. Although D. Meschi and R. Myers, J. Mol. Spectry. 3, 405 (1959) and U. Blukis and R. Myers, J. Phys. Chem. 69, 1154 (1965), have certainly concluded in their microwave spectroscopic studies that the S<sub>2</sub>O species was one of the important products in the Sulfur - SO<sub>2</sub> equilibrium which was considered as unimportant by Dewing and Richardson, the value,  $\Delta H_f^\circ$  298 (SO; g) = 0 kcal. mole<sup>-1</sup> derived from Dewing and Richardson is still very close to the selected value,  $\Delta H_f^\circ$  298 (SO; g) = 1.64 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The molecular constants  $\omega_e$ ,  $\omega_e x_e$  and  $\alpha_e$  were obtained from R. Norrish and G. Oldershaw, loc. cit., and the values of  $r_e$  and  $B_0$  were recently measured in the microwave spectrum by P. X. Powell and D. R. Lide, Jr., J. Chem. Phys. 41, 1413 (1964).

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

T, °K.	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298<sup>o</sup>)/T</sub>	H <sup>o</sup> -H <sub>298<sup>o</sup></sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.957	45.366	2.090	1.640	1.640	1.640	INFINITE
200	6.996	50.194	53.672	1.818	1.818	1.818	∞.757
298	7.212	53.021	∞.000	1.640	1.640	1.640	∞.363
300	7.217	53.066	∞.013	1.637	1.637	1.637	∞.362
400	7.543	55.186	∞.751	1.920	1.920	1.920	3.642
500	7.846	56.903	∞.861	1.521	1.521	1.521	3.715
600	8.087	58.356	∞.432	2.318	∞.051	∞.235	3.728
700	8.272	59.617	∞.176	3.137	∞.421	11.879	3.708
800	8.413	60.731	∞.577	3.971	13.811	14.761	4.032
900	8.520	61.728	∞.575	4.818	13.809	14.879	3.613
1000	8.605	62.631	∞.956	5.674	13.807	14.998	3.278
1100	8.672	63.454	∞.519	6.538	13.806	15.118	3.004
1200	8.726	64.211	∞.077	7.407	13.805	15.237	2.775
1300	8.770	64.909	∞.639	8.280	13.804	15.355	2.581
1400	8.808	65.543	∞.201	9.154	13.803	15.472	2.418
1500	8.840	66.171	∞.847	10.043	13.803	15.586	2.272
1600	8.867	66.743	∞.911	10.930	13.804	15.715	2.146
1700	8.891	67.281	∞.325	11.818	13.807	15.834	2.035
1800	8.912	67.790	∞.708	12.708	13.811	15.954	1.937
1900	8.931	68.272	∞.114	13.600	13.816	16.071	1.848
2000	8.948	68.731	∞.484	14.494	13.823	16.191	1.769
2100	8.963	69.168	∞.819	15.390	13.832	16.310	1.697
2200	8.978	69.585	∞.212	16.287	13.843	16.426	1.632
2300	8.991	69.984	∞.513	17.185	13.856	16.543	1.572
2400	9.003	70.367	∞.832	18.085	13.870	16.659	1.517
2500	9.015	70.735	∞.141	18.986	13.886	16.776	1.466
2600	9.026	71.089	∞.440	19.888	13.904	16.891	1.420
2700	9.036	71.430	∞.729	20.791	13.924	17.007	1.377
2800	9.046	71.759	∞.010	21.695	13.946	17.123	1.336
2900	9.056	72.076	∞.283	22.600	13.970	17.233	1.299
3000	9.065	72.383	∞.548	23.506	13.997	17.343	1.263
3100	9.074	72.681	∞.805	24.413	14.023	17.456	1.231
3200	9.082	72.969	∞.056	25.321	14.053	17.567	1.200
3300	9.090	73.248	∞.300	26.230	14.084	17.676	1.171
3400	9.098	73.520	∞.538	27.139	14.117	17.784	1.143
3500	9.106	73.784	∞.770	28.049	14.152	17.895	1.117
3600	9.114	74.040	∞.996	28.960	14.187	17.997	1.093
3700	9.121	74.290	∞.217	29.872	14.225	18.102	1.069
3800	9.129	74.534	∞.432	30.785	14.263	18.209	1.047
3900	9.136	74.771	∞.643	31.698	14.303	18.314	1.026
4000	9.143	75.002	∞.849	32.612	14.344	18.412	1.006
4100	9.150	75.228	∞.7051	33.527	14.385	18.514	∞.987
4200	9.157	75.449	∞.7248	34.442	14.429	18.616	∞.969
4300	9.164	75.664	∞.7441	35.358	14.473	18.712	∞.951
4400	9.171	75.875	∞.7631	36.275	14.518	18.813	∞.934
4500	9.178	76.081	∞.7816	37.192	14.564	18.907	∞.918
4600	9.184	76.283	∞.7998	38.110	14.611	19.004	∞.903
4700	9.191	76.481	∞.8176	39.029	14.658	19.102	∞.888
4800	9.197	76.674	∞.8351	39.948	14.706	19.194	∞.874
4900	9.204	76.864	∞.8523	40.869	14.754	19.282	∞.860
5000	9.210	77.050	∞.8692	41.789	14.804	19.382	∞.847
5100	9.217	77.232	∞.8858	42.711	14.854	19.467	∞.834
5200	9.223	77.411	∞.9020	43.633	14.904	19.558	∞.822
5300	9.230	77.587	∞.9180	44.555	14.954	19.647	∞.810
5400	9.236	77.760	∞.9338	45.479	15.005	19.739	∞.799
5500	9.242	77.929	∞.9492	46.402	15.056	19.822	∞.788
5600	9.248	78.096	∞.9644	47.327	15.106	19.911	∞.777
5700	9.255	78.259	∞.9794	48.252	15.156	19.994	∞.767
5800	9.261	78.420	∞.9942	49.178	15.212	20.075	∞.756
5900	9.267	78.579	∞.1007	50.104	15.267	20.167	∞.745
6000	9.273	78.735	∞.1073	51.031	15.316	20.245	∞.737

(IDEAL GAS)

DISULFUR MONOXIDE (S<sub>2</sub>O)

Point Group C<sub>s</sub>  
 $\Delta H_f^0 = [-13 \pm 8] \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 298.15 = [-13.5 \pm 8] \text{ kcal. mole}^{-1}$

S-O = 63.8 cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
679 (1)
388 (1)
1185 (1)

Bond Distances: S-S = 1.684 Å S-O = 1.465 Å

Bond Angle: S-S-O = 118°

Product of the Moment of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 6.27441 X 10<sup>-115</sup> g.<sup>3</sup> cm.<sup>6</sup>

C<sub>v</sub> = 1

Heat of Formation.

There is no direct measurement of the standard enthalpy of formation for S<sub>2</sub>O(g). U. Blukis and R. Myers, J. Phys. Chem., 69, 1154 (1965), have discussed the discrepancy of the values of  $\Delta H_f^0$  which vary from -1 to -35 kcal. mole<sup>-1</sup>. R. Hagsmann, Compt. Rend., 225, 1102 (1962), reported  $\Delta H_f^0 = -17 \text{ kcal. mole}^{-1}$  from his ionization and appearance potential measurements by mass spectrometry. R. Stuedel and P. W. Schenk, Z. Physik Chem., 43, 33 (1964), estimated the enthalpy of formation as -22.7 kcal. mole<sup>-1</sup>. If the bond dissociation energies D<sub>0</sub>(S-O) = 123.5 kcal. mole<sup>-1</sup> and D<sub>0</sub>(S-S) = 101 kcal. mole<sup>-1</sup> were used to estimate the dissociation energy of S<sub>2</sub>O (i.e. D<sub>0</sub>(S<sub>2</sub>O) = 224.5 kcal. mole<sup>-1</sup>), one will obtain  $\Delta H_f^0 = -35.3 \text{ kcal. mole}^{-1}$ . A. V. Jones, J. Chem. Phys. 18, 1263 (1950), reported the predissociation energy, 91 kcal. mole<sup>-1</sup>, for sulfur monoxide from the infrared and ultraviolet spectra. [D. Meschi and R. Myers, J. Mol. Spectro. 3, 405 (1959), have concluded from their experiment that the so called sulfur monoxide is S<sub>2</sub>O.] Therefore, if SO(g) + S(g), were the dissociation products, the  $\Delta H_f^0$  would be -25.4 kcal. mole<sup>-1</sup>; and if S<sub>2</sub>(g) + O(g) were the products, the  $\Delta H_f^0$  would be -1.2 kcal. mole<sup>-1</sup>. (All JANAF auxiliary data used in calculation.)

E. Dewing and F. Richardson, Trans. Faraday Soc., 54, 679 (1958), have investigated the gas phase equilibria in the sulfur-oxygen vapor at 1250° and 1500°C respectively. U. Blukis and R. Myers (loc. cit.) recalculated their data based on the assumption that the S<sub>2</sub>O (instead of SO) was the major product in the equilibrium, and obtained  $\Delta H_f^0 = -13 \text{ kcal. mole}^{-1}$  for S<sub>2</sub>O(g) which is adopted in this table.

Heat Capacity and Entropy.

The bond distance, angle, and vibrational frequencies were obtained from the microwave and infrared spectra measurements by D. Meschi and R. Myers, loc. cit., and U. Blukis and R. Myers, loc. cit. The three principal moments of inertia are I<sub>A</sub> = 2.0219 X 10<sup>-39</sup>, I<sub>B</sub> = 16.6342 X 10<sup>-39</sup> and I<sub>C</sub> = 16.6560 X 10<sup>-39</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S° -(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup> kcal. mole <sup>-1</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞	∞	2.660	13.016	13.016	INFINITE
100	8.195	53.775	1.861	12.902	15.610	34.114
200	9.423	59.816	.982	13.149	18.240	19.931
298	10.544	63.796	.000	13.500	20.665	15.187
300	10.562	63.861	.020	13.507	20.709	15.086
400	11.624	67.024	1.821	14.959	23.011	12.572
500	12.641	69.644	2.496	16.025	24.899	10.885
600	12.477	71.860	3.523	16.890	26.589	9.684
700	12.076	73.520	4.693	17.573	28.089	8.746
800	11.517	74.703	5.988	18.099	29.446	8.019
900	11.303	75.468	7.312	18.498	30.554	7.419
1000	11.303	75.868	8.672	18.788	31.447	6.942
1100	11.399	76.761	10.047	18.988	32.147	6.563
1200	11.476	77.643	11.391	19.107	32.700	6.247
1300	11.536	78.511	12.742	19.149	33.124	5.971
1400	11.585	79.364	14.098	19.114	33.431	5.726
1500	11.625	80.203	15.458	19.003	33.624	5.501
1600	11.658	81.028	16.822	18.817	33.707	5.291
1700	11.686	81.840	18.190	18.557	33.681	5.091
1800	11.709	82.640	19.559	18.224	33.547	4.901
1900	11.729	83.428	20.931	17.828	33.306	4.721
2000	11.747	84.203	22.305	17.374	32.961	4.551
2100	11.761	84.964	23.681	16.863	32.524	4.391
2200	11.774	85.711	25.057	16.303	31.999	4.241
2300	11.786	86.444	26.436	15.694	31.388	4.101
2400	11.796	87.164	27.815	15.040	30.703	3.971
2500	11.805	87.871	29.195	14.346	29.956	3.851
2600	11.813	88.564	30.576	13.616	29.159	3.741
2700	11.820	89.243	31.957	12.853	28.316	3.641
2800	11.826	89.908	33.339	12.059	27.430	3.551
2900	11.832	90.560	34.722	11.238	26.505	3.471
3000	11.837	91.199	36.106	10.394	25.546	3.401
3100	11.841	91.824	37.490	9.530	24.557	3.341
3200	11.844	92.435	38.874	8.648	23.543	3.291
3300	11.846	93.032	40.259	7.750	22.509	3.251
3400	11.848	93.615	41.644	6.839	21.460	3.221
3500	11.850	94.184	43.029	5.918	20.399	3.191
3600	11.851	94.738	44.415	5.000	19.330	3.171
3700	11.852	95.277	45.801	4.087	18.257	3.151
3800	11.854	95.801	47.187	3.181	17.184	3.141
3900	11.856	96.311	48.574	2.284	16.114	3.131
4000	11.858	96.807	49.961	1.399	15.050	3.121
4100	11.871	97.289	51.348	0.528	14.000	3.111
4200	11.871	97.757	52.736	-0.326	12.964	3.101
4300	11.874	98.211	54.122	-1.104	11.944	3.091
4400	11.876	98.651	55.510	-1.888	10.940	3.081
4500	11.878	99.077	56.898	-2.681	9.954	3.071
4600	11.879	99.499	58.285	-3.484	8.987	3.061
4700	11.880	99.911	59.673	-4.297	8.040	3.051
4800	11.882	100.300	61.061	-5.120	7.114	3.041
4900	11.883	100.679	62.450	-5.964	6.209	3.031
5000	11.884	101.050	63.838	-6.821	5.326	3.021
5100	11.885	101.415	65.226	-7.692	4.464	3.011
5200	11.886	101.774	66.615	-8.577	3.624	3.001
5300	11.887	102.129	68.004	-9.476	2.806	2.991
5400	11.888	102.479	69.392	-10.389	2.011	2.981
5500	11.889	102.824	70.781	-11.316	1.240	2.971
5600	11.889	103.164	72.170	-12.257	0.493	2.961
5700	11.890	103.500	73.559	-13.212	-0.219	2.951
5800	11.891	103.831	74.948	-14.181	-0.954	2.941
5900	11.891	104.157	76.337	-15.164	-1.707	2.931
6000	11.892	104.477	77.726	-16.161	-2.476	2.921

Ground State Configuration  $1\Sigma^+$   
 $\Delta H_f^0 = 14.26 \pm 12$  kcal. mole<sup>-1</sup>  
 $S_{298.15}^0 = 54.35 \pm 2$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^0 298.15 = 14.0 \pm 12$  kcal. mole<sup>-1</sup>

Electronic Levels and Quantum Weight

$\epsilon_i$ , cm. <sup>-1</sup>	$g_i$	$\epsilon_i$ , cm. <sup>-1</sup>	$g_i$
0	1	[18000]	2
[4000]	6	[22000]	6
[6000]	2	[25500]	2
15500	2	27300	1
[15700]	6	[28500]	6
[17500]	6		

$\omega_e = 978$  cm.<sup>-1</sup>  
 $\omega_e x_e = 4$  cm.<sup>-1</sup>  
 $B_e = 0.4142$  cm.<sup>-1</sup>  
 $\alpha_e = 0.0023$  cm.<sup>-1</sup>  
 $r_e = 1.711 \text{ \AA}$   
 $\sigma = 1$

Heat of Formation.

The  $\Delta H_f^0 298.15 = 14.0 \pm 12$  kcal. mole<sup>-1</sup> was calculated from the  $\Delta H_f^0 298.15 = 290.342 \pm 12.8$  kcal. mole<sup>-1</sup> for the reaction  $Zr(c) + ZrO_2(c) = 2ZrO(g)$ . The value of  $\Delta H_f^0 298.15$  was obtained by the third law analysis from the mass spectrometric studies of W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. **26**, 1207 (1957). They observed the variation of the  $ZrO^+$  ion intensity over the system  $Zr + ZrO_2$  and reported equilibrium constants for the reaction  $Zr + ZrO_2 \rightarrow 2ZrO$  in the range 2124-2322°K. The third law drift is  $-58 \pm 28$  e.u.

Heat Capacity and Entropy.

The ground state of  $ZrO(g)$  was assumed to be  $1\Sigma^+$  as determined from the matrix isolation spectra of W. Weltner, Jr., and D. McLeod, Jr., J. Phys. Chem. **69**, 3488 (1965). Previously this had been described as the lower state in the A band system reported by V. Uhler and L. Akerlind, Arkiv Fysik **10**, 431 (1955).

All molecular constants were obtained from Uhler and Akerlind, loc. cit., except  $\omega_e = 978$  cm.<sup>-1</sup> and  $\omega_e x_e = 4$  cm.<sup>-1</sup> which were calculated from  $\omega$  and  $\alpha_e = 0.0023$  cm.<sup>-1</sup> using the equations

$$\alpha_e = \frac{6 \sqrt{\omega_e x_e \cdot B_e^3}}{\omega_e} \quad \text{and} \quad \omega = \omega_e - 2\omega_e x_e = 969.76 \text{ cm.}^{-1}$$

The higher electronic levels were obtained or estimated from the correlation diagram given by Weltner and McLeod, loc. cit.

T. °K.	C <sub>v</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	6.957	46.626	2.100	14.255	14.255	14.255	INFINITE
200	7.048	51.463	1.405	14.381	12.132	26.513	-26.513
300	7.107	54.695	1.065	14.417	9.437	10.858	-10.858
400	7.143	56.553	0.814	14.432	7.882	5.777	-5.777
500	7.165	57.818	0.627	14.438	6.844	3.184	-3.184
600	7.178	58.813	0.542	14.438	6.196	2.518	-2.518
700	7.183	59.605	0.487	14.432	5.828	2.161	-2.161
800	7.188	60.229	0.448	14.414	5.609	1.968	-1.968
900	7.191	60.717	0.418	14.386	5.507	1.852	-1.852
1000	7.193	61.176	0.393	14.354	5.476	1.793	-1.793
1100	7.194	61.609	0.371	14.318	5.482	1.766	-1.766
1200	7.194	62.014	0.351	14.279	5.528	1.741	-1.741
1300	7.193	62.391	0.332	14.236	5.609	1.717	-1.717
1400	7.191	62.741	0.315	14.191	5.729	1.685	-1.685
1500	7.188	63.066	0.300	14.144	5.882	1.647	-1.647
1600	7.184	63.368	0.287	14.095	6.066	1.604	-1.604
1700	7.179	63.647	0.276	14.044	6.278	1.557	-1.557
1800	7.173	63.904	0.266	13.991	6.517	1.506	-1.506
1900	7.166	64.141	0.257	13.936	6.782	1.451	-1.451
2000	7.158	64.359	0.250	13.879	7.072	1.394	-1.394
2100	7.149	64.558	0.244	13.821	7.386	1.336	-1.336
2200	7.139	64.739	0.239	13.762	7.724	1.277	-1.277
2300	7.128	64.902	0.235	13.702	8.086	1.218	-1.218
2400	7.116	65.048	0.232	13.641	8.472	1.159	-1.159
2500	7.104	65.178	0.230	13.579	8.882	1.100	-1.100
2600	7.091	65.293	0.228	13.516	9.316	1.042	-1.042
2700	7.078	65.394	0.227	13.452	9.774	0.985	-0.985
2800	7.064	65.481	0.226	13.387	10.256	0.930	-0.930
2900	7.050	65.555	0.225	13.321	10.762	0.877	-0.877
3000	7.036	65.617	0.225	13.254	11.292	0.826	-0.826
3100	7.021	65.667	0.225	13.187	11.845	0.777	-0.777
3200	7.006	65.706	0.225	13.119	12.420	0.730	-0.730
3300	6.990	65.734	0.225	13.051	13.017	0.685	-0.685
3400	6.974	65.752	0.225	12.982	13.636	0.642	-0.642
3500	6.958	65.760	0.225	12.913	14.276	0.601	-0.601
3600	6.941	65.759	0.225	12.844	14.937	0.562	-0.562
3700	6.924	65.749	0.225	12.774	15.619	0.525	-0.525
3800	6.907	65.730	0.225	12.704	16.322	0.490	-0.490
3900	6.890	65.702	0.225	12.633	17.046	0.457	-0.457
4000	6.873	65.666	0.225	12.562	17.791	0.426	-0.426
4100	6.856	65.622	0.225	12.491	18.557	0.397	-0.397
4200	6.839	65.571	0.225	12.420	19.344	0.370	-0.370
4300	6.821	65.513	0.225	12.349	20.152	0.345	-0.345
4400	6.803	65.449	0.225	12.277	20.981	0.321	-0.321
4500	6.785	65.379	0.225	12.205	21.831	0.299	-0.299
4600	6.767	65.304	0.225	12.132	22.702	0.278	-0.278
4700	6.749	65.224	0.225	12.059	23.594	0.259	-0.259
4800	6.731	65.139	0.225	11.985	24.507	0.241	-0.241
4900	6.713	65.049	0.225	11.911	25.441	0.225	-0.225
5000	6.695	64.955	0.225	11.836	26.396	0.210	-0.210
5100	6.677	64.857	0.225	11.761	27.372	0.196	-0.196
5200	6.659	64.755	0.225	11.686	28.369	0.183	-0.183
5300	6.641	64.649	0.225	11.610	29.387	0.171	-0.171
5400	6.623	64.539	0.225	11.534	30.425	0.160	-0.160
5500	6.605	64.425	0.225	11.458	31.483	0.150	-0.150
5600	6.587	64.307	0.225	11.381	32.561	0.141	-0.141
5700	6.569	64.185	0.225	11.304	33.659	0.133	-0.133
5800	6.551	64.059	0.225	11.227	34.777	0.126	-0.126
5900	6.533	63.929	0.225	11.149	35.914	0.120	-0.120
6000	6.515	63.795	0.225	11.071	37.070	0.115	-0.115

(REFERENCE STATE - IDEAL GAS)

OXYGEN, DIATOMIC (O<sub>2</sub>)

Ground State Configuration  $3 \sum_g^-$   $\Delta H_f^0 = 0$

$S_{298.15}^0 = 49.00 \pm 0.01$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>  $\Delta H_f^0 298.15 = 0$

$\sigma^- = 2$

$r_e = 1.2074 \text{ \AA}$

$\omega_e x_e = 12.071$  cm.<sup>-1</sup>

$B_e = 1.445$  cm.<sup>-1</sup>  $\alpha_e = 0.0158$  cm.<sup>-1</sup>

Heat of Formation.

The heat of formation ( $\Delta H_f^0$ ) for O<sub>2</sub>(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here are based on those of H. W. Woolley, J. Research, Nat. Bur. Standards 40, 163 (1946), who used a direct summation to 5000°K. The spectroscopic constants used were the same as those listed by G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Co., 1950. Raman measurements of rotation-vibration levels by A. Weber and E. A. McGinnis, J. Molec. Spect., 4, 195 (1960), support the constants selected by Strominger, J. M. Hollander, and T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The entropies listed by Woolley were reduced by 0.0065 cal. deg.<sup>-1</sup> mole<sup>-1</sup> which was added by Woolley to account for the contribution due to the presence of both odd and even rotational levels in 0<sup>16</sup>-0<sup>17</sup> and 0<sup>16</sup>-0<sup>18</sup> molecules. This correction is not necessary when isotope mixing entropy is neglected, cf. W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. 54, 1731 (1932).

T, °K.	C <sub>v</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.000	INFINITE	2.075	.000	.000
100	6.958	41.395	55.205	.000	.000
200	6.961	46.218	49.643	.000	.000
298	7.020	49.004	.000	.000	.000
300	7.023	49.047	.013	.000	.000
400	7.196	51.091	49.282	.000	.000
500	7.431	52.722	1.455	.000	.000
600	7.670	54.098	2.210	.000	.000
700	7.883	55.297	51.028	.000	.000
800	8.063	56.361	51.629	.000	.000
900	8.212	57.320	4.600	.000	.000
1000	8.336	58.192	52.765	.000	.000
1100	8.439	58.991	53.295	.000	.000
1200	8.527	59.729	53.801	.000	.000
1300	8.604	60.415	54.283	.000	.000
1400	8.674	61.055	54.744	.000	.000
1500	8.738	61.656	55.185	.000	.000
1600	8.800	62.222	10.583	.000	.000
1800	8.918	62.726	11.465	.000	.000
1900	8.973	63.198	12.259	.000	.000
2000	9.029	64.210	14.149	.000	.000
2100	9.084	64.682	15.054	.000	.000
2200	9.139	65.076	15.966	.000	.000
2300	9.194	65.493	16.882	.000	.000
2400	9.248	65.876	17.804	.000	.000
2500	9.301	66.254	18.732	.000	.000
2600	9.354	66.620	19.664	.000	.000
2700	9.405	66.974	20.602	.000	.000
2800	9.455	67.317	21.545	.000	.000
2900	9.503	67.650	22.493	.000	.000
3000	9.551	67.973	23.446	.000	.000
3100	9.596	68.287	24.403	.000	.000
3200	9.640	68.592	25.365	.000	.000
3300	9.682	68.889	26.331	.000	.000
3400	9.723	69.179	27.302	.000	.000
3500	9.762	69.461	28.276	.000	.000
3600	9.799	69.737	29.254	.000	.000
3700	9.835	70.006	30.236	.000	.000
3800	9.869	70.269	31.221	.000	.000
3900	9.901	70.525	32.209	.000	.000
4000	9.932	70.776	33.201	.000	.000
4100	9.961	71.022	34.196	.000	.000
4200	9.988	71.262	35.193	.000	.000
4300	10.015	71.498	36.190	.000	.000
4400	10.041	71.730	37.188	.000	.000
4500	10.066	71.959	38.186	.000	.000
4600	10.084	72.176	39.184	.000	.000
4700	10.104	72.393	40.181	.000	.000
4800	10.123	72.606	41.179	.000	.000
4900	10.140	72.814	42.176	.000	.000
5000	10.156	73.019	43.173	.000	.000
5100	10.172	73.221	44.170	.000	.000
5200	10.187	73.418	45.167	.000	.000
5300	10.200	73.613	46.163	.000	.000
5400	10.213	73.803	47.158	.000	.000
5500	10.225	73.991	48.153	.000	.000
5600	10.237	74.175	49.147	.000	.000
5700	10.247	74.356	50.140	.000	.000
5800	10.258	74.535	51.132	.000	.000
5900	10.267	74.710	52.124	.000	.000
6000	10.276	74.883	53.116	.000	.000

$\Delta H_f^0 = -261.0 \pm 0.4 \text{ kcal. mole}^{-1}$

$\Delta H_f^{298.15} = -262.3 \pm 0.4 \text{ kcal. mole}^{-1}$

$\Delta H_c^0 = 1.42 \pm 0.1 \text{ kcal. mole}^{-1}$

$\Delta H_m = [20.8] \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = [12.036 \pm 0.08] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_f = 1478 \pm 5^\circ\text{K.}$

$T_m = 2950^\circ\text{K.}$

Heat of Formation.

The  $\Delta H_f^{298.15}$  is the average value of the  $\Delta H_f^{298.15} = -261.5 \pm 0.2 \text{ kcal. mole}^{-1}$  and  $\Delta H_f^{298.15} = -263.1 \pm 0.5 \text{ kcal. mole}^{-1}$  measured (by combustion calorimetry) by G. L. Humphrey, J. Am. Chem. Soc. 75, 978 (1954) and E. J. Huber, Jr., E. L. Head and C. E. Holley, Jr., J. Phys. Chem. 68, 3040 (1964) respectively. Also the heat of formation was measured calorimetrically by B. Neumann, C. Kröger and H. Kunz, Z. anorg. Chem. 218, 379 (1934), by W. A. Roth, E. Bbrger, and H. Slemenson, *ibid.*, 239, 321 (1938) and by A. Sieverts, A. Gotta and S. Halberstadt, *ibid.*, 187, 155 (1930) and was found  $-258.2$ ,  $-258.8$  and  $-256.1 \text{ kcal. mole}^{-1}$  respectively. However more weight was given to the Humphrey and Huber values.

Heat Capacity and Entropy.

The low temperature heat capacities,  $54.3$ - $295^\circ\text{K.}$ , were measured by K. K. Kelley, Ind. Eng. Chem. 36, 377 (1944). The heat capacities in the temperature range  $298$ - $1478^\circ\text{K.}$  were calculated by using the J. P. Coughlin and E. G. King equation  $C_p = 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^{-5}T^2$  obtained from their measured enthalpy data in the range  $396.8$ - $1841^\circ\text{K.}$ , J. Am. Chem. Soc. 72, 2262 (1950). The values from the two sources join smoothly at  $298^\circ\text{K.}$  Above the transition  $1478^\circ\text{K.}$  the heat capacity was taken as constant at  $17.80 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ , Coughlin and King, loc. cit. The entropy was calculated at  $54.30$  using the Debye and Einstein function  $D(\frac{513}{T}) + E(\frac{861}{T})$  given by Kelley, loc. cit. The value of  $S_{54.3}^0 = 0.5507 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Transition Data.

$T_f$  and  $\Delta H_c^0$  were taken from Coughlin and King loc. cit.

Melting Data.

The  $T_m$  and  $\Delta H_m^0$  were taken from Natl. Bur. Standards Circ. 500 Washington (1952).

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S <sup>0</sup> -(F <sup>0</sup> -H <sub>298</sub> <sup>0)/T</sup>	H <sup>0</sup> -H <sub>298</sub> <sup>0</sup> kcal. mole <sup>-1</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞∞∞	INFINITE	-2.091	-260.999	-260.999	INFINITE
100	4.524	2.268	1.934	-261.767	-257.504	562.748
200	10.224	7.3173	1.174	-262.210	-253.930	278.430
298	13.430	12.036	∞∞∞	-262.300	-248.502	182.148
300	13.447	12.119	∞25	-262.299	-248.416	180.962
400	15.260	16.268	1.471	-262.195	-243.802	133.201
500	16.196	19.782	3.048	-262.024	-239.221	104.558
600	16.787	22.791	4.699	-261.832	-234.678	85.477
700	17.214	25.412	6.400	-261.634	-230.168	71.858
800	17.555	27.733	8.139	-261.431	-225.687	61.652
900	17.845	29.818	9.909	-261.220	-221.231	53.726
1000	18.104	31.717	11.707	-261.003	-216.798	47.379
1100	18.342	33.449	13.529	-260.790	-212.390	42.196
1200	18.567	35.054	15.375	-260.580	-207.959	37.871
1300	18.781	36.549	17.242	-260.374	-203.496	34.209
1400	18.989	37.948	19.131	-260.173	-199.009	31.073
1500	19.180	39.256	21.043	-259.977	-194.461	28.361
1600	19.360	41.355	23.024	-259.786	-190.347	25.999
1700	19.530	43.146	25.090	-259.608	-186.640	23.916
1800	19.690	44.631	27.270	-259.442	-183.327	22.065
1900	19.840	45.841	29.560	-259.287	-180.401	20.409
2000	19.980	46.877	31.930	-259.142	-177.841	18.920
2100	20.110	47.730	34.390	-259.007	-175.616	17.572
2200	20.230	48.414	36.930	-258.882	-173.696	16.331
2300	20.340	48.947	39.550	-258.766	-172.042	15.192
2400	20.440	49.439	42.230	-258.659	-170.632	14.147
2500	20.530	49.891	44.960	-258.561	-169.447	13.186
2600	20.610	50.305	47.730	-258.471	-168.456	12.299
2700	20.680	50.681	50.540	-258.388	-167.628	11.478
2800	20.740	51.019	53.390	-258.312	-166.927	10.715
2900	20.790	51.319	56.280	-258.242	-166.327	10.005
3000	20.830	51.574	59.200	-258.178	-165.816	9.342
3100	20.860	51.792	62.150	-258.120	-165.379	8.722
3200	20.880	51.971	65.130	-258.068	-165.004	8.141
3300	20.890	52.111	68.140	-258.021	-164.688	7.595
3400	20.890	52.211	71.170	-257.979	-164.420	7.081
3500	20.880	52.281	74.230	-257.941	-164.198	6.596
3600	20.860	52.321	77.320	-257.907	-164.026	6.138
3700	20.830	52.331	80.440	-257.877	-163.894	5.704
3800	20.790	52.311	83.590	-257.850	-163.802	5.294
3900	20.740	52.261	86.770	-257.826	-163.749	4.904
4000	20.680	52.181	90.000	-257.804	-163.723	4.534



T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	(H°-H° <sub>298</sub> )/T	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>p</sub>
0							
100							
200							
298	13.430	17.841	17.841	0.000	-244.550	-232.483	170.406
300	13.447	17.924	17.941	0.025	-244.549	-232.408	169.301
400	15.260	22.072	18.195	1.471	-244.649	-228.373	124.771
500	16.196	25.587	19.491	3.048	-244.274	-224.373	98.069
600	16.787	28.595	20.764	4.699	-244.082	-220.410	80.281
700	17.214	31.217	22.074	6.400	-243.884	-216.481	67.585
800	17.555	33.538	23.365	8.139	-243.681	-212.581	58.072
900	17.845	35.623	24.613	9.909	-243.470	-208.706	50.678
1000	18.134	37.517	25.810	11.707	-243.253	-204.853	44.769
1100	18.342	39.253	26.954	13.529	-243.040	-201.024	39.938
1200	18.567	40.859	28.047	15.375	-242.780	-197.166	35.907
1300	18.781	42.354	29.091	17.242	-242.544	-193.292	32.494
1400	18.989	43.753	30.088	19.131	-242.301	-189.436	29.571
1500	19.180	45.011	31.058	21.043	-242.050	-185.618	27.043
1600	19.350	46.160	32.029	22.979	-241.793	-181.885	24.863
1700	19.500	47.210	32.995	24.930	-241.533	-178.159	22.973
1800	19.630	48.256	33.859	26.770	-241.270	-174.436	21.178
1900	19.750	49.218	34.666	28.550	-241.007	-170.710	19.529
2000	19.860	50.132	35.467	30.290	-240.743	-167.009	18.029
2100	19.960	51.000	36.277	32.030	-240.485	-163.304	16.594
2200	20.050	51.820	37.000	33.780	-240.230	-159.604	15.230
2300	20.130	52.600	37.702	35.530	-240.000	-155.904	13.930
2400	20.200	53.350	38.406	37.300	-239.776	-152.204	12.700
2500	20.260	54.080	39.086	41.930	-239.554	-148.504	11.530
2600	20.310	54.740	39.745	43.300	-239.336	-144.804	10.430
2700	20.350	55.340	40.386	46.030	-239.124	-141.104	9.390
2800	20.380	55.890	41.008	48.130	-238.917	-137.404	8.410
2900	20.400	56.400	41.614	50.230	-238.715	-133.704	7.490
3000	20.410	56.860	42.203	52.330	-238.518	-130.004	6.630
3100	20.410	57.280	42.777	54.430	-238.325	-126.304	5.830
3200	20.400	57.660	43.336	56.530	-238.137	-122.604	5.090
3300	20.380	58.000	43.881	58.630	-237.953	-118.904	4.410
3400	20.350	58.275	44.413	60.730	-237.774	-115.204	3.790
3500	20.310	58.500	44.932	62.830	-237.600	-111.504	3.230
3600	20.260	58.675	45.439	64.930	-237.432	-107.804	2.730
3700	20.200	58.800	45.934	67.030	-237.270	-104.104	2.290
3800	20.130	58.910	46.418	69.130	-237.114	-100.404	1.910
3900	20.050	59.000	46.892	71.230	-236.963	-96.704	1.590
4000	20.000	59.068	47.355	73.330	-236.817	-93.004	1.330
4100	20.000	59.100	47.809	75.430	-236.676	-89.304	1.130
4200	20.000	59.110	48.253	77.530	-236.540	-85.604	0.980
4300	20.000	59.100	48.688	79.630	-236.410	-81.904	0.870
4400	20.000	59.068	49.114	81.730	-236.286	-78.204	0.790
4500	20.000	59.000	49.532	83.830	-236.168	-74.504	0.730
4600	20.000	58.920	49.942	85.930	-236.056	-70.804	0.690
4700	20.000	58.820	50.342	88.030	-235.950	-67.104	0.660
4800	20.000	58.700	50.739	90.130	-235.850	-63.404	0.640
4900	20.000	58.560	51.127	92.230	-235.756	-59.704	0.630
5000	20.000	58.400	51.508	94.330	-235.668	-56.004	0.630
5100	20.000	58.220	51.882	96.430	-235.586	-52.304	0.640
5200	20.000	58.020	52.249	98.530	-235.510	-48.604	0.660
5300	20.000	57.800	52.611	100.630	-235.440	-44.904	0.690
5400	20.000	57.560	52.966	102.730	-235.376	-41.204	0.730
5500	20.000	57.300	53.315	104.830	-235.318	-37.504	0.780
5600	20.000	57.020	53.650	106.930	-235.266	-33.804	0.840
5700	20.000	56.720	53.970	109.030	-235.220	-30.104	0.910
5800	20.000	56.400	54.280	111.130	-235.180	-26.404	0.990
5900	20.000	56.060	54.580	113.230	-235.146	-22.704	1.080
6000	20.000	55.700	54.880	115.330	-235.118	-19.004	1.180

ΔH<sub>f</sub><sup>o</sup> 298.15 = [-244.55] kcal. mole<sup>-1</sup>  
 ΔH<sub>m</sub><sup>o</sup> = [20.8] kcal. mole<sup>-1</sup>  
 ΔH<sub>v</sub><sup>o</sup> = [149.2] kcal. mole<sup>-1</sup>

S<sup>o</sup> 298.15 = [17.841] cal. deg.  
 T<sub>m</sub> = 2950°K.  
 T<sub>b</sub> = 4548°K.

Heat of Formation.

The ΔH<sub>f</sub><sup>o</sup> 298.15 (1) was obtained from ΔH<sub>f</sub><sup>o</sup> 298.15 (c) by adding ΔH<sub>m</sub><sup>o</sup> and the difference between H<sub>m</sub><sup>o</sup> and H<sub>v</sub><sup>o</sup> for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 2000°K. The heat capacity below 2000°K. was obtained from the heat capacity of the crystal. Above 2000°K. the heat capacity was assumed constant and estimated to be 21.0 cal. deg.<sup>-1</sup> mole<sup>-1</sup> or 7 cal. deg.<sup>-1</sup> per g-atom as suggested by O. Kubaschewski and E. L.L. Evans, "Metallurgical Thermochemistry" Pergamon Press, New York (1958). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See ZrO<sub>2</sub>(c) table.

Vaporization Data.

T<sub>b</sub> was calculated as the temperature at which the free energy change of the reaction ZrO<sub>2</sub>(l) → ZrO<sub>2</sub>(g) approaches zero. The difference between ΔH<sub>f</sub><sup>o</sup> 4548 for ZrO<sub>2</sub>(g) and ZrO<sub>2</sub>(l) is ΔH<sub>v</sub><sup>o</sup>.

MOL. WT. = 123.2168

ZIRCONIUM DIOXIDE (ZrO<sub>2</sub>) (IDEAL GAS)

Point Group C<sub>2v</sub>

$\Delta H_f^0 = -67.9 \pm 11$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -68.4 \pm 11$  kcal. mole<sup>-1</sup>

S<sup>298.15</sup> = 65.402 cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
884 (1)
[137](1)
818 (1)

Bond Distance: O-Zr = 1.711 Å  
 Bond Angle: O-Zr-O = 109°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 5.679636 X 10<sup>-115</sup> g.<sup>3</sup> cm.<sup>6</sup>

σ = 2

Heat of Formation.

The  $\Delta H_f^{298.15} = -68.4 \pm 11$  kcal. mole<sup>-1</sup> was calculated from the  $\Delta H_f^{298.15} = 193.867 \pm 11.25$  kcal. mole<sup>-1</sup> for the reaction ZrO<sub>2</sub>(c) → ZrO<sub>2</sub>(g). The value of  $\Delta H_f^{298.15}$  was obtained by the third law method using the determined vapor pressures (at the range 2331-2480°K) by W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 26, 1207 (1957). They observed the variation of the ZrO<sub>2</sub><sup>+</sup> ion intensity over ZrO<sub>2</sub> and reported equilibrium constants for the reaction ZrO<sub>2</sub>(c) → ZrO<sub>2</sub>(g) in the range 2331-2480°K. The third law drift is 80 ± 23 e.u.

Heat Capacity and Entropy.

The vibrational frequencies  $\nu_1 = 884$ ,  $\nu_2 = [137]$ ,  $\nu_3 = 818$  and angle O-Zr-O = 109° were obtained from M. J. Linevsky, Spectroscopic Studies of the Vaporization of Refractory Materials, Technical Report Nr. AFML TR-64-420 Air Force Materials Lab. Research and Technology Division, Wright Patterson Air Force Base, Ohio (1965). The bond distances (r<sub>e</sub>) O-Zr = 1.711 Å was obtained from U. Uhler and L. Akerlind, Arkiv Fysik 10, 431 (1955). The three principal moments of inertia are: I<sub>A</sub> = 1.03083 X 10<sup>-38</sup>, I<sub>B</sub> = 3.8826 X 10<sup>-39</sup>, I<sub>C</sub> = 1.41909 X 10<sup>-38</sup> g. cm.<sup>2</sup>

T, °K.	C <sub>v</sub> <sup>o</sup>	S <sup>o</sup>	-(F <sup>o</sup> -H <sub>298<sup>o</sup>})/T</sub>	H <sup>o</sup> -H <sub>298<sup>o</sup></sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	9.454	54.403	74.481	2.870	67.878	67.878	INFINITE
200	10.115	61.194	66.379	2.012	67.945	68.952	150.578
298	11.009	65.402	65.402	1.036	68.172	69.776	76.243
300	11.026	65.470	65.402	∞	68.404	70.526	51.376
400	11.818	68.756	65.845	1.165	68.605	71.203	36.902
500	12.378	71.457	66.705	2.1376	68.796	71.830	31.395
600	12.759	73.750	67.693	3.634	68.997	72.418	26.377
700	13.022	75.738	68.703	4.924	69.210	72.952	22.782
800	13.207	77.489	69.804	6.236	69.434	73.438	19.077
900	13.342	78.953	71.064	7.584	69.667	73.868	15.706
1000	13.442	80.184	71.361	8.963	69.907	74.254	12.711
1100	13.518	81.249	72.630	10.261	70.168	74.598	10.000
1200	13.578	82.198	73.756	11.606	71.459	75.267	7.682
1300	13.625	83.017	74.642	12.987	71.669	75.580	5.628
1400	13.663	83.728	75.391	14.431	71.843	75.871	3.860
1500	13.694	84.372	75.506	15.699	72.242	76.140	2.453
1600	13.720	84.956	76.188	17.070	72.543	76.388	1.434
1700	13.741	85.489	76.840	18.443	72.855	76.621	0.850
1800	13.759	85.975	77.465	19.818	73.178	76.832	0.528
1900	13.774	86.419	78.064	21.195	73.512	77.025	0.328
2000	13.787	86.826	78.640	22.573	73.858	77.204	0.216
2100	13.798	87.199	79.193	23.952	74.214	77.362	0.151
2200	13.808	87.541	79.726	25.332	74.586	77.508	0.100
2300	13.817	87.855	80.240	26.714	74.970	77.642	0.060
2400	13.824	88.143	80.737	28.096	75.365	77.760	0.038
2500	13.831	88.408	81.216	29.478	75.768	77.865	0.026
2600	13.837	88.650	81.680	30.862	76.184	77.958	0.018
2700	13.842	88.873	82.130	32.246	76.613	78.040	0.012
2800	13.847	89.076	82.565	33.630	77.054	78.112	0.008
2900	13.851	89.259	82.988	35.015	77.506	78.175	0.005
3000	13.855	89.423	83.398	36.401	77.969	78.230	0.003
3100	13.859	89.568	83.797	37.786	78.443	78.278	0.002
3200	13.862	89.696	84.185	39.172	78.934	78.319	0.001
3300	13.865	89.803	84.562	40.559	79.436	78.355	0.000
3400	13.868	89.891	84.930	41.945	79.949	78.387	0.000
3500	13.870	89.969	85.288	43.332	80.474	78.416	0.000
3600	13.872	90.060	85.638	44.719	81.011	78.442	0.000
3700	13.874	90.140	85.978	46.107	81.558	78.465	0.000
3800	13.876	90.210	86.311	47.494	82.115	78.486	0.000
3900	13.878	90.270	86.636	48.882	82.682	78.505	0.000
4000	13.879	90.322	86.954	50.270	83.259	78.522	0.000
4100	13.881	90.364	87.265	51.658	83.846	78.537	0.000
4200	13.882	90.400	87.569	53.046	84.443	78.550	0.000
4300	13.884	90.432	87.866	54.434	85.050	78.561	0.000
4400	13.885	90.460	88.158	55.823	85.667	78.570	0.000
4500	13.886	90.485	88.443	57.211	86.294	78.578	0.000
4600	13.887	90.510	88.723	58.600	86.931	78.585	0.000
4700	13.888	90.530	88.997	59.988	87.578	78.590	0.000
4800	13.889	90.550	89.266	61.376	88.235	78.594	0.000
4900	13.890	90.568	89.530	62.764	88.902	78.598	0.000
5000	13.891	90.584	89.789	64.152	89.579	78.602	0.000
5100	13.892	90.600	90.043	65.540	90.266	78.606	0.000
5200	13.893	90.615	90.293	66.928	90.963	78.610	0.000
5300	13.894	90.630	90.538	68.316	91.670	78.614	0.000
5400	13.895	90.645	90.777	69.704	92.387	78.618	0.000
5500	13.896	90.660	91.017	71.092	93.114	78.622	0.000
5600	13.896	90.675	91.250	72.480	93.851	78.626	0.000
5700	13.897	90.690	91.479	73.868	94.598	78.630	0.000
5800	13.898	90.705	91.704	75.256	95.355	78.634	0.000
5900	13.899	90.720	91.926	76.644	96.122	78.638	0.000
6000	13.899	90.735	92.145	78.032	96.899	78.642	0.000

June 30, 1961; Dec. 31, 1965

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S° -(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub> kcal. mole <sup>-1</sup>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞
100	10.680	8.883	3.876	-272.011	-272.011	INFINITE
200	17.343	12.343	3.348	-273.039	-266.727	582.904
298	21.520	16.273	2.819	-273.514	-260.197	284.316
			0.000	-273.660	-253.620	185.000
300	21.500	16.273	2.819	-273.660	-253.620	184.653
400	24.580	19.046	2.385	-273.572	-248.782	134.529
500	26.700	20.776	1.927	-273.320	-240.112	104.948
600	28.380	22.006	1.488	-272.954	-233.503	85.049
700	29.500	22.869	1.085	-272.484	-226.770	70.797
800	30.250	23.320	0.724	-271.921	-220.101	60.126
900	30.780	23.574	0.467	-271.271	-213.491	51.840
1000	31.150	23.744	0.274	-270.544	-206.938	45.224
1100	31.440	23.854	0.111	-270.000	-200.441	39.822
1200	31.690	23.911	0.011	-269.529	-194.091	35.329
1300	31.890	23.938	0.000	-269.129	-187.889	31.535
1400	32.080	23.942	0.000	-268.792	-181.732	28.290
1500	32.270	23.922	0.000	-268.507	-175.614	25.584
1600	32.420	23.880	0.000	-268.272	-169.535	23.033
1700	32.550	23.819	0.000	-268.080	-163.493	20.662
1800	32.690	23.739	0.000	-267.929	-157.491	18.463
1900	32.780	23.639	0.000	-267.814	-151.526	16.417
2000	32.850	23.517	0.000	-267.731	-145.594	14.514

LEAD METASILICATE (PbSiO<sub>3</sub>)

(CRYSTAL)

MOL. WT. = 283.2742

$$\Delta H_f^0 = -272.01 \pm 1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -273.66 \pm 1 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 26.273 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1037^\circ\text{K.}$$

Heat of Formation.

The heat of the reaction  $\text{PbO}(\text{red}) + \text{SiO}_2 \rightarrow \text{PbSiO}_3(\text{c})$  was reported by K. K. Kelley, U. S. Bureau of Mines, Report Investigation 5901 (1962). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAF values for  $\text{PbO}(\text{c})$  (March 31, 1962) and for  $\text{SiO}_2(\text{c})$  (Dec. 31, 1962). The above  $\Delta H_f^{298.15} = -3.75 \pm 0.12 \text{ kcal. mole}^{-1}$ .

Heat Capacity and Entropy.

In the low temperature region (53.25-298.15°K.) the  $C_p$  values are those determined by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). Above 298.15°K. values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.25°K. using the Debye and Einstein functions  $D(\frac{h\nu}{T}) + E(\frac{2h\nu}{T}) + 2E(\frac{3h\nu}{T}) + E(\frac{4h\nu}{T})$  given by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). The  $S_{53.25}^0 = 3.662 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Melting Data.

$T_m$  was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).

SULFUR TRIOXIDE (SO<sub>3</sub>) (IDEAL GAS)

MOL. WT. = 80.0622

Point Group D<sub>3h</sub>  
 $\Delta H_f^0 = -83.22 \pm 0.17$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^{298.15} = -94.59 \pm 0.17$  kcal. mole<sup>-1</sup>  
 $S_{298.15} = 61.344$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>  
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>
1068 (1)
495 (1)
1391 (2)
529 (2)

Bond Distance: S-O = 1.43 Å  
 Bond Angle: O-S-O = 120°

Product of the Moments of Inertia:  $I_A I_B I_C = 1.0813 \times 10^{-114}$  g.<sup>3</sup> cm.<sup>6</sup>

Heat of Formation.

The heat of formation was calculated from the reaction  $SO_2 + 1/2 O_2 \rightarrow SO_3$  for which three sets of equilibrium constants are available. A summary of the second and third law treatment of the data is given below.

Ref.	Temp. Range	Points	$\Delta H_{298}^0$ kcal. mole <sup>-1</sup>	$\Delta H_{298}^0$ kcal. mole <sup>-1</sup>	Drift
1	933-945°K	5	-27.67 ± 2.7	-23.608	3.7 ± 2.9
2	801-1170°K	8	-23.45 ± 0.1	-23.661	-0.8 ± 0.1
3	850-1001°K	11	-22.74 ± 0.6	-23.614	-1.5 ± 0.6
4	801-1170°K	23*	-23.40 ± 0.2	-23.638	-0.9 ± 0.2

References

- G. B. Taylor and S. Lehner, Z. Physik. Chem. **530**, (1931).
- M. Bodenstein and W. Pohl, Z. Electrochem. **11**, 373 (1905).
- A. F. Kapustinsky and L. M. Shamovsky, Acta Physicochem. URSS **4**, 791 (1936).
- Combination of above references, with one point omitted due to failure of a statistical test.

The combined set was adopted though it appears that the three sets are not in excellent agreement, and the combination heavily favors Ref. 2. Although there is a definite trend in all the data it cannot be considered definitive enough for use in the modification of the SO<sub>3</sub> functions.

Heat Capacity and Entropy.

The bond length and angles were taken from the electron diffraction data of K. J. Palmer, J. Am. Chem. Soc. **50**, 2360 (1928). The vibrational frequencies were taken from the infrared studies of R. W. Lovejoy, J. H. Colwell, D. F. Eggers and G. D. Halsey, J. Chem. Phys. **36**, 612 (1962), which are in excellent accord with those of R. Bent and W. R. Ladner, Spectrochim. Acta **19**, 931 (1963) using different techniques. These values differ from the assignment used by W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley, J. Chem. Phys. **12**, 408 (1944) in their analysis of the thermodynamic properties of SO<sub>3</sub>.

The individual moments of inertia were  $I_A = I_B = 8.148 \times 10^{-39}$  g. cm.<sup>2</sup> and  $I_C = 16.296 \times 10^{-39}$  g. cm.<sup>2</sup>

T, K.	C <sub>v</sub>	S°	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞	∞
100	8.165	50.733	24.796	4.796	93.220	93.220	INFINITE
200	10.110	56.920	1.094	93.656	92.205	92.205	2.11504
298	12.168	61.344	∞	94.590	90.555	90.555	98.949
300	12.142	61.345	∞	94.597	88.662	88.669	65.007
400	15.784	65.146	1.322	95.463	86.597	86.597	64.580
500	15.082	66.367	2.768	96.052	84.310	84.310	67.312
600	16.075	71.209	4.328	96.481	81.919	81.919	29.837
700	16.824	73.746	5.975	96.861	79.441	79.441	24.801
800	17.391	76.031	7.687	110.111	78.213	78.213	21.366
900	17.823	78.105	9.448	110.009	74.230	74.230	18.025
1000	18.157	80.001	11.248	109.891	70.260	70.260	15.354
1100	18.419	81.745	13.077	109.763	66.306	66.306	13.173
1200	18.628	83.357	14.930	109.626	62.360	62.360	11.357
1300	18.796	84.855	16.802	109.485	58.426	58.426	9.822
1400	18.933	86.253	18.688	109.341	54.504	54.504	8.508
1500	19.046	87.563	20.587	109.197	50.593	50.593	7.371
1600	19.140	88.795	22.497	109.051	46.689	46.689	6.377
1700	19.219	89.958	24.415	108.905	42.796	42.796	5.502
1800	19.286	91.058	26.340	108.763	38.911	38.911	4.724
1900	19.344	92.103	28.272	108.624	35.034	35.034	4.030
2000	19.393	93.096	30.209	108.488	31.166	31.166	3.405
2100	19.436	94.044	32.150	108.356	27.304	27.304	2.841
2200	19.474	94.949	34.096	108.230	23.447	23.447	2.329
2300	19.507	95.815	36.045	108.108	19.596	19.596	1.862
2400	19.536	96.646	37.997	107.992	15.748	15.748	1.434
2500	19.562	97.444	39.952	107.882	11.910	11.910	1.041
2600	19.585	98.212	41.909	107.777	8.072	8.072	0.678
2700	19.605	98.951	43.869	107.676	4.228	4.228	0.335
2800	19.623	99.664	45.830	107.578	0.383	0.383	0.010
2900	19.640	100.353	47.793	107.483	-3.473	-3.473	-0.268
3000	19.655	101.019	49.758	107.391	-7.284	-7.284	-0.528
3100	19.669	101.664	51.724	107.305	-11.054	-11.054	-0.780
3200	19.681	102.289	53.692	107.224	-14.879	-14.879	-1.016
3300	19.692	102.895	55.660	107.148	-18.693	-18.693	-1.238
3400	19.702	103.483	57.630	107.076	-22.510	-22.510	-1.447
3500	19.712	104.054	59.601	107.006	-26.319	-26.319	-1.643
3600	19.721	104.609	61.573	107.058	-30.136	-30.136	-1.829
3700	19.729	105.150	63.545	107.018	-33.945	-33.945	-2.005
3800	19.736	105.676	65.518	106.980	-37.756	-37.756	-2.171
3900	19.743	106.189	67.492	106.947	-41.559	-41.559	-2.329
4000	19.749	106.689	69.467	106.920	-45.368	-45.368	-2.479
4100	19.755	107.176	71.442	106.896	-49.179	-49.179	-2.621
4200	19.761	107.652	73.418	106.876	-52.985	-52.985	-2.757
4300	19.766	108.117	75.394	106.859	-56.794	-56.794	-2.886
4400	19.770	108.572	77.371	106.848	-60.594	-60.594	-3.010
4500	19.775	109.016	79.348	106.839	-64.404	-64.404	-3.128
4600	19.779	109.451	81.326	106.833	-68.211	-68.211	-3.241
4700	19.783	109.876	83.304	106.831	-72.016	-72.016	-3.349
4800	19.787	110.293	85.283	106.831	-75.819	-75.819	-3.452
4900	19.790	110.700	87.261	106.834	-79.621	-79.621	-3.551
5000	19.793	111.101	89.241	106.840	-83.423	-83.423	-3.646
5100	19.796	111.493	91.220	106.849	-87.234	-87.234	-3.738
5200	19.799	111.877	93.200	106.859	-91.037	-91.037	-3.826
5300	19.802	112.254	95.180	106.871	-94.850	-94.850	-3.911
5400	19.805	112.625	97.160	106.886	-98.664	-98.664	-3.992
5500	19.807	112.988	99.141	106.901	-102.460	-102.460	-4.071
5600	19.809	113.345	101.122	106.921	-106.263	-106.263	-4.147
5700	19.812	113.695	103.103	106.941	-110.070	-110.070	-4.220
5800	19.816	114.040	105.084	106.962	-113.882	-113.882	-4.291
5900	19.818	114.379	107.065	106.985	-117.682	-117.682	-4.359
6000	19.817	114.712	109.047	107.009	-121.498	-121.498	-4.425

Dec. 31, 1960; Sept. 30, 1985

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	∞	∞	∞	∞	∞	∞
100	17.636	32.210	6.198	-327.311	-327.311	INFINITE
200	27.239	32.672	5.250	-328.690	-370.263	695.901
298	32.740	44.654	0.000	-329.320	-311.554	340.434
					-302.839	221.575
300	32.800	44.857	0.061	-329.318	-302.675	220.488
400	36.330	54.794	3.523	-329.090	-293.822	160.529
500	40.140	63.217	7.301	-328.670	-285.051	124.590
600	44.430	70.561	11.335	-328.099	-276.377	100.665
700	48.050	77.077	15.564	-329.756	-267.428	83.491
800	44.020	82.893	19.921	-329.039	-258.574	70.636
900	44.640	88.114	24.354	-328.274	-249.809	60.659
1000	45.200	92.848	28.848	-327.473	-241.132	52.697
1100	45.600	97.175	33.389	-326.640	-232.540	46.199
1200	45.900	101.155	37.963	-325.782	-224.021	40.798
1300	46.300	104.845	42.573	-324.900	-215.577	36.240
1400	46.680	108.291	47.222	-323.995	-207.204	32.344
1500	47.000	111.522	51.907	-323.069	-198.890	28.977
1600	47.300	114.565	56.622	-322.133	-190.642	26.039
1700	47.570	117.441	61.365	-321.288	-182.343	23.441
1800	47.810	120.167	66.135	-320.287	-173.495	21.064
1900	48.110	122.761	70.932	-321.290	-164.703	18.944
2000	48.400	125.236	75.758	-320.292	-155.960	17.042

LEAD ORTHOSILICATE (Pb<sub>2</sub>SiO<sub>4</sub>) (CRYSTAL)

MOL. WT. = 506.4636

ΔH<sub>f</sub>° 0 = -327.3 ± 3.5 kcal. mole<sup>-1</sup>

ΔH<sub>f</sub>° 298.15 = -329.3 ± 3.5 kcal. mole<sup>-1</sup>

S° 298.15 = 44.654 ± 0.5 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>m</sub> = 1016°K.

Heat of Formation.

The heat of the reaction 2PbO(c) + SiO<sub>2</sub>(c) → Pb<sub>2</sub>SiO<sub>4</sub>(c) was reported by O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York (1958). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAF values for PbO(c) (March 31, 1962) and for SiO<sub>2</sub>(c) (Dec. 31, 1962). The above ΔH<sub>f</sub>° 298.15 = -7.00 ± 3.5 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

In the low temperature region (53.07-298.15°K.) the C<sub>p</sub> values are those determined by E. G. King, J. Am. Chem. Soc., 81, 799-800 (1959). Above 298.15 C<sub>p</sub> values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.07°K. using the Debye and Einstein functions D( $\frac{h\nu}{RT}$ ) + 2E( $\frac{h\nu}{RT}$ ) + 3E( $\frac{547}{T}$ ) + E( $\frac{1373}{T}$ ) given by E. G. King, J. Am. Chem. Soc., 81, 799-800 (1959). The S° 53.07 = 8.248 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Data.

T<sub>m</sub> was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1954).

T, °K.	C <sub>p</sub>	S°	-(F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>p</sub>
0	.000	.000	INFINITE	- 3.562	- 481.062	- 481.062	INFINITE
100	7.417	3.363	36.589	- 3.123	- 482.525	- 474.128	1036.155
200	17.519	11.869	22.058	- 2.034	- 483.400	- 465.137	508.175
298	23.580	20.083	.000	.000	- 483.736	- 456.386	334.324
300	23.690	20.083	.044	.044	- 483.738	- 456.216	332.337
400	27.400	27.576	21.060	2.607	- 483.740	- 447.036	244.238
500	30.100	33.996	23.019	5.489	- 483.541	- 437.879	191.387
600	31.950	39.657	25.330	8.596	- 483.221	- 428.775	156.174
700	33.180	44.679	27.742	11.855	- 482.833	- 419.731	131.040
800	34.100	49.173	30.145	15.222	- 482.402	- 410.748	112.206
900	34.720	53.226	32.488	18.664	- 481.947	- 401.815	97.569
1000	35.200	56.910	34.749	22.161	- 481.483	- 392.935	85.872
1100	35.550	60.283	36.919	25.700	- 481.024	- 384.105	76.311
1200	35.780	63.387	38.997	29.287	- 481.529	- 375.266	68.342
1300	35.900	66.235	40.985	32.851	- 481.075	- 366.429	61.599
1400	35.950	68.917	42.886	36.443	- 480.639	- 357.628	55.826
1500	36.000	71.399	44.705	40.041	- 480.220	- 348.856	50.456
1600	36.000	73.723	46.447	43.641	- 479.820	- 340.109	46.455
1700	36.000	75.903	48.116	47.241	- 479.443	- 331.780	42.587
1800	36.000	77.943	49.716	50.841	- 479.083	- 323.865	39.078
1900	36.000	79.809	51.256	54.441	- 478.762	- 316.422	35.841
2000	36.000	81.456	52.635	58.041	- 478.489	- 309.310	33.120
2100	36.000	83.512	54.159	61.641	- 478.262	- 293.742	30.569
2200	36.000	85.187	55.532	65.241	- 478.059	- 279.238	28.235
2300	36.000	86.787	56.856	68.841	- 477.874	- 265.093	26.100
2400	36.000	88.320	58.136	72.441	- 477.701	- 251.138	24.143
2500	36.000	89.789	59.373	76.041	- 477.539	- 237.467	22.344
2600	36.000	91.201	60.570	79.641	- 477.387	- 224.087	20.684
2700	36.000	92.560	61.730	83.241	- 477.246	- 211.016	19.149
2800	36.000	93.869	62.854	86.841	- 477.116	- 198.259	17.723
2900	36.000	95.132	63.946	90.441	- 477.000	- 185.811	16.397
3000	36.000	96.353	65.006	94.041	- 476.893	- 173.689	15.159

ΔH<sub>f</sub>° = -481.1 ± 0.7 kcal. mole<sup>-1</sup>

ΔH<sub>f</sub>° 298.15 = -483.7 ± 0.7 kcal. mole<sup>-1</sup>

S°<sub>298.15</sub> = 20.083 ± 0.3 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

T<sub>d</sub> = 1811°K.

Heat of Formation.

The ΔH<sub>f</sub>° 298.15 was calculated from the ΔH<sub>f</sub>° 298.15 of its constituent oxides ZrO<sub>2</sub>(c) + SiO<sub>2</sub>(c) = ZrSiO<sub>4</sub>(c) and from the ΔH<sub>f</sub>° 298.15 of ZrO<sub>2</sub>(c) (June 30, 1961) and SiO<sub>2</sub>(c) (Dec. 31, 1962) in JANAF tables. The ΔH<sub>f</sub>° 298.15 = -4.736 kcal. mole<sup>-1</sup> was based on the free energy of formation of its constituent oxides at the decomposition temperature 1811°K.

Heat Capacity and Entropy.

At low temperatures C<sub>p</sub> were used from K. K. Kelley, J. Am. Chem. Soc. 63, 2750 (1941). From 298-940°K. C<sub>p</sub> was calculated by using the J. P. Coughlin and E. G. King equation C<sub>p</sub> = 31.48 + 3.92 X 10<sup>-3</sup>T - 8.08 X 10<sup>-5</sup>T<sup>2</sup>, J. Am. Chem. Soc., 72, 2262 (1950), which joined smoothly with the low temperature data. Above 940°K. the data was estimated by extending the curve smoothly. The entropy was calculated at 52.7°K. using the Debye and Einstein functions D(321/T) + 2E(407/T) + 2E(1624/T) given by K. K. Kelley, J. Am. Chem. Soc., 63, 2750 (1941). S°<sub>52.7</sub> = 0.65404 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Temperature of Decomposition.

T<sub>d</sub> is the temperature at which ΔF<sub>r</sub>° = 0 for the reaction ZrSiO<sub>4</sub>(c) → ZrO<sub>2</sub>(c) + SiO<sub>2</sub>(c). T<sub>d</sub> = 1811°K. was taken from C. E. Curtis and H. G. Sowman, J. Am. Chem. Soc., 36, 190 (1963).

T, °K.	C <sub>p</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	Log K <sub>f</sub>
0	∞	∞	∞	∞	∞	∞
100	18.550	89.940	8.117	696.994	-696.994	INFINITE
200	36.940	37.260	7.441	699.947	-680.441	1487.032
298	50.690	54.680	4.000	701.810	-660.134	721.326
300	50.830	54.994	4.094	702.707	-639.450	468.707
400	62.200	71.218	5.761	702.727	-639.058	465.531
500	71.700	86.135	12.463	701.964	-617.815	337.542
600	80.300	99.982	20.071	700.535	-575.725	209.698
700	88.000	112.950	28.493	698.535	-555.074	173.594
800	94.800	125.153	37.640	777.710	-555.992	151.883
900	100.800	136.675	47.428	773.736	-528.506	128.333
1000	105.800	147.560	57.763	769.292	-501.492	109.596
1100	110.200	157.858	68.572	764.442	-474.948	94.359
1200	113.600	167.598	79.768	759.258	-448.857	81.744
1300	116.200	176.797	91.263	753.824	-423.206	71.144
1400	118.300	185.487	102.991	748.196	-397.983	62.125
1500	120.000	193.710	114.909	742.417	-373.168	54.368

DIPHOSPHORUS PENTOXIDE, DIMERIC ((P<sub>2</sub>O<sub>5</sub>)<sub>2</sub>) (CRYSTAL)

MOL. WT. = 285.8892

ΔH<sub>f</sub><sup>o</sup> P<sub>2</sub>O<sub>5</sub> = -697.0 ± 2.1 kcal. mole<sup>-1</sup>  
 ΔH<sub>f</sub><sup>o</sup> 298.15 = -702.7 ± 2.1 kcal. mole<sup>-1</sup>  
 ΔH<sub>f</sub><sup>o</sup> 298.15 = 25.34 ± 0.08 kcal. mole<sup>-1</sup>

S<sup>o</sup> 298.15 = 54.68 ± 0.10 cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 T<sub>g</sub> = 631°K.

Heat of Formation.

The heat of formation (ΔH<sub>f</sub><sup>o</sup> 298.15) of P<sub>4</sub>O<sub>10</sub>(c) has been reported by many investigators. The most recent value, ΔH<sub>f</sub><sup>o</sup> 298.15 = -719.4 ± 2.0 kcal. mole<sup>-1</sup> for the reaction P<sub>4</sub>(α, white, c) + 5O<sub>2</sub>(g) = P<sub>4</sub>O<sub>10</sub>(hex. c), was determined by E. P. Egan, Jr. and B. B. Luff, "Heats of Formation of Phosphorus Oxides", June 1, 1963 to Nov. 30, 1963, Tennessee Valley Authority, Office of Agriculture and Chemical Development, Fundamental Research Branch, Willson Dam, Alabama. This ΔH<sub>f</sub><sup>o</sup> 298.15 value was derived from energy of combustion, ΔE<sub>c</sub> = -716.397 kcal. mole<sup>-1</sup>, which is an average value of many measurements using three different sample forms, i.e. uncoated phosphorus, lucite-coated phosphorus and cellulose acetate-coated phosphorus. The adopted ΔH<sub>f</sub><sup>o</sup> 298.15 (P<sub>4</sub>O<sub>10</sub>, c) value was recalculated based on the P(red, V, c) as reference state.

The heat of combustion of white phosphorus was determined as -713.2 ± 1.0 kcal. mole<sup>-1</sup> by W. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962), yielding ΔH<sub>f</sub><sup>o</sup> 298.15 (P<sub>4</sub>O<sub>10</sub>, c) = -696.5 ± 1.3 kcal. mole<sup>-1</sup>, based on P(red, V, c) as reference state. The heat of formation of P<sub>2</sub>O<sub>5</sub> from red phosphorus was reported to be -355 ± 2 kcal. mole<sup>-1</sup> by W. E. Koerner and P. Daniels, J. Chem. Phys. 20, 113 (1952). The product, P<sub>2</sub>O<sub>5</sub>, was considered to be a mixture of two forms, i.e. crystalline and amorphous. The other ΔH<sub>f</sub><sup>o</sup> 298.15 (P<sub>4</sub>O<sub>10</sub>, c) values reported by early investigators were reviewed by Egan and Luff, loc. cit.

Heat Capacity and Entropy.

The heat capacities (12-324°K.) and S<sup>o</sup> 298.15 adopted were taken from R. J. L. Andon, J. F. Counsell, H. McKerrell and J. P. Martin, Trans. Faraday Soc. 59, 2702 (1963). The C<sub>v</sub> values above 324°K. were obtained by graphical extrapolation. The S<sup>o</sup> 298.15 value was calculated based on S<sup>o</sup> 10 = 0.36 e.u.

Low temperature (15-310°K.) and high temperature (298.15-623.15°K.) heat capacities were also measured by Thermal Laboratory, The Dow Chemical Company, private communication, June 18, 1962, and M. Frandsen, J. Res. Natl. Bur. Std. 10, 35 (1933), respectively. The low temperature data were not adopted because they are less satisfactory than the data of Andon et al. The high temperature data were not used because the sample employed for enthalpy measurements was not explicitly reported as pure hexagonal form.

Sublimation Data.

The value of ΔH<sub>f</sub><sup>o</sup> 298.15 was derived from the vapor pressure data by both the second and third law analyses. See the P<sub>4</sub>O<sub>10</sub>(g) table for details. T<sub>g</sub> is the temperature at which the free energy change of the reaction P<sub>4</sub>O<sub>10</sub>(hex. c) = P<sub>4</sub>O<sub>10</sub>(g) approaches zero. Sublimation temperature for P<sub>4</sub>O<sub>10</sub>(c) was derived to be 632°K., 636°K. (average of three determinations) and 623.7°K. (average of two determinations) by M. Frandsen, loc. cit. from the vapor pressure data reported by J. M. Hoeflake and M. P. Scheffer, Rec. trav. chim. 45, 191 (1926); A. Smits, Z. physik. Chem. 149, 357 (1930); and A. Smits and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924), respectively.

DIPHOSPHORUS PENTOXIDE, DIMERIC ((P<sub>2</sub>O<sub>5</sub>)<sub>2</sub>) (IDEAL GAS)

Point Group T<sub>d</sub>  
 $\Delta H_f^0 = -671.0 \pm 2.1$  kcal. mole<sup>-1</sup>  
 $\Delta H_f^0$  298.15 = [96.5] cal. deg.<sup>-1</sup> mole<sup>-1</sup>  
 $\Delta H_f^0$  298.15 = -677.4  $\pm$  2.1 kcal. mole<sup>-1</sup>  
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>	$\omega$ , cm. <sup>-1</sup>
424 (1)	650 (2)	764 (3)	764 (3)
721 (1)	952 (2)	1015 (3)	1015 (3)
1417 (1)	1707(3)	329 (3)	1390 (3)
278 (2)	4707(5)	573 (3)	

Bond Distance: P-O<sub>optical</sub> = 1.40  $\pm$  0.03 Å P-O = 1.60  $\pm$  0.01 Å P-P = 2.83  $\pm$  0.03 Å  
 Bond Angle: Optical-P-O = 117  $\pm$  1° O-P-O = 101  $\pm$  1° P-O-P = 124°30'  $\pm$  1°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = 2.93796 X 10<sup>11</sup> g.<sup>3</sup> cm.<sup>6</sup>  $\sigma = 12$

Heat of Formation.

The value of  $\Delta H_f^0$  298.15 (P<sub>2</sub>O<sub>5</sub>, g) was calculated from the heats of formation and sublimation for P<sub>4</sub>O<sub>10</sub> (hex., c). The heat of sublimation ( $\Delta H_s^0$  298.15) was derived from vapor pressure data by the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K	Second Law Value	Third Law Value	Drift, e.u.
Hoeflake and Scherff <sup>1</sup>	260 - 401	25.42±0.07	25.33	-0.39±0.13
Southard and Nelson <sup>2</sup>	216.2-300.4	25.55±0.06	25.35	-0.18±0.14
	285.6-389.3	25.45±0.07	25.35	-0.10±0.07

1. J. M. A. Hoeflake and P. E. C. Scherff, Rec. trav. chim. 45, 191 (1928).  
 2. J. C. Southard and R. A. Nelson, J. Am. Chem. Soc. 59, 911 (1937).

The value of  $\Delta H_s^0$  298.15 adopted was 25.34  $\pm$  0.08 kcal. mole<sup>-1</sup>. There are many vapor pressure measurements reported but only the above two over P<sub>4</sub>O<sub>10</sub> (hex., c).

It has been shown that P<sub>4</sub>O<sub>10</sub> has three solid phases and two liquid phases. The three solid phases are hexagonal, orthorhombic and tetragonal. As temperature increases, the thermal stability of P<sub>4</sub>O<sub>10</sub> follows the same order. The metastable liquid, according to data of Hoeflake and Scherff, loc. cit., is from hexagonal form. The stable liquid is from tetragonal form. W. L. Hill, G. T. Paust and S. B. Hendricks, J. Am. Chem. Soc. 65, 794 (1943) reported that molecules of P<sub>4</sub>O<sub>10</sub> having the same structure as in the vapor are present in the hexagonal form of the solid. The vapor pressures of P<sub>4</sub>O<sub>10</sub> over different condensed phases have been measured by many investigators and reviewed by T. D. Parr, "Phosphorus, Properties of the Elements and Some of Its Compounds", Tennessee Valley Authority, Wilson Dam, Alabama, 1950. The complexity of the solid state of P<sub>4</sub>O<sub>10</sub> has also been discussed by A. Smits and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924); A. Smits, Z. Physik. Chem. 149, 337 (1930); A. Smits, J. A. A. Ketselaar and J. L. Meyerling, ibid., 841, 87 (1936); and A. Smits, ibid., 846, 43 (1940).

Heat Capacity and Entropy.

The molecular structure and constants were obtained from P. A. Akishin, N. G. Rabbidi and E. Z. Zaslavin, Kristallografiya, 4, 360 (1959). The molecular structure of P<sub>4</sub>O<sub>10</sub> (g) has also been studied by the electron diffraction method by L. R. Maxwell, S. B. Hendricks and L. S. Deming, J. Chem. Phys. 5, 626 (1937), and G. C. Hampson and A. J. Stosick, J. Am. Chem. Soc. 60, 184 (1938). The model of the P<sub>4</sub>O<sub>10</sub> molecule was later confirmed by the X-ray method reported by H. C. J. Decker and C. H. McGilvray, Rec. trav. chim. 50, 153 (1941); and spectroscopic studies reported by H. Gerding and H. C. J. Decker, Rec. trav. chim. 51, 191 (1945), and T. A. Sidorov and N. N. Sobolev, Opt. Spectr. (USSR), 2, 717 (1957). All vibrational frequencies were obtained from E. P. Egan, Jr., private communication, Feb. 23, 1960, except nine frequencies, i.e. 170 (3), 470 (3) and 750 (3) cm.<sup>-1</sup> which were estimated in order to make the second and third law values of  $\Delta H_f^0$  298.15 agree. The three principal moments of inertia are: I<sub>A</sub> = I<sub>B</sub> = I<sub>C</sub> = 1.4322 X 10<sup>-37</sup> g. cm.<sup>2</sup>. The heat capacities (549-1098°C. or 822-1371°K.) of P<sub>4</sub>O<sub>10</sub> (g) have been determined by M. Prandeen, J. Res. Natl. Bur. Std. 10, 35 (1933). His results are in fair agreement with the calculated ones.

T, °K.	C <sub>v</sub>	S° - (F° - H° <sub>298</sub> )/T	H° - H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	∞.00	INFINITE	7.308	-670.975	-670.975	INFINITE
100	16.835	66.368	173.811	-658.929	-658.929	14.40-018
200	32.689	81.525	308.277	-646.105	-646.105	7.57-319
298	45.126	96.525	465.252	-626.627	-626.627	4.29-308
300	45.325	96.805	465.526	-626.311	-626.311	4.56-245
400	54.377	111.461	86.622	-609.157	-609.157	3.24-812
500	60.662	128.113	101.667	-591.896	-591.896	2.26-705
600	65.643	135.844	106.875	-574.633	-574.633	2.09-300
700	68.849	142.157	111.705	-557.370	-557.370	1.74-020
800	70.599	147.152	116.152	-540.107	-540.107	1.53-374
900	71.650	151.004	120.100	-522.844	-522.844	1.30-346
1000	72.329	153.809	123.609	-505.581	-505.581	1.11-957
1100	72.704	156.102	126.500	-488.318	-488.318	96.940
1200	72.829	157.945	128.925	-471.055	-471.055	86.449
1300	72.841	159.345	130.867	-453.792	-453.792	73.400
1400	72.775	160.263	132.382	-436.529	-436.529	64.876
1500	72.581	201.532	146.338	-419.266	-419.266	57.071
1600	72.918	206.486	149.944	-402.003	-402.003	50.225
1700	72.200	211.158	153.409	-384.740	-384.740	44.253
1800	71.439	215.777	156.741	-367.477	-367.477	38.929
1900	70.642	219.370	159.949	-350.214	-350.214	34.175
2000	70.817	223.757	163.041	-332.951	-332.951	29.906
2100	70.969	227.557	166.023	-315.688	-315.688	26.049
2200	70.101	231.188	168.903	-298.425	-298.425	22.550
2300	70.216	234.662	171.687	-281.162	-281.162	19.363
2400	70.318	237.993	174.381	-263.899	-263.899	16.446
2500	70.408	241.192	176.990	-246.636	-246.636	13.767
2600	70.489	244.269	179.519	-229.373	-229.373	11.300
2700	70.560	247.232	181.972	-212.110	-212.110	9.019
2800	70.625	250.091	184.354	-194.847	-194.847	6.905
2900	70.682	252.851	186.669	-177.584	-177.584	4.940
3000	70.735	255.519	188.920	-160.321	-160.321	3.110
3100	70.782	258.101	191.110	-143.058	-143.058	1.400
3200	70.825	260.603	193.243	-125.795	-125.795	1.199
3300	70.864	263.030	195.321	-108.532	-108.532	1.098
3400	70.900	265.384	197.347	-91.269	-91.269	1.008
3500	70.933	267.672	199.324	-74.006	-74.006	1.018
3600	70.963	269.896	201.254	-56.743	-56.743	1.028
3700	70.991	272.060	203.138	-39.480	-39.480	1.038
3800	70.017	274.167	204.980	-22.217	-22.217	1.048
3900	70.041	276.220	206.780	-4.954	-4.954	1.058
4000	70.063	278.221	208.541	12.309	12.309	1.068
4100	70.083	280.174	210.265	29.572	29.572	1.078
4200	70.102	282.080	211.952	46.835	46.835	1.088
4300	70.120	283.941	213.605	64.098	64.098	1.098
4400	70.137	285.760	215.224	81.361	81.361	1.108
4500	70.152	287.539	216.811	98.624	98.624	1.118
4600	70.167	289.279	218.368	115.887	115.887	1.128
4700	70.180	290.981	219.895	133.150	133.150	1.138
4800	70.193	292.649	221.393	150.413	150.413	1.148
4900	70.205	294.282	222.860	167.676	167.676	1.158
5000	70.216	295.882	224.300	184.939	184.939	1.168
5100	70.227	297.451	225.727	202.202	202.202	1.178
5200	70.237	298.989	227.141	219.465	219.465	1.188
5300	70.246	300.499	228.542	236.728	236.728	1.198
5400	70.255	301.980	229.936	253.991	253.991	1.208
5500	70.263	303.434	231.314	271.254	271.254	1.218
5600	70.271	304.863	232.687	288.517	288.517	1.228
5700	70.279	306.266	234.050	305.780	305.780	1.238
5800	70.286	307.645	235.412	323.043	323.043	1.248
5900	70.293	308.999	236.765	340.306	340.306	1.258
6000	70.299	310.333	238.118	357.569	357.569	1.268

Dec. 31, 1962; Dec. 31, 1965



(REFERENCE STATE)

SULFUR (S)

0° to 368.54°K. Crystal, Rhombic  
 368.54° to 388.36°K. Crystal, Monoclinic  
 388.36° to 717.75°K. Liquid  
 717.75° to 6000°K. Ideal Gas, Diatomic

See crystal, liquid and diatomic gas for details.

T, °K.	C <sub>p</sub>	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	$\Delta H_f^{\circ}$	$\Delta F_f^{\circ}$	Log K <sub>p</sub>
0	.000	INFINITE	1.053	.000	.000	.000
100	3.060	2.965	.889	.000	.000	.000
200	4.634	5.022	8.104	.000	.000	.000
298	5.440	7.631	17.461	.000	.000	.000
300	5.442	7.665	17.632	.000	.000	.000
400	7.734	10.674	31.059	.000	.000	.000
500	9.081	12.768	44.504	.000	.000	.000
600	8.200	14.333	57.002	.000	.000	.000
700	7.759	15.601	68.552	.000	.000	.000
800	7.368	16.657	79.257	.000	.000	.000
900	4.396	17.416	89.106	.000	.000	.000
1000	4.418	17.936	98.100	.000	.000	.000
1100	4.435	18.265	106.351	.000	.000	.000
1200	4.450	18.432	113.857	.000	.000	.000
1300	4.461	18.524	120.609	.000	.000	.000
1400	4.471	18.580	126.607	.000	.000	.000
1500	4.480	18.614	131.852	.000	.000	.000
1600	4.488	18.638	136.343	.000	.000	.000
1700	4.495	18.657	140.080	.000	.000	.000
1800	4.501	18.671	143.063	.000	.000	.000
1900	4.507	18.681	145.292	.000	.000	.000
2000	4.513	18.688	146.766	.000	.000	.000
2100	4.518	18.692	147.485	.000	.000	.000
2200	4.523	18.694	147.450	.000	.000	.000
2300	4.528	18.694	146.661	.000	.000	.000
2400	4.532	18.692	145.117	.000	.000	.000
2500	4.537	18.687	142.820	.000	.000	.000
2600	4.541	18.680	139.773	.000	.000	.000
2700	4.545	18.671	135.984	.000	.000	.000
2800	4.549	18.659	131.451	.000	.000	.000
2900	4.553	18.644	126.174	.000	.000	.000
3000	4.557	18.628	120.161	.000	.000	.000
3100	4.561	18.611	113.421	.000	.000	.000
3200	4.565	18.592	105.964	.000	.000	.000
3300	4.568	18.571	97.800	.000	.000	.000
3400	4.572	18.548	88.927	.000	.000	.000
3500	4.575	18.524	79.354	.000	.000	.000
3600	4.579	18.498	69.081	.000	.000	.000
3700	4.583	18.471	58.108	.000	.000	.000
3800	4.586	18.442	46.445	.000	.000	.000
3900	4.590	18.411	34.092	.000	.000	.000
4000	4.593	18.378	21.050	.000	.000	.000
4100	4.596	18.343	7.319	.000	.000	.000
4200	4.600	18.306	-13.100	.000	.000	.000
4300	4.603	18.267	-28.214	.000	.000	.000
4400	4.607	18.226	-43.042	.000	.000	.000
4500	4.610	18.183	-57.584	.000	.000	.000
4600	4.613	18.138	-71.841	.000	.000	.000
4700	4.617	18.091	-85.814	.000	.000	.000
4800	4.620	18.042	-99.503	.000	.000	.000
4900	4.624	17.991	-112.908	.000	.000	.000
5000	4.627	17.938	-126.030	.000	.000	.000
5100	4.630	17.883	-138.869	.000	.000	.000
5200	4.633	17.826	-151.426	.000	.000	.000
5300	4.637	17.767	-163.701	.000	.000	.000
5400	4.640	17.706	-175.694	.000	.000	.000
5500	4.643	17.643	-187.415	.000	.000	.000
5600	4.647	17.578	-198.864	.000	.000	.000
5700	4.650	17.511	-210.041	.000	.000	.000
5800	4.653	17.442	-220.946	.000	.000	.000
5900	4.656	17.371	-231.579	.000	.000	.000
6000	4.660	17.298	-241.940	.000	.000	.000

$\Delta H_f^0 = 0 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^{298.15} = 0 \text{ kcal. mole}^{-1}$   
 $\Delta H_{t1} = 96.01 \pm 0.5 \text{ cal. mole}^{-1}$   
 $\Delta H_{t2} = 0.38 \pm 0.2 \text{ cal. mole}^{-1}$   
 $\Delta H_m = 410.52 \pm 0.5 \text{ cal. mole}^{-1}$   
 $\Delta H_g^{298.15} = 66.68 \pm 0.3 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 7.63 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_{t1} = 368.54^\circ \text{K.}$   
 $T_{t2} = 374^\circ \text{K.}$   
 $T_m = 388.36^\circ \text{K.}$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

E. D. Eastman and W. C. McGavock, J. Am. Chem. Soc. 59, 145 (1937), have measured the low temperature heat capacities of sulfur from 15° to 375°K. E. D. West, J. Am. Chem. Soc. 81, 29 (1959), has measured the high temperature heat capacities from 298° to 678°K. These two sets of data were joined smoothly at 298.15 K. by a graphical method.

The values of entropy at 110°C and above in E. D. West's paper (table VIII) have been lowered by 0.5641 Joule. deg.<sup>-1</sup> mole<sup>-1</sup> because of a calculational error which was pointed out by J. P. McCullough and D. W. Scott, private communication, Sept. 27, 1960.

The entropy of rhombic sulfur at 298.15°K. was taken from E. D. Eastman and W. C. McGavock, loc. cit., based on an extrapolation of  $S_{15}^0 = 0.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ .

Transition Data.

The enthalpies of transition at 368.54°K. and 374°K. were obtained from E. D. West, loc. cit. The first transition at 368.54°K. was the known rhombic-monoclinic transition, but the second one near 374°K. was a previously unreported transition.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Heat of Sublimation.

The heat of sublimation of sulfur (c) is the heat of formation of monatomic sulfur (g). See S(g) table for details. Since S<sub>8</sub> and lower polymers are major vapor species at room temperature, the heat of sublimation to the equilibrium gas is much smaller. See S<sub>8</sub>(g) table for details.

T, °K.	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> <sup>0</sup>	ΔF <sub>f</sub> <sup>0</sup>	Log K <sub>p</sub>
0	.000	.000	INFINITE	1.053	.000	.000	.000
100	3.060	2.965	11.855	.489	.000	.000	.000
200	4.639	5.422	8.104	.469	.000	.000	.000
298	5.441	7.631	7.631	.000	.000	.000	.000
300	5.442	7.665	7.632	.013	.000	.000	.000
400	7.133	9.571	7.871	.683	.429	.012	.007
500	8.419	11.013	8.352	1.327	.720	.158	.069
600	9.504	12.317	8.911	2.044	.860	.349	.127
700	10.419	13.525	9.485	2.828	.876	.577	.180
800	11.176	14.664	10.062	3.682	13.847	.486	.133
900	11.804	15.749	10.634	4.603	13.164	1.134	.280
1000	12.327	16.792	11.198	5.584	12.814	2.738	.598
1100	12.753	17.800	11.752	6.623	12.198	4.283	.847
1200	13.104	18.781	12.283	7.719	11.195	5.731	1.044
1300	13.384	19.738	12.797	8.872	10.743	7.134	1.200
1400	13.606	20.672	13.282	10.081	9.946	8.485	1.325
1500	13.776	21.585	13.737	11.357	9.000	9.770	1.423
1600	13.901	22.490	14.168	12.697	8.107	10.996	1.502
1700	14.007	23.390	14.582	14.087	7.085	12.158	1.563
1800	14.093	24.270	14.985	15.526	5.996	13.259	1.610
1900	14.161	25.139	15.375	17.019	4.839	14.298	1.645
2000	14.214	25.998	15.746	18.556	3.613	15.274	1.669

$\Delta H_f^{298.15} = 8.44 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_m^{\circ} = 410.52 \pm 0.5 \text{ cal. mole}^{-1}$   
 $\Delta H_v^{\circ} = [2.30] \text{ kcal. mole}^{-1}$

$S_{298.15}^{\circ} = 8.44 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $T_m = 308.36^{\circ}\text{K.}$   
 $T_b = 717.75^{\circ}\text{K.}$

Heat of Formation.

The  $\Delta H_f^{298.15} (S, l)$  was obtained from that of the crystal by adding  $\Delta H_m^{\circ}$  and the difference between  $H_{398.36}^{\circ}$  and  $H_{298.15}^{\circ}$  for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was obtained from E. D. West, J. Am. Chem. Soc. 81, 29 (1959). No simple equation fits the curve of  $C_p$  against T which shows a peak.

The value of  $S_{298.15}^{\circ} (S, l)$  was obtained in a manner analogous to that of the heat of formation. The heat capacity of sulfur (liquid) below the melting point was assumed to be constant as 7.579 cal. deg.<sup>-1</sup> mole<sup>-1</sup>; and above the boiling point, it was assumed as 7.694 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Vaporization Data.

According to the international practical temperature scale, the boiling point is 717.75°K. The heat of vaporization to the equilibrium vapor mixture was estimated by D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., 1956. The equilibrium vapor involves monomeric and several polymeric species; S<sub>2</sub> and S predominate above 1000°K. while S<sub>8</sub>, S<sub>6</sub> and possible S<sub>4</sub> and S<sub>3</sub> are favored at lower temperatures.

T, °K.	C <sub>p</sub> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	S <sup>o</sup> -(F <sup>o</sup> -H <sub>298</sub> )/T	H <sup>o</sup> -H <sub>298</sub> kcal. mole <sup>-1</sup>	ΔF <sup>o</sup>	Log K <sub>p</sub>
0					
100	7.579	8.444	+0.00	+0.93	-0.068
200	7.579	8.444	+0.00	+0.92	-0.067
300	7.579	8.444	+0.00	+0.92	-0.067
400	7.579	8.444	+0.00	+0.92	-0.067
500	7.579	8.444	+0.00	+0.92	-0.067
600	7.579	8.444	+0.00	+0.92	-0.067
700	7.579	8.444	+0.00	+0.92	-0.067
800	7.579	8.444	+0.00	+0.92	-0.067
900	7.579	8.444	+0.00	+0.92	-0.067
1000	7.579	8.444	+0.00	+0.92	-0.067
1100	7.694	8.444	+0.00	+0.93	-0.068
1200	7.694	8.444	+0.00	+0.93	-0.068
1300	7.694	8.444	+0.00	+0.93	-0.068
1400	7.694	8.444	+0.00	+0.93	-0.068
1500	7.694	8.444	+0.00	+0.93	-0.068
1600	7.694	8.444	+0.00	+0.93	-0.068
1700	7.694	8.444	+0.00	+0.93	-0.068
1800	7.694	8.444	+0.00	+0.93	-0.068
1900	7.694	8.444	+0.00	+0.93	-0.068
2000	7.694	8.444	+0.00	+0.93	-0.068

SULFUR, MONATOMIC (S) (IDEAL GAS) AT. WT. = 32.064

Ground State Configuration  $3p_2$   
 $\Delta H_f^0 = 40.1 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 $\Delta H_f^0 = 66.14 \pm 0.5 \text{ kcal. mole}^{-1}$   
 $\Delta H_f^0 = 66.68 \pm 0.5 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\epsilon_1$	$\epsilon_1$ , cm. <sup>-1</sup>	$g_1$	$\epsilon_1$	$\epsilon_1$ , cm. <sup>-1</sup>	$g_1$
0	0.0	5	67,878.03	9	75,921.14
3	596.8	3	67,880.45	7	74,269.2
5	573.6	1	67,888.25	5	74,270.28
9	9,239.0	3	67,885.97	3	74,272.32
1	22,181.4	1	67,884.67	1	75,342.02
5	52,623.68	5	69,238.7	5	76,706.70
5	55,331.15	3	70,165.9	3	77,986.31
3	63,446.36	3	70,166.8	5	78,338.35
5	63,457.33	5	70,170.7	7	79,014.3
7	63,475.26	7	[70,706.0]	5	79,782.1
1	64,891.71	1	71,352.5	3	80,158.61
3	64,889.23	3	72,025.5	5	80,634.
5	64,892.89	5	72,382.5	3	81,089.9
7	67,816.87	3	72,572.4	1	81,405.23
5	67,825.72	5	73,911.53	3	81,864.6
7	67,843.38	7	73,915.16	5	82,353.3

Heat of Formation.

L. Brewer, J. Chem. Phys. 21, 1143 (1959), has reviewed the three possible values of  $D_0^0(S_2)$ , i.e. 4.4 e.v., 3.6 e.v. and 3.3 e.v., which were due to the ambiguity of defining the excitation state of the atomic products resulting from predissociation in the spectroscopic measurements. The value of 4.4 e.v. (101.5 kcal. mole<sup>-1</sup>) was shown to be the most probable one. Since this review, further support for his value have been given by the following investigators. J. R. Marquart, Dissertation Abstract 24, 5027 (1964), has found that the value of  $D_0^0(S_2)$  to be consistent with the value of 4.4 e.v. in mass spectrometric studies. R. Collin, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. 60, 306 (1964), have found  $D_0^0(S_2) = 97 \pm 5 \text{ kcal. mole}^{-1}$  in their mass-spectrometric studies of the vaporization of  $CaS$ ,  $Bas$ ,  $Sns$  and  $Pbs$ , but they reported a revised value, i.e.  $D_0^0(S_2) = 101 \pm 1 \text{ kcal. mole}^{-1}$ , which was given in the note in proof. A. N. Singh and D. K. Rai, J. Chem. Phys. 43, 2151 (1965), have selected the best value of  $D_0^0(S_2) = 4.4 \text{ e.v.}$  in theoretical comparisons of the potential-energy curve. As pointed out by L. Brewer, loc. cit., and A. G. Daydon, "Dissociation Energies", Chapman and Hall Ltd., 2nd. Ed., London, 1953, the old vapor pressure measurements which are not consistent with  $D_0^0(S_2) = 4.4 \text{ e.v.}$  (101.5 kcal. mole<sup>-1</sup>) are probably not reliable.

The value  $D_0^0(S_2, g) = 4.4 \text{ e.v.}$  (101.5 kcal. mole<sup>-1</sup>) was selected as the dissociation energy of diatomic sulfur, and combination of this value with heat of formation of diatomic sulfur gives the heat of formation of monatomic sulfur,  $\Delta H_f^0$  298 (S, g) = 66.68 kcal. mole<sup>-1</sup>.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weight were obtained from C. E. Moore, "Atomic Energy Levels", Vol. 1, National Bureau of Standards Circular 467, June, 1949.

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

T, °K.	$C_p$	$S^0$	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\Delta H_f^0$	$\Delta F_f^0$	Log K <sub>p</sub>
0	4.000	INFINITE	-	1.591	66.142	66.142	INFINITE
100	5.253	34.127	45.046	1.092	63.761	-138.468	-
200	5.589	37.631	40.604	1.555	60.621	-65.758	-
298	5.659	40.986	40.086	4.000	57.004	-41.783	-
300	5.658	40.121	40.086	4.010	56.944	-41.481	-
400	5.534	41.736	40.407	1.272	60.143	-29.349	-
500	5.436	42.967	40.770	1.421	65.754	-22.161	-
600	5.340	43.944	41.176	1.659	67.363	-17.363	-
700	5.250	44.762	41.634	2.134	64.753	-11.972	-
800	5.171	45.491	42.049	2.715	60.580	-6.587	-
900	5.109	46.142	42.426	3.332	59.795	-6.512	-
1000	5.137	46.815	42.766	3.747	52.019	-6.250	-
1100	5.112	47.103	43.231	4.260	36.317	-7.215	-
1200	5.079	47.547	43.672	4.770	34.881	-6.532	-
1300	5.079	47.954	43.864	5.279	33.440	-5.622	-
1400	5.070	48.331	44.198	5.786	31.992	-4.994	-
1500	5.064	48.680	44.466	6.293	30.540	-4.449	-
1600	5.062	49.007	44.758	6.709	29.085	-3.973	-
1700	5.063	49.314	45.017	7.305	27.626	-3.551	-
1800	5.068	49.603	45.263	7.812	26.165	-3.177	-
1900	5.075	49.877	45.499	8.319	24.701	-2.841	-
2000	5.085	50.138	45.725	8.827	23.232	-2.539	-
2100	5.097	50.386	45.941	9.336	21.761	-2.265	-
2200	5.112	50.624	46.148	9.846	20.287	-2.015	-
2300	5.127	50.851	46.346	10.358	18.811	-1.787	-
2400	5.144	51.070	46.540	10.872	17.332	-1.578	-
2500	5.162	51.280	46.725	11.387	15.851	-1.386	-
2600	5.181	51.483	46.905	11.904	14.367	-1.208	-
2700	5.200	51.679	47.078	12.423	12.879	-1.042	-
2800	5.219	51.869	47.246	12.944	11.387	-0.889	-
2900	5.239	52.052	47.408	13.467	9.898	-0.746	-
3000	5.258	52.230	47.566	13.992	8.405	-0.612	-
3100	5.277	52.403	47.719	14.519	6.908	-0.487	-
3200	5.295	52.571	47.866	15.048	5.408	-0.369	-
3300	5.313	52.734	48.013	15.578	3.907	-0.259	-
3400	5.331	52.893	48.154	16.110	2.406	-0.155	-
3500	5.347	53.047	48.292	16.644	0.901	-0.056	-
3600	5.363	53.198	48.426	17.180	-0.606	0.037	-
3700	5.378	53.345	48.557	17.717	-2.115	0.125	-
3800	5.392	53.489	48.685	18.255	-3.628	0.209	-
3900	5.406	53.629	48.810	18.793	-5.142	0.288	-
4000	5.419	53.766	48.932	19.336	-6.655	0.364	-
4100	5.430	53.900	49.052	19.879	-8.174	0.436	-
4200	5.441	54.031	49.165	20.422	-9.694	0.504	-
4300	5.451	54.159	49.273	20.967	-11.216	0.570	-
4400	5.460	54.285	49.386	21.513	-12.742	0.633	-
4500	5.470	54.408	49.506	22.059	-14.267	0.693	-
4600	5.477	54.528	49.613	22.607	-15.795	0.750	-
4700	5.485	54.646	49.719	23.155	-17.326	0.806	-
4800	5.491	54.761	49.822	23.703	-18.857	0.858	-
4900	5.497	54.875	49.925	24.253	-20.390	0.909	-
5000	5.502	54.986	50.025	24.803	-21.927	0.958	-
5100	5.507	55.095	50.124	25.353	-23.462	1.005	-
5200	5.511	55.202	50.220	25.904	-25.001	1.051	-
5300	5.515	55.307	50.315	26.456	-26.542	1.094	-
5400	5.518	55.410	50.409	27.007	-28.082	1.136	-
5500	5.521	55.511	50.500	27.559	-29.625	1.177	-
5600	5.523	55.611	50.591	28.111	-31.172	1.216	-
5700	5.525	55.708	50.680	28.664	-32.716	1.250	-
5800	5.526	55.805	50.767	29.216	-34.269	1.279	-
5900	5.528	55.899	50.853	29.769	-35.818	1.317	-
6000	5.529	55.992	50.938	30.322	-37.366	1.361	-

T, °K	C <sub>p</sub>	S°	-(F°-H° <sub>298</sub> )/T	H°-H° <sub>298</sub>	ΔH <sub>f</sub> °	ΔF <sub>f</sub> °	Log K <sub>f</sub>
0	.000	INFINITE	-	2.141	30.805	30.805	INFINITE
100	6.964	46.623	61.075	1.445	27.104	27.104	- 59.232
200	7.265	51.515	55.704	.738	23.040	23.040	- 25.176
298	7.759	54.510	.000	.000	19.138	19.138	- 14.028
300	7.768	54.528	.014	.014	19.066	19.066	- 13.889
400	8.144	56.848	54.819	.811	15.233	15.233	- 8.323
500	8.389	58.693	55.416	1.639	11.806	11.806	- 5.160
600	8.549	60.238	56.094	2.486	8.575	8.575	- 3.123
700	8.658	61.594	56.783	3.344	5.423	5.423	- 1.762
800	8.735	62.726	57.455	4.217	.000	.000	.000
900	8.782	63.758	58.099	5.093	.000	.000	.000
1000	8.836	64.687	58.712	5.975	.000	.000	.000
1100	8.870	65.521	59.294	6.860	.000	.000	.000
1200	8.899	66.304	59.846	7.749	.000	.000	.000
1300	8.922	67.037	60.371	8.640	.000	.000	.000
1400	8.942	67.719	60.870	9.533	.000	.000	.000
1500	8.959	68.356	61.344	10.428	.000	.000	.000
1600	8.976	68.975	61.797	11.325	.000	.000	.000
1700	8.992	69.574	62.230	12.223	.000	.000	.000
1800	9.007	69.934	62.643	13.123	.000	.000	.000
1900	9.014	70.121	63.040	14.024	.000	.000	.000
2000	9.023	70.884	63.421	14.926	.000	.000	.000
2100	9.036	71.324	63.787	15.829	.000	.000	.000
2200	9.046	71.745	64.139	16.733	.000	.000	.000
2300	9.055	72.147	64.479	17.638	.000	.000	.000
2400	9.064	72.533	64.806	18.544	.000	.000	.000
2500	9.073	72.903	65.123	19.451	.000	.000	.000
2600	9.081	73.259	65.429	20.358	.000	.000	.000
2700	9.090	73.602	65.725	21.267	.000	.000	.000
2800	9.098	73.932	66.012	22.176	.000	.000	.000
2900	9.106	74.252	66.291	23.086	.000	.000	.000
3000	9.113	74.561	66.562	23.997	.000	.000	.000
3100	9.121	74.860	66.824	24.909	.000	.000	.000
3200	9.129	75.149	67.080	25.822	.000	.000	.000
3300	9.136	75.430	67.329	26.735	.000	.000	.000
3400	9.143	75.703	67.571	27.649	.000	.000	.000
3500	9.150	75.968	67.807	28.563	.000	.000	.000
3600	9.158	76.226	68.038	29.479	.000	.000	.000
3700	9.165	76.477	68.262	30.395	.000	.000	.000
3800	9.172	76.722	68.482	31.312	.000	.000	.000
3900	9.179	76.960	68.696	32.229	.000	.000	.000
4000	9.186	77.193	68.906	33.148	.000	.000	.000
4100	9.192	77.419	69.111	34.066	.000	.000	.000
4200	9.199	77.641	69.311	34.986	.000	.000	.000
4300	9.206	77.858	69.507	35.906	.000	.000	.000
4400	9.213	78.069	69.698	36.827	.000	.000	.000
4500	9.220	78.276	69.886	37.749	.000	.000	.000
4600	9.226	78.479	70.072	38.671	.000	.000	.000
4700	9.233	78.678	70.252	39.594	.000	.000	.000
4800	9.240	78.873	70.427	40.518	.000	.000	.000
4900	9.247	79.063	70.605	41.442	.000	.000	.000
5000	9.253	79.250	70.776	42.367	.000	.000	.000
5100	9.260	79.433	70.944	43.293	.000	.000	.000
5200	9.266	79.613	71.109	44.219	.000	.000	.000
5300	9.273	79.789	71.271	45.146	.000	.000	.000
5400	9.280	79.963	71.431	46.074	.000	.000	.000
5500	9.286	80.133	71.587	47.002	.000	.000	.000
5600	9.293	80.300	71.741	47.931	.000	.000	.000
5700	9.299	80.465	71.893	48.861	.000	.000	.000
5800	9.306	80.627	72.042	49.791	.000	.000	.000
5900	9.312	80.786	72.189	50.722	.000	.000	.000
6000	9.319	80.942	72.334	51.653	.000	.000	.000

SULFUR, DIATOMIC (S<sub>2</sub>)

(IDEAL GAS)

MOL. WT. = 64.128

Ground State Configuration  $3 \Sigma_g^-$

$\Delta H_f^0 = 30.80 \pm 0.2$  kcal. mole<sup>-1</sup>

$\Delta H_f^{298.15} = 54.51$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>

$\Delta H_f^{298.15} = 30.84 \pm 0.2$  kcal. mole<sup>-1</sup>

Electronic Levels and Quantum Weight

E, cm. <sup>-1</sup>	g <sub>l</sub>
0	3

$\omega_e x_e = 2.852$  cm.<sup>-1</sup>

$\omega_e = 724.66$  cm.<sup>-1</sup>

$\alpha_e = 0.2948$  cm.<sup>-1</sup>

$\alpha_e = 0.0016$  cm.<sup>-1</sup>

$\sigma = 2$

$r_e = 1.889$  Å

Heat of Formation.

The standard enthalpy of formation of gaseous diatomic sulfur,  $\Delta H_f^{298} = 30.84$  kcal. mole<sup>-1</sup>, was calculated from  $\Delta H_f^{298} = -20.30$  kcal. mole<sup>-1</sup> for the reaction  $H_2(g) + 0.5 S_2(g) \rightarrow H_2S(g)$  with JANAF value  $\Delta H_f^{298}(H_2S, g) = -4.88 \pm 0.15$  kcal. mole<sup>-1</sup>. The  $\Delta H_f^{298}$  was obtained by the second and third law analyses of equilibrium constants which have been determined by G. Freuner and W. Schupp (ref. 1) and M. Randall and P. R. Bichowsky (ref. 2). The results obtained are presented as follows:

Ref.	Temp. Range	Points	ΔH <sub>f</sub> <sup>298</sup> kcal. mole <sup>-1</sup>	2nd law ΔH <sub>f</sub> <sup>298</sup> kcal. mole <sup>-1</sup>	3rd law ΔH <sub>f</sub> <sup>298</sup> kcal. mole <sup>-1</sup>	Drift cal. mole <sup>-1</sup> deg. <sup>-1</sup>
1	1023-1405°K	5	-19.92 ± 0.13	-20.285	-20.285	-0.282 ± 0.097
2	1362-1667°K	4	-20.74 ± 0.40	-20.74 ± 0.40	-20.307	+0.281 ± 0.269
3	1023-1667°K	9	-20.13 ± 0.12	-20.13 ± 0.12	-20.300	-0.066 ± 0.093

References

- G. Freuner and W. Schupp, Z. Physik Chem. **58**, 157 (1910).
- M. Randall and P. R. Bichowsky, J. Am. Chem. Soc. **40**, 368 (1918).
- Combination of above references.

The third law value of the combination set was selected to calculate the heat of formation of diatomic sulfur.

The dissociation energy of gaseous diatomic sulfur,  $D_0(S_2) = 101.5$  kcal. mole<sup>-1</sup>, was chosen. For discussions see JANAF monatomic sulfur (g) and sulfur monoxide (g) tables.

Heat Capacity and Entropy.

The molecular constants which were taken from G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, have been modified for the natural isotopic abundances reported by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. **30**, 585 (1958).

# INDEX TO TABLES IN THIS PUBLICATION

The tables prefixed by asterisks (\*) are revisions superseding the corresponding tables in PB 166370, issued August 1965. The rest are new tables.

Filing Order	Table Title	Filing Order	Table Title	Filing Order	Table Title
A1	*Aluminum (ref. st.)	CB <sub>4</sub>	*Boron Carbide (1)	Cl <sub>2</sub> Mg	*Magnesium Dichloride (g)
A1	*Aluminum (c)	CC10	Carbonyl Monochloride (g)	Cl <sub>2</sub> O	*Chlorine Monoxide (g)
A1	*Aluminum (1)	CPO	Carbonyl Monofluoride (g)	Cl <sub>3</sub> Co <sub>3</sub>	Copper Monochloride, Trimeric (g)
A1	*Aluminum, Monatomic (g)	CKN	*Potassium Cyanide (c)	Cl <sub>3</sub> Fe	Iron Trichloride (c)
A1 <sup>+</sup>	*Aluminum Unipositive Ion (g)	CKN	*Potassium Cyanide (1)	HNao	*Sodium Hydroxide (c)
AlF <sub>3</sub>	*Aluminum Trifluoride (c)	CKN	*Potassium Cyanide (g)	HNao	*Sodium Hydroxide (1)
AlF <sub>3</sub>	*Aluminum Trifluoride (g)	CK <sub>2</sub> O <sub>3</sub>	*Potassium Carbonate (c)	HNao	*Sodium Hydroxide (g)
AlF <sub>3</sub> Ne <sub>3</sub>	*Cryolite (c)	CK <sub>2</sub> O <sub>3</sub>	*Potassium Carbonate (1)	HO	*Hydroxyl (g)
AlO	*Aluminum Monoxide (g)	CLi <sub>2</sub> O <sub>3</sub>	Lithium Carbonate (c)	HO <sup>+</sup>	Hydroxyl Unipositive Ion (g)
Al <sub>2</sub> O	*Aluminum Suboxide (g)	CLi <sub>2</sub> O <sub>3</sub>	Lithium Carbonate (1)	HO <sup>+</sup>	Hydroxyl Unipositive Ion (g)
Al <sub>2</sub> O <sub>2</sub>	*Aluminum Monoxide, Dimeric (g)	CNNa	*Sodium Cyanide (c)	H <sub>2</sub> P <sub>2</sub> O <sub>2</sub>	*Potassium Hydroxide, Dimeric (g)
Al <sub>2</sub> O <sub>3</sub>	*Aluminum Oxide (c, gamma)	CNNa	*Sodium Cyanide (1)	H <sub>2</sub> P <sub>2</sub> O <sub>2</sub>	*Lithium Hydroxide, Dimeric (g)
BBF <sub>2</sub> H	*Boron Dibromide Hydride (g)	CNNa	*Sodium Cyanide (g)	H <sub>2</sub> N <sub>2</sub>	*Amidogen (g)
BCl <sub>2</sub> H	*Boron Dichloride Hydride (g)	CNNa	*Sodium Cyanide (g)	H <sub>2</sub> N <sub>2</sub>	Dimide (g)
BF <sub>2</sub> H	*Boron Dichloride Hydride (g)	CNa <sub>2</sub> O <sub>3</sub>	*Sodium Carbonate (c)	H <sub>2</sub> Na <sub>2</sub> O <sub>2</sub>	Sodium Hydroxide, Dimeric (g)
BF <sub>2</sub> O	Difluoroborane (g)	CNa <sub>2</sub> O <sub>3</sub>	*Sodium Carbonate (1)	H <sub>2</sub> S	*Hydrogen Sulfide (g)
BF <sub>3</sub>	*Boron Trifluoride (g)	CO	*Carbon Dioxide (g)	H <sub>3</sub> N	*Ammonia (g)
BT1	*Titanium Monoboride (c)	CO <sub>2</sub>	*Carbon Dioxide (g)	H <sub>4</sub> N <sub>2</sub>	Hydrazine (1)
B <sub>2</sub> BeO <sub>4</sub>	*Beryllium Diborate (g)	C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane (g)	H <sub>4</sub> N <sub>2</sub>	Hydrazine (1)
B <sub>2</sub> H <sub>4</sub> O <sub>4</sub>	*Boron Dihydroxide, Dimeric (c)	C <sub>2</sub> H <sub>4</sub>	*Ethylene (g)	MgO	*Magnesium Oxide (c)
B <sub>2</sub> H <sub>4</sub> O <sub>4</sub>	*Boron Dihydroxide, Dimeric (g)	C <sub>2</sub> H <sub>4</sub> O	*Ethylene Oxide (g)	MgO	*Magnesium Oxide (1)
B <sub>2</sub> Tl	*Titanium Diboride (1)	C <sub>2</sub> K <sub>2</sub> N <sub>2</sub>	*Potassium Cyanide, Dimeric (g)	Mg <sub>4</sub> S	*Magnesium Sulfate (c)
B <sub>2</sub> Tl	*Titanium Diboride (c)	C <sub>2</sub> N <sub>2</sub> Ne <sub>2</sub>	*Sodium Cyanide, Dimeric (g)	Mg <sub>4</sub> S	*Magnesium Sulfate (1)
B <sub>2</sub> Zr	*Zirconium Diboride (1)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (c)	Mg <sub>2</sub> S	*Magnesium Sulfate (1)
B <sub>3</sub> PH <sub>2</sub> O <sub>3</sub>	*Monofluoroboroxin (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	NO <sub>2</sub>	*Nitrogen Dioxide Negative Ion (g)
B <sub>3</sub> P <sub>2</sub> HO <sub>3</sub>	*Difluoroboroxin (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	N <sub>2</sub>	Nitrogen (ref. st., g)
B <sub>4</sub> Li <sub>2</sub> O <sub>7</sub>	*Dilithium Tetraborate (1)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	Ne <sub>2</sub> O <sub>3</sub> S1	*Sodium Metasilicate (c)
B <sub>4</sub> Li <sub>2</sub> O <sub>7</sub>	*Beryllium Unipositive Ion (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	Ne <sub>2</sub> O <sub>3</sub> S1	*Sodium Metasilicate (1)
Be <sup>+</sup>	*Beryllium Unipositive Ion (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	Ne <sub>2</sub> O <sub>3</sub> S1 <sub>2</sub>	*Sodium Disilicate (c)
BeBr <sub>2</sub>	*Beryllium Dibromide (1)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	Ne <sub>2</sub> O <sub>3</sub> S1 <sub>2</sub>	*Sodium Disilicate (1)
BeBr <sub>2</sub>	*Beryllium Dibromide (c)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sup>-</sup>	Oxygen Unipositive Ion (g)
BeBr <sub>2</sub>	*Beryllium Dibromide (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	OS	*Sulfur Monoxide (g)
BeCl <sub>2</sub>	*Beryllium Chloride Fluoride (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	OS <sub>2</sub>	Disulfur Monoxide (g)
BeCl <sub>2</sub>	*Beryllium Chloride, Alpha-(c, alpha)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	OZr	*Zirconium Monoxide (g)
BeCl <sub>2</sub>	*Beryllium Chloride, Beta-(c, beta)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>2</sub> Zr	*Zirconium Dioxide (1)
BeCl <sub>2</sub>	*Beryllium Dichloride (1)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>2</sub> Zr	*Zirconium Dioxide (g)
BeCl <sub>2</sub>	*Beryllium Dichloride (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>3</sub> PBS1	Lead Metasilicate (c)
BeI <sub>2</sub>	*Beryllium Diiodide (c)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>3</sub> S	*Sulfur Trioxide (g)
BeI <sub>2</sub>	*Beryllium Diiodide (1)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>3</sub> Pb <sub>2</sub> S1	Lead Orthosilicate (c)
BeI <sub>2</sub>	*Beryllium Diiodide (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>4</sub> SiZr	*Zirconium Orthosilicate (c)
Be <sub>2</sub> Cl <sub>4</sub>	*Beryllium Dichloride, Dimeric (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>10</sub> P <sub>4</sub>	*Phosphorus Pentoxide, Dimeric (c)
Be <sub>2</sub> O <sub>4</sub> S1	*Beryllium Orthosilicate (c)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	O <sub>10</sub> P <sub>4</sub>	*Phosphorus Pentoxide, Dimeric (g)
BrCl	*Bromine Monochloride (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	S	*Sulfur (c)
BrF	*Bromine Monofluoride (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	S	*Sulfur (1)
BrF <sub>3</sub>	*Bromine Trifluoride (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	S	*Sulfur, Monatomic (g)
BrF <sub>5</sub>	*Bromine Pentafluoride (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)	S <sub>2</sub>	*Sulfur, Monatomic (g)
BrH	*Hydrogen Bromide (g)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)		
BrH <sub>4</sub> N	*Ammonium Bromide (c)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)		
CB <sub>4</sub>	*Boron Carbide (c)	C <sub>3</sub> Al <sub>4</sub>	*Aluminum Carbide (1)		