

Beryllium (Be) $A_1 = 9.01218$ Beryllium (Be) $Be_1(\text{ref})$

REFERENCE STATE

0 to 1577 K crystal, alpha
 1577 to 1560 K crystal, beta
 1560 to 2741.437 K liquid
 above 2741.437 K ideal monatomic gas

Refer to the individual tables for details.

T/K	C_p^0	Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^0 = 0.1$ MPa		$\log K_r$
		$S^0 - [G^0 - H^0(T_r)]/T$	$S^0 - [G^0 - H^0(T_r)]/T$	$H^0 - H^0(T_r)$	$\Delta_r G^0$	
0	0.	0.	INFINITE	-1.932	0.	0.
100	1.819	0.503	19.434	-1.893	0.	0.
200	9.984	4.174	10.751	-1.315	0.	0.
298.15	16.380	9.440	9.440	0.	0.	0.
300	16.472	9.542	9.440	0.030	0.	0.
400	19.965	14.817	10.136	1.872	0.	0.
500	21.943	19.501	11.551	3.975	0.	0.
600	23.336	23.630	13.227	6.242	0.	0.
700	24.463	27.314	14.981	8.634	0.	0.
800	25.458	30.647	16.734	11.130	0.	0.
900	26.384	33.699	18.452	13.723	0.	0.
1000	27.274	36.525	20.119	16.406	0.	0.
1100	28.147	39.166	21.732	19.177	0.	0.
1200	29.016	41.652	23.290	22.035	0.	0.
1300	29.886	44.009	24.793	24.980	0.	0.
1400	30.763	46.256	26.247	28.013	0.	0.
1500	31.650	48.409	27.653	31.133	0.	0.
1527.000	31.892	48.975	28.025	31.991	0.	0.
1527.000	30.000	53.461	28.025	38.840	0.	0.
1560.000	30.000	54.102	28.570	39.830	0.	0.
1560.000	28.788	59.163	28.570	47.725	0.	0.
1600	28.874	59.893	29.344	48.879	0.	0.
1700	29.089	61.650	31.193	51.777	0.	0.
1800	29.304	63.319	32.932	54.696	0.	0.
1900	29.519	64.909	34.573	57.638	0.	0.
2000	29.734	66.429	36.128	60.600	0.	0.
2100	29.949	67.884	37.606	63.584	0.	0.
2200	30.164	69.283	39.014	66.590	0.	0.
2300	30.379	70.628	40.360	69.617	0.	0.
2400	30.584	71.926	41.648	72.666	0.	0.
2500	30.809	73.179	42.885	75.736	0.	0.
2600	31.024	74.391	44.073	78.828	0.	0.
2700	31.239	75.566	45.218	81.941	0.	0.
2741.437	31.328	76.043	45.680	83.237	0.	0.
2741.437	20.883	182.400	45.680	374.809	0.	0.
2800	20.905	182.842	48.545	376.032	0.	0.
2900	20.949	183.576	53.188	378.125	0.	0.
3000	21.006	184.287	57.546	380.223	0.	0.
3100	21.075	184.977	61.646	382.327	0.	0.
3200	21.159	185.648	65.511	384.438	0.	0.
3300	21.259	186.300	69.161	386.559	0.	0.
3400	21.376	186.937	72.616	388.691	0.	0.
3500	21.512	187.558	75.891	390.835	0.	0.
3600	21.668	188.166	79.001	392.994	0.	0.
3700	21.844	188.762	81.960	395.169	0.	0.
3800	22.041	189.347	84.778	397.363	0.	0.
3900	22.259	189.923	87.467	399.578	0.	0.
4000	22.500	190.489	90.035	401.816	0.	0.
4100	22.761	191.048	92.492	404.079	0.	0.
4200	23.045	191.600	94.845	406.369	0.	0.
4300	23.349	192.146	97.102	408.688	0.	0.
4400	23.674	192.686	99.268	411.039	0.	0.
4500	24.019	193.222	101.350	413.424	0.	0.
4600	24.383	193.754	103.553	415.844	0.	0.
4700	24.764	194.284	105.782	418.301	0.	0.
4800	25.162	194.806	107.942	420.797	0.	0.
4900	25.576	195.311	108.936	423.334	0.	0.
5000	26.003	195.852	110.669	425.913	0.	0.
5200	26.894	196.889	113.965	431.202	0.	0.
5400	27.822	197.921	117.056	436.673	0.	0.
5600	28.776	198.950	119.962	442.332	0.	0.
5800	29.743	199.977	122.704	448.184	0.	0.
6000	30.711	201.001	125.297	454.229	0.	0.

PREVIOUS: September 1961 (1 atm)

CURRENT: September 1983 (1 bar)

Beryllium (Be)

$Be_1(\text{ref})$

Be₁(cr)

Beryllium (Be)

A_r = 9.01218

CRYSTAL(α-β)

Beryllium (Be)

$S^{\circ}(298.15\text{ K}) = 9.44 \pm 0.15\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $\Delta_{\text{cr}}H^{\circ} = 4.527 \pm 25\text{ K} (\alpha \rightarrow \beta)$
 $T_{\text{fus}} = 1560 \pm 5\text{ K} (\beta \rightarrow \text{l})$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted thermal functions for Be(α, β, cr) are derived from the studies of Ahlers (1.4–30 K),¹ Hill and Smith (4–300 K),² Ginnings *et al.* (367–1169 K),³ and Kantor *et al.* (600–3200 K).⁴ The mathematical and graphical treatment of these four studies yields a continuous and smooth heat capacity curve for α-Be(cr).

There are no heat capacity or enthalpy measurements for β-Be(cr). We assume a constant value of $C_p = 30.0\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the β-region. The entropy at 298.15 K is $0.06\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ less than that recommended by CODATA.⁵ This is undoubtedly due to the manner in which the data of Ahlers¹ and Hill and Smith² were merged. A detailed discussion of the heat capacities of all alkaline earth metals is in preparation.

Phase and Fusion Data

Cannon⁶ has summarized the data on the polymorphic phase changes and the variation of the melting temperature of beryllium with pressure. His critical evaluation results in the recommendation that at ambient pressure there are two stable phases. His recommendations are entirely attributable to the resistance studies of Francois and Contre.⁷ The phases are denoted alpha(hcp) and beta(bcc). The melting point of beryllium is fairly well defined. We adopt $T_{\text{fus}} = 1560 \pm 5\text{ K}$ based on the studies of Kantor *et al.*,⁴ Martin and Moore,⁸ Teitel and Cohen,⁹ and Loasby and Dearden.¹⁰

The alpha-beta transition is ill-defined. There are many conflicting studies as to the value of the transition temperature and the value and sign of the derivative (dT/dP) for this transition. We adopt $T_{\text{tr}} = 1527 \pm 25\text{ K}$ based on the study of Ammonenko, *et al.*¹¹

The enthalpies of transition and fusion are also poorly defined. Kantor, *et al.*,⁴ has measured the enthalpy of the crystal and liquid. No data points were obtained in the beta phase region. As a result, we can only derive a combined value for the enthalpy of transition and fusion. Following the suggestion of Ahey,¹² the enthalpy values of Loasby and Dearden¹⁰ and Ahey¹² have the same value for the ratio of the transition enthalpy to fusion enthalpy, even though the actual values for each enthalpy are quite different. Thus, using this ratio and the sum of the enthalpies, as determined by Kantor *et al.*,⁴ we calculate the individual enthalpies of transition and fusion. A much more detailed discussion is in progress.

Sublimation Data

Refer to the ideal gas table for details.

References

- G. Ahlers, *Phys. Rev.* **145**, 419 (1966).
- R. W. Hill and P. L. Smith, *Phil. Mag.* **44**, 636 (1953).
- D. C. Ginnings, T. B. Douglas, and A. F. Bail, *J. Am. Chem. Soc.* **73**, 1236 (1951).
- P. B. Kantor, R. M. Krasovitskaya, and A. N. Kisev, *Fiz. Metal. i Metalloved.*, Akad. Nauk SSSR **10**, 835 (1960) [*Phys. Metals Metallog.* **10** (6), 42 (1960)].
- J. D. Cox, Chairman, ICSU-CODATA Task Group on Key Values for Thermodynamics, *J. Chem. Thermodyn.* **10**, 903 (1978).
- J. F. Cannon, *J. Phys. Chem. Ref. Data* **3**, 781 (1974).
- M. Francois and M. Contre, *Conf. Int. Met. Beryllium, Commun.*, 3rd., pp. 201–11, (1965).
- A. J. Martin and A. Moore, *J. Less-Common Metals* **1**, 85 (1959).
- R. J. Teitel and M. Cohen, *J. Metl.* **185**, 285 (1949).
- R. G. Loasby and D. Dearden, *J. Less-Common Metals* **52**, 137 (1977).
- V. M. Amonenko, V. E. Ivanov, *et al.*, *Phys. Metals Metallog.* **12**, 77 (1962).
- A. Ahey, Lawrence Livermore National Laboratory, UCRL-55567, (1984).

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa	
		S ^o J·K ⁻¹ ·mol ⁻¹	-(G ^o -H ^o (T _r))/T	H ^o -H ^o (T _r)	Δ _r G ^o
0	0	0	INFINITE	-1.932	0
100	1.819	0.503	19.434	-1.893	0
200	9.984	4.174	10.751	-1.315	0
230	13.574	6.801	9.695	-0.723	0
298.15	16.380	9.440	9.440	0	0
300	16.472	9.542	9.440	0.030	0
350	18.570	12.245	9.649	0.909	0
400	19.965	14.817	10.136	1.872	0
450	21.061	17.235	10.792	2.899	0
500	21.943	19.501	11.551	3.975	0
600	23.336	23.630	13.227	6.242	0
700	24.463	27.314	14.981	8.634	0
800	25.438	30.647	16.734	11.130	0
900	26.384	33.699	18.452	13.723	0
1000	27.274	36.525	20.119	16.406	0
1100	28.147	39.166	21.732	19.177	0
1200	29.016	41.652	23.290	22.035	0
1300	29.886	44.009	24.793	24.980	0
1400	30.763	46.236	26.247	28.013	0
1500	31.650	48.409	27.653	31.133	0
1527.000	31.892	48.975	28.025	31.991	0
1527.000	30.000	53.461	28.025	38.840	0
1560.000	30.000	54.102	28.570	39.830	0
1600	30.000	54.862	29.218	41.030	0.202
1700	30.000	56.680	30.780	44.030	0.702
1800	30.000	58.395	32.267	47.030	1.196
1900	30.000	60.017	33.685	50.030	1.687
2000	30.000	61.556	35.041	53.030	2.175

ALPHA <- -> BETA
 TRANSITION
 BETA <- -> LIQUID

PREVIOUS September 1961

CURRENT: September 1983

Beryllium (Be)

Be₁(cr)

Be(l)

Beryllium (Be)

LIQUID

Beryllium (Be)

$S^{\circ}(298.15\text{ K}) = [19.539]\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 1560 \pm 5\text{ K}$ ($\beta \rightarrow \alpha$)
 $\Delta H^{\circ}(298.15\text{ K}) = [15.508]\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{liq}}H^{\circ} = 7.895 \pm 0.05\text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation of liquid beryllium is calculated from that of the crystal by adding $\Delta_{\text{liq}}H^{\circ}$ and the difference in enthalpy, $H^{\circ}(1560\text{ K}) - H^{\circ}(298.15\text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid is derived from the measured enthalpy data of Kantor *et al.*,¹ 17 data points in the liquid region, 1560 to 2200 K. The data was presented graphically. We adopt the reported equation: $C_p^{\circ} = 6.079 + 5.138 \times 10^{-4} T\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This equation is used to calculate extrapolated values from 2200 K to 3500 K and from 1150 K to 1560 K.

A glass transition temperature is assumed at 1150 K, below which the heat capacity values of crystalline beryllium are adopted. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Transition and Fusion Data

Refer to the crystal table for details.

Vaporization Data

There is only one reported vaporization study for Be(l): Baur and Brunner (926–1283 K).² This study was not considered in the analysis as it had an incorrect temperature dependence, as was also noted by Hultgren *et al.*³

The boiling point ($f = 1\text{ bar}$), $T_{\text{vap}} = 2741.437\text{ K}$, is calculated as the temperature for which $\Delta G^{\circ} = 0$ for Be(l) = Be(g). The difference in the enthalpy of formation of Be(l) and Be(g) at T_{vap} is the enthalpy of vaporization, $\Delta_{\text{vap}}H^{\circ} = 291.572\text{ kJ}\cdot\text{mol}^{-1}$.

References

- ¹P. B. Kantor, R. M. Krasovitskaya, and A. N. Kisel, *Fiz Metal and Metalloved.*, Akad. Nauk SSSR, **10**, 835 (1960).
- ²E. Baur and R. Brunner, *Helv. Chim. Acta* **17**, 958 (1934).
- ³R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals, Metals Park, Ohio, 636 pp. (1973).

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P ^o = 0.1 MPa		log K _r
		S ^o - [C _p ^o - F(T _r)]/T	H ^o - H ^o (T _r)	Δ _{liq} H ^o	ΔG ^o	
0						
100						
200						
250						
298.15	16.380	19.539	0.	15.508	12.497	-2.189
300	16.472	19.540	0.030	15.508	12.478	-2.173
350	18.570	22.344	0.909	15.508	11.973	-1.787
400	19.965	24.917	2.025	15.508	11.468	-1.498
450	21.061	27.334	2.879	15.508	10.963	-1.273
500	21.943	29.600	3.975	15.508	10.458	-1.093
600	23.336	33.730	6.242	15.508	9.448	-0.823
700	24.465	37.414	8.634	15.508	8.438	-0.630
800	25.458	40.746	11.150	15.508	7.428	-0.485
900	26.384	43.799	13.723	15.508	6.418	-0.372
1000	27.274	46.625	16.406	15.508	5.408	-0.282
1100	28.147	49.265	19.177	15.508	4.398	-0.209
1150.000	28.582	50.526	20.595	GLASS <--> LIQUID		
1150.000	27.907	50.526	20.595	TRANSITION		
1200	28.014	51.716	21.993	15.466	3.389	-0.148
1300	28.279	53.967	24.805	15.333	2.388	-0.096
1400	28.444	56.067	27.639	15.134	1.399	-0.052
1500	28.659	58.037	30.494	14.869	0.427	-0.015
1560.000	28.788	59.163	32.218	--- BETA <--> LIQUID ---		
1600	28.874	59.893	33.371	0.	0.	0.
1700	29.089	61.650	36.269	0.	0.	0.
1800	29.304	63.319	39.189	0.	0.	0.
1900	29.519	64.909	42.130	0.	0.	0.
2000	29.734	66.429	45.093	0.	0.	0.
2100	29.949	67.884	48.077	0.	0.	0.
2200	30.164	69.283	51.082	0.	0.	0.
2300	30.379	70.628	54.110	0.	0.	0.
2400	30.594	71.926	57.158	0.	0.	0.
2500	30.809	73.179	60.228	0.	0.	0.
2600	31.024	74.391	63.320	0.	0.	0.
2700	31.239	75.566	66.433	0.	0.	0.
2741.437	31.328	76.043	67.729	--- FUGACITY = 1 bar ---		
2800	31.454	76.706	69.568	-290.957	6.723	-0.116
2900	31.669	77.814	72.724	-289.894	16.817	-0.303
3000	31.884	78.891	75.901	-288.814	27.375	-0.477
3100	32.099	79.940	79.101	-287.718	37.897	-0.639
3200	32.314	80.963	82.321	-286.609	48.383	-0.790
3300	32.529	81.960	85.563	-285.488	58.834	-0.931
3400	32.744	82.934	88.877	-284.356	69.251	-1.064
3500	32.959	83.887	92.112	-283.215	79.635	-1.188

PREVIOUS: September 1961

CURRENT: September 1983

Beryllium (Be)

Be(l)

Be₁(cr,l)A₁ = 9.01218 Beryllium (Be)

CRYSTAL(α-β)-LIQUID

0 to 1527 K crystal, alpha
1527 to 1560 K crystal, beta
above 1560 K liquid

Refer to the individual tables for details.

Beryllium (Be)

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa		log K _r
		S ^o / J·K ⁻¹ ·mol ⁻¹	-[G ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r) / kJ·mol ⁻¹	ΔG ^o	
0	0	0	INFINITE	-1.932	0	0
100	1.819	0.503	19.434	-1.893	0	0
200	9.984	4.174	10.751	-1.315	0	0
250	13.574	6.801	9.695	-0.723	0	0
298.15	16.380	9.440	9.440	0	0	0
300	16.472	9.542	9.440	0.030	0	0
350	18.570	12.245	9.649	0.909	0	0
400	19.965	14.817	10.136	1.872	0	0
450	21.061	17.235	10.792	2.899	0	0
500	21.943	19.501	11.551	3.975	0	0
600	23.336	23.650	13.227	6.242	0	0
700	24.463	27.314	14.981	8.634	0	0
800	25.458	30.647	16.734	11.130	0	0
900	26.384	33.699	18.452	13.723	0	0
1000	27.274	36.525	20.119	16.406	0	0
1100	28.147	39.166	21.732	19.177	0	0
1200	29.016	41.652	23.290	22.035	0	0
1300	29.886	44.009	24.793	24.980	0	0
1400	30.763	46.256	26.247	28.013	0	0
1500	31.650	48.409	27.653	31.133	0	0
1527.000	31.892	48.975	28.025	31.991	ALPHA <--> BETA	
1527.000	30.000	53.461	28.025	38.840	TRANSITION	
1560.000	30.000	54.102	28.570	39.830	BETA <--> LIQUID	
1560.000	28.788	59.163	28.570	47.725	TRANSITION	
1600	28.874	59.893	29.344	48.879	0	0
1700	29.089	61.650	31.193	51.777	0	0
1800	29.304	63.319	32.932	54.696	0	0
1900	29.519	64.909	34.573	57.638	0	0
2000	29.734	66.429	36.128	60.600	0	0
2100	29.949	67.884	37.606	63.584	0	0
2200	30.164	69.283	39.014	66.590	0	0
2300	30.379	70.628	40.360	69.617	0	0
2400	30.594	71.926	41.648	72.666	0	0
2500	30.809	73.179	42.885	75.736	0	0
2600	31.024	74.391	44.073	78.828	0	0
2700	31.239	75.566	45.218	81.941	0	0
2741.437	31.328	76.043	45.680	83.237	--- FUGACITY = 1 bar ---	
2800	31.454	76.706	46.322	85.075	-290.957	6.223
2900	31.669	77.814	47.389	88.232	-289.894	-0.303
3000	31.884	78.891	48.421	91.409	-288.814	-0.477
3100	32.099	79.940	49.421	94.608	-287.718	-0.659
3200	32.314	80.963	50.391	97.829	-286.609	-0.790
3300	32.529	81.960	51.333	101.071	-285.488	-0.931
3400	32.744	82.934	52.248	104.335	-284.356	-1.064
3500	32.959	83.887	53.138	107.620	-283.215	-1.188

PREVIOUS:

CURRENT: September 1983

Beryllium (Be)

Be₁(cr,l)

Be(g)

Beryllium (Be)

IDEAL GAS

Beryllium (Be)

IP(Be, g) = 75192.07 ± 0.1 cm⁻¹
 S^o(298.15 K) = 136.274 ± 0.020 J·K⁻¹·mol⁻¹
 ΔH^o(0 K) = 320 ± 5 kJ·mol⁻¹
 ΔH^o(298.15 K) = 324 ± 5 kJ·mol⁻¹

Electronic Levels and Quantum Weights	g _i
State	
1S ₀	0.0
1P ₀	21978.28
3P ₀	21978.92
3P ₂	21981.27
3P ₁	42565.35
1D ₂	74443.20
1P	75192.29

Enthalpy of Formation

The enthalpy of formation is derived from the sublimation studies of Holden *et al.* (1172–1552 K),¹ Gulbranson and Andrew (1103–1229 K),² and Hildenbrand and Murad (1400–1500 K).³ The adopted value, ΔH^o(Be, g, 298.15 K) = 324 ± 5 kJ·mol⁻¹, is that recommended by CODATA.⁵ There are additional vapor pressure studies (~20), but they have been omitted in this analysis.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,^{6,7} is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function⁸ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the three levels at ~22000 cm⁻¹; the next excited state is approximately 42565 cm⁻¹ above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in S^o(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.⁸

The thermal functions at 298.15 K agree with the CODATA recommendations⁵ except that the entropy differs by 0.1094 J·K⁻¹·mol⁻¹, since this table uses a standard state pressure of 1 bar (CODATA recommendations are based on 1 atm).

References

- ¹R. B. Holden, R. Speiser, and H. L. Johnston, *J. Am. Chem. Soc.* **70**, 3897 (1948).
- ²E. A. Gulbranson and R. F. Andrew, *J. Electrochem. Soc.* **97**, 383 (1950).
- ³G. P. Kovtun, A. A. Kruglykh, and V. S. Pavlov, *Izvest. Akad. Nauk SSSR, Met. Corn. Delo* **2**, 177 (1964).
- ⁴D. L. Hildenbrand and E. Murad, *J. Chem. Phys.* **44**, 1524 (1966).
- ⁵J. D. Cox, chairman, ICSU-CODATA Task Group on Key Values for Thermodynamics, *J. Chem. Thermodynamics* **10**, 903 (1978).
- ⁶C. E. Moore, *U. S. Nat. Bur. Stand., NSRDS-NBS-34*, 8 pp. (1970).
- ⁷C. E. Moore, *U. S. Nat. Bur. Stand., NSRDS-NBS-35*, Volume 1, 1970 [Reprint of NBS Circular 467, Volume 1, (1949)].
- ⁸J. R. Downey, Jr., The Dow Chemical Company, AFOSR-TR-78-0960, Contract No. F44620-75-1-0048, (1978).

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P ^o = 0.1 MPa		log K _r
	C _p ^o	S ^o - [(C _p ^o - H(T _r))/T _r]	H ^o - H(T _r)	ΔH ^o	
0	0.	0.	INFINITE	319.735	INFINITE
90	20.786	113.567	-6.197	321.774	-162.172
200	20.786	127.975	-2.040	323.275	-77.964
250	20.786	132.613	-1.001	323.723	-292.269
298.15	20.786	136.274	0.	324.000	286.184
300	20.786	136.403	0.038	324.008	-50.138
350	20.786	139.607	1.078	324.169	-49.788
400	20.786	142.385	1.917	324.248	-51.730
450	20.786	144.851	3.156	324.257	-30.974
500	20.786	147.021	4.196	324.221	-27.210
600	20.786	150.811	6.274	324.032	-21.566
700	20.786	154.015	8.353	323.719	-23.5029
800	20.786	156.791	10.431	323.501	-17.538
900	20.786	159.239	12.510	322.787	-14.520
1000	20.786	161.429	14.589	322.183	-12.177
1100	20.786	163.410	16.667	321.490	-10.303
1200	20.786	165.219	18.746	320.711	-8.776
1300	20.786	166.882	20.824	319.844	-7.506
1400	20.786	168.423	22.903	318.890	-6.433
1500	20.786	169.857	24.982	317.848	-5.517
1600	20.786	171.198	27.060	302.182	-4.725
1700	20.786	172.458	29.139	301.362	-4.051
1800	20.787	173.647	31.218	300.521	-3.472
1900	20.787	174.770	33.296	299.659	-2.958
2000	20.789	175.837	35.375	298.775	-2.500
2100	20.791	176.851	37.454	297.870	-2.088
2200	20.795	177.818	39.533	296.943	-1.717
2300	20.801	178.743	41.613	295.996	-1.381
2400	20.811	179.628	43.694	295.028	-1.075
2500	20.824	180.478	45.779	294.039	-0.795
2600	20.844	181.295	47.859	293.031	-0.539
2700	20.870	182.082	49.944	292.003	-0.303
2741.437	20.883	182.400	50.809	291.000	-0.085
2800	20.905	182.842	52.033	0.	0.
2900	20.949	183.576	54.126	0.	0.
3000	21.006	184.287	56.223	0.	0.
3100	21.075	184.977	58.327	0.	0.
3200	21.159	185.648	60.439	0.	0.
3300	21.259	186.300	62.559	0.	0.
3400	21.376	186.937	64.691	0.	0.
3500	21.512	187.558	66.835	0.	0.
3600	21.668	188.166	68.994	0.	0.
3700	21.844	188.762	71.170	0.	0.
3800	22.041	189.347	73.364	0.	0.
3900	22.259	189.923	75.578	0.	0.
4000	22.500	190.489	77.816	0.	0.
4100	22.761	191.048	80.079	0.	0.
4200	23.045	191.600	82.369	0.	0.
4300	23.349	192.146	84.689	0.	0.
4400	23.674	192.686	87.040	0.	0.
4500	24.019	193.222	89.424	0.	0.
4600	24.383	193.754	91.844	0.	0.
4700	24.764	194.282	94.301	0.	0.
4800	25.162	194.808	96.798	0.	0.
4900	25.576	195.331	99.334	0.	0.
5000	26.003	195.852	101.913	0.	0.
5100	26.443	196.371	104.535	0.	0.
5200	26.894	196.889	107.202	0.	0.
5300	27.354	197.405	109.914	0.	0.
5400	27.822	197.921	112.673	0.	0.
5500	28.296	198.436	115.479	0.	0.
5600	28.776	198.950	118.333	0.	0.
5700	29.258	199.464	121.234	0.	0.
5800	29.743	199.977	124.184	0.	0.
5900	30.227	200.489	127.183	0.	0.
6000	30.711	201.001	130.230	0.	0.

PREVIOUS: September 1961 (1 atm)

CURRENT: September 1983 (1 bar)

Beryllium (Be)

Be(g)

Be₁Br₁(g)

Beryllium Bromide (BeBr)

IDEAL GAS

Beryllium Bromide (BeBr)

T/K	C _p ^o	S ^o - [C _p ^o - H ^o (T)]/T	H ^o - H ^o (T)	ΔH ^o	ΔG ^o	log K _f
0	0	0	0	0	0	INFINITE
100	29.145	195.462	-8.971	125.326	-57.455	INFINITE
200	30.486	215.960	-3.098	126.799	-57.455	INFINITE
250	31.597	222.881	-1.546	126.735	-57.455	INFINITE
298.15	32.598	228.534	0	126.735	-57.455	INFINITE
300	32.633	228.736	0.060	126.735	-57.455	INFINITE
350	33.508	233.834	1.715	126.735	-57.455	INFINITE
400	34.218	238.357	3.408	126.735	-57.455	INFINITE
450	34.787	242.421	5.134	126.735	-57.455	INFINITE
500	35.246	246.111	6.885	126.735	-57.455	INFINITE
600	35.922	252.601	10.446	126.735	-57.455	INFINITE
700	36.386	258.175	14.063	126.735	-57.455	INFINITE
800	36.721	263.721	17.719	126.735	-57.455	INFINITE
900	36.973	269.397	21.404	126.735	-57.455	INFINITE
1000	37.170	275.112	25.112	126.735	-57.455	INFINITE
1100	37.330	280.854	28.837	126.735	-57.455	INFINITE
1200	37.465	286.618	32.577	126.735	-57.455	INFINITE
1300	37.580	292.392	36.329	126.735	-57.455	INFINITE
1400	37.681	298.174	40.092	126.735	-57.455	INFINITE
1500	37.772	303.962	43.865	126.735	-57.455	INFINITE
1600	37.854	309.754	47.646	126.735	-57.455	INFINITE
1700	37.931	315.550	51.436	126.735	-57.455	INFINITE
1800	38.002	321.350	55.232	126.735	-57.455	INFINITE
1900	38.069	327.152	59.033	126.735	-57.455	INFINITE
2000	38.134	332.956	62.846	126.735	-57.455	INFINITE
2100	38.195	338.762	66.663	126.735	-57.455	INFINITE
2200	38.255	344.570	70.485	126.735	-57.455	INFINITE
2300	38.312	350.379	74.313	126.735	-57.455	INFINITE
2400	38.369	356.189	78.147	126.735	-57.455	INFINITE
2500	38.424	362.000	81.987	126.735	-57.455	INFINITE
2600	38.479	367.812	85.832	126.735	-57.455	INFINITE
2700	38.533	373.625	89.683	126.735	-57.455	INFINITE
2800	38.586	379.439	93.539	126.735	-57.455	INFINITE
2900	38.640	385.254	97.400	126.735	-57.455	INFINITE
3000	38.694	391.070	101.267	126.735	-57.455	INFINITE
3100	38.749	396.886	105.139	126.735	-57.455	INFINITE
3200	38.805	402.702	109.017	126.735	-57.455	INFINITE
3300	38.862	408.518	112.899	126.735	-57.455	INFINITE
3400	38.921	414.334	116.789	126.735	-57.455	INFINITE
3500	38.982	420.150	120.684	126.735	-57.455	INFINITE
3600	39.045	425.966	124.586	126.735	-57.455	INFINITE
3700	39.111	431.782	128.494	126.735	-57.455	INFINITE
3800	39.180	437.598	132.408	126.735	-57.455	INFINITE
3900	39.252	443.414	136.330	126.735	-57.455	INFINITE
4000	39.328	449.230	140.259	126.735	-57.455	INFINITE
4100	39.408	455.046	144.195	126.735	-57.455	INFINITE
4200	39.492	460.862	148.140	126.735	-57.455	INFINITE
4300	39.581	466.678	152.094	126.735	-57.455	INFINITE
4400	39.674	472.494	156.057	126.735	-57.455	INFINITE
4500	39.772	478.310	160.029	126.735	-57.455	INFINITE
4600	39.876	484.126	164.011	126.735	-57.455	INFINITE
4700	39.984	490.000	168.004	126.735	-57.455	INFINITE
4800	40.098	495.874	172.008	126.735	-57.455	INFINITE
4900	40.218	501.748	176.024	126.735	-57.455	INFINITE
5000	40.342	507.622	180.052	126.735	-57.455	INFINITE
5100	40.473	513.496	184.093	126.735	-57.455	INFINITE
5200	40.609	519.370	188.147	126.735	-57.455	INFINITE
5300	40.751	525.244	192.215	126.735	-57.455	INFINITE
5400	40.898	531.118	196.297	126.735	-57.455	INFINITE
5500	41.051	537.000	200.395	126.735	-57.455	INFINITE
5600	41.209	542.882	204.507	126.735	-57.455	INFINITE
5700	41.372	548.764	208.636	126.735	-57.455	INFINITE
5800	41.541	554.646	212.782	126.735	-57.455	INFINITE
5900	41.714	560.528	216.945	126.735	-57.455	INFINITE
6000	41.892	566.410	221.125	126.735	-57.455	INFINITE

S^o(298.15 K) = [228.5 ± 0.4] J·K⁻¹·mol⁻¹ ΔH^o(0 K) = 125.3 ± 41.8 kJ·mol⁻¹ ΔH^o(298.15 K) = 120.1 ± 41.8 kJ·mol⁻¹

Electronic Levels and Quantum Weights	g _e
State	
X ² Σ ⁺	2
A ₁ ¹ Π _{1/2}	2
A ₂ ¹ Π _{3/2}	2
B ² Σ ⁺	[2]
C ¹ Π	[4]

ω_eX_e = 4.30 cm⁻¹ σ = 1
B_e = [0.62155] cm⁻¹ r_e = [1.83] Å

Enthalpy of Formation

No thermochemical measurement of the enthalpy of formation has been made. The selected value, Δ_fH^o(BeBr, g, 0 K) = 30.0 ± 10.0 kcal·mol⁻¹, is obtained from an analysis of spectroscopic data. The adopted values for the ground state vibrational constants give D₀^o = 3.64 eV by a linear Birge-Sponer extrapolation.¹ Based on the ionicity correction developed by Hildenbrand,² this value adjusts to D₀^o = 3.27₂ eV (75.46 kcal·mol⁻¹) which is adopted. Δ_fH^o(298.15 K) corresponds to 28.7 kcal·mol⁻¹.
Ionic model calculations^{3,4} and bond energy correlations⁵ have led to D₀^o values of (in eV) 1.2,⁴ 4^{1,5} and 2.1.⁶ The latter value which is based on a Rittner potential⁷ is believed to represent a minimum value for D₀^o. Additional support for the adopted value of Δ_fH^o is provided by a comparison of values for the ratio D₀^o(MX₂, 298.15 K)/Δ_fH^o(MX₂, 298.15 K) for the alkaline-earth halides.¹ We find D₀^o(BeBr, 298.15 K)/Δ_fH^o(BeBr, 298.15 K) = 0.41 which is quite consistent with values of this ratio for other alkaline-earth halides.

Heat Capacity and Entropy

We estimate r_e to be 0.08 Å less than that for BeBr₂.³ This estimation is made based on the observation that the ratio r_e(MX₂)/r_e(MX₂) is near 0.96 for several alkaline-earth halides.³ The value of B_e is calculated from r_e. The value of α_e is obtained from the other constants by assuming a Morse potential function.
The ground state vibrational constants are taken from the results of a recent vibrational analysis of the A¹Π-X²Σ⁺ system by Reddy *et al.*⁸ Other values⁹ for these constants are slightly different than ours, but we consider them to be less accurate. It should also be noted that the values for ω_eX_e tabulated by Rosen⁹ for the ground and first excited states have been inadvertently reversed. The electronic level for the A₂Π_{1/2} state is also taken from Reddy *et al.*⁸ The doublet splitting of this state is assumed to be 197 cm⁻¹ as was observed in the emission spectrum of BeBr by Reddy and Rao.^{10,11} We also include a B²Σ⁺ level at 27000 cm⁻¹ and a C¹Π level at 40000 cm⁻¹. These levels are estimated by analogy with those for CaBr, SrBr, and BaBr.³

References

- A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall, Ltd., London, 330 pp (1968); refer to p. 264.
- D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, Ed by L. Eyring, Academic Press, New York, (1967).
- JANAF Thermochemical Tables: BeBr₂(g), 6-30-75; CaBr(g), SrBr(g), and BaBr(g), 12-31-74.
- J. L. Margrave, J. Phys. Chem. 58, 258 (1954).
- S. P. Tandon and K. Tandon, Indian J. Phys. 38, 460 (1964).
- K. S. Krasnov and N. V. Karaseva, Optics and Spectroscopy 19, 14 (1965).
- E. S. Rittner, J. Chem. Phys. 19, 1030 (1951).
- B. R. Reddy, Y. P. Reddy, and P. T. Rao, J. Phys. B, 3, L1 (1970).
- R. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 515 pp. (1970).
- Y. P. Reddy and P. T. Rao, Proc. Phys. Soc., London, At. Mol. Phys. 1, 482 (1968).
- Y. P. Reddy and P. T. Rao, Curr. Sci. 36, 399 (1967).

PREVIOUS: June 1975 (1 atm)

CURRENT: June 1975 (1 bar)

Beryllium Bromide (BeBr)

Be₁Br₁(g)

Beryllium Bromide (BeBr₂)

CRYSTAL

Beryllium Bromide (BeBr₂)Be₂Br₂(cr)

$S^{\circ}(298.15 \text{ K}) = [100.4 \pm 4.2] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $T_{\text{fus}} = 781 \pm 15 \text{ K}$
 $\Delta H_f^{\circ}(0 \text{ K}) = \text{Unknown}$
 $\Delta H_f^{\circ}(298.15 \text{ K}) = [-355.6 \pm 12.6] \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_{\text{sub}}H^{\circ} = [9.83 \pm 8.4] \text{ kJ} \cdot \text{mol}^{-1}$

Enthalpy of Formation

A direct measurement of the enthalpy of formation has not been made. An estimate of ΔH_f° is obtained by a method suggested by Parker,¹ Biltz and Messerknecht² have measured the enthalpies of solution of BeCl₂(cr) and BeBr₂(cr) in aqueous HCl (18.69%). Samples³ of the dihalides were prepared from reactions of BeO-C mixtures, with the halogens at elevated temperatures. We assume that the two dihalides had similar structures, i.e. α form. $\Delta H_f^{\circ}(\text{BeBr}_2, \text{ in } 18.7\% \text{ HCl}, 298.15 \text{ K})$ is estimated as $-140.1 \text{ kcal} \cdot \text{mol}^{-1}$ by combining $\Delta_{\text{sol}}H^{\circ}$ of BeCl₂(cr) with $\Delta H_f^{\circ}(\alpha\text{-BeCl}_2, \text{ cr}, 298.15 \text{ K}) = -117.3 \pm 0.8 \text{ kcal} \cdot \text{mol}^{-1}$,⁴ and twice the difference in $\Delta H_f^{\circ}(\text{HCl} \cdot 8.8\text{H}_2\text{O}, 298.15 \text{ K})$ and $\Delta H_f^{\circ}(\text{HBr} \cdot 8.8\text{H}_2\text{O}, 298.15 \text{ K})$ which is $-21.2 \text{ kcal} \cdot \text{mol}^{-1}$.⁵ The heat associated with the interchange of the aqueous anions is assumed to be negligible. Combination of the estimated value for $\Delta H_f^{\circ}(\text{BeBr}_2, \text{ in } 18.7\% \text{ HCl}, 298.15 \text{ K})$ with $\Delta_{\text{sub}}H^{\circ} = -55.7 \text{ kcal} \cdot \text{mol}^{-1}$ gives $\Delta H_f^{\circ}(\text{BeBr}_2, \text{ cr}, 298.15 \text{ K}) = -84.4 \text{ kcal} \cdot \text{mol}^{-1}$ which is essentially the value adopted by NBS.⁶ Subsequent measurements by Biltz *et al.*⁷ in less concentrated HCl (1.48%) solutions lead to $\Delta H_f^{\circ}(298.15 \text{ K})$ equal to $-85.6 \text{ kcal} \cdot \text{mol}^{-1}$ by a similar route. We adopt an average value of $-85.0 \text{ kcal} \cdot \text{mol}^{-1}$ ($-355.64 \text{ kJ} \cdot \text{mol}^{-1}$) but emphasize that the uncertainty in ΔH_f° is much greater than that indicated ($-1.0 \text{ kcal} \cdot \text{mol}^{-1}$) by the agreement of these two results. A combined total uncertainty of $\pm 3.0 \text{ kcal} \cdot \text{mol}^{-1}$ ($\pm 12.552 \text{ kJ} \cdot \text{mol}^{-1}$) is believed to be more realistic.

Heat Capacity and Entropy

No low-temperature heat capacity or high-temperature enthalpy measurements have been reported. We estimate $C_p^{\circ}(298.15 \text{ K}) = 15.78 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ from the reaction $\text{BeF}_2(\text{cr}) + 2\text{LiBr}(\text{cr}) = \text{BeBr}_2(\text{cr}) + 2\text{LiF}(\text{cr})$ by assuming $\Delta C_p^{\circ} = 0$. Comparison of this value with C_p° data for α -BeBr₂ and MgCl₂,⁴ suggests that our estimate is reasonable. C_p° data above 298 K are estimated graphically by comparison with those for α -BeCl₂ and MgCl₂.

Several methods of estimation predict that the value of $S^{\circ}(298.15 \text{ K})$ should lie near $24.0 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Application of the Benhelot principle⁸ to the process $\text{SrBr}_2(\text{cr}) + \text{Be}(\text{cr}) = \text{Sr}(\text{cr}) + \text{BeBr}_2(\text{cr})$ and additive entropy constants⁹ give values of 24.1 and $24.0 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively. A graphical comparison of the standard entropies for other alkaline-earth dihalides⁹ suggests values for $S^{\circ}(298.15 \text{ K})$ in the range $23.5\text{--}24.5 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Literature estimates have included (in $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) 29¹⁰ and 22.¹¹ We adopt $S^{\circ}(298.15 \text{ K}) = 24.0 \pm 1.0 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ($100.416 \pm 4.184 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$).

Fusion Data

The reported melting points for BeBr₂ show an unusual amount of scatter. Values of T_{fus} include 761 K ,¹² 763 K ,¹³ and $779\text{--}781 \text{ K}$.¹⁴ Semenenko and Naumova¹⁴ reported encountering difficulties in handling BeBr₂ due to its hygroscopic nature and susceptibility to oxidation by traces of oxygen. These factors could account for the discrepancies in the T_{fus} values. We tentatively adopt the highest value of 781 K ¹⁴ but believe that T_{fus} is more uncertain ($\pm 15 \text{ K}$) than the accuracy ($\pm 5 \text{ K}$) claimed in their temperature measurements.

A thermal analysis¹⁴ of BeBr₂ up to temperatures near the melting point showed no polymorphic modifications. Also, the interpretation of electron-diffraction patterns for freshly sublimed BeBr₂ indicated that it is isostructural with the α form of BeCl₂. Thus, we estimate $\Delta_{\text{sub}}H^{\circ} = 2.35 \pm 2.0 \text{ kcal} \cdot \text{mol}^{-1}$ from $\Delta_{\text{sub}}S^{\circ} = 3.0 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ which is calculated for $\alpha\text{-BeCl}_2$.⁴

Sublimation Data

$\Delta_{\text{sub}}H^{\circ}(298.15 \text{ K})$ is obtained from an analysis of the sublimation pressures reported by Rahlfs and Fischer.¹² Further details of the analysis are given on the gas-phase table. The value, $T_{\text{sub}} = 752 \text{ K}$, is the temperature at which ΔG approaches zero for the process $\text{BeBr}_2(\text{cr}) = \text{BeBr}_2(\text{g})$. T_{sub} has been measured as 746 K .¹² The good agreement between the calculated and observed values of T_{sub} is believed to indicate the presence of only small amounts of dimer in the saturated vapor of BeBr₂ near the melting point. However, this conflicts with other evidence which is discussed on the gas-phase table. Our results show that $T_{\text{sub}} < T_{\text{fus}}$ which implies that the liquid phase is thermodynamically unstable under ordinary conditions.

References

- ¹V. B. Parker, personal communication, U. S. Nat. Bur. Stand., March (1975).
- ²W. Biltz and C. Messerknecht, *Z. Anorg. Chem.* **148**, 157 (1925).
- ³C. Messerknecht and W. Biltz, *Z. Anorg. Chem.* **148**, 152 (1925).
- ⁴JANAF Thermochemical Tables: α -Be-BeCl₂(cr), 6-30-65; MgCl₂(cr), 12-31-65.
- ⁵U. S. Nat. Bur. Stand. Tech. Note 270-3, 264 pp. (1968).
- ⁶U. S. Nat. Bur. Stand. Tech. Note 270-6, 119 pp. (1971).
- ⁷W. Biltz, K. A. Klante, and E. Rahlfs, *Z. Anorg. Chem.* **166**, 339 (1927).
- ⁸N. N. Drozin, *Zhur. Fiz. Khim.* **35**, 879 (1961).
- ⁹D. R. Stull and H. Prophet in "The Characterization of High Temperature Vapors," J. L. Margrave, Ed., John Wiley and Sons, Inc., New York, (1966).
- ¹⁰L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren in "Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics," L. L. Quill, Ed., National Nuclear Energy Series IV-19B, McGraw-Hill Book Co., New York, (1950).
- ¹¹L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Revs.* **63**, 111 (1963).
- ¹²O. Rahlfs and W. Fischer, *Z. Anorg. Chem.* **211**, 349 (1933).
- ¹³P. Lebeau, *Ann. Chim. Phys.* **16**, 472 (1899).
- ¹⁴K. N. Semenenko and T. N. Naumova, *Russ. J. Structural Chem.* **4**, 59 (1963).

T/K	Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		$H^{\circ} - H^{\circ}(T_r)$	$\Delta_r H^{\circ}$	$\Delta_r G^{\circ}$	log K _r
	C_p°	$S^{\circ} - [C_p^{\circ} - H^{\circ}(T_r)]/T_r$				
0						
100						
200						
298.15	66.024	100.416	100.416	0.	-337.384	59.108
300	66.149	100.825	100.417	0.122	-337.271	58.724
400	70.626	120.475	103.066	6.963	-324.995	42.440
500	74.810	136.710	108.216	14.247	-310.120	32.398
600	77.613	150.608	114.151	21.874	-295.560	25.731
700	79.705	162.735	120.244	29.744	-281.283	20.990
800	81.337	173.487	126.240	37.998	-267.260	17.450
900	82.634	183.144	132.035	45.998	-253.467	14.711
1000	83.764	191.909	137.591	54.318	-239.879	12.530
1100	84.810	199.942	142.899	62.747	-226.479	10.755
1200	85.856	207.366	147.966	71.280	-213.250	9.283
1300	86.902	214.280	152.804	79.919	-200.178	8.043
1400	87.864	220.755	157.429	88.656	-187.252	6.986
1500	88.910	226.852	161.856	97.494	-174.462	6.075

PREVIOUS June 1965

CURRENT: June 1975

Beryllium Bromide (BeBr₂)Be₂Br₂(cr)

Be₂Br₂(g)

Beryllium Bromide (BeBr₂)

IDEAL GAS

Beryllium Bromide (BeBr₂)

Table with columns: T/K, Cp, S, -[G° - HF(T)]/T, H° - H(T), ΔH°, ΔG°, log Kr. Rows include vibrational frequencies, ground state quantum weight, point group, bond distance, bond angle, rotational constant, and thermodynamic data from 0 to 6000 K.

Enthalpy of Formation: Rahlfs and Fischer have reported measurements of the sublimation pressures (624-695 K) and vapor densities (736-799 K) for BeBr2. Both measurements were complicated by significant reaction of the dibromide with the quartz apparatus. Assuming the reaction to be 2BeBr2(cr) + SiO2(cr) = SiBr4(g) + 2BeO(cr), Rahlfs and Fischer corrected their measured total pressure for the partial pressure of the tetrabromide. Results of a 2nd and 3rd law analyses of their data are tabulated below.

Heat Capacity and Entropy: Information available on the structure of BeBr2 tend to indicate that the molecule is linear. Electron-diffraction patterns... for BeBr2 vapor have been successfully interpreted in terms of a linear configuration.

References: O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 349 (1953). J. Janaf Thermochemical Tables: Be2Cl4(g), 6-30-65; Mg2Br4(g), 6-30-74; Mg2Cl4(g), 12-31-69; Mg2F4(g), 3-31-66; BeBr(g), 6-30-75; BeCl(g), 12-31-72.

Be₂Br₂(g)

Beryllium Bromide (BeBr₂)

Continued on page 428

Beryllium Chloride, Ion (BeCl⁺)

S^o(298.15 K) = [213.0 ± 8] J·K⁻¹·mol⁻¹

IDEAL GAS

M_r = 44.464631

ΔH^f°(0 K) = [970 ± 84] kJ·mol⁻¹
ΔH^f°(298.15 K) = [979 ± 84] kJ·mol⁻¹

Table with 3 columns: Electronic State, Levels (ε_r, cm⁻¹), and Quantum Weights (g_r). Rows include Σ_g⁺, Π_g⁻, Π_g⁺, Σ_g⁻, Σ_g⁺, Δ_g⁻, and Σ_g⁺.

ω_ex_e = [700] cm⁻¹
B_e = [0.7241] cm⁻¹
ω_ex_e = [4.8] cm⁻¹
α_e = [0.0071] cm⁻¹
σ = 1
r_e = [1.8] Å

Enthalpy of Formation

Krasnov¹ has reported calculations of the ionization potentials (IP) for the monohalides (MX, where X = F, Cl, Br, and I) of Group IIA elements (M = Mg, Ca, Sr, and Ba). Based on his data we obtain graphically the value IP(BeCl, g) = 8.9 ± 0.5 eV. The value of ΔH^f°(298.15 K) is derived as 219 ± 15 kcal·mol⁻¹, using ΔH^f°(BeCl, g, 0 K) = 13.9 kcal·mol⁻¹. Beckett² reported the ionization potential of BeCl(g) to be approximately 9 ± 1 eV, yielding ΔH^f°(298.15 K) = 222 ± 23 kcal·mol⁻¹. Hildenbrand³ measured the appearance potential (AP) of BeCl(g) to be 9.5 ± 0.7 cal·K⁻¹·mol⁻¹, which is on the same order of the above IP values, and assumed that IP(BeCl⁺, g) = AP(BeCl⁺, g) = 9.5 ± 0.7 eV. Using this IP value, we obtain ΔH^f°(298.15 K) = 234 ± 20 kcal·mol⁻¹, which is adopted.

Heat Capacity and Entropy

The six electronic states are obtained from Fougere.¹ The electronic levels are estimated by comparison with those of the isoelectronic molecules, BeS,⁴ BeO,⁵ and MgO.⁵ The values of ω_ex_e and α_e are estimated by comparison with those for BeCl(g) and LiCl(g). B_e and α_e are calculated using the method suggested by Herzberg.⁶ The bond distance is estimated.⁷

References

- ¹K. S. Krasnov, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR, 3, 927 (1965).
- ²C. W. Beckett and E. C. Cassidy, U. S. Nat. Bur. Stand. Report 8628, 111 pp. (January 1965) refer to App. IV, p. 89.
- ³P. F. Fougere and R. K. Nesbet, J. Chem. Phys. 44, 285 (1965).
- ⁴G. Verhaegen and W. G. Richards, Proc. Phys. Soc. 90, 579 (1967).
- ⁵G. Herzberg, "Molecular Spectra and Molecular Structure of Diatomic Molecules," 2nd ed., D. Van Nostrand Co., Inc., New York, (1950).
- ⁶G. Verhaegen and W. G. Richards, J. Chem. Phys. 45, 1828 (1966).
- ⁷L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).
- ⁸K. S. Krasnov, Zh. Strukt. Khim. 1, 209 (1960).
- ⁹D. L. Hildenbrand, E. Murad, L. P. Theard, and F. Ju, Aeronutronic, Philco Corporation, Report No. U-3197, (July 30, 1965).

Beryllium Chloride, Ion (BeCl⁻)

Enthalpy Reference Temperature = T_r = 298.15 K

Standard State Pressure = P^o = 0.1 MPa

Main data table with columns: T/K, C_p^o, S^o - [G^o - H^o(T_r)]/T, H^o - H^o(T_r), ΔH^f°, ΔG^o, log K_r. Rows include 0, 100, 200, 250, 298.15, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1800, 1900, 2000, 2100, 2200, 2300, 2400, 2500, 2600, 2800, 2900, 3000, 3100, 3200, 3300, 3400, 3500, 3600, 3700, 3800, 3900, 4000, 4100, 4200, 4300, 4400, 4500, 4600, 4700, 4800, 4900, 5000, 5100, 5200, 5300, 5400, 5500, 5600, 5700, 5800, 5900, 6000.

PREVIOUS: June 1968 (1 atm)

CURRENT: June 1968 (1 bar)

Beryllium Chloride, Ion (BeCl⁺)

Be₂Cl₂(g)

Beryllium Chloride Fluoride (BeClF)

IDEAL GAS

M_r = 63.633583

Beryllium Chloride Fluoride (BeClF)

Be₂Cl₂F₂(g)

$$\Delta_f H^\circ(0 \text{ K}) = [-574 \pm 42] \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = [-573 \pm 42] \text{ kJ} \cdot \text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = [246.49] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies

 ν, cm^{-1}

[500] (1)
[270] (2)
[1300] (1)

Ground State Quantum Weight: 1

Point Group: C_{2v} D_{2h}

Bond Distances: Be-Cl = [1.77] Å; Be-F = [1.43] Å

Bond Angle: Cl-Be-F = [180]°

Rotational Constant: B₀ = [0.129706] cm⁻¹

σ = 1

Enthalpy of Formation

The enthalpy of formation was estimated by assuming Δ_fH° = 0 for the reaction BeF₂ + BeCl₂ → 2BeClF.

Heat Capacity and Entropy

The structure, bond lengths and frequencies were all estimated from the properties of BeCl₂ and BeF₂.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	$\int_0^T C_p^o \cdot \text{mol}^{-1} dT$	$H^\circ - H^\circ(T_r)$	$\Delta_f G^\circ$	
0	0	INFINITE	-11.704	-573.977	INFINITE
100	34.801	200.224	-8.654	-573.876	300.808
200	44.577	377.702	-4.633	-573.816	150.974
230	47.364	437.961	-2.332	-573.267	121.026
298.15	49.413	466.486	0	-573.208	101.683
300	49.483	246.792	0.091	-573.207	101.064
350	51.183	254.552	2.609	-573.221	86.806
400	52.601	261.482	2.488	-573.280	76.112
450	53.805	267.748	7.866	-573.368	67.793
500	54.832	273.472	10.583	-573.474	61.137
600	56.463	283.621	16.152	-573.725	51.150
700	57.663	292.469	21.861	-574.019	44.013
800	58.536	300.180	26.588	-574.357	38.638
900	59.231	307.118	31.654	-574.746	34.489
1000	59.749	313.387	37.515	-575.192	31.152
1100	60.152	319.101	45.511	-575.702	28.420
1200	60.472	324.349	55.543	-576.283	26.141
1300	60.729	329.200	57.603	-576.938	24.210
1400	60.938	333.708	63.687	-577.673	22.553
1500	61.109	337.919	69.789	-578.491	21.115
1600	61.252	341.867	75.908	-579.333	19.838
1700	61.373	345.584	82.039	-579.527	18.697
1800	61.474	349.095	88.182	-579.142	17.682
1900	61.562	352.421	94.334	-578.781	16.772
2000	61.636	355.581	100.494	-578.443	15.953
2100	61.701	358.590	106.661	-578.128	15.211
2200	61.758	361.462	112.834	-577.836	14.535
2300	61.808	364.208	119.012	-577.566	13.918
2400	61.851	366.830	125.185	-577.318	13.351
2500	61.890	369.365	131.382	-577.090	12.829
2600	61.925	371.793	137.573	-576.883	12.346
2700	61.956	374.131	143.767	-576.696	11.899
2800	61.983	376.385	149.964	-576.533	11.367
2900	62.008	378.560	156.163	-576.392	10.792
3000	62.031	380.663	162.365	-576.268	10.256
3100	62.051	382.697	168.570	-576.159	9.754
3200	62.070	384.667	174.776	-576.062	9.284
3300	62.087	386.578	180.984	-575.976	8.843
3400	62.102	388.431	187.193	-575.903	8.427
3500	62.117	390.232	193.404	-575.842	8.036
3600	62.130	391.982	199.616	-575.790	7.666
3700	62.142	393.684	205.830	-575.748	7.316
3800	62.153	395.342	212.045	-575.715	6.985
3900	62.163	396.956	218.261	-575.690	6.671
4000	62.173	398.530	224.477	-575.672	6.372
4100	62.182	400.066	230.695	-575.664	6.089
4200	62.190	401.566	236.914	-575.664	5.816
4300	62.198	403.028	243.133	-575.672	5.561
4400	62.205	404.457	249.353	-575.687	5.315
4500	62.211	405.855	255.574	-575.708	5.080
4600	62.218	407.223	261.795	-575.734	4.856
4700	62.224	408.561	268.017	-575.764	4.641
4800	62.229	409.871	274.240	-575.798	4.434
4900	62.234	411.154	280.463	-575.836	4.237
5000	62.239	412.412	286.687	-575.877	4.047
5100	62.244	413.644	292.911	-575.921	3.865
5200	62.248	414.853	299.136	-575.968	3.690
5300	62.252	416.039	305.361	-576.018	3.521
5400	62.256	417.202	311.586	-576.070	3.359
5500	62.260	418.345	317.812	-576.124	3.202
5600	62.263	419.467	324.038	-576.180	3.051
5700	62.266	420.569	330.264	-576.238	2.906
5800	62.270	421.652	336.491	-576.298	2.765
5900	62.272	422.716	342.718	-576.359	2.629
6000	62.275	423.763	348.946	-576.421	2.498

PREVIOUS: June 1965 (1 atm)

CURRENT: June 1965 (1 bar)

Beryllium Chloride Fluoride (BeClF)

Be₂Cl₂F₂(g)

Be₁Cl₂(cr)

Beryllium Chloride, Alpha (BeCl₂)

CRYSTAL(α)

Beryllium Chloride, Alpha (α-BeCl₂)

$M_r = 79.91818$

$\Delta_f H^\circ(0 \text{ K}) = -491.8 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15 \text{ K}) = -490.9 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{cr}} H^\circ = 8.66 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
T/K	C _p ^o / J·K ⁻¹ ·mol ⁻¹	H° - H°(T) / kJ·mol ⁻¹	Δ _r G°
0	0	INFINITE	
100	33.660	28.974	-491.795
200	53.555	131.942	-477.011
298.15	64.852	88.261	-461.208
300	65.019	82.676	-446.254
400	72.760	83.078	-445.977
500	77.530	102.907	-431.234
600	80.082	119.678	-416.927
688.000	81.278	134.040	-403.007
700	81.358	145.083	ALPHA ← -> LIQUID
800	82.257	146.489	-389.422
900	83.023	137.413	-376.125
1000	83.680	114.967	-360.074
1100	84.230	175.929	-350.239
1200	84.672	183.931	-337.593
1300	85.007	191.280	-325.117
1400	85.234	198.071	-312.790
1500	85.354	204.380	-300.597
		210.265	-288.523

$S^\circ(298.15 \text{ K}) = 82.68 \pm 0.25 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 688 \text{ K}$

Enthalpy of Formation
 Johnson and Gilliland¹ have directly reacted beryllium and chlorine and obtained $\Delta_f H^\circ = -118.03 \pm 0.56 \text{ kcal}\cdot\text{mol}^{-1}$ though the crystal form of the product was unknown. Gross, Heyman, Greene and Bingham² also by direct combustion of the elements obtain $\Delta_f H^\circ = -117.1 \pm 0.4 \text{ kcal}\cdot\text{mol}^{-1}$. The crystal form of the sample was deduced to be α' by a comparison experiment, the assumption is made here that α and α' are identical. Thompson, Sinke and Stull³ by solution calorimetry report a $\Delta_f H^\circ = -118.25 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$. Initially this sample was reported to be of unknown crystal form. However, Sinke⁴ reports that an x-ray of the sample used has been reinterpreted, in the light of more recent data, as being approximately 50% α' and 50% β. Using the enthalpies of transition adopted for these tables, enthalpies of formation of $-117.3 \pm 0.8 \text{ kcal}\cdot\text{mol}^{-1}$ for α and $-118.6 \pm 0.8 \text{ kcal}\cdot\text{mol}^{-1}$ for β have been adopted as being the most consistent with all measurements.

Heat Capacity and Entropy
 McDonald and Oetting⁵ have measured the heat capacity of the α' form from 13 and 304 K and the enthalpy (relative to the α' form) from 676 to 688 K. The assumption has been made that the α and α' 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 $S^\circ(13 \text{ K}) = 0.16 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The sample was identified as α' by x-ray diffraction both before and after the experiments.

Fusion Data

The temperature and enthalpy of melting were reported by McDonald and Oetting.⁵ 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 α-liquid melting point.

Sublimation Data

The adopted enthalpy of sublimation was calculated from that of the β form and enthalpy of the α-β transition at 298.15 K.

References

- ¹W. H. Johnson and A. A. Gilliland, J. Res. Nat. Bur. Stand. 65A, 59 (1961).
- ²P. 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.
- ³C. J. Thompson, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 380 (1962).
- ⁴G. C. Sinke, personal communication, (February 1965)
- ⁵R. A. McDonald and F. L. Oetting, J. Phys. Chem., 69, 3839 (1965).

PREVIOUS:

CURRENT: June 1965

Beryllium Chloride, Alpha (BeCl₂)

J. Phys. Chem. Ref. Data, Monograph 9

Be₂Cl₂(cr)Beryllium Chloride, Beta (BeCl₂)M_r = 9.91818

CRYSTAL(β)

Beryllium Chloride, Beta (β-BeCl₂)

$$\Delta_f H^\circ(0 \text{ K}) = -496.5 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = -496.2 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{tr}} H^\circ = [15.27 \pm 0.63] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{tr}} H^\circ = [6.82 \pm 0.63] \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = 75.81 \pm 0.21 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T_{\text{fus}} = [682] \text{ K}$$

$$T_{\text{tr}} = 676 \text{ K } (\beta \rightarrow \alpha)$$

Enthalpy of FormationSee the α -crystal table for details.**Heat Capacity and Entropy**

McDonald and Oetting¹ have measured the heat capacity of the β -form from 13 to 304 K and the enthalpy of the β -form from 298 to 676 K. The entropy was obtained by integration of the heat capacity curve based on $S^\circ(13 \text{ K}) = 0.06 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The sample was identified as β -BeCl₂, both before and after the low temperature experiments.

Fusion DataThe temperature and enthalpy of melting were obtained from cross over point of the tables for β -BeCl₂ and liquid BeCl₂.**Transition Data**

The temperature of the $\beta \rightarrow \alpha$ transition was obtained from McDonald and Oetting.¹ The enthalpy of the transition is a function of the heat capacity curve chosen for α -BeCl₂ between 298 and 676 K. A straight line interpolation was used by McDonald and Oetting, which gives a different result (1.49 kcal·mol⁻¹) than the curve employed here. It should also be noted that the transitional enthalpy is not included in this table, which is for β -BeCl₂ only.

Sublimation DataThe enthalpy of sublimation was determined by 2nd and 3rd law analysis of vapor pressure data as described fully on the table for BeCl₂(g).**References**¹R. A. McDonald and F. L. Oetting, *J. Phys. Chem.*, **69**, 3839 (1965).

Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P ^o = 0.1 MPa				
T/K	C _p ^o	S ^o - [C _p ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r)	Δ _f H ^o	Δ _f G ^o	log K _r
0	0	0	INFINITE	-496.527	-496.527	INFINITE
100	31.777	24.104	127.616	-498.412	-481.871	251.704
200	51.798	52.928	81.211	-497.332	-465.090	121.469
298.15	62.425	75.814	75.814	0	-449.501	78.751
300	62.593	76.201	75.815	0.116	-496.200	78.215
400	68.701	95.099	78.350	6.700	-433.736	56.640
500	72.802	110.900	83.324	13.788	-418.599	43.731
600	75.814	124.449	89.075	21.224	-403.758	35.150
700	78.157	136.327	94.995	28.933	-389.184	29.041
800	79.956	146.885	100.833	36.841	-374.851	24.475
900	81.379	156.387	106.487	44.910	-360.735	20.936
1000	82.550	165.025	111.915	53.109	-346.816	18.116
1100	83.387	172.934	117.108	61.408	-333.075	15.816
1200	84.015	180.217	122.088	69.780	-319.495	13.907
1300	84.475	186.961	126.803	78.203	-306.060	12.298
1400	84.782	193.234	131.277	86.669	-292.734	10.923
1500	84.935	199.089	135.652	95.157	-279.564	9.755

PREVIOUS:

CURRENT: June 1965

Beryllium Chloride, Beta (BeCl₂)Be₂Cl₂(cr)

Be₁Cl₂(l)

Beryllium Chloride (BeCl₂)

LIQUID

Beryllium Chloride (BeCl₂)

Be₁Cl₂(l)

$M_r = 79.91818$ Beryllium Chloride (BeCl₂)

$\Delta_f H^\circ(298.15 \text{ K}) = [-491.313] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{vap}} H^\circ = 8.66 \pm 0.25 \text{ kJ}\cdot\text{mol}^{-1}$

$S^\circ(298.15 \text{ K}) = [79.727] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 688 \text{ K}$

Enthalpy of Formation
 The enthalpy of formation is calculated from that of the α -BeCl₂ by adding $\Delta_{\text{fus}} H^\circ$ and the difference in enthalpy, $H^\circ(688 \text{ K}) - H^\circ(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy
 McDonald and Oetting¹ have measured the enthalpy of the liquid, relative to α -BeCl₂, 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 -BeCl₂. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion
 Refer to the α -crystal table for details.

Vaporization Data
 The boiling point and enthalpy of vaporization are calculated from the cross over point of the BeCl₂ (l) and (g) tables. The analysis of the liquid vapor pressure data is given on the table for BeCl₂(g).

References
¹R. A. McDonald and F. L. Oetting, J. Phys. Chem., **69**, 3839 (1965).

T/K	C _p ^o	S ^o - [G ^o - H ^o (T)]/T	H ^o - H ^o (T)	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K _r
0						
100						
200						
298.15	62.425	79.727	0.	-491.313	-445.758	78.095
300	62.593	79.728	0.116	-491.291	-445.475	77.564
400	68.701	82.263	6.700	-490.019	-430.392	56.203
460.100	71.356	85.103	10.912			
460.100	121.420	108.819	10.912			
500	121.420	118.917	15.757	-486.636	-415.729	43.431
600	121.420	141.054	27.898	-480.393	-402.138	35.009
688.000	121.420	157.671	38.583			
700	121.420	159.771	40.040	-474.314	-389.578	29.071
800	121.420	175.984	52.182	-468.369	-377.880	24.673
900	121.420	190.286	64.324	-462.540	-366.920	21.295
1000	121.420	203.078	76.466	-456.817	-356.603	18.627
1100	121.420	214.651	88.608	-451.107	-346.854	16.471
1200	121.420	225.216	100.750	-445.475	-337.615	14.995
1300	121.420	234.933	112.892	-440.050	-328.829	13.613
1400	121.420	243.933	125.034	-434.922	-320.468	12.396
1500	121.420	252.310	137.176	-429.692	-312.465	10.881
1600	121.420	260.146	149.318	-424.095	-304.293	9.934
1700	121.420	267.507	161.460	-418.360	-296.034	9.096
1800	121.420	274.447	173.602	-412.555	-288.095	8.360
1900	121.420	281.012	185.744	-406.681	-280.455	7.710
2000	121.420	287.240	197.886	-400.746	-273.097	7.133

PREVIOUS September 1961

CURRENT June 1965

Beryllium Chloride (BeCl₂)

Beryllium Chloride (BeCl₂)

Be₁Cl₂(l)

Beryllium Chloride (BeCl₂)

M_r = 79.91818 Beryllium Chloride (BeCl₂)

CRYSTAL (β-α)-LIQUID

0 to 676 K crystal, beta
676 to 688 crystal, alpha
above 688 liquid

Refer to the individual tables for details.

Beryllium Chloride (BeCl₂)

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S° - [(C _p ^o - H°(T _r))/T]	H° - H°(T _r)	Δ _r H°	
0	0	0	-11.979	-491.795	INFINITE
100	33.660	28.974	-10.297	-477.011	249.165
200	53.555	59.036	-5.845	-461.208	120.455
298.15	64.852	82.676	0	-490.930	78.182
300	65.019	83.078	0.120	-490.903	77.651
400	72.760	102.907	7.031	-489.303	56.313
500	77.530	119.678	14.556	-487.453	43.556
600	80.082	134.040	22.437	-485.471	35.085
688.000	81.278	145.083	29.539	-483.000	—
688.000	121.420	157.671	38.200	—	ALPHA <- -> LIQUID TRANSITION
700	121.420	159.771	39.657	-474.314	29.071
800	121.420	175.984	51.799	-468.369	24.673
900	121.420	190.286	63.941	-462.540	21.295
1000	121.420	203.078	76.083	-456.817	18.627
1100	121.420	214.651	88.225	-451.197	16.471
1200	121.420	225.216	100.367	-445.675	14.696
1300	121.420	234.933	112.509	-440.250	13.212
1400	121.420	243.933	124.651	-434.922	11.956
1500	121.420	252.310	136.793	-429.692	10.881
1600	121.420	260.146	148.935	-424.595	9.934
1700	121.420	267.507	161.077	-419.660	9.096
1800	121.420	274.447	173.219	-414.825	8.360
1900	121.420	281.012	185.361	-410.055	7.710
2000	121.420	287.240	197.503	-417.540	7.133

PREVIOUS:

CURRENT: June 1965

Beryllium Chloride (BeCl₂)

Be₂Cl₂(cr,l)

BeCl₂(g)

Beryllium Chloride (BeCl₂)

IDEAL GAS

Beryllium Chloride (BeCl₂)

T/K	C _p ^o	S ^o - (G ^o - H ^o (T))/T	H ^o - H ^o (T)/T	Standard State Pressure = p ^o = 0.1 MPa	log K _r
Enthalpy Reference Temperature = T _r = 298.15 K		J·K ⁻¹ ·mol ⁻¹		kJ·mol ⁻¹	
0	0	INFINITE	INFINITE	-361.451	INFINITE
100	37.378	202.989	294.816	-361.263	189.409
200	47.267	256.831	4.873	-360.568	95.128
250	49.785	243.300	-2.443	-360.350	76.300
298.15	51.622	252.232	0	-360.242	64.143
300	51.685	252.552	0.096	-360.240	63.753
350	53.221	260.638	2.719	-360.213	54.793
400	54.497	267.531	5.413	-360.234	48.073
450	55.563	274.313	8.166	-360.285	42.846
500	56.455	280.215	10.967	-360.355	38.664
600	57.830	290.636	16.685	-360.536	32.388
700	58.809	299.629	22.520	-360.764	27.903
800	59.517	307.530	28.438	-361.043	24.537
900	60.042	314.572	34.417	-361.376	21.916
1000	60.438	320.920	40.442	-361.771	19.818
1100	60.744	326.695	46.502	-362.233	18.099
1200	60.983	331.991	52.588	-362.766	16.664
1300	61.174	336.880	58.697	-363.375	15.499
1400	61.329	341.419	64.822	-364.064	14.405
1500	61.455	345.655	70.961	-364.836	13.498
1600	61.560	349.625	77.112	-380.230	12.686
1700	61.648	353.360	83.273	-380.776	11.956
1800	61.722	356.885	89.441	-381.345	11.303
1900	61.785	360.224	95.617	-381.938	10.722
2000	61.840	363.395	101.798	-382.557	10.197
2100	61.887	366.413	107.985	-383.203	9.721
2200	61.928	369.293	114.175	-383.879	9.287
2300	61.964	372.047	120.370	-384.585	8.890
2400	61.995	374.685	126.568	-385.325	8.526
2500	62.023	377.216	132.769	-386.099	8.190
2600	62.048	379.649	138.972	-386.900	7.880
2700	62.070	381.991	145.178	-387.726	7.597
2800	62.089	384.249	151.386	-388.579	7.307
2900	62.108	386.428	157.596	-389.460	7.018
3000	62.124	388.534	163.808	-390.373	6.730
3100	62.139	390.571	170.021	-391.318	6.443
3200	62.152	392.544	176.236	-392.293	6.157
3300	62.164	394.457	182.451	-393.298	5.872
3400	62.176	396.313	188.668	-394.332	5.587
3500	62.186	398.115	194.887	-395.395	5.302
3600	62.195	399.867	201.106	-396.487	5.017
3700	62.204	401.571	207.326	-397.608	4.732
3800	62.212	403.230	213.546	-398.758	4.447
3900	62.219	404.846	219.768	-399.937	4.162
4000	62.226	406.422	225.990	-401.145	3.877
4100	62.232	407.958	232.213	-402.382	3.592
4200	62.238	409.458	238.436	-403.647	3.307
4300	62.244	410.923	244.659	-404.940	3.022
4400	62.249	412.354	250.885	-406.261	2.737
4500	62.253	413.753	257.110	-407.610	2.452
4600	62.258	415.121	263.336	-408.987	2.167
4700	62.262	416.460	269.562	-410.392	1.882
4800	62.266	417.769	275.788	-411.825	1.597
4900	62.270	419.055	282.015	-413.286	1.312
5000	62.273	420.313	288.242	-414.774	1.027
5100	62.277	421.546	294.470	-416.288	0.742
5200	62.280	422.755	300.698	-417.827	0.457
5300	62.283	423.942	306.931	-419.391	0.172
5400	62.285	425.106	313.154	-420.980	-0.113
5500	62.288	426.249	319.383	-422.594	-0.398
5600	62.290	427.371	325.617	-424.233	-0.683
5700	62.293	428.474	331.841	-425.897	-0.968
5800	62.295	429.557	338.070	-427.586	-1.253
5900	62.297	430.622	344.300	-429.300	-1.538
6000	62.299	431.669	350.530	-431.039	-1.823

ΔH^o(0 K) = -361.5 ± 10.5 kJ·mol⁻¹
 ΔH^o(298.15 K) = -360.2 ± 10.5 kJ·mol⁻¹

Vibrational Frequencies and Degeneracies
 ν, cm⁻¹

[375] (1)
 [230] (2)
 1113 (1)

σ = 2

Point Group: D_{2h}
 Bond Distance: Be-Cl = [1.77] Å
 Bond Angle: Cl-Be-F = [180]^o
 Rotational Constant: B₀ = 0.075887 cm⁻¹

Enthalpy 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 Gibbs energy functions based on a bending frequency of 170 cm⁻¹ but no significant improvement of the results was noted.

Source	T/K	Δ _{sub} H ^o (298.15 K), kcal·mol ⁻¹	Drift
		2nd law	3rd law
1	680-740*	33.5 ± 0.6	31.38
2	680-740	34.3	31.22
3	613-663	31.6 ± 1.6	30.91
4	638-668	35.6	31.07
5	441-518	31.4 ± 0.8	32.45
6	510-600*	31.8 ± 0.3	32.07
7	460-504*	32.45 ± 0.4	32.48

*Points rejected due to failure of a statistical test.

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 3rd law trend, that is Δ_{sub}H^o = 32.5 ± 1 kcal·mol⁻¹ from.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 20-30% 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 BeCl₂(g) has been confirmed by the electric deflection experiments of Buchler.⁷ The bond length was obtained from the electron diffraction data of Akishin, Spirodinov and Sobolev.⁸ Buchler and Klemperer⁹ have reported the infra-red spectrum and assigned 1113 as the asymmetric stretch ν₃ and 482 as the bending frequency ν₂. However, Snelson⁸ 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 BeF₂(g). This gives 230 cm⁻¹ for ν₂ and 375 cm⁻¹ for the symmetric stretch.

References

- O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).
- W. 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 F. Ju, Ford Motor Co., Aeronautics Div., Report U-3068, April 1965 under Contract AF (04) 611-8523.
- A. Buchler, A. D. Little, Inc., Progress Report No. 8, Dec. 1963 under contract No. DA-19-020-ORD-5584.
- P. A. Akishin, V. P. Spirodinov and G. A. Sobolev, Dokl. Akad. Nauk SSSR 118, 1134 (1958).
- A. Buchler and W. Klemperer, J. Chem. Phys. 29, 121 (1958).
- A. Snelson, IIT Research Institute, Report No. IITRI-C6013-4, May 1964 under Contract No. DA-31-124-ARO (O)-111.

PREVIOUS: June 1965 (1 atm)

CURRENT: June 1965 (1 bar)

BeCl₂(g)

Beryllium Chloride (BeCl₂)

Be₂F₂(cr)

Beryllium Fluoride (BeF₂)

CRYSTAL(I-II)

Beryllium Fluoride (BeF₂)

$M_r = 47.008986$ Beryllium Fluoride (BeF₂)

$\Delta_f H^\circ(0\text{ K}) = -1024.5 \pm 4.2\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = -1026.8 \pm 4.2\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{cr}} H^\circ = 0.2201\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{cr}} H^\circ = 4.757\text{ kJ}\cdot\text{mol}^{-1}$

$S^\circ(298.15\text{ K}) = 53.354 \pm 0.17\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 500\text{ K}$ (low quartz \rightarrow high quartz)
 $T_{\text{tr}} = 825\text{ K}$

Enthalpy of Formation
 $\Delta_f H^\circ$ is the value selected by Parker,¹ based on a thorough review of data for BeF₂(cr, vitreous, aq) and BeO(cr) and BeO(cr), Parker's analysis remains essentially unchanged for BeO(cr) and BeF₂(cr), even though the results for BeF₂(HF, aq) become more negative by 0.93 kcal·mol⁻¹ due to JANAF selections for HF(aq). Three values derived by Parker for BeF₂(cr) from PbF₂(cr) are changed due to JANAF auxiliary data; these values become -246.9, -246.0 and -247.2 for the three paths used by Parker.
 The adopted $\Delta_f H^\circ$ was derived by combination of calorimetric data for Be(cr) + F₂(g) \rightarrow BeF₂(vitreous) and BeF₂(cr) \rightarrow BeF₂(vitreous). Churney and Armstrong² obtained $\Delta_f H^\circ(298.15\text{ K}) = -244.32 \pm 0.8\text{ kcal}\cdot\text{mol}^{-1}$ for vitreous BeF₂ by combustion in fluorine of polytetrafluoroethylene and mixtures of Be(cr) with polytetrafluoroethylene. $\Delta_f H^\circ(298.15\text{ K}, \text{cr} \rightarrow \text{vitreous}) = 1.125 \pm 0.016\text{ kcal}\cdot\text{mol}^{-1}$ was measured via solution calorimetry by Taylor and Gardner.³

Heat Capacity and Entropy
 C_p° is based on JANAF curve fits of measurements by adiabatic calorimetry (8–300 K) and by ice calorimetry (354–776 K) as reported by Taylor and Gardner.³ The sample was estimated as approximately 99.5% BeF₂. Analyses indicated that the major impurity was about 0.3% oxygen, mainly in the form of absorbed water. Petrographic examination and x-ray diffraction showed the sample to be composed almost completely of quartz-type crystals. The entropy is derived from the smoothed C_p° based on the extrapolation $S^\circ(8\text{ K}) = 0.0065\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The adopted C_p° above 300 K agrees closely with the relative enthalpy data and shows a remarkable similarity to that of SiO₂ (low quartz, high quartz).

Transition Data
 T_{tr} is the value selected by Taylor and Gardner³ from their relative enthalpy data. $\Delta_{\text{cr}} H^\circ$ is the corresponding difference in relative enthalpy from the JANAF curve fits for the two crystalline forms. Levina⁴ studied the polymorphism of BeF₂ by observing the peaks in C_p near the transition temperatures. For low quartz \rightarrow high quartz, Levina's peak began near 438 K, was complete near 503 K, and gave $\Delta_{\text{cr}} H^\circ = 0.17\text{ kcal}\cdot\text{mol}^{-1}$. Levina found a 2nd transition attributed to a form analogous to tridymite, this began above 670 K, was complete by 740 K, and gave $\Delta_{\text{cr}} H^\circ = 0.24\text{ kcal}\cdot\text{mol}^{-1}$. There is no evidence for this transition in the relative enthalpy data, so we suspect that its occurrence may be due to impurities in Levina's sample. Levina also found that the cristobalite-like phase transformed in the region 380 to 420 K with $\Delta_{\text{cr}} H^\circ = 1.27\text{ kcal}\cdot\text{mol}^{-1}$.

Fusion Data
 Refer to the liquid table for details.

Sublimation Data
 Refer to the ideal gas table for details.

References
¹V. B. Parker, Nat. Bur. Stand. Report 10004, Chapter 3, p. 58, (January 1, 1969).
²K. L. Churney and G. T. Armstrong, J. Res. Nat. Bur. Stand. 73A, 281 (1969).
³A. R. Taylor and T. Estelle Gardner, U. S. Bur. Mines RI-6664, 15 pp. (1965).
⁴M. E. Levina, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Teknol. 8 (2), 177 (1965).

Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
T/K	C _p ^o J·K ⁻¹ ·mol ⁻¹	H° - H°(T _r) kJ·mol ⁻¹	log K _r
0	0	INFINITE	INFINITE
100	21.004	-8.468	-1024.465
200	39.083	-7.550	-1010.881
298.15	51.819	-4.486	-995.024
300	52.028	0	-979.385
400	62.522	0.096	-979.091
500	76.048	5.822	-963.292
500.000	76.048	12.710	-1024.661
500.000	64.099	12.930	---
600	67.446	19.508	-1023.604
700	70.793	26.420	-1022.636
800	74.140	33.666	-1021.495
825.000	74.977	35.530	---
900	77.488	41.248	-1020.160
1000	80.835	49.164	-1018.617
1100	84.182	57.415	-1016.858
1200	87.529	66.000	-1014.876
1300	90.876	74.920	-1012.670

II \leftarrow I \rightarrow LIQUID
 TRANSITION

PREVIOUS: June 1964

CURRENT: June 1970

Beryllium Fluoride (BeF₂)

Be₂F₂(cr)

Beryllium Fluoride (BeF₂)

$$S^{\circ}(298.15 \text{ K}) = [59.920] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{fus}} = 825 \text{ K}$$

LIQUID

$$M_r = 47.008986$$

$$\Delta H_f^{\circ}(298.15 \text{ K}) = [-1022.048] \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{liq}} H_f^{\circ} = 4.757 \text{ kJ} \cdot \text{mol}^{-1}$$

Enthalpy of Formation

ΔH_f° is calculated from that of the crystal by means of $\Delta H_f^{\circ} = 1.125 \pm 0.016 \text{ kcal} \cdot \text{mol}^{-1}$ for $\rightarrow \text{BeF}_2(\text{vitreous})$ at 298.15 K. Further details are given in the section on Fusion Data. $\Delta H_f^{\circ}(\text{l})$ actually is based on the direct determination of $\Delta H_f^{\circ}(\text{vitreous})$ by Chumney and Armstrong¹ as discussed on the crystal table.

Heat Capacity and Entropy

C_p° is based on a JANAF curve fit of relative enthalpies of Taylor and Gardner² for the liquid (828–1183 K) and vitreous (320–473 K) forms of BeF₂. The combined data yield a normal C_p° curve and reveal no need for a glass transition. Scatter in the data is somewhat larger than for the crystal, presumably due to minor variations in the vitreous state at the conclusion of each drop. $S^{\circ}(298.15 \text{ K}, \text{l})$ is calculated from that of the crystal by addition of $\Delta_{\text{liq}} S^{\circ}$ and the difference-for crystal and liquid of $S^{\circ}(825 \text{ K}) - S^{\circ}(298.15 \text{ K})$.

Fusion Data

T_{fus} is the value selected by Taylor and Gardner² from their relative enthalpy data. These showed premelting starting near 804 K and complete melting above 828 K. Cooling of the liquid produced the vitreous state. T_{fus} has also been reported as 815,³ 821,⁴ 818,⁵ and 816 \pm 5 K.⁶

Solution calorimetry⁷ gave $\Delta H_f^{\circ} = 1.125 \pm 0.016 \text{ kcal} \cdot \text{mol}^{-1}$ for BeF₂(low quartz) \rightarrow BeF₂(vitreous) at 298.15 K. Confirmation of this result came from temperature-drop calorimetry⁷ and calorimetric conversion.⁸ These gave 1.1 \pm 0.2 and 1.1 \pm 0.5 kcal \cdot mol⁻¹, respectively. Combination of $\Delta H_f^{\circ} = 1.125$ with JANAF enthalpies yields $\Delta_{\text{vap}} H_f^{\circ} = 1.137 \text{ kcal} \cdot \text{mol}^{-1}$.

Vaporization Data

T_{vap} is the calculated temperature at which $\Delta_{\text{liq}} G^{\circ} = 0$ for BeF₂(l) \rightarrow BeF₂(g); $\Delta_{\text{vap}} H_f^{\circ}$ is the corresponding value of ΔH_f° at T_{vap} . These calculations neglect the presence of dimer, which is assumed to be negligible based on extrapolation of the equations of Belousov.⁹ Cantor¹⁰ obtained $T_{\text{vap}} = 1442 \text{ K}$ by extrapolation of his vapor pressures (1146–1372 K).

References

1. K. L. Chumney and G. T. Armstrong, *J. Res. Nat. Bur. Stand.* **73A**, 281 (1969).
2. A. R. Taylor and T. E. Gardner, *U. S. Bur. Mines RI-6664*, 15 pp. (1965).
3. M. A. Greenbaum, J. N. Foster, M. L. Arin and M. Farber, *J. Phys. Chem.* **67**, 36 (1963).
4. R. E. Thoma, H. Insley, H. A. Friedman and C. F. Weaver, *J. Phys. Chem.* **64**, 865 (1960).
5. K. A. Sasse and R. W. Stone, *J. Phys. Chem.* **62**, 453 (1958).
6. D. M. Roy, R. Roy and E. F. Osborn, *J. Amer. Ceram. Soc.* **36**, 185 (1953).
7. M. E. Melnichak, unpublished result quoted by J. L. Holm and O. J. Kleppa, *Inorg. Chem.* **8**, 207 (1969).
8. P. Gross, *Fulmer Res. Inst. Report R.163/19/April 1965*, Stokes Poges, England.
9. V. I. Belousov, L. N. Sidorov, S. A. Komarov and P. A. Aktishin, *Zh. Fiz. Khim.* **41**, 2969 (1967); *Russ. J. Phys. Chem.* **41**, 1598 (1967).
10. S. Cantor, *J. Chem. Eng. Data* **10**, 237 (1965).

Beryllium Fluoride (BeF₂)Be₁F₂(l)

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P ^o = 0.1 MPa	
		S ^o - (G ^o - H ^o (T _r))/T	H ^o - H ^o (T _r)	ΔH ^o	ΔG ^o
0	0				
100	49.903	59.970	59.920	-1022.048	-976.637
200	50.112	60.229	59.921	-1022.044	-976.355
300	59.208	75.979	62.006	-1021.608	-961.180
400	65.559	89.906	66.222	-1020.823	-946.157
500	70.551	102.314	71.222	-1019.751	-931.320
600	74.810	113.516	76.477	-1018.421	-916.684
700	78.647	123.761	81.756	-1016.851	-902.254
825.000	79.538	126.195	83.066	---	---
900	82.278	133.232	86.956	-1015.054	-888.035
1000	85.642	142.073	92.030	-1013.032	-874.028
1100	88.943	150.391	96.961	-1010.793	-860.234
1200	92.165	158.269	101.745	-1008.342	-846.654
1300	95.332	165.771	106.383	-1005.681	-833.286
1400	98.458	172.950	110.884	-1002.814	-820.131
1500	101.550	179.849	115.253	-999.744	-807.188
1600	104.621	186.501	119.499	-997.203	-793.931
1700	107.671	192.935	123.631	-995.139	-780.481
1800	110.709	199.175	127.655	-993.459	-767.266
1900	113.734	205.242	131.580	-992.137	-754.289
2000	116.750	211.153	135.411	-991.163	-741.551

PREVIOUS: June 1964

CURRENT: June 1970

Beryllium Fluoride (BeF₂)Be₁F₂(l)

Beryllium Fluoride (BeF₂) M_r = 47.008986 Beryllium Fluoride (BeF₂) Be₁F₂(cr,l)

0 to 500 K crystal, low quartz
 500 to 825 K crystal, high quartz
 above 825 K liquid
 Refer to the individual tables for details.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S° - [G° - f(T _r)]/T _r	H° - H°(T _r)	Δ _f H°	
0	0	0	INFINITE	INFINITE	INFINITE
100	21.004	14.753	90.253	-1024.465	-1024.465
200	39.083	35.371	57.702	-1026.493	-1010.881
298.15	51.819	53.354	0	-1026.535	-993.024
300	52.028	53.676	0.096	-1026.754	-979.385
400	62.522	70.077	5.822	-1026.746	-979.091
500	76.048	85.392	12.710	-1024.661	-947.738
500.000	76.048	85.392	12.710	-1024.661	99.009
500.000	64.099	85.832	12.930	TRANSITION	
600	67.446	97.814	65.302	-1023.604	-932.474
700	70.793	108.463	70.720	-1022.636	-917.360
800	74.140	118.134	76.051	-1021.495	-902.396
825.000	74.977	120.428	77.362	35.530	58.920
900	82.278	133.232	81.727	-1015.054	-888.035
1000	85.642	142.073	87.524	-1013.032	-874.028
1100	88.943	150.391	92.683	-1010.793	-860.234
1200	92.165	158.268	97.823	-1008.342	-846.653
1300	95.332	165.771	102.763	-1005.681	-833.286
1400	98.458	172.950	107.522	-1002.814	-820.131
1500	101.550	179.849	112.115	-999.744	-807.188
1600	104.621	186.501	116.558	-996.481	-794.591
1700	107.671	192.935	120.862	-993.035	-782.319
1800	110.709	199.175	125.041	-989.444	-770.481
1900	113.734	205.242	129.103	-985.750	-759.066
2000	116.750	211.153	133.058	-982.000	-748.151

PREVIOUS:

CURRENT: June 1970

Beryllium Fluoride (BeF₂)

Be₁F₂(cr,l)

Be₃F₃Li₃(cr)

Lithium Trifluoroberyllate (LiBeF₃)

CRYSTAL

Lithium Trifluoroberyllate (LiBeF₃)

M_r = 72.98389

$\Delta_f H^\circ(298.15 \text{ K}) = 89.24 \pm 4.2 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = [650 \text{ K}]$
 $\Delta_f H^\circ(0 \text{ K}) = \text{Unknown}$
 $\Delta_f H^\circ(298.15 \text{ K}) = -1651.8 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{ion}} H^\circ = [27.196] \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

Interpolation of the calorimetric enthalpies of mixing of Holm and Kleppa¹ yields $\Delta_f H^\circ = -0.56 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$ for $\text{LiF}(\text{l}) + \text{BeF}_2(\text{l}) \rightarrow \text{LiBeF}_3(\text{l})$ at 1135 K. Reduction with the estimated JANAF functions yields $\Delta_f H^\circ = -3.07 \pm 1.0 \text{ kcal}\cdot\text{mol}^{-1}$ at 298.15 K for $\text{LiF}(\text{cr}) + \text{BeF}_2(\text{l}) \rightarrow \text{LiBeF}_3(\text{cr})$, where $\text{BeF}_2(\text{l})$ is the supercooled liquid. $\Delta_f H^\circ(298.15 \text{ K})$ for the latter reaction may also be calculated as $-2.77 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1}$ from the difference of two calorimetric reactions measured by Gross.² These results at 298.15 K were $\Delta_f H^\circ = -2.28 \pm 0.12 \text{ kcal}\cdot\text{mol}^{-1}$ for $\text{LiF}(\text{cr}) + \text{LiBeF}_3(\text{cr}) \rightarrow \text{Li}_2\text{BeF}_4(\text{cr})$ and $\Delta_f H^\circ = -5.06 \pm 0.06 \text{ kcal}\cdot\text{mol}^{-1}$ for $2\text{LiF}(\text{cr}) + \text{BeF}_2(\text{l}) \rightarrow \text{Li}_2\text{BeF}_4(\text{cr})$. We adopt the high-temperature results of Holm and Kleppa since the entropy must be calculated by combination of $\Delta_f H^\circ$ with $\Delta_f G^\circ$ obtained at high temperature.

Heat Capacity and Entropy

C_p° is estimated from C_p° of $\text{Li}_2\text{BeF}_4(\text{cr})$ minus C_p° of $\text{LiF}(\text{cr})$. Existing information leads to three values for S° at 298.15 K; namely 21.41 $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for mixing of molten LiF and BeF_2 , 21.33 $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from $\Delta_f G^\circ = 552 \text{ K}$ for disproportionation of $\text{LiBeF}_3(\text{cr})$ to $\text{Li}_2\text{BeF}_4(\text{cr})$ and $\text{BeF}_2(\text{cr})$, and 21.28 $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ estimated from S° of $\text{LiF}(\text{cr})$ and $\text{BeF}_2(\text{cr})$. We adopt the intermediate value but emphasize that $S^\circ(298.15 \text{ K})$ is much more uncertain than indicated by the consistency of the three values. There is less uncertainty in $S^\circ(900 \text{ K})$ since it does not involve large contributions from the estimated values of C_p° and $\Delta_{\text{ion}} H^\circ$.

Hitch and Baes³ reported emf data and activity coefficients which yield $\Delta_f G^\circ = -5.91 \text{ kcal}\cdot\text{mol}^{-1}$ at 900 K for $\text{LiF}(\text{l}) + \text{BeF}_2(\text{l}) \rightarrow \text{LiBeF}_3(\text{l})$. Combining $\Delta_f G^\circ$ with $\Delta_f H^\circ = -1.05 \text{ kcal}\cdot\text{mol}^{-1}$ derived with JANAF functions from data of Holm and Kleppa,¹ we obtain $\Delta_f S^\circ = 5.4$ and $S^\circ(\text{LiBeF}_3, \text{l}) = 64.46 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, both at 900 K. The corresponding values from the adopted tables are $\Delta_f G^\circ = -5.84 \text{ kcal}\cdot\text{mol}^{-1}$ and $S^\circ(\text{LiBeF}_3, \text{l}) = 64.38 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Disproportionation Data

No transitions are known between room temperature and T_{fus} , but $\text{LiBeF}_3(\text{cr})$ does disproportionate into $\text{Li}_2\text{BeF}_4(\text{cr})$ and BeF_2 (high quartz). Disproportionation occurs at 553 K according to the latest phase diagrams^{4,5} or at 573 K according to Roy *et al.*⁶ The adopted tables yield $\Delta_d G^\circ = 0$ at 552 K, but this temperature is very sensitive to the value selected for S° , which in turn depends on the estimates of C_p° and $\Delta_{\text{ion}} H^\circ$.

Fusion Data

Refer to the liquid table for details.

References

- ¹J. L. Holm and O. J. Kleppa, *Inorg. Chem.* **8**, 207 (1969).
- ²P. Gross, *Fulmer Res. Inst. Report*, R.163/23/May 1966 and R.163/22/Jan. 1966, contract AF 61(052)-863; R.163/18/Dec. 1964, contract AF 61(052)-447.
- ³B. F. Hitch and C. F. Baes, *Inorg. Chem.* **8**, 201 (1969); U. S. Atomic Energy Comm., ORNL-4257, 46 pp., (1968).
- ⁴K. A. Romberger, J. Braunstein and R. E. Thoma, *J. Phys. Chem.* **76**, 1154 (1972).
- ⁵R. Thoma, H. Inley, H. A. Friedman, and G. M. Hebert, *J. Nucl. Materials* **27**, 166 (1968).
- ⁶D. M. Roy, R. Roy and E. F. Osborn, *J. Amer. Ceram. Soc.* **37**, 300 (1954).

Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa			
T/K	C _p ^o J·K ⁻¹ ·mol ⁻¹	S° - [G° - H°(T _r)]/T J·K ⁻¹ ·mol ⁻¹	H° - H°(T _r) kJ·mol ⁻¹	Δ _f G° kJ·mol ⁻¹	log K _r
0					
100					
200					
298.15	91.816	89.245	0.	-1651.843	276.156
300	92.048	89.246	0.170	-1651.836	274.372
400	104.600	93.007	10.002	-1651.275	202.479
500	117.152	100.522	21.090	-1653.272	159.331
600	129.704	109.450	33.433	-1651.389	130.559
650.0	135.980	114.147	40.075	---	---
700	142.256	118.921	47.031	---	---
800	154.808	128.568	61.884	-1648.435	110.037
900	167.360	138.223	77.992	-1644.389	94.678
1000	179.912	147.808	95.356	-1639.246	82.766
1100	192.464	157.286	113.975	-1632.986	73.269
1200	205.016	166.644	133.849	-1625.600	65.531
				-1617.079	59.114

PREVIOUS: June 1966

CURRENT: December 1971

Lithium Trifluoroberyllate (LiBeF₃)

Be₃F₃Li₃(cr)

Lithium Trifluoroberyllate (LiBeF₃)

LIQUID

M_r = 72.948389Lithium Trifluoroberyllate (LiBeF₃)Be₁F₃Li₁(l)

$$S^{\circ}(298.15 \text{ K}) = [111.681] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T_{\text{fus}} = [650] \text{ K}$$

$$\Delta_f H^{\circ}(298.15 \text{ K}) = [-1634.323] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{mix}} H^{\circ} = [27.2] \text{ kJ}\cdot\text{mol}^{-1}$$

Enthalpy of Formation

$\Delta_f H^{\circ}$ is calculated from that of the crystal by addition of $\Delta_{\text{mix}} H^{\circ}$ and the difference in enthalpy, $H^{\circ}(650 \text{ K}) - H^{\circ}(298.15 \text{ K})$, between the crystal and liquid. Note that the result is based on direct measurements of the enthalpy of mixing of molten LiF and BeF₂ at 1135 K.¹

Heat Capacity and Entropy

C_p° is estimated on the basis of 7.6 cal·K⁻¹·mol⁻¹ by comparison with the liquid phases of LiF, BeF₂, and Li₃BeF₄. A glass transition is assumed at 400 K and below this temperature C_p° is obtained from that of the crystal. The entropy is calculated in a manner analogous to that used for $\Delta_f H^{\circ}$. Note that the resulting value of $S^{\circ}(900 \text{ K})$ differs by only 0.08 cal·K⁻¹·mol⁻¹ from that based on measurements of $\Delta_f H^{\circ}(1135 \text{ K})$ and $\Delta_r G^{\circ}(900 \text{ K})$ for mixing of molten LiF and BeF₂.

Fusion Data

The composition corresponding to LiBeF₃ melts incongruently,³ starting with the eutectic composition of 53 mole percent BeF₂ at 636.6 ± 0.5 K and finishing at a liquidus temperature near 653 K. Just below the melting region, the solid consists of an equimolar mixture of Li₃BeF₄(cr) and BeF₂(high quartz). We arbitrarily adopt 650 K as the hypothetical, congruent melting point of metastable LiBeF₃. We estimate $\Delta_{\text{mix}} H^{\circ}$ on the basis of $\Delta_{\text{mix}} S^{\circ} = 2.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{g}\cdot\text{atom}^{-1}$ by comparison with Li₃BeF₄.

Vaporization Data

Mass-spectrometric data^{4,5} for the LiF-BeF₂ system suggest that the vapor consists mainly of BeF₂(g), some LiBeF₃(g), and traces of other molecules.

References

- J. L. Holm and O. J. Kleppa, *Inorg. Chem.* **8**, 207 (1969).
- B. F. Hitch and C. F. Baes, *Inorg. Chem.* **8**, 201 (1969); U. S. Atomic Energy Comm., ORNL-4257, 46 pp., (1968).
- K. A. Romberger, J. Braunstein and R. E. Thoma, *J. Phys. Chem.*, **76**, 1154 (1972).
- A. Buchler and J. L. Stauffer, *Thermodynamics, Proc. Symp.*, Vienna, 1965, **1**, 271, Intl. At. Energy Agency, Vienna, (1966).
- J. Berkowitz, and W. A. Chupka, *Ann. New York Acad. Sci.* **79**, Art. 11, 1073 (1960).

T/K	C _p ^o	S ^o - [G ^o - F(T _r)]/T	H ^o - H ^o (T _r)	Δ _r H ^o	Δ _r G ^o	log K _r
Enthalpy Reference Temperature = T _r = 298.15 K						
Standard State Pressure = P ^o = 0.1 MPa						
J·K ⁻¹ ·mol ⁻¹ kJ·mol ⁻¹						
0						
100						
200						
298.15	91.816	111.681	0.	-1634.323	-1565.442	274.259
300	92.048	111.683	0.170	-1634.315	-1565.014	272.493
400	104.600	115.443	10.002	-1633.755	-1541.988	201.563
400.001	104.600	115.443	10.003	GLASS ← → LIQUID		
400.001	158.992	140.449	10.003	TRANSITION		
500	158.992	175.927	25.902	-1630.939	-1519.428	158.734
600	158.992	204.915	41.801	-1625.501	-1497.640	130.381
650.000	158.992	217.641	49.750	--- CRYSTAL ← → LIQUID ---		
700	158.992	229.423	57.700	-1620.246	-1476.748	110.196
800	158.992	250.654	73.599	-1615.154	-1456.597	95.106
900	158.992	269.380	89.498	-1610.219	-1437.076	83.406
1000	158.992	286.132	105.398	-1605.424	-1418.096	74.074
1100	158.992	301.285	121.297	-1600.757	-1399.590	66.461
1200	158.992	315.119	137.196	-1596.211	-1381.792	60.135
1300	158.992	327.846	153.095	-1591.783	-1363.792	54.798
1400	158.992	339.628	168.994	-1587.468	-1346.417	50.235
1500	158.992	350.597	184.894	-1583.263	-1329.346	46.292
1600	158.992	360.859	200.793	-1579.202	-1312.027	42.833
1700	158.992	370.497	216.692	-1575.146	-1295.380	39.556
1800	158.992	379.585	232.591	-1571.191	-1279.437	36.600
1900	158.992	388.181	248.490	-1567.337	-1264.300	33.962
2000	158.992	396.337	264.142	-1563.577	-1249.743	31.595

PREVIOUS:

CURRENT: December 1971

Lithium Trifluoroberyllate (LiBeF₃)Be₁F₃Li₁(l)

Lithium Trifluoroberyllate (LiBeF₃)

M_r = 72.948389 Lithium Trifluoroberyllate (LiBeF₃)

Be₁F₃Li₁(Cr₁)

0 to 650 K crystal
above 650 K liquid

Refer to the individual tables for details.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S ^o - [C _p ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r)	ΔH ^o	
	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹	
0					
100	91.816	89.245	0.	-1651.843	276.156
200	92.048	89.246	0.170	-1651.836	274.372
300	104.600	118.013	10.002	-1651.275	202.479
400	117.152	142.702	21.090	-1653.272	159.331
500	129.704	165.171	33.433	-1651.389	130.559
600	135.980	175.801	40.075	CRYSTAL → LIQUID	
650.000	158.992	217.641	67.271	TRANSITION	
700	158.992	229.423	75.221	-1620.246	110.196
800	158.992	250.654	91.120	-1615.154	95.106
900	158.992	269.380	107.019	-1610.219	83.406
1000	158.992	286.132	122.918	-1605.424	74.074
1100	158.992	301.285	138.817	-1600.757	66.461
1200	158.992	315.119	154.717	-1596.211	60.135
1300	158.992	327.846	170.616	-1591.783	54.798
1400	158.992	339.628	186.515	-1587.468	50.235
1500	158.992	350.597	202.414	-1583.263	46.292
1600	158.992	360.859	218.313	-1579.202	42.833
1700	158.992	370.497	234.212	-1575.246	39.556
1800	158.992	379.385	250.112	-1571.438	36.609
1900	158.992	388.181	266.011	-1567.768	33.962
2000	158.992	396.537	281.910	-1564.237	31.595

PREVIOUS:

CURRENT December 1971

Lithium Trifluoroberyllate (LiBeF₃)

Be₁F₃Li₁(Cr₁)

Lithium Trifluoroberyllate (LiBeF₃)

IDEAL GAS

M_r = 72.948389Lithium Trifluoroberyllate (LiBeF₃)Be₃F₃Li₃(g)

S^o(298.15 K) = [267.42] J·K⁻¹·mol⁻¹ ΔH^o(0 K) = -880 kJ·mol⁻¹
 ΔH^o(298.15 K) = -887 kJ·mol⁻¹

Vibrational Frequencies and D-Generacities

v, cm ⁻¹	D, cm ⁻¹
[1530] (1)	[485] (2)
[820] (2)	[800] (3)
[700] (1)	

Point Group: [C_{3v}]

Bond Distances: Be-F = [1.40] Å; Li-Be = [1.209] Å; Li-F = [1.85] Å

Bond Angles: F-Be-F = [120]^o; Li-Be-F = [90]^oProduct of the Moments of Inertia: I_AI_BI_C = [2.1635 × 10⁻¹¹⁴] g³·cm⁶

Enthalpy of Formation

ΔH^o(298.15 K) is calculated from ΔH^o(900 K) = 53 kcal mol⁻¹ for the reaction LiF(g) + BeF₂(g) = LiBeF₃(g) reported by Hildenbrand, et al.¹

Heat Capacity and Entropy

The molecular structure was assumed to be pyramidal with Li atom at the top and BeF₃ located at the bottom. Beryllium atom was taken at the center of the equilateral triangle formed by the three F atoms. The Be-F distance was estimated from that of BeF₂(g). The bond distance of Li-F was taken from Porter and Zeller.² Vibrational frequencies were estimated by comparison with related fluorides. The principal moments of inertia are: I_A = I_B = 10.7996 × 10⁻³⁹ and I_C = 18.5503 × 10⁻³⁹ g·cm².

References

1. D. L. Hildenbrand, et al., Aeronutronic, Division of Ford Motor Co., Publication No. U-1734, (June 1962).
2. R. F. Porter and E. E. Zeller, J. Chem. Phys., 33, 858 (1960).

T/K	C _p ^o	S ^o	H ^o - H ^o (T)	ΔH _f ^o	ΔG _f ^o	log K _f
Enthalpy Reference Temperature = T _r = 298.15 K						
Standard State Pressure = P ^o = 0.1 MPa						
J·K ⁻¹ ·mol ⁻¹						
KJ·mol ⁻¹						
0	0	0	INFINITE	-12.459	-879.675	INFINITE
100	34.100	219.860	311.078	-9.122	-876.878	458.034
200	45.467	246.303	272.513	-5.242	-881.430	227.594
250	53.629	257.524	268.384	-2.765	-885.662	181.374
298.15	61.090	267.419	267.419	0	-887.008	151.467
300	61.360	267.798	267.420	0.113	-887.058	150.509
350	68.105	277.777	268.193	3.354	-888.341	86.545
400	73.789	287.253	269.988	6.906	-889.536	18.429
450	78.517	296.226	272.410	10.717	-890.676	11.846
500	82.442	304.708	275.219	14.744	-891.782	98.932
600	88.434	320.301	281.438	23.306	-892.852	88.555
700	92.665	334.269	288.022	32.373	-893.885	72.959
800	95.721	346.853	294.603	41.891	-894.882	61.797
900	97.986	358.264	301.052	51.490	-895.838	53.413
1000	99.700	368.681	307.502	61.379	-896.764	46.881
1100	101.024	378.248	313.323	71.418	-897.659	41.649
1200	102.064	387.085	319.106	81.574	-898.518	37.363
1300	102.895	395.288	324.655	91.824	-899.340	33.786
1400	103.568	402.939	329.976	102.148	-900.128	30.755
1500	104.121	410.104	335.082	112.533	-900.890	28.154
1600	104.579	416.839	339.963	122.969	-901.621	25.896
1700	104.963	423.191	344.693	133.447	-902.322	23.901
1800	105.288	429.200	349.222	143.960	-902.997	22.194
1900	105.566	434.900	353.583	154.503	-903.647	20.777
2000	105.804	440.321	357.785	165.071	-904.271	18.441
2100	106.011	445.488	361.839	175.662	-904.871	16.969
2200	106.190	450.424	365.755	186.273	-905.447	15.636
2300	106.348	455.148	369.530	196.900	-906.000	14.424
2400	106.487	459.677	373.201	207.542	-906.531	13.318
2500	106.610	464.027	376.748	218.197	-907.043	12.303
2600	106.719	468.210	380.186	228.863	-907.527	11.369
2700	106.817	472.240	383.521	239.540	-907.983	10.506
2800	106.905	476.126	386.759	250.226	-908.413	9.708
2900	106.984	479.879	389.906	260.921	-908.818	8.950
3000	107.055	483.507	392.966	271.623	-909.199	8.233
3100	107.120	487.018	395.944	282.332	-909.557	7.553
3200	107.179	490.420	398.843	293.047	-909.893	6.908
3300	107.232	493.719	401.668	303.767	-910.206	6.295
3400	107.281	496.921	404.423	314.493	-910.497	5.711
3500	107.326	500.032	407.111	325.223	-910.767	5.153
3600	107.368	503.056	409.734	335.958	-911.017	4.619
3700	107.406	505.999	412.296	346.697	-911.247	4.107
3800	107.441	508.863	414.800	357.439	-911.457	3.615
3900	107.473	511.654	417.248	368.185	-911.647	3.141
4000	107.503	514.375	419.642	378.934	-911.817	2.683
4100	107.531	517.030	421.985	389.685	-911.967	2.241
4200	107.557	519.622	424.779	400.440	-912.097	1.815
4300	107.581	522.153	427.276	411.197	-912.207	1.405
4400	107.604	524.626	429.727	421.956	-912.297	1.009
4500	107.625	527.045	432.085	432.718	-912.367	0.627
4600	107.645	529.411	433.902	443.481	-912.417	0.259
4700	107.663	531.726	435.078	454.247	-912.447	0.000
4800	107.681	533.993	437.115	465.014	-912.457	-0.227
4900	107.697	536.213	439.115	475.783	-912.447	-0.472
5000	107.712	538.389	441.078	486.553	-912.417	-0.728
5100	107.727	540.522	443.007	497.325	-912.367	-1.069
5200	107.741	542.614	444.903	508.099	-912.297	-1.495
5300	107.754	544.667	446.766	518.873	-912.207	-1.907
5400	107.766	546.681	448.598	529.649	-912.097	-2.305
5500	107.777	548.658	450.399	540.426	-911.967	-2.688
5600	107.788	550.600	452.171	551.205	-911.817	-3.057
5700	107.799	552.508	453.915	561.984	-911.647	-3.411
5800	107.808	554.383	455.631	572.764	-911.457	-3.750
5900	107.818	556.226	457.320	583.546	-911.247	-4.075
6000	107.827	558.038	458.984	594.328	-911.017	-4.386

PREVIOUS: December 1962 (1 atm)

CURRENT: December 1962 (0.1 bar)

Lithium Trifluoroberyllate (LiBeF₃)Be₃F₃Li₃(g)

Lithium Tetrafluoroberyllate (Li₂BeF₄)

CRYSTAL

Lithium Tetrafluoroberyllate (Li₂BeF₄)

$S^{\circ}(298.15\text{ K}) = 130.58 \pm 2.1\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 732.2 \pm 0.2\text{ K}$

Enthalpy of Formation
 Interpolation of the calorimetric enthalpies of Holm and Kleppa¹ yields $\Delta_f H^{\circ} = -3.2 \pm 0.1\text{ kcal}\cdot\text{mol}^{-1}$ for $2\text{LiF}(l) + \text{BeF}_2(l) \rightarrow \text{Li}_2\text{BeF}_4(l)$ at 1135 K. Reduction with the estimated JANAF functions yields $\Delta_f H^{\circ} = -4.24 \pm 0.2\text{ kcal}\cdot\text{mol}^{-1}$ at 298.15 K for $2\text{LiF}(cr) + \text{BeF}_2(l) \rightarrow \text{Li}_2\text{BeF}_4(cr)$, where $\text{BeF}_2(l)$ is the supercooled liquid. Gross² studied the latter reaction calorimetrically and obtained $\Delta_f H^{\circ} = -5.05 \pm 0.06\text{ kcal}\cdot\text{mol}^{-1}$ at 298.15 K. The difference of 0.8 kcal·mol⁻¹ between the two results is greater than the combined uncertainties but probably is not unreasonable in this case. We adopt the high-temperature results of Holm and Kleppa since the entropy must be calculated by combination of $\Delta_f H^{\circ}$ with $\Delta_f G^{\circ}$ obtained at high temperature.

Heat Capacity and Entropy
 C_p° is taken from the enthalpy study (323–873 K) of Douglas and Payne.³ Their sample was only 98.6% pure and extensive premelting corrections were necessary above 650 K. Thus, C_p° may be more uncertain than usual in this region. The premelting corrections could also be affected by new phase data which show that pure Li₂BeF₄ melts congruently at a temperature 12° lower than assumed in the premelting analysis. The magnitude of the adopted C_p° is confirmed by data by Levina *et al.*⁴ for samples prepared by fusion. Hitch and Baes⁵ reported emf data and activity coefficients which yield $\Delta_f G^{\circ} = -9.33\text{ kcal}\cdot\text{mol}^{-1}$ at 900 K for $2\text{LiF}(l) + \text{BeF}_2(l) \rightarrow \text{Li}_2\text{BeF}_4(l)$. Combining $\Delta_f G^{\circ}$ with $\Delta_f H^{\circ} = -4.19\text{ kcal}\cdot\text{mol}^{-1}$ derived from data of Holm and Kleppa,¹ we obtain $\Delta_f S^{\circ} = 5.71\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 900 K and $S^{\circ} = 31.21 \pm 0.5\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Li₂BeF₄(cr) at 298.15 K. This experimental entropy may be compared with $29.8 \pm 2\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ estimated by assuming $\Delta_f S^{\circ} = 0\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for formation from LiF(cr) and BeF₂(cr).

T/K	Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure = P° = 0.1 MPa	
	C _p ^o	S° - [G° - HF(T)]/T	H° - H°(T)	Δ _f G°
0				
100				
200				
298.15	135.269	130.583	0.	-2171.438
300	135.520	130.585	0.250	-2170.804
400	150.457	136.079	14.550	-2136.665
500	165.352	146.947	30.340	-2102.147
600	180.247	159.724	47.620	-2067.220
700	195.184	173.152	66.391	-2032.747
732.200	199.995	177.519	72.753	---
800	210.100	186.715	86.656	-1998.858
900	225.004	200.641	108.411	-1965.643
1000	239.911	213.462	131.657	-1933.176
1100	254.819	226.509	156.393	-1901.516
1200	269.729	239.312	182.620	-1870.714
1300	284.640	251.875	210.339	-1840.813
1400	299.554	264.208	239.549	-1811.848
1500	314.469	276.323	270.250	-1783.850

Transition Data

Li₂BeF₄ has a hexagonal unit cell (space group R3̄) isotopic with phenacite.⁶ This structure shows no phase transitions between room temperature and T_{fus},^{3,4} but exposure to traces of moisture at elevated temperatures causes decomposition to LiF and BeO.^{7,8} Metastable forms have been reported⁹ but not confirmed or identified.

Fusion Data

New electrochemical measurements⁹ of the liquidus in the LiF-BeF₂ system show that Li₂BeF₄ melts congruently at 459.1 ± 0.2°C with the eutectic point at 458.9 ± 0.2°C and 32.8 mole percent BeF₂. The close proximity of the eutectic explains previous conflicting reports of incongruent⁴ and congruent^{4,10} melting. We adopt T_{fus} = 732.2 ± 0.2 K and derive $\Delta_{\text{fus}} H^{\circ} = 10.515\text{ kcal}\cdot\text{mol}^{-1}$ from the difference in smoothed enthalpies for liquid and crystal.⁹ The uncertainty estimated for $\Delta_{\text{fus}} H^{\circ}$ emphasized the nature of the premelting corrections.

References

¹J. L. Holm and O. J. Kleppa, *Inorg. Chem.* **8**, 207 (1969).
²P. Gross, *Fulmer Res. Inst. Report R.163/23/May 1966* and *R.163/22/Jan. 1966*, Contract AF 61(052)-863; *R.163/18/December 1964*, Contract AF 61(052)-447.
³T. B. Douglas and W. H. Payne, *J. Res. Nat. Bur. Stand.* **73A**, 479 (1969).
⁴M. W. Levina, V. I. Kalitin and V. T. Kalinnikov, *Vestnik Moskov. Univ., Khim. Ser.* **III**, No. 4, 43 (1961).
⁵B. F. Hitch and C. F. Baes, *Inorg. Chem.* **8**, 201 (1969); *U. S. Atomic Energy Comm., ORNL-4257*, 46 pp., (1968).
⁶J. H. Burns and E. K. Gordon, *Acta Cryst.* **20**, 135 (1966).
⁷T. Hahn, H. Bielen, W. Eysel and F. Weber, *Chem. Erde* **22**, 175 (1962).
⁸R. Thoma, H. Insley, H. A. Friedman, and G. M. Hebert, *J. Nucl. Materials* **27**, 166 (1968).
⁹K. A. Romberger, J. Braunstein and R. E. Thoma, *J. Phys. Chem.*, **76**, 1154 (1972).

Enthalpy Reference Temperature = T, = 298.15 K

Standard State Pressure = P° = 0.1 MPa

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

Standard State Pressure = P° = 0.1 MPa

log K_t

PREVIOUS: June 1966

CURRENT: December 1971

Lithium Tetrafluoroberyllate (Li₂BeF₄)

Be₁₂F₄Li₂(cr)

Be₁₂F₄Li₂(cr)

Be₃F₄Li₂(l)Lithium Tetrafluoroberyllate (Li₂BeF₄)M_r = 98.887792

LIQUID

Lithium Tetrafluoroberyllate (Li₂BeF₄)

$S^{\circ}(298.15 \text{ K}) = [171.395] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $T_{\text{fus}} = 732.2 \pm 0.2 \text{ K}$

$\Delta H^{\circ}(298.15 \text{ K}) = [-2241.068] \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_{\text{mix}} H^{\circ} = 43.995 \pm 2.09 \text{ kJ} \cdot \text{mol}^{-1}$

Enthalpy of Formation

ΔH° is calculated from that of the crystal by addition of $\Delta_{\text{mix}} H^{\circ}$ and the difference in enthalpy, $H^{\circ}(732.2 \text{ K}) - H^{\circ}(298.15 \text{ K})$, between the crystal and liquid. Note that the result is based on direct measurements of the enthalpy of mixing of molten LiF and BeF₂ at 1135 K.¹

Heat Capacity and Entropy

The constant C_p° is derived from enthalpy data (743–873 K) of Douglas and Payne.² A glass transition is assumed at 500 K and below this temperature C_p° is obtained from that of the crystal. The entropy is calculated in a manner analogous to that used for $\Delta_{\text{mix}} H^{\circ}$. Note that the result is based on measurements of $\Delta_{\text{mix}} H^{\circ}(1135 \text{ K})^1$ and $\Delta G^{\circ}(900 \text{ K})^3$ for mixing of molten LiF and BeF₂.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

Mass spectra of vapor effusing from twin-crucible Knudsen cells⁴ suggest that the vapor consists of BeF₂, LiBeF₃, and traces of other molecules.

References

- ¹J. L. Holm and O. J. Kleppa, *Inorg. Chem.* **8**, 207 (1969).
- ²T. B. Douglas and W. H. Payne, *J. Res. Nat. Bur. Stand.* **73A**, 479 (1969).
- ³B. F. Hitch and C. F. Baes, *Inorg. Chem.* **8**, 201 (1969); U. S. Atomic Energy Comm., ORNL-4257, 46 pp., (1968).
- ⁴A. Buchler and J. L. Stauffer, "Thermodynamics, Proc. Symp., Vienna, 1965," **1**, 271, Int. At. Energy Agency, Vienna, (1966).

T/K	C_p°	$S^{\circ} - (G^{\circ} - H^{\circ}(T))/T$	$H^{\circ} - H^{\circ}(T)$	$\Delta_{\text{mix}} H^{\circ}$	ΔG°	$\log K_f$
0						
100						
200						
298.15	135.269	171.395	171.395	0.	-2241.068	376.862
300	135.520	172.232	171.397	0.250	-2241.055	374.441
400	150.457	213.265	176.891	14.550	-2240.238	376.905
500	165.352	248.440	187.759	30.340	-2245.147	218.345
500.001	165.352	248.440	187.759	30.341	GLASS \leftarrow LIQUID	
500.001	232.086	248.440	187.759	30.341	TRANSITION	
600	232.086	290.754	201.506	53.549	-2237.119	179.319
700	232.086	326.530	216.877	76.758	-2229.255	151.543
732.200	232.086	336.968	221.930	84.231	CRYSTAL \leftarrow LIQUID	
800	232.086	357.521	232.553	99.966	-2221.555	130.784
900	232.086	384.857	247.996	123.175	-2214.079	114.693
1000	232.086	409.310	262.926	146.384	-2206.655	101.864
1100	232.086	431.430	277.255	169.592	-2199.420	91.402
1200	232.086	451.624	290.957	192.801	-2192.313	82.712
1300	232.086	470.201	304.040	216.010	-2185.333	75.383
1400	232.086	487.400	316.530	239.218	-2178.470	69.121
1500	232.086	503.413	328.461	262.427	-2171.718	63.710
1600	232.086	518.391	339.869	285.635	-2179.611	58.974
1700	232.086	532.461	350.788	308.844	-2463.146	54.353
1800	232.086	545.727	361.253	332.053	-2454.737	50.156
1900	232.086	558.275	371.296	355.261	-2446.377	46.413
2000	232.086	570.180	380.945	378.470	-2438.061	43.056
2100	232.086	581.503	390.228	401.679	-2429.783	40.079
2200	232.086	592.300	399.169	424.887	-2421.540	37.286
2300	232.086	602.617	407.792	448.096	-2413.325	34.790
2400	232.086	612.494	416.117	471.305	-2405.134	32.511
2500	232.086	621.968	424.163	494.513	-2396.963	30.420

PREVIOUS: June 1966

CURRENT: December 1971

Lithium Tetrafluoroberyllate (Li₂BeF₄)Be₃F₄Li₂(l)

Lithium Tetrafluoroberyllate (Li₂BeF₄) Be₁F₄Li₂(cr,l)

CRYSTAL-LIQUID

0 to 732.2 K crystal
above 732.2 K liquid
Refer to the individual tables for details.

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa		log K _r
		S ^o - [G ^o - F ^o (T _r)]/T	H ^o - H ^o (T _r)	Δ _r H ^o	Δ _r G ^o	
	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·mol ⁻¹	J·mol ⁻¹	J·mol ⁻¹	
0			0.			
100	135.269	130.583	0.250	-2273.586	-2171.438	380.427
200	135.520	131.420	0.250	-2273.573	-2170.804	377.971
300	150.457	172.453	14.550	-2272.755	-2136.665	279.020
400	165.352	207.627	30.340	-2277.665	-2102.147	219.610
500	180.247	239.090	67.620	-2275.565	-2067.220	179.967
600	195.184	267.997	66.591	-2272.139	-2032.747	151.685
700	199.995	276.882	72.753	CRYSTAL <- -> LIQUID		
732.200	232.086	336.968	116.748	TRANSITION		
800	232.086	357.521	132.484	-2221.555	-2003.019	130.784
900	232.086	384.857	155.692	-2214.029	-1976.156	114.693
1000	232.086	409.310	178.901	-2206.655	-1950.122	101.864
1100	232.086	431.430	202.110	-2199.420	-1924.820	91.402
1200	232.086	451.624	225.318	-2192.313	-1900.171	82.712
1300	232.086	470.201	248.577	-2185.333	-1876.140	75.383
1400	232.086	487.400	271.736	-2178.470	-1852.882	69.321
1500	232.086	503.413	294.944	-2171.718	-1829.940	63.710
1600	232.086	518.391	318.153	-2179.611	-1806.420	58.974
1700	232.086	532.461	341.361	-2463.146	-1768.956	54.353
1800	232.086	545.727	364.570	-2454.737	-1728.364	50.156
1900	232.086	558.275	387.779	-2446.377	-1688.238	46.413
2000	232.086	570.180	410.987	-2438.061	-1648.551	43.056
2100	232.086	581.503	434.196	-2429.783	-1609.280	40.029
2200	232.086	592.300	457.405	-2421.540	-1570.402	37.286
2300	232.086	602.617	480.613	-2413.325	-1531.897	34.790
2400	232.086	612.494	503.822	-2405.134	-1493.750	32.511
2500	232.086	621.968	527.031	-2396.963	-1455.944	30.420

PREVIOUS:

CURRENT December 1971

Lithium Tetrafluoroberyllate (Li₂BeF₄)

Be₁F₄Li₂(cr,l)

Beryllium Hydride (BeH)

IDEAL GAS

Beryllium Hydride (BeH)

Be₂H₂(g)

$$S^{\circ}(298.15 \text{ K}) = 176.822 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta H_f^{\circ}(0 \text{ K}) = 319 \pm 29 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^{\circ}(298.15 \text{ K}) = 321 \pm 29 \text{ kJ}\cdot\text{mol}^{-1}$$

Electronic Levels and Quantum Weight State	$\epsilon_i, \text{cm}^{-1}$	Quantum Weight g_i
$\sum \epsilon_i^*$	0	2

$$\omega_e x_e = 2058.6 \text{ cm}^{-1}$$

$$B_e = 10.308 \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = 1.3431 \text{ \AA}$$

Enthalpy of Formation

Gaydon¹ selected a value of $2.3 \pm 0.3 \text{ eV}$ ($53 \pm 7 \text{ kcal}\cdot\text{mol}^{-1}$) for D_0° . Herzberg² estimated D_0° as being 2.2 eV ($50.7 \text{ kcal}\cdot\text{mol}^{-1}$). Gaydon's¹ value was used in this table.

Heat Capacity and Entropy

Molecular constants were found in Herzberg.²

References

- ¹A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall Ltd., London, 261 pp. (1953); refer to p. 221.
²G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," D. Van Nostrand Co. Inc., New York, (1950).

T/K	Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^{\circ} = 0.1 \text{ MPa}$		log K _r
	C_p°	$S^{\circ} - [G^{\circ} - H^{\circ}(T_r)]/T$	$H^{\circ} - H^{\circ}(T_r)$	ΔH_f°	
0	0	INFINITE	INFINITE	INFINITE	INFINITE
100	29.128	144.978	202.751	318.716	310.636
200	29.149	165.173	179.492	320.047	-162.260
250	29.171	171.680	177.303	321.036	300.778
298.15	29.224	176.822	176.822	321.204	295.689
300	29.227	177.003	176.822	321.197	290.773
350	29.344	181.516	177.179	321.056	290.585
400	29.538	185.446	177.972	320.835	285.493
450	29.809	188.940	179.000	320.561	280.620
500	30.144	192.098	180.154	320.253	275.391
600	30.932	197.620	183.620	320.479	270.389
700	31.769	202.402	185.122	318.849	260.479
800	32.570	206.788	187.166	318.093	250.686
900	33.296	210.667	188.921	317.307	241.000
1000	33.937	214.209	192.175	316.485	231.410
1100	34.496	217.470	194.328	315.617	221.910
1200	34.982	220.493	196.384	314.694	212.494
1300	35.404	223.310	198.348	313.708	203.159
1400	35.774	225.947	200.227	312.653	193.904
1500	36.098	228.427	202.025	311.522	184.728
1600	36.381	230.766	203.749	310.328	175.629
1700	36.641	232.980	205.404	309.072	167.134
1800	36.871	235.081	206.994	307.764	159.121
1900	37.079	237.080	208.526	306.412	151.162
2000	37.269	238.987	210.001	305.022	143.253
2100	37.443	240.809	211.425	303.598	135.394
2200	37.603	242.535	212.801	302.138	127.583
2300	37.732	244.230	214.131	300.642	119.819
2400	37.839	245.839	215.419	299.112	112.100
2500	38.023	247.389	216.667	297.552	104.426
2600	38.146	248.883	217.878	295.965	96.795
2700	38.264	250.324	219.053	294.352	89.208
2800	38.376	251.718	220.195	292.725	81.662
2900	38.483	253.067	221.305	291.087	74.150
3000	38.585	254.373	222.386	289.434	66.646
3100	38.684	255.640	223.438	287.764	59.143
3200	38.780	256.869	224.464	286.088	51.637
3300	38.872	258.064	225.464	284.402	44.131
3400	38.962	259.226	226.440	282.706	36.624
3500	39.049	260.357	227.393	281.002	29.118
3600	39.135	261.458	228.324	279.292	21.612
3700	39.218	262.531	229.234	277.578	14.106
3800	39.300	263.578	230.124	275.862	6.600
3900	39.380	264.600	230.995	274.144	-0.906
4000	39.459	265.598	231.848	272.424	-3.412
4100	39.536	266.573	232.683	270.704	-5.918
4200	39.613	267.527	233.501	268.984	-8.424
4300	39.688	268.460	234.303	267.264	-10.930
4400	39.762	269.373	235.090	265.544	-13.436
4500	39.835	270.268	235.862	263.824	-15.942
4600	39.908	271.144	236.619	262.104	-18.448
4700	39.980	272.003	237.363	260.384	-20.954
4800	40.051	272.846	238.093	258.664	-23.460
4900	40.121	273.672	238.811	256.944	-25.966
5000	40.191	274.483	239.517	255.224	-28.472
5100	40.261	275.280	240.210	253.504	-30.978
5200	40.329	276.062	240.892	251.784	-33.484
5300	40.398	276.831	241.563	250.064	-35.990
5400	40.466	277.587	242.223	248.344	-38.496
5500	40.533	278.330	242.873	246.624	-41.002
5600	40.600	279.061	243.512	244.904	-43.508
5700	40.667	279.780	244.142	243.184	-46.014
5800	40.733	280.488	244.765	241.464	-48.520
5900	40.800	281.185	245.374	239.744	-51.026
6000	40.865	281.871	245.977	238.024	-53.532

PREVIOUS: March 1963 (1 atm)

CURRENT: March 1963 (1 bar)

Beryllium Hydride (BeH)

Be₂H₂(g)

IDEAL GAS

Beryllium Hydride, Ion (BeH⁺)

S⁰(298.15 K) = 170.65 J·K⁻¹·mol⁻¹

ΔH⁰(298.15 K) = 1156.5 ± 42 kJ·mol⁻¹
 ΔH⁰(0 K) = 1147.8 ± 42 kJ·mol⁻¹

Electronic Levels and Quantum Weights	g _i
Σ ⁺	0
Σ ⁻	[20000]
Σ ⁺	1
Σ ⁻	[3]

ω_e = 2221.7 cm⁻¹ ω₂ = 39.79 cm⁻¹ σ = 1
 B_e = 10.7996 cm⁻¹ α_e = 0.2935 cm⁻¹ r_e = 1.31216 Å

Enthalpy of Formation

The enthalpy of formation is calculated from the equation BeH(g) → BeH⁺(g) + e⁻ with the JANAF auxiliary data for BeH(g)¹ using an ionization potential of 8.6 ± 0.4 eV (198.34 ± 9.23 kcal·mol⁻¹) obtained from Beckett and Cassidy.²

The dissociation energy, D₀(Be⁺-H) = 3.2 ± 0.2 eV (73.8 kcal·mol⁻¹), has been reported by Gaydon.³ This yields ΔH⁰(BeH⁺, g, 0 K) = 270.0 kcal·mol⁻¹ which is in agreement with the value adopted.

Heat Capacity and Entropy

The molecular constants were obtained from the ultraviolet spectroscopic studies by Watson and Humphrey.⁴ The ground state configuration was given by Herzberg.⁵ The estimated electronic level and quantum weight were obtained by assuming a Σ⁻ level lies below the first observed excited state (Σ⁺) at 40,000 cm⁻¹.

References

- ¹JANAF Thermochemical Tables, BeH(g), 3-31-63.
- ²C. W. Beckett and E. C. Cassidy, NBS Report 8628, 111 pp. (January 1965); refer to App. IV, p. 109.
- ³A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall Ltd., London, 261 pp (1953); refer to p. 221.
- ⁴W. W. Watson and R. F. Humphreys, Phys. Rev. 52, 318 (1937).
- ⁵G. Herzberg, "Molecular Spectra and Molecular Structure of Diatomic Molecules," 2nd ed., D. Van Nostrand Company, New York, (1950).

Beryllium Hydride, Ion (BeH⁺)

Be.Ht(g)

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ⁰ = 0.1 MPa		log K _r
	C _p ⁰	S ⁰ - [G ⁰ - H ⁰ (T _r)]/T	H ⁰ - H ⁰ (T _r)	ΔH ⁰	
0	0	INFINITE	-8.644	1147.782	
100	29.126	138.816	-5.776	1121.402	-196.503
200	29.144	159.009	-2.862	1115.481	-195.253
250	29.159	165.514	-1.405	1109.438	-166.478
298.15	29.193	170.653	0	1103.296	-128.067
300	29.195	170.833	0.054	1101.072	-114.610
350	29.274	175.339	1.515	1086.493	-94.407
400	29.413	179.256	2.982	1069.438	-79.960
450	29.621	182.732	4.458	1058.205	-69.112
500	29.892	185.866	5.946	1045.260	-60.665
600	30.571	191.374	8.968	1021.052	-53.901
700	31.339	196.144	12.063	995.643	-48.361
800	32.105	200.379	15.235	969.481	-43.740
900	32.823	204.203	18.482	942.889	-39.876
1000	33.471	207.695	21.797	916.098	-36.468
1100	34.046	210.913	25.174	889.272	-33.556
1200	34.551	213.897	28.604	862.514	-31.023
1300	34.994	216.681	32.082	835.826	-28.779
1400	35.384	219.289	35.601	809.205	-26.820
1500	35.728	221.742	39.157	782.654	-25.047
1600	36.033	224.057	42.746	756.172	-23.451
1700	36.304	226.250	46.363	729.754	-22.005
1800	36.549	228.332	50.006	703.396	-20.689
1900	36.770	230.314	53.672	677.097	-19.487
2000	36.971	232.206	57.326	650.854	-18.383
2100	37.156	234.014	61.065	624.660	-17.372
2200	37.328	235.747	64.790	598.526	-16.429
2300	37.489	237.409	68.531	572.450	-15.560
2400	37.642	239.008	72.287	546.432	-14.867
2500	37.788	240.548	76.059	520.472	-14.301
2600	37.930	242.033	79.845	494.572	-13.772
2700	38.069	243.467	83.645	468.732	-13.279
2800	38.207	244.854	87.458	442.952	-12.808
2900	38.345	246.197	91.286	417.232	-12.369
3000	38.484	247.499	95.127	391.572	-11.955
3100	38.627	248.763	98.983	365.972	-11.563
3200	38.773	249.992	102.853	340.432	-11.193
3300	38.924	251.187	106.738	314.952	-10.841
3400	39.080	252.352	110.638	289.532	-10.508
3500	39.242	253.487	114.554	264.172	-10.191
3600	39.410	254.595	118.486	238.872	-9.889
3700	39.586	255.677	122.436	213.632	-9.601
3800	39.768	256.735	126.404	188.452	-9.327
3900	39.958	257.770	130.390	163.332	-9.064
4000	40.154	258.784	134.395	138.272	-8.813
4100	40.358	259.778	138.421	113.282	-8.573
4200	40.568	260.754	142.467	88.352	-8.343
4300	40.785	261.711	146.535	63.482	-8.122
4400	41.008	262.651	150.624	38.672	-7.909
4500	41.237	263.575	154.732	13.922	-7.706
4600	41.472	264.484	158.872	-10.822	-7.510
4700	41.712	265.378	163.031	-36.042	-7.321
4800	41.956	266.259	167.214	-61.282	-7.139
4900	42.204	267.127	171.422	-86.542	-6.964
5000	42.455	267.982	175.655	-111.812	-6.795
5100	42.709	268.825	179.913	-137.082	-6.632
5200	42.966	269.657	184.107	-162.352	-6.474
5300	43.224	270.478	188.507	-187.622	-6.322
5400	43.484	271.288	192.842	-212.892	-6.174
5500	43.744	272.088	197.204	-238.162	-6.032
5600	44.004	272.879	201.591	-263.432	-5.894
5700	44.264	273.660	206.004	-288.702	-5.762
5800	44.522	274.432	210.444	-313.972	-5.632
5900	44.779	275.195	214.909	-339.242	-5.502
6000	45.035	275.950	219.399	-364.512	-5.372

PREVIOUS September 1966 (1 atm) CURRENT September 1966 (1 bar)

Beryllium Hydride, Ion (BeH⁺)

Be.Ht(g)

Beryllium Hydroxide (BeOH)

Beryllium Hydroxide (BeOH)

$M_r = 26.01952$

$\Delta H_f^\circ(0\text{ K}) = -113.7 \pm 37.7\text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15\text{ K}) = -114.6 \pm 37.7\text{ kJ mol}^{-1}$

IDEAL GAS

Electronic Levels and Quantum Weights	
ϵ_n , cm ⁻¹	g_n
0	[2]
[30000]	[4]
Vibrational Frequencies and Degeneracies	
ν_i , cm ⁻¹	
[1266](1)	
[606](2)	
[3650](1)	

Point Group: $[C_{\infty v}]$
 Bond Distances: Be-O = [1.38] Å; O-H = [0.96] Å
 Bond Angle: Be-O-H = [180]°
 Rotational Constant: $B_0 = [1.29312]\text{ cm}^{-1}$

Enthalpy of Formation

The adopted $\Delta H_f^\circ(298.15\text{ K}) = -27.4 \pm 10\text{ kcal mol}^{-1}$, which corresponds to $D_0(\text{Be-OH}) = 113.9 \pm 10\text{ kcal mol}^{-1}$, is derived from 3rd law analysis of Knudsen-cell mass-spectrometric studies and Knudsen-cell weight-loss studies of several BeOH(g) producing reactions.¹⁻³ The earlier Knudsen-cell mass-spectrometric measurement by Hildenbrand *et al.*⁴ had indicated a minimum absolute value of $\Delta H_f^\circ(\text{BeOH}, \text{g}, 298.15\text{ K}) = -25 \pm 10\text{ kcal mol}^{-1}$.

Source	Reaction	Data Points	$\Delta H_f^\circ(298.15\text{ K})$, kcal mol ⁻¹	3rd law $\Delta H_f^\circ(298.15\text{ K})$, kcal mol ⁻¹	Drift cal K ⁻¹ mol ⁻¹
Inami and Ju ¹	A	3	2422-2485	9.73 ± 0.93	-13.0 ± 2.0
	B	3	2422-2485	0.82 ± 0.59	6.2 ± 5.5
	C	3	2422-2485	75.56 ± 1.3	-5.3 ± 17
Inami and Ju ²	D	3	2422-2485	12.09 ± 1.8	3.6 ± 25
	E	3	2425-2518	22.11 ± 2.1	-21.3 ± 8.6
	F	3	2107-2368	106.01 ± 1.40	5.1 ± 1.7

Reactions:
 A) BeO(g) + OH(g) = BeOH(g) + O(g)
 B) Be₂O(g) + OH(g) = BeOH(g) + BeO(g)
 C) BeO(ct, β) + H(g) = BeOH(g)

The average $\Delta H_f^\circ(\text{BeOH}, \text{g}, 298.15\text{ K})$ from the measurements of Inami and Ju^{1,2} is $-27.4\text{ kcal mol}^{-1}$. The $\Delta H_f^\circ(\text{Be-OH}, \text{g}, 298.15\text{ K}) = 115\text{ kcal mol}^{-1}$ from $\Delta H_f^\circ(298.15\text{ K})$ of $-27.4\text{ kcal mol}^{-1}$ appears more reasonable than a $\Delta H_f^\circ(\text{Be-OH}, \text{g}, 298.15\text{ K}) = 127\text{ kcal mol}^{-1}$ from the $\Delta H_f^\circ(298.15\text{ K})$ of $-39.4\text{ kcal mol}^{-1}$, derived from Ko, Greenbaum, and Farber³ above. This is based on a comparison of the trends in D_0 values of the alkaline earth monofluorides and monochlorides and in the adopted D_0 values for the other alkaline earth monohydroxides.⁵ The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has already been recognized.⁶⁻⁹ Accordingly, $\Delta H_f^\circ(\text{BeOH}, \text{g}, 298.15\text{ K}) = -27.4 \pm 10\text{ kcal mol}^{-1}$ is adopted.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh¹⁰ and the evidence that the gaseous alkali metal monohydroxides are linear.¹¹⁻¹³ By analogy with BeF and BeCl¹³ the ground state is assumed to be $^2\Sigma^+$ and the first excited state is estimated at 30000 cm⁻¹. The Be-O bond distance is estimated to be slightly larger, 0.02 Å, than the Be-F bond distance³ after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is that in water.³

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

Continued on page 428

T/K	C _p ^o	S ^o - [G ^o - F(T)]/T	Standard State Pressure = P ^o = 0.1 MPa		
			H ^o - H(T)	ΔH ^o	log K _i
0	0	INFINITE	-9.528	-113.662	INFINITE
100	29.307	174.021	-6.620	-113.745	61.371
200	33.323	195.328	-3.523	-114.028	31.594
250	35.983	203.052	-1.790	-114.314	25.631
298.15	38.321	209.594	0	-114.642	21.769
300	38.405	209.831	0.071	-114.655	21.645
350	40.511	215.914	2.045	-115.022	18.789
400	42.314	221.444	4.117	-115.390	16.640
450	43.849	226.519	6.272	-115.750	14.963
500	45.157	231.208	8.498	-116.102	13.617
600	47.250	239.636	13.123	-116.788	11.590
700	48.862	247.045	17.932	-117.467	10.134
800	50.175	253.658	22.886	-118.155	9.035
900	51.295	259.634	27.961	-118.862	8.175
1000	52.281	265.090	33.140	-119.598	7.483
1100	53.162	270.115	38.413	-120.371	6.914
1200	53.956	274.776	43.770	-121.186	6.436
1300	54.672	279.123	49.202	-122.051	6.029
1400	55.319	283.199	54.702	-122.972	5.677
1500	55.901	287.036	60.264	-123.955	5.370
1600	56.426	290.661	65.881	-124.989	5.082
1700	56.898	294.096	71.547	-126.067	4.813
1800	57.324	297.360	77.259	-127.188	4.573
1900	57.708	300.470	83.011	-128.351	4.357
2000	58.053	303.439	88.799	-129.556	4.162
2100	58.366	306.272	94.620	-130.803	3.984
2200	58.648	309.001	100.471	-132.093	3.822
2300	58.904	311.614	106.349	-133.433	3.673
2400	59.136	314.126	112.251	-134.824	3.535
2500	59.347	316.544	118.175	-136.261	3.408
2600	59.540	318.876	124.120	-137.740	3.290
2700	59.715	321.126	130.083	-139.256	3.180
2800	59.876	323.301	136.063	-140.803	3.078
2900	60.024	325.404	142.035	-142.383	2.981
3000	60.159	327.442	148.067	-144.017	2.888
3100	60.284	329.416	154.089	-145.700	2.800
3200	60.400	331.332	160.094	-147.435	2.717
3300	60.507	333.192	166.069	-149.224	2.639
3400	60.606	335.000	172.000	-151.064	2.565
3500	60.700	336.758	178.000	-152.956	2.494
3600	60.787	338.470	184.064	-154.900	2.426
3700	60.869	340.136	190.047	-156.896	2.361
3800	60.947	341.760	196.038	-158.944	2.300
3900	61.021	343.345	202.036	-161.044	2.242
4000	61.092	344.890	208.042	-163.196	2.188
4100	61.160	346.400	214.055	-165.400	2.138
4200	61.226	347.874	220.074	-167.656	2.091
4300	61.290	349.316	226.100	-169.964	2.046
4400	61.353	350.726	232.132	-172.324	2.003
4500	61.415	352.105	238.171	-174.734	1.962
4600	61.477	353.456	244.216	-177.194	1.922
4700	61.538	354.778	250.266	-179.704	1.883
4800	61.598	356.073	256.320	-182.264	1.845
4900	61.656	357.345	262.378	-184.874	1.808
5000	61.721	358.592	268.440	-187.534	1.772
5100	61.784	359.814	274.506	-190.244	1.737
5200	61.847	361.015	280.576	-193.004	1.702
5300	61.911	362.194	286.650	-195.814	1.667
5400	61.977	363.351	292.726	-198.674	1.632
5500	62.043	364.486	298.803	-201.584	1.597
5600	62.111	365.608	304.884	-204.544	1.562
5700	62.181	366.708	310.969	-207.554	1.527
5800	62.252	367.790	317.056	-210.614	1.492
5900	62.324	368.854	323.144	-213.724	1.457
6000	62.399	369.903	329.232	-216.884	1.422

PREVIOUS: December 1975 (1 atm)

CURRENT: December 1975 (1 bar)

Beryllium Hydroxide (BeOH)

Beryllium Hydroxide (BeOH)

$M_r = 26.01952$

IDEAL GAS

Heat Capacity and Entropy

Beryllium Hydroxide, Ion (BeOH⁺) Be₂H₂O₂(g)

$M_r = 26.018971$ $\Delta_f H^\circ(0\text{ K}) = 754.70 \pm 50\text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_f H^\circ(298.15\text{ K}) = 759.93 \pm 50\text{ kJ}\cdot\text{mol}^{-1}$

T/K	Enthalpy Reference Temperature = T, T = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S° - [C _p ° - H(T)]/T	H° - H(T)	Δ _f H°	
0	0.	INFINITE	-9.546	754.698	-130.654
100	29.321	168.260	-6.638		-129.833
200	33.428	189.606	-3.535		-110.922
250	36.103	197.356	-1.706		-85.675
298.15	38.441	203.919	0.		-76.826
300	38.525	204.157	0.071	759.934	-75.959
350	40.625	210.257	2.051	760.638	-74.235
400	42.420	215.803	4.129	761.314	-72.703
450	43.946	220.889	6.289	761.998	-71.314
500	45.245	225.589	8.519	762.690	-69.991
600	47.323	234.031	13.153	764.091	-67.800
700	48.922	241.450	17.968	765.497	-65.024
800	50.224	248.071	22.927	766.894	-61.746
900	51.336	254.052	28.007	768.269	-57.945
1000	52.316	259.512	33.190	769.615	-53.646
1100	53.192	264.540	38.466	770.925	-48.906
1200	53.982	269.203	43.826	772.191	-43.733
1300	54.695	273.553	49.260	773.407	-38.138
1400	55.338	277.630	54.767	774.567	-32.130
1500	55.918	281.468	60.326	775.664	-25.738
1600	56.441	285.094	65.944	776.716	-19.005
1700	56.912	288.550	71.612	777.732	-12.045
1800	57.336	291.795	77.325	778.710	-4.778
1900	57.719	294.906	83.078	779.653	2.800
2000	58.063	297.875	88.868	780.562	10.315
2100	58.375	300.716	94.690	781.438	17.678
2200	58.657	303.438	100.542	782.282	24.808
2300	58.912	306.051	106.420	783.095	31.713
2400	59.143	308.563	112.323	783.878	38.402
2500	59.354	310.982	118.248	784.631	44.875
2600	59.546	313.314	124.193	785.364	51.142
2700	59.712	315.564	130.157	786.076	57.207
2800	59.861	317.739	136.137	786.766	63.080
2900	60.027	319.843	142.132	787.434	68.771
3000	60.162	321.880	148.142	788.080	74.282
3100	60.285	323.855	154.164	788.706	79.614
3200	60.399	325.771	160.199	789.311	84.777
3300	60.503	327.631	166.249	789.896	89.771
3400	60.602	329.449	172.304	790.461	94.605
3500	60.692	331.197	178.364	791.006	99.289
3600	60.775	332.908	184.438	791.531	103.832
3700	60.853	334.574	190.519	792.036	108.245
3800	60.925	336.198	196.608	792.521	112.528
3900	60.992	337.781	202.704	792.986	116.681
4000	61.055	339.326	208.806	793.431	120.714
4100	61.113	340.833	214.915	793.856	124.637
4200	61.168	342.308	221.029	794.261	128.452
4300	61.220	343.748	227.148	794.646	132.159
4400	61.268	345.156	233.273	795.011	135.759
4500	61.313	346.533	239.402	795.356	139.254
4600	61.355	347.881	245.535	795.681	142.645
4700	61.395	349.201	251.673	795.986	145.931
4800	61.433	350.494	257.814	796.271	149.114
4900	61.469	351.761	263.959	796.536	152.205
5000	61.502	353.003	270.108	796.781	155.205
5100	61.534	354.222	276.260	797.006	158.114
5200	61.564	355.417	282.415	797.211	160.933
5300	61.593	356.590	288.572	797.396	163.662
5400	61.620	357.741	294.733	797.561	166.301
5500	61.645	358.872	300.896	797.706	168.850
5600	61.670	359.983	307.062	797.831	171.309
5700	61.693	361.075	313.230	797.936	173.678
5800	61.715	362.148	319.401	798.021	175.957
5900	61.735	363.203	325.573	798.086	178.146
6000	61.755	364.241	331.748	798.131	180.245

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

Beryllium Hydroxide, Ion (BeOH⁺) $M_r = 26.018971$ $\Delta_f H^\circ(0\text{ K}) = 754.70 \pm 50\text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_f H^\circ(298.15\text{ K}) = 759.93 \pm 50\text{ kJ}\cdot\text{mol}^{-1}$

IDEAL GAS

Vibrational Frequencies and Degeneracies
 ν , cm⁻¹
 [1260] (1)
 [600] (2)
 [3650] (1)

Ground State Quantum Weight: [1] $\sigma = 1$
 Point Group: [C_{2v}]
 Bond Distances: Be-O = [1.38] Å; O-H = [0.96] Å
 Bond Angle Be-O-H = [180]°
 Rotational Constant: B₀ = [1.2932] cm⁻¹

Enthalpy of Formation
 Using mass spectrometric techniques, Inami and Ju¹ determined the appearance potential of BeOH(g) to be 9.0 ± 0.5 eV (207.55 ± 11.53 kcal·mol⁻¹). In the same study, Porter² was reported to have said that the appearance potential of a metal hydroxide is expected to be about the same as the corresponding fluoride. In this case, the appearance potential of BeF(g) is 9.1 eV¹, which is within 0.1 eV of the value for BeOH(g). It is also interesting to note that the ionization potential of Be(g) is 9.32 eV. We adopt the experimentally determined appearance potential of 9.0 ± 0.5 eV which refers to the process BeOH(g) + e⁻ = BeOH⁺(g) + 2e⁻. Using auxiliary data,³ we calculate Δ_fH°(0 K) = 180.39 ± 12.0 kcal mol⁻¹ for BeOH⁺(g). This leads to Δ_fH°(298.15 K) = 181.63 ± 12.0 kcal·mol⁻¹.

Heat Capacity and Entropy
 The molecular configuration is assumed to be linear since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.^{4,5,6} In addition, Walsh⁷ had predicted that BAH molecules (H-hydrogen atom) with ten or less valence electrons (BeOH⁺ has 8 valence electrons) will be linear in their ground state. The molecule BeOH⁺ is isoelectronic with LiOH.
 The bond dissociation energy for BeOH⁺(121.2 kcal·mol⁻¹)³ for the process BeOH⁺(g) = Be⁺(g) + OH(g) is fairly close to that for BeOH(113.9 kcal·mol⁻¹).³ This suggests a similar bonding in these two molecules. Thus, bond distances are assumed to be the same as those adopted for BeOH(g).³ The vibrational frequencies are assumed to be similar to those adopted for BeOH(g).³ The ground state quantum weight is assumed to be the same as that of LiOH(g).¹

References
¹Y. H. Inami and F. Ju, Philco-Ford Corp., Aeronutronic Dev., Report U-4307, Contract F 04611-68-C-0012, (February 1, 1968).
²R. F. Porter, personal communication, as referenced by Inami and Ju.
³JANAF Thermochemical Tables: e⁻(ref), 3-31-65, Be⁺(g), 6-30-71; BeOH(g), 12-31-75.
⁴N. Acquista, S. Abramowitz, and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
⁵R. L. Kuczowski and D. R. Lide, J. Chem. Phys. 44, 3131 (1966).
⁶N. Acquista, and S. Abramowitz, U. S. Nat. Bur. Stand. Report 9905, Ch. 6 (July, 1968); refer to pp. 99-111.
⁷A. D. Walsh, J. Chem. Soc. 1953, 2288.

Beryllium Hydroxide, Ion (BeOH⁺)

Beryllium Hydride (BeH₂)Beryllium Hydride (BeH₂)Be₁H₂(g)

$$\Delta H_f^\circ(\text{K}) = [127.21] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^\circ(298.15 \text{ K}) = [125.52] \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = [173.1] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

IDEAL GAS

Vibrational Frequencies and Multiplicities

 ν, cm^{-1}

[2200] (1)

[1500] (2)

[1300] (1)

Ground State Quantum Weight: 1

Point Group: [D_{∞h}]

Bond Distance: Be-H = [1.34] Å

Bond Angle: H-Be-H = [180]°

Rotational constant: B_v = [4.657172] cm⁻¹

σ = 2

Enthalpy of Formation

Estimated by O'Brien, Perrin and Perrine.¹

Heat Capacity and Entropy

Molecular and spectroscopic parameters estimated.

References

¹C. J. O'Brien and J. R. Perrin, Marquardt Corp., Van Nuys, Calif. and J. Perrine, Olin Mathieson Chemical Corp. New York 22, N. Y., Estimation of the Heats of Formation of Gaseous Combustion Product Molecules, (October, 1959).

T/K	C _p ^o	S ^o - (G ^o - HF(T)) / T	Standard State Pressure = p ^o = 0.1 MPa	log K _r
	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	kJ·mol ⁻¹	
0	0	INFINITE	-8.714	INFINITE
100	29.101	141.109	127.206	127.206
200	29.204	161.292	-5.822	123.071
300	29.588	173.842	-2.910	119.159
400	29.588	167.843	-1.442	117.379
500	30.370	173.115	0	117.379
600	30.408	173.303	0.056	115.682
700	31.659	178.079	1.666	115.622
800	35.253	182.466	3.227	114.037
900	34.999	186.421	4.953	112.566
1000	36.842	190.204	6.729	111.195
1100	40.446	197.244	10.595	109.908
1200	43.678	203.727	14.805	107.540
1300	46.434	209.744	19.315	105.378
1400	48.733	215.351	24.077	103.363
1500	50.634	220.587	29.048	101.458
1600	52.204	225.489	34.192	99.637
1700	53.505	230.088	39.480	97.885
1800	54.589	234.415	44.896	96.192
1900	55.496	238.493	50.392	94.554
2000	56.262	242.351	55.981	92.968
2100	56.912	246.003	61.640	91.433
2200	57.467	249.470	67.360	90.475
2300	57.944	252.769	73.131	89.499
2400	58.357	255.913	78.947	88.492
2500	58.716	258.916	84.801	87.448
2600	59.030	261.788	90.688	86.332
2700	59.306	264.541	96.627	85.221
2800	59.550	267.183	102.548	84.115
2900	59.766	269.722	108.514	83.015
3000	59.958	272.165	114.501	81.916
3100	60.131	274.520	120.505	80.816
3200	60.285	276.793	126.526	79.716
3300	60.425	278.988	132.562	78.616
3400	60.551	281.110	138.611	77.516
3500	60.665	283.163	144.672	76.416
3600	60.768	285.156	150.743	75.316
3700	60.863	287.087	156.825	74.216
3800	60.950	288.961	162.916	73.116
3900	61.029	290.782	169.015	72.016
4000	61.102	292.552	175.121	70.916
4100	61.169	294.274	181.235	69.816
4200	61.231	295.951	187.355	68.716
4300	61.288	297.585	193.481	67.616
4400	61.341	299.177	199.612	66.516
4500	61.390	300.731	205.749	65.416
4600	61.436	302.247	211.890	64.316
4700	61.478	303.728	218.036	63.216
4800	61.518	305.175	224.186	62.116
4900	61.555	306.590	230.339	61.016
5000	61.590	307.974	236.497	59.916
5100	61.622	309.328	242.657	58.816
5200	61.653	310.653	248.821	57.716
5300	61.681	311.952	254.988	56.616
5400	61.708	313.224	261.157	55.516
5500	61.734	314.471	267.329	54.416
5600	61.758	315.693	273.504	53.316
5700	61.780	316.893	279.681	52.216
5800	61.802	318.070	285.860	51.116
5900	61.822	319.225	292.041	50.016
6000	61.841	320.360	298.224	48.916
6100	61.859	321.474	304.409	47.816
6200	61.876	322.569	310.596	46.716
6300	61.893	323.646	316.785	45.616
6400	61.908	324.704	322.975	44.516
6500	61.923	325.744	329.166	43.416
6600				42.316
6700				41.216
6800				40.116
6900				39.016
7000				37.916
7100				36.816
7200				35.716
7300				34.616
7400				33.516
7500				32.416
7600				31.316
7700				30.216
7800				29.116
7900				28.016
8000				26.916
8100				25.816
8200				24.716
8300				23.616
8400				22.516
8500				21.416
8600				20.316
8700				19.216
8800				18.116
8900				17.016
9000				15.916
9100				14.816
9200				13.716
9300				12.616
9400				11.516
9500				10.416
9600				9.316
9700				8.216
9800				7.116
9900				6.016
10000				4.916

PREVIOUS: December 1960 (1 atm)

CURRENT: December 1960 (1 bar)

Beryllium Hydride (BeH₂)Be₁H₂(g)

Beryllium Hydroxide, Alpha (α -Be(OH)₂)CRYSTAL(α)M_r = 43.02686Beryllium Hydroxide, Alpha (Be(OH)₂)Be₂H₂O₂(cr)

Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure = p° = 0.1 MPa			
T/K	C _p ^o J·K ⁻¹ ·mol ⁻¹	S° - [G° - H°(T)]/T J·K ⁻¹ ·mol ⁻¹	H° - H°(T) kJ·mol ⁻¹	Δ _f G° kJ·mol ⁻¹	log K _r
0					
100					
200					
298.15	65.701	53.555	0.	-902.907	142.948
300	66.053	53.963	0.122	-902.923	141.973
400	82.902	75.434	7.626	-903.139	102.661
500	92.994	95.086	16.451	-902.397	79.081
600	99.387	112.633	26.086	-901.119	63.378
700	103.956	128.310	36.261	-899.527	52.180
800	107.495	142.430	46.839	-897.735	43.798
900	110.399	155.262	57.737	-895.810	37.292
1000	112.905	167.027	68.906	-893.790	32.098

$S^{\circ}(298.15\text{ K}) = [53.6 \pm 8] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $\Delta_f H^{\circ}(0\text{ K}) = \text{Unknown}$
 $\Delta_f H^{\circ}(298.15\text{ K}) = -902.9 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

Bear and Turnbull¹ measured the enthalpy of solution of α -Be(OH)₂ and Be in 22.6% HF(aq) at 21°C. Combining these results, adjusting to 25°C, and correcting for the small HF concentration differences in the two systems, we calculate $\Delta_f H^{\circ}(298.15\text{ K}) = -79.16 \text{ kcal}\cdot\text{mol}^{-1}$ for the reaction $\text{Be}(\text{cr}) + 2\text{H}_2\text{O}(\text{l}) = \text{Be}(\text{OH})_2(\alpha, \text{cr}) + \text{H}_2(\text{g})$. Using auxiliary data,^{2,3} we derive $\Delta_f H^{\circ}(298.15\text{ K}) = -215.8 \text{ kcal}\cdot\text{mol}^{-1}$ for α -Be(OH)₂. Since this adopted value is calorimetrically determined and based on well characterized samples, we assign an uncertainty of $\pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$.

Parker⁴ recently reviewed data pertaining to the enthalpy of formation of the beryllium hydroxides. Her analyses were intended to give additional support to the thermochemical values chosen for BeO(cr). Our interpretation would differ slightly due to the fact that our $\Delta_f H^{\circ}$ value for BeO(cr) is different (by 0.3 kcal·mol⁻¹ at 298.15 K) from that adopted by Parker.⁴ Discussed in her review are the enthalpy of solution studies by Fricks and Wullhorst⁵ [involving BeO and α -Be(OH)₂ in 11.59% HF] and Matignon and Marchal^{6,7} [amorphous Be(OH)₂ in 30% HF]. In addition there is also an earlier study by Mulet⁸ involving amorphous Be(OH)₂ in 20% HF. All these studies are in fair agreement with our adopted value for $\Delta_f H^{\circ}(298.15\text{ K})$. These latter studies are thought to be less reliable, however, due to incomplete characterization of the beryllium compounds.

Heat Capacity and Entropy

The heat capacity is assumed to be identical to that of the β -phase. The entropy difference between the α and β phases may be obtained from the solubility data of Fricke and Humme.⁹ Both crystalline forms of Be(OH)₂ were dissolved in varying concentrations of aqueous NaOH. By relating the quantities dissolved, we calculate $\Delta_f G^{\circ}(303\text{ K}) = -0.5 (\pm 0.2) \text{ kcal}\cdot\text{mol}^{-1}$ for the process $\alpha\text{-Be}(\text{OH})_2 = \beta\text{-Be}(\text{OH})_2$. Using auxiliary data,² we find $\Delta_f S^{\circ}(303\text{ K}) = -0.8 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, from which we calculate and adopt $S^{\circ}(298.15\text{ K}) = 12.8 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for α -Be(OH)₂. We assign an uncertainty of $\pm 2 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to reflect the possible error in this calculation of $\Delta_f S^{\circ}(303\text{ K})$.

Phase Data

The structural information for α -Be(OH)₂ via x-ray techniques is not complete.¹⁰⁻¹¹ A tetragonal unit cell has been suggested by Guillemat and Lecoq¹¹ without supporting data. Bear and Turnbull,¹ following this suggestion and using their x-ray data, calculated a crystal density which was consistent with the two experimentally determined values of Fricke and Severin¹² (helium densitometry and a pycnometric method). This lends support to the premise that α -Be(OH)₂ has a tetragonal unit cell. The alpha phase is metastable.

Decomposition Data

T_{dem} is calculated as the temperature at which $\Delta_f G^{\circ}$ is zero for the reaction $\text{Be}(\text{OH})_2(\alpha, \text{cr}) = \text{BeO}(\alpha, \text{cr}) + \text{H}_2\text{O}(\text{g})$.

References

- J. J. Bear and A. G. Turnbull, *J. Phys. Chem.* **69**, 2828 (1965).
- JANAF Thermochemical Tables: Be(cr), 9-30-61, H₂(g) and H₂O(g), 3-31-61; BeO(aq, cr), 6-30-75, Be(OH)₂(β , cr), 12-31-75.
- U. S. Nat. Bur. Stand. Tech. Note 270-3, 264 pp. (1968).
- V. B. Parker, *J. Res. Nat. Bur. Stand.* **77A**, 227 (1973); U. S. Nat. Bur. Stand. Report 10004, pp 58-81, (January, 1969).
- R. Fricke and B. Wullhorst, *Z. anorg. allgem. Chem.* **205**, 127 (1932).
- C. Matignon and G. Marchal, *Bull. Soc. Chim. France* **39**, 167 (1926).
- C. Matignon and G. Marchal, *Compt. Rend.* **181**, 859 (1925).
- O. Mulet, *Z. anorg. allgem. Chem.* **75**, 198 (1912).
- R. Fricke and H. Humme, *Z. anorg. allgem. Chem.* **178**, 400 (1929).
- M. Bernier, *Commission Energie Atomique (France) Rapport CEA2326* (1963).
- A. Guillemat and A. Lecoq, *Compt. Rend.* **257**, 1260 (1963).
- R. Fricke and H. Severin, *Z. anorg. allgem. Chem.* **205**, 287 (1932).

PREVIOUS: December 1966

CURRENT: December 1975

Beryllium Hydroxide, Alpha (Be(OH)₂)Be₂H₂O₂(cr)

Beryllium Hydroxide, Beta (β -Be(OH)₂)CRYSTAL(β)M_r = 43.02686Beryllium Hydroxide, Beta (Be(OH)₂)Be₂H₂O₂(cr)

S°(298.15 K) = [50.2 ± 4.2] J K⁻¹·mol⁻¹
 T_{am} = [366] K

Δ_rH°(298.15 K) = -905.8 ± 2.1 kJ·mol⁻¹
 Δ_rH°(0 K) = Unknown

Enthalpy of Formation

Bear and Turnbull¹ measured the enthalpy of solution of β-Be(OH)₂ and Be in 22.6% HF(aq) at 21°C. Combining these results, adjusting to 25°C, and correcting for the small HF concentration differences in the two systems, we calculate Δ_rH°(298.15 K) = -79.89 kcal·mol⁻¹ for the reaction Be(cr) + 2H₂O(l) = Be(OH)₂(β, cr) + H₂(g). Using auxiliary data,^{2,3} we derive Δ_rH°(298.15 K) = -216.5 kcal·mol⁻¹ for β-Be(OH)₂. Since this adopted value is calorimetrically determined and based on well characterized samples, we assign an uncertainty of ±0.5 kcal·mol⁻¹.

Parker⁴ recently reviewed data pertaining to the enthalpy of formation of the beryllium hydroxides. Her analyses were intended to give additional support to the thermochemical values chosen for BeO(cr). Our interpretation would differ slightly due to the fact that our Δ_rH° value for BeO(cr) is different (by 0.3 kcal·mol⁻¹) at 298.15 K from that adopted by Parker.⁴ Discussed in her review were the enthalpy of solution studies by Fricke and Wulthors⁵ [involving BeO and β-Be(OH)₂ in 11.59% HF] and Matignon and Marchal⁶ [amorphous Be(OH)₂ in 30% HF]. In addition there is also an earlier study by Muler⁷ involving amorphous Be(OH)₂ in 20% HF. These latter three studies are in fair agreement with our adopted value for Δ_rH°(298.15 K) but are thought to be less reliable, however, due to incomplete characterization of the beryllium compounds.

Fricke and Severin⁸ and Baur and Lecoq¹⁰ measured the decomposition pressure of water vapor over β-Be(OH)₂, Fricke and Severin⁹ observed a decomposition temperature at 105°C at a pressure of 100 mm Hg while Baur and Lecoq¹⁰ observed 223°C for the equilibrium with saturated water vapor at 24.2 atm. We reduce the latter data to a standard state value Δ_rG°(496 K) = -3028 cal·mol⁻¹ for the decomposition reaction Be(OH)₂(β, cr) → BeO(α, cr) + H₂O(g). The 3rd law analyses for these two decomposition studies are given below where Δ_rH°(298.15 K) refers to the enthalpy of formation of β-Be(OH)₂.

Source	T/K	Method	Δ _r H°(298.15 K) kcal·mol ⁻¹	Δ _r H°(298.15 K)
Fricke and Severin ⁹	378	K _p	15.27	≥ -218.5
Baur and Lecoq ¹⁰	496	K _p	14.88	≥ -218.1

These values are within 2 kcal·mol⁻¹ of our adopted Δ_rH°(298.15 K) value. The difference may be due to the formation of metastable BeO. Fricke and Severin⁹ reported that BeO had a distorted lattice which would suggest a Δ_rH° value more positive than -145.4 kcal·mol⁻¹. Thus, we conclude that these two studies^{9,10} are consistent with our adopted value but are not sufficiently definitive for further consideration.

Heat Capacity and Entropy

The heat capacity is estimated from that for Mg(OH)₂ by subtracting the values for MgO(cr) and adding those for BeO(α, cr).² The entropy is estimated to be S°(298.15 K) = 12.0 cal·K⁻¹·mol⁻¹. This value is a compromise of values suggested by two different paths. Additive entropy constants of Kelley¹¹ yield S°(298.15 K) = 13.20 cal·K⁻¹·mol⁻¹, whereas a comparison of entropy differences for the alkali metal and alkaline earth chlorides and hydroxides suggest values in the range 10.2 to 12.4 cal·K⁻¹·mol⁻¹. Our adopted value is the same as that selected by NBS.¹²

Phase Data

Bear and Turnbull¹ and Seitz *et al.*,¹³ using x-ray powder techniques, determined that β-Be(OH)₂ has an orthorhombic structure, the ε-Zn(OH)₂ structure. The β-structure is the stable crystalline form for Be(OH)₂, whereas the α-structure is metastable.

Decomposition Data

T_{am} is calculated as the temperature at which Δ_rG° is zero for the reaction Be(OH)₂(β, cr) → BeO(α, cr) + H₂O(g).

References

1. J. Bear and A. G. Turnbull, *J. Phys. Chem.* **69**, 2828 (1965).
2. JANAF Thermochemical Tables: Be(cr), 9-30-61; H₂(g) and H₂O(g), 3-31-61; BeO(α, cr), 6-30-75; BeO(β, cr) and MgO(cr), 12-31-74; Mg(OH)₂(cr), 12-31-75.
3. U. S. Nat. Bur. Stand. Tech. Note 270-3, 264 pp. (1968).
4. V. B. Parker, *J. Res. Nat. Bur. Stand.* **77A**, 227 (1973); U. S. Nat. Bur. Stand. Report 10004, pp. 58-81, (January, 1969).
5. R. Fricke and B. Wulthors, *Z. anorg. allgem. Chem.* **205**, 127 (1932).
6. C. Matignon and G. Marchal, *Bull. Soc. Chim. France* **39**, 167 (1926).
7. C. Matignon and G. Marchal, *Compt. Rend.* **181**, 859 (1925).
8. O. Muler, *Z. anorg. allgem. Chem.* **178**, 198 (1912).
9. R. Fricke and H. Severin, *Z. anorg. allgem. Chem.* **205**, 287 (1932).
10. A. Baur and A. Lecoq, *Comm. Energie At. (France)*, *Rapport. CEA-R2611*, 17 pp. (1964).
11. D. R. Stull and H. Prophet in "The Characterization of High Temperature Vapors," J. L. Margrave, ed., John Wiley and Sons Inc., New York (1966).
12. U. S. Nat. Bur. Stand. Tech. Note 270-6, 119 pp. (1971).
13. A. Seitz, U. Rosler, and K. Schubert, *Z. anorg. allgem. Chem.* **261**, 94 (1960).

PREVIOUS: December 1966

CURRENT: December 1975

Beryllium Hydroxide, Beta (Be(OH)₂)Be₂H₂O₂(cr)

Beryllium Hydroxide (Be(OH)₂)

IDEAL GAS

Beryllium Hydroxide (Be(OH)₂)

Be₁H₂O₂(g)

S°(298.15 K) = [233.97 ± 12.6] J·K⁻¹·mol⁻¹

Δ_fH°(298.15 K) = -677 ± 38 kJ·mol⁻¹

M_r = 43.02686

Standard State Pressure = p° = 0.1 MPa

Table with 2 columns: Vibrational Frequencies and Degeneracies (v, cm⁻¹) and values: [670](1), [3650](2), [945](2), [606](4), [1530](1).

Ground State Quantum Weight: [1]

Point Group: [C_{2v}]

Bond Distances: Be-O = [1.42] Å; O-H = [0.96] Å

Bond Angles: Be-O-H = [180]°; O-Be-O = [180]°

Rotational Constant: B₀ = [0.22198] cm⁻¹

σ = 2

Enthalpy of Formation

The equilibrium reaction BeO(α, cr) + H₂O(g) = Be(OH)₂(g) has been studied by several investigators... all inferred that Be(OH)₂ was the major product, but there was no direct proof of this.

Table with 4 columns: Investigator, Data Points, Δ_fH°(298.15 K), kcal·mol⁻¹ (2nd and 3rd law), and Drift (cal·K⁻¹·mol⁻¹). Includes entries from Stuart and Price, Young, Grossweiner and Seifert, Blauer et al., Brewer and Elliott, and Moritze et al.

*One (or two) point(s) rejected due to a statistical test.

Three of these studies were conducted under similar conditions. Each of these investigations varied the H₂O(g) flow rate without a detectable change in K_p value. However, one study used a considerably larger flow rate than the others.

We adopt Δ_fH°(298.15 K) = -161.7 kcal·mol⁻¹ for Be(OH)₂(g) which is an average value of three studies... We assign an uncertainty of ±0.0 kcal·mol⁻¹.

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized. The O-Be-O angle is assumed to be the same as the F-Be-F angle...

Main data table with 13 columns: T/K, C_p, S°, H° - H°(T)/T, Δ_fH°, Δ_fG°, log K_p. Rows range from 0 to 6000 K.

PREVIOUS: December 1975 (1 atm)

CURRENT: December 1975 (1 bar)

Continued on page 428

Beryllium Hydroxide (Be(OH)₂)

Be₁H₂O₂(g)

Beryllium Iodide (BeI)

IDEAL GAS

Beryllium Iodide (BeI)

BeI₂(g)

$S^{\circ}(298.15 \text{ K}) = 237.30 \pm 0.21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $\Delta H_f^{\circ}(0 \text{ K}) = 169.5 \pm 41.8 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta H_f^{\circ}(298.15 \text{ K}) = 170.0 \pm 41.8 \text{ kJ} \cdot \text{mol}^{-1}$

Electronic Levels and Quantum Weights	
State	g_i
$X^1\Sigma^+$	0
$A_1^3\Pi_{1/2}$	2
$A_2^3\Pi_{3/2}$	2

$\omega_e = 611.7 \text{ cm}^{-1}$ $\sigma = 1$
 $B_e = 0.4466 \text{ cm}^{-1}$ $\alpha_e = [3.36] \text{ cm}^{-1}$ $r_e = 2.132 \text{ \AA}$
 $\alpha_e = [0.0042] \text{ cm}^{-1}$

Enthalpy of Formation

No thermochemical measurements of the enthalpy of formation has been made. The selected value, $\Delta H_f^{\circ}(\text{BeI}, 0 \text{ K}) = 40.5 \text{ kcal} \cdot \text{mol}^{-1}$, is obtained from an analysis of spectroscopic data. The adopted values for the ground state vibrational constants give $D_0^{\circ} = 3.41 \text{ eV}$ (78.73 kcal·mol⁻¹) via a linear Bergs-Spencer extrapolation.¹ Based on the ionicity correction developed by Hildenbrand,² this value adjusts to $D_0^{\circ} = 2.70 \text{ eV}$ (62.43 kcal·mol⁻¹). We adopt $D_0^{\circ} = 62.4 \pm 10 \text{ kcal} \cdot \text{mol}^{-1}$, which corresponds to $\Delta H_f^{\circ}(0 \text{ K}) = 40.5 \pm 10.0 \text{ kcal} \cdot \text{mol}^{-1}$.

Support for the adopted D_0° value is provided by an examination of the trends in the dissociation energies for all alkaline earth monohalides and a comparison of the values for the ratio $\Delta_e H_f^{\circ}(\text{MX}, 298.15 \text{ K}) / \Delta_e H_f^{\circ}(\text{MX}_2, 298.15 \text{ K})$ for the alkaline earth halides.³ For the beryllium iodides this ratio is 0.44 which is consistent with the values of this ratio for other alkaline earth halides.

Heat Capacity and Entropy

The ground state vibrational and rotational constants are derived from spectroscopic studies by Murty and Rao.^{4,5} The reported value for ω_e (1.6 cm⁻¹) appears to be inconsistent with the values obtained for other alkaline earth monohalides. By a comparison of $(\omega_e/\omega_e \cdot x_e)$ and x_e/r_e^2 values, we estimate ω_e to be 3.36 cm⁻¹ and adopt this value. The reported B_e value is converted to B_e by using a calculated value for α_e . We calculate α_e from the relation $\alpha_e/B_e = 13.2 (B_e/\omega_e)$ as suggested by Calder and Ruedenberg.⁷ Initially we use the B_e value in this relationship and then iterate to obtain consistent values for B_e and α_e . We calculate $r_e = 2.132 \text{ \AA}$ from B_e . This corresponds well with the 2.12 Å Be-I distance for BeI₂(g) obtained via the electron diffraction study of Akishin *et al.*⁸

The electronic levels are also from the study by Murty and Rao.^{4,5} The possibility of additional levels (²I and ²Σ⁺) near 15000 cm⁻¹ is suggested by a comparison with Cal, Srl, and Bal.³ Including these levels does not change the entropy at 298.15 K but does increase the entropy at 6000 K by 0.7 cal·K⁻¹·mol⁻¹.

References

- ¹A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall, London, 330 pp. (1968); refer to p. 264.
- ²D. L. Hildenbrand in "Advances in High Temperatures Chemistry", Vol. 1, Ed. by L. Eyring, Academic press, New York, (1967).
- ³JANAF Thermochemical Tables: BeI₂(g), 12–31–75, Bal(g), Srl(g), and Cal(g), 6–30–74.
- ⁴P. S. Murty and P. T. Rao, *Curr. Sci.* 38, 187 (1969).
- ⁵P. S. Murty and P. T. Rao, *Curr. Sci.* 38, 537 (1969).
- ⁶P. S. Murty and P. T. Rao, *Proc. Roy. Ir. Acad., Sect. A72*, 71 (1972).
- ⁷G. V. Calder and K. Ruedenberg, *J. Chem. Phys.* 49, 5399 (1968).
- ⁸P. A. Akishin, V. P. Spiridonov, and G. A. Sobolev, *Dokl. Akad. Nauk SSSR* 118, 1134 (1958).

T/K	C _p ^o	S ^o - (C _p ^o - RT)/T	Standard State Pressure = P ^o = 0.1 MPa		
			H ^o - H ^o (T)	ΔH ^o	log K _r
0	0	0	INFINITE	169.452	INFINITE
100	29.217	203.629	-9.098	169.452	169.452
200	31.228	224.384	-6.188	170.798	170.798
300	32.473	231.489	-3.182	170.760	170.760
400	33.473	237.297	-1.589	170.447	170.447
500	33.509	237.505	0	170.018	170.018
600	34.321	242.734	0.062	170.000	170.000
700	34.949	247.359	1.759	169.412	169.412
800	35.437	251.505	3.491	167.767	167.767
900	35.821	255.259	5.251	165.923	165.923
1000	36.277	261.843	7.033	164.319	164.319
1100	36.755	267.481	8.652	162.976	162.976
1200	37.258	272.407	10.405	161.900	161.900
1300	37.785	276.781	12.289	161.066	161.066
1400	38.335	280.574	14.307	160.418	160.418
1500	38.902	283.776	16.469	160.000	160.000
1600	39.484	286.399	18.774	159.856	159.856
1700	40.080	288.542	21.224	159.914	159.914
1800	40.689	290.217	23.818	160.166	160.166
1900	41.309	291.525	26.555	160.600	160.600
2000	41.937	292.567	29.434	161.200	161.200
2100	42.571	293.344	32.454	161.950	161.950
2200	43.209	293.867	35.614	162.822	162.822
2300	43.850	294.143	38.914	163.798	163.798
2400	44.492	294.171	42.354	164.866	164.866
2500	45.134	293.954	45.924	166.014	166.014
2600	45.774	293.492	49.624	167.232	167.232
2700	46.412	292.796	53.454	168.518	168.518
2800	47.047	291.877	57.414	169.862	169.862
2900	47.678	290.744	61.504	171.254	171.254
3000	48.304	289.407	65.734	172.684	172.684
3100	48.924	287.867	70.104	174.154	174.154
3200	49.537	286.122	74.614	175.664	175.664
3300	50.143	284.171	79.254	177.204	177.204
3400	50.741	282.024	84.024	178.774	178.774
3500	51.330	279.681	88.924	180.374	180.374
3600	51.910	277.143	93.954	182.004	182.004
3700	52.480	274.411	99.114	183.654	183.654
3800	53.040	271.485	104.404	185.324	185.324
3900	53.590	268.367	109.814	187.004	187.004
4000	54.130	265.057	115.344	188.694	188.694
4100	54.660	261.557	121.004	190.394	190.394
4200	55.180	257.867	126.794	192.104	192.104
4300	55.690	253.987	132.704	193.824	193.824
4400	56.190	249.917	138.734	195.554	195.554
4500	56.680	245.657	144.874	197.294	197.294
4600	57.160	241.207	151.124	199.044	199.044
4700	57.630	236.567	157.484	200.804	200.804
4800	58.090	231.737	163.954	202.574	202.574
4900	58.540	226.717	170.534	204.354	204.354
5000	58.980	221.507	177.224	206.144	206.144
5100	59.410	216.107	184.024	207.944	207.944
5200	59.830	210.517	190.914	209.754	209.754
5300	60.240	204.737	197.914	211.574	211.574
5400	60.640	198.767	205.024	213.404	213.404
5500	61.030	192.607	212.134	215.244	215.244
5600	61.410	186.257	218.964	217.094	217.094
5700	61.780	179.717	226.404	218.954	218.954
5800	62.140	172.987	234.454	220.864	220.864
5900	62.490	166.067	243.114	222.794	222.794
6000	62.830	158.957	252.284	224.744	224.744

CURRENT: December 1975 (1 bar)

PREVIOUS: December 1975 (1 atm)

Beryllium Iodide (BeI)

BeI₂(g)

Be₁₂(cr)

M_r = 262.82118 Beryllium Iodide (BeI₂)

CRYSTAL

Beryllium Iodide (BeI₂)

$S^{\circ}(298.15\text{ K}) = [120.5 \pm 4.2] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 753 \pm 15 \text{ K}$
 $\Delta H_f^{\circ}(0\text{ K}) = \text{Unknown}$
 $\Delta H_f^{\circ}(298.15\text{ K}) = [-188.7 \pm 21] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{sub}}H^{\circ} = [20.9 \pm 12.6] \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

A direct measurement of the enthalpy of formation has not been made. An estimate of ΔH_f° is obtained by a method suggested by Parker¹ and used in the BeBr₂(cr) table.² Biltz and Messerknecht³ have measured the enthalpies of solution of BeCl₂(cr) and BeI₂(cr) in aqueous HCl (18.69%). Samples⁴ of the dihalides were prepared from reactions of BeO-C mixtures with the halogens at elevated temperatures. We assume that the two dihalides had similar structures, i.e. the α -form (orthorhombic). $\Delta H_f^{\circ}(\text{BeI}_2)$ in 18.7% HCl, 298.15 K is estimated at -109.1 kcal·mol⁻¹ by combining ΔH_f° of BeCl₂(cr) with $\Delta H_f^{\circ}(\text{BeCl}_2)$, cr, α , 298.15 K = -117.3 ± 0.8 kcal·mol⁻¹,² and twice the difference in $\Delta H_f^{\circ}(\text{HCl}18\text{H}_2\text{O}, 298.15\text{ K})$ and $\Delta H_f^{\circ}(\text{HCl}9\text{H}_2\text{O}, 298.15\text{ K})$ which is -52.3 kcal·mol⁻¹.⁵ The enthalpy associated with the aqueous anions is assumed to be negligible. Combination of the estimated value for $\Delta H_f^{\circ}(\text{BeI}_2)$ in 18.8% HCl, 298.15 K with $\Delta H_f^{\circ} = -62.5 \text{ kcal}\cdot\text{mol}^{-1}$ gives $\Delta H_f^{\circ}(\text{BeI}_2, \text{ cr}, 298.15\text{ K}) = -46.6 \text{ kcal}\cdot\text{mol}^{-1}$ which is within 0.6 kcal·mol⁻¹ of the value suggested by NBS.⁶ Subsequent measurements by Biltz *et al.*,⁷ in less concentrated HCl (1.48%) solution leads to $\Delta H_f^{\circ}(298.15\text{ K}) = -43.6 \text{ kcal}\cdot\text{mol}^{-1}$ by a similar route. We adopt an average value of -45.1 kcal·mol⁻¹, but emphasize that the uncertainty in ΔH_f° is much greater than indicated (3 kcal·mol⁻¹) by the closeness of these two values. An uncertainty of ±0.5 kcal·mol⁻¹ is believed to be more realistic.

Heat Capacity and Entropy

No low-temperature heat capacity or high-temperature enthalpy measurements have been reported. We estimate $C_p^{\circ}(298.15\text{ K}) = 16.482 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from the reaction $\text{BeCl}_2(\text{cr}, \alpha) + 2\text{LiI}(\text{cr}) = \text{BeI}_2(\text{cr}) + 2\text{LiCl}(\text{cr})$ by assuming $\Delta C_p^{\circ} = 0$. Similar results are obtained using $\text{BeF}_2(\text{cr})$ C_p° values above 298.15 K as assumed to parallel those for $\alpha\text{-BeCl}_2$.²

Application of the Berthelot principle⁸ to the process $\text{BaI}_2(\text{cr}) + \text{Be}(\text{cr}) \rightarrow \text{Ba}(\text{cr}) + \text{BeI}_2(\text{cr})$ suggests $S^{\circ}(298.15\text{ K}) = 26.8 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. A graphical comparison of the standard entropies for other alkaline-earth dihalides⁹ indicates that this value is reasonable. Other estimated values are given by additive entropy constants (27.4 cal·K⁻¹·mol⁻¹),⁹ Brewer (31.0 cal·K⁻¹·mol⁻¹),¹⁰ and Brewer *et al.* (25 cal·K⁻¹·mol⁻¹).¹¹ For additional information of the heat capacity and entropy, refer to the enthalpy of formation discussion for gaseous BeI₂.²

Fusion Data

Refer to the liquid table for details.

Phase Data

Semenko and Naumova¹² studied the BeI₂ crystal modifications by thermal and x-ray techniques. The study was complicated by the extreme hygroscopicity, high vapor pressures near the melting point, and susceptibility to oxidation on heating by traces of oxygen. As stated by Semenko and Naumova,¹² the sequence of polymorphic conversion and the character of the resulting modifications of BeI₂, which are largely dependent on the heating and cooling conditions, parallel those of BeCl₂.¹³ They detected thermally transitions at 290°C, 370°C, 470°C, and a melting at 490°C. However, this data does not appear to be fully consistent in terms of crystallographic structures with that proposed by Johnson, Startzky, and Douglas¹⁴ and Messerknecht and Biltz.¹⁵ These latter works suggested two structures with a transition at 350°C. We assume the similarity with BeCl₂ with a transition in the vicinity of 350–370°C. Further study is necessary to resolve all possible phases and their structures.

Sublimation Data

Refer to the ideal gas table for details.

References

- ¹V. B. Parker, personal communication, Nat. Bur. Stand., (March, 1975).
- ²JANAF Thermochemical Tables: BeBr₂(cr), 6-30-75; BeI₂(cr) and BeI₂(g), 12-31-75; BeCl₂(cr, α), 6-30-75.
- ³W. Biltz and C. Messerknecht, Z. Anorg. Chem. 148, 157 (1925).
- ⁴C. Messerknecht and W. Biltz, Z. Anorg. Chem. 148, 152 (1925).
- ⁵U. S. Nat. Bur. Stand. Tech. Note 270-3, 264 pp. (1968).
- ⁶U. S. Nat. Bur. Stand. Tech. Note 270-6, 119 pp. (1971).
- ⁷W. Biltz, K. A. Klante, and E. Rahlf, Z. Anorg. Chem. 166, 339 (1927).
- ⁸N. N. Drozin, Zhur. Fiz. Khim. 35, 879 (1961).
- ⁹D. R. Stull and H. Prophet in "The Characterization of High Temperature Vapors," J. L. Margrave, Ed., John Wiley and Sons, Inc., New York, (1966).
- ¹⁰L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., National Nuclear Energy Series IV-19B, McGraw-Hill Book Co., New York, (1950).
- ¹¹L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
- ¹²O. N. Semenko and T. N. Naumova, Russ J. Structural Chem. 4, 59 (1963).
- ¹³O. N. Semenko, O. N. Breusov, A. V. Novoselova, and K. N. Semenko, Zhur. Fiz. Khim. 34, 343 (1960).
- ¹⁴R. E. Johnson, E. Startzky, and R. M. Douglas, J. Amer. Chem. Soc. 79, 2037 (1957).
- ¹⁵C. Messerknecht and W. Biltz, Z. anorg. allgem. Chem. 48, 152 (1925).

T/K	C _p ^o	S ^o - [G ^o - F(T _o)]/T	H ^o - H ^o (T _o)/T	Standard State Pressure = P ^o = 0.1 MPa	
				ΔH ^o	ΔG ^o
0					
100					
200					
298.15	68.961	120.499	0.	-188.698	-187.183
300	69.128	120.501	0.128	-188.702	-187.174
400	76.668	141.944	7.452	-204.858	-186.084
500	81.638	159.651	15.396	-247.213	-177.328
600	84.190	174.780	23.698	-244.932	-163.563
700	83.467	187.860	32.185	-247.604	-150.186
753.000	85.944	194.116	36.728	---	LIQUID <--> CRYSTAL
800	86.366	199.331	40.777	-240.288	-137.142
900	87.132	209.549	49.453	-237.995	-124.386
1000	87.789	218.764	58.200	-235.733	-111.885
1100	88.337	227.158	67.007	-233.512	-99.608
1200	88.780	234.864	75.864	-231.346	-87.531
1300	89.115	241.984	84.759	-229.252	-75.632
1400	89.341	248.597	93.683	-227.247	-63.891
1500	89.462	254.766	102.624	-225.354	-52.289

log K_r

32.794
32.590
24.300
18.525
14.239
11.207

PREVIOUS: June 1965

CURRENT: December 1975

Beryllium Iodide (BeI₂)

Be₁₂(cr)

Beryllium Iodide (BeI₂)

LIQUID

M_r = 262.82118Beryllium Iodide (BeI₂)BeI₂(l)

$$S^{\circ}(298.15 \text{ K}) = [128.999] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{fus}} = 753 \pm 15 \text{ K}$$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{\text{fus}}H^{\circ}$ and the difference enthalpy, $H^{\circ}(753 \text{ K}) - H^{\circ}(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with the measured value for BeCl₂.¹ A glass transition is assumed at 400 K below which the heat capacity is that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Rahfs and Fischer² reported a melting point of 753 K. Semenenko and Naumova,³ using thermal analysis techniques, implied a melting point of 763 K. Since this latter value was derived from a thermogram, it is probable that this value represents a maximum, with the true melting point somewhat lower. We adopt $T_{\text{fus}} = 753 \pm 15 \text{ K}$.

We estimate the enthalpy of melting, $\Delta_{\text{fus}}H^{\circ} = 5.0 \pm 3.0 \text{ kcal} \cdot \text{mol}^{-1}$. This estimate includes a contribution for melting (based on the entropy of melting for other alkaline earth dihalides) and a contribution for a phase transition. There is no experimental data available pertaining to the enthalpy of melting.

Vaporization Data

T_{vap} is the temperature at which $\Delta G^{\circ} = 0$ for the process BeI₂(l) = BeI₂(g). $\Delta_{\text{vap}}H^{\circ}$ is the corresponding difference in the ΔH° values for the liquid and gas at T_{vap} .

References

- ¹JANAF Thermochemical Table: BeCl₂(l), 6-30-65.
- ²O. Rahfs and W. Fischer, Z. Anorg. Chem. 211, 349 (1933).
- ³K. N. Semenenko and J. N. Naumova, Russ. J. Structural Chem. 4, 59 (1963).

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P ^o = 0.1 MPa	
	C _p ^o	S ^o - [C _p ^o - H ^o (T _r)]/T _r	H ^o - H ^o (T _r)/T	ΔG ^o
0				
100				
200				
298.15	68.961	128.999	0.	-178.377
300	69.128	129.426	0.128	-178.380
400	76.868	131.812	7.449	-179.402
400.000	76.868	131.812	7.449	-194.539
400.000	76.868	131.812	7.449	GLASS <---> LIQUID
400.000	112.968	131.812	7.449	TRANSITION
500	112.968	138.151	18.746	-233.542
600	112.968	146.168	30.043	-228.266
700	112.968	154.597	41.339	-223.128
753.000	112.968	159.047	47.327	--- CRYSTAL <---> LIQUID
800	112.968	162.943	52.636	-218.107
900	112.968	171.007	63.933	-213.193
1000	112.968	178.716	75.230	-208.581
1100	112.968	186.053	86.527	-203.671
1200	112.968	193.023	97.823	-199.065
1300	112.968	199.646	109.120	-194.569
1400	112.968	205.944	120.417	-190.192
1500	112.968	211.941	131.714	-185.943
				-138.486
				-128.830
				-119.715
				-111.077
				-102.863
				-94.578
				-87.538
				-80.355

PREVIOUS: June 1965

CURRENT: December 1975

Beryllium Iodide (BeI₂)BeI₂(l)

Beryllium Iodide (BeI₂)

CRYSTAL-LIQUID

0 to 753 K crystal
above 753 K liquid

Refer to the individual tables for details.

M_r = 262.82118 Beryllium Iodide (BeI₂)

BeI₂(cr,l)

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa		log K _r
		J·K ⁻¹ ·mol ⁻¹	S ^o - [G ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r)	Δ _r H ^o	
0						
100						
200						
298.15	68.961	120.499	0.	-188.698	-187.183	32.794
300	69.128	120.501	0.128	-188.702	-187.174	32.590
400	76.868	141.944	7.452	-204.858	-186.084	24.300
500	81.638	159.651	15.396	-247.213	-177.328	18.525
600	84.190	174.780	23.698	-244.932	-163.563	14.239
700	85.467	187.860	32.185	-242.604	-150.186	11.207
753.000	85.944	194.116	36.728			
753.000	112.968	221.898	57.648			
800	112.968	228.738	62.958	-218.107	-138.486	9.042
900	112.968	242.044	74.254	-213.193	-128.830	7.477
1000	112.968	253.946	85.551	-208.381	-119.715	6.253
1100	112.968	264.713	96.848	-203.671	-111.077	5.275
1200	112.968	274.542	108.145	-199.065	-102.863	4.478
1300	112.968	283.585	119.442	-194.569	-95.030	3.818
1400	112.968	291.957	130.738	-190.192	-87.538	3.266
1500	112.968	299.751	142.035	-185.943	-80.354	2.798

PREVIOUS.

CURRENT. December 1975

Beryllium Iodide (BeI₂)

BeI₂(cr,l)

Beryllium Iodide (BeI₂)

IDEAL GAS

Beryllium Iodide (BeI₂)BeI₂(g)

$$S^{\circ}(298.15 \text{ K}) = [291.52 \pm 2.1] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta H_f^{\circ}(0 \text{ K}) = -62.5 \pm 33.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^{\circ}(298.15 \text{ K}) = -64.0 \pm 33.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies

 ν, cm^{-1}

[160] (1)

[175] (2)

873 (1)

[1] (1)

Ground State Quantum Weight: [1]

Point Group: D_{2h}

Bond Distance: Be-I = 2.12 ± 0.05 Å

Bond Angle: I-Be-I = 180° ± 10°

Rotational Constant: B₀ = 0.014778 cm⁻¹

σ = 2

Enthalpy of Formation

Rahlfis and Fischer¹ have reported measurements of the sublimation pressures (578–703 K, 9 pts) for BeI₂. The measurements were complicated by reaction of the diiodide with the quartz apparatus. Assuming the reaction to be BeI₂(cr) + SiO₂(cr) = SiI₄(g) + 2BeO(cr), Rahlfis and Fischer¹ corrected their measured total pressure for the partial pressure of the tetraiodide. A 2nd and 3rd law analysis of their corrected data yields $\Delta_{\text{sub}}H_f^{\circ}(298.15 \text{ K}) = 29.81 \pm 0.29 \text{ kcal}\cdot\text{mol}^{-1}$ (3rd law) and $28.34 \pm 0.74 \text{ kcal}\cdot\text{mol}^{-1}$ (2nd law) with a drift of $2.2 \pm 1.1 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. We adopt $\Delta_{\text{sub}}H_f^{\circ}(298.15 \text{ K}) = 29.8 \pm 2.0 \text{ kcal}\cdot\text{mol}^{-1}$. We have assumed negligible dimer formation $\Delta H_f^{\circ}(298.15 \text{ K}) = -15.3 \text{ kcal}\cdot\text{mol}^{-1}$ for BeI₂(g) when the adopted $\Delta_{\text{sub}}H_f^{\circ}(298.15 \text{ K})$ value is added to the $\Delta H_f^{\circ}(298.15 \text{ K})$ value for BeI₂(cr).

The drift could be reduced by further adjusting the Gibbs energy functions for the crystal. These functions may be changed by altering the C_p° values and/or the $S^{\circ}(298.15 \text{ K})$ value. Such changes would yield values which are unreasonable when compared to other alkaline earth dihalides. Note also that a similar sublimation study for BeCl₂ gives a drift of $-1.3 \pm 2.6 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. We tentatively assume the drift is due to the data rather than our choice of functions.

Heat Capacity and Entropy

Electron diffraction patterns for BeI₂ vapor^{3,4} have been interpreted in terms of a linear configuration, with the latter study reporting the Be-I bond distance as 2.12 Å. Other studies also suggest a linear molecule. For example, the electric deflection of mass spectrometrically detected molecular beams⁵ showed that all the beryllium dihalides are linear.

Snelson⁶ observed the infrared spectra of BeI₂ in the spectral range 4000–200 cm⁻¹ using a matrix isolation technique. Assuming a linear geometry, ν_2 was assigned as 873 cm⁻¹. Snelson⁶ estimated a value for ν_3 based on force constant values for the other three beryllium dihalides. The values of ν_1 were calculated using a simple valence force field approximation. We adopt the two estimated and one measured vibrational frequency as reported by Snelson.⁶ The ground state quantum weight of one is assigned by analogy with BaCl₂².

Brewer *et al.*⁷ have tabulated Gibbs energy functions for BeI₂ up to 2000 K. Their values are consistently lower than ours due primarily to their use of a higher bending frequency ($\nu_2 = 395 \text{ cm}^{-1}$).

References

- ¹O. Rahlfis and W. Fischer, *Z. Anorg. Chem.* **211**, 349 (1933).
- ²JANAF Thermochemical Tables BeCl₂(f), 6–30–65.
- ³P. S. Akishin and V. P. Spiridonov, *Kristallografiya* **2**, 472 (1957).
- ⁴P. S. Akishin, V. P. Spiridonov and G. A. Sobalov, *Dokl. Akad. Nauk SSSR* **118**, 1134 (1958).
- ⁵A. Buchler, J. L. Stauffer, and W. Klemperer, *J. Amer. Chem. Soc.* **86**, 4544 (1964).
- ⁶A. Snelson, *J. Phys. Chem.* **72**, 250 (1968).
- ⁷L. Brewer, G. R. Somoyajulu, and E. Brackett, *Chem. Revs.* **63**, 111 (1963).

T/K	C _p ^o	S ^o	S ^o - [(C ^o - H(T))/T]	H ^o - H(T)	ΔH ^o	log K _r
0	0	0	INFINITE	-13.633	-62.517	INFINITE
100	44.605	236.565	236.565	-10.143	-79.634	41.591
200	51.767	270.220	296.456	-5.247	-96.949	25.320
250	53.542	281.970	292.421	-2.613	-105.439	22.030
298.15	54.939	291.524	291.524	0	-113.491	19.883
300	54.988	291.864	291.525	0.102	-113.798	19.814
350	56.181	300.433	292.199	2.882	-122.021	18.211
400	57.156	308.001	293.710	5.716	-129.559	16.919
450	57.948	314.780	295.681	8.594	-135.385	15.715
500	58.591	320.920	297.903	11.508	-142.617	14.330
600	59.544	331.692	302.662	17.418	-152.307	12.128
700	60.192	340.973	307.484	23.407	-162.659	10.555
800	60.648	348.992	311.179	29.450	-172.531	9.370
900	60.977	356.155	314.675	35.532	-181.989	8.449
1000	61.222	362.593	320.930	41.643	-191.066	7.709
1100	61.408	368.437	325.005	47.775	-199.801	7.102
1200	61.552	373.787	328.851	53.923	-208.204	6.594
1300	61.667	378.718	332.499	60.084	-216.283	6.163
1400	61.759	383.292	335.966	66.256	-224.131	5.791
1500	61.834	387.555	339.265	72.436	-231.758	5.466
1600	61.895	391.548	342.409	78.622	-239.182	5.163
1700	61.947	395.302	345.411	84.814	-246.417	4.882
1800	61.990	398.844	348.282	91.011	-253.464	4.630
1900	62.027	402.179	351.032	97.212	-260.323	4.403
2000	62.059	405.377	353.671	103.417	-267.000	4.198
2100	62.086	408.408	356.206	109.624	-273.495	4.011
2200	62.110	411.296	358.643	115.834	-279.810	3.839
2300	62.131	414.058	360.994	122.046	-285.946	3.682
2400	62.149	416.702	363.261	128.266	-291.904	3.536
2500	62.165	419.240	365.450	134.476	-297.688	3.401
2600	62.180	421.678	367.566	140.691	-303.300	3.275
2700	62.193	424.025	369.614	146.911	-308.743	3.157
2800	62.204	426.287	371.598	153.131	-314.017	3.041
2900	62.214	428.470	373.521	159.352	-319.125	2.924
3000	62.224	430.580	375.388	165.574	-324.067	2.809
3100	62.232	432.620	377.202	171.797	-328.843	2.694
3200	62.240	434.596	378.965	178.021	-333.455	2.578
3300	62.247	436.511	380.680	184.245	-337.904	2.461
3400	62.253	438.370	382.349	190.470	-342.192	2.344
3500	62.259	440.174	383.976	196.696	-346.420	2.227
3600	62.265	441.928	385.561	202.922	-350.498	2.110
3700	62.270	443.634	387.108	209.149	-354.426	1.993
3800	62.274	445.295	388.617	215.376	-358.204	1.876
3900	62.278	446.913	390.091	221.603	-361.832	1.759
4000	62.282	448.489	391.532	227.831	-365.310	1.642
4100	62.286	450.027	392.940	234.060	-368.648	1.525
4200	62.289	451.528	394.317	240.289	-371.846	1.408
4300	62.292	452.994	395.664	246.518	-374.904	1.291
4400	62.295	454.426	396.984	252.747	-377.822	1.174
4500	62.298	455.826	398.276	258.977	-380.600	1.057
4600	62.301	457.196	399.542	265.207	-383.238	0.940
4700	62.303	458.535	400.783	271.437	-385.736	0.823
4800	62.305	459.847	402.000	277.667	-388.094	0.706
4900	62.308	461.132	403.193	283.898	-390.312	0.589
5000	62.310	462.391	404.365	290.129	-392.390	0.472
5100	62.311	463.625	405.515	296.360	-394.328	0.355
5200	62.313	464.835	406.644	302.591	-396.126	0.238
5300	62.315	466.022	407.753	308.822	-397.784	0.121
5400	62.316	467.186	408.843	315.054	-399.302	0.004
5500	62.318	468.330	409.914	321.286	-400.680	-0.113
5600	62.319	469.453	410.967	327.518	-401.918	-0.229
5700	62.321	470.556	412.003	333.750	-402.916	-0.345
5800	62.322	471.640	413.022	339.982	-403.774	-0.461
5900	62.323	472.705	414.025	346.214	-404.492	-0.577
6000	62.324	473.752	415.011	352.446	-405.066	-0.693

PREVIOUS December 1975 (1 atm)

CURRENT December 1975 (1 bar)

Beryllium Iodide (BeI₂)BeI₂(g)

Beryllium Nitride (BeN)

$S^\circ(298.15\text{ K}) = [208.77] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$\Delta_f H^\circ(0\text{ K}) = [424] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = [427] \text{ kJ}\cdot\text{mol}^{-1}$

Beryllium Nitride (BeN)

Be₃N₂(g)

Electronic Levels and Multiplicities state	$\epsilon_i, \text{cm}^{-1}$	g_i
$^2\Pi$	0	[4]

$\sigma = 1$
 $r_e = [1.406] \text{ \AA}$

$\omega_e x_e = [1194] \text{ cm}^{-1}$
 $B_e = [1.555] \text{ cm}^{-1}$

Enthalpy of Formation

The enthalpy of formation was taken from Gordon.¹

Heat Capacity and Entropy

The molecular constants were taken from Gordon.¹

Reference

¹J. S. Gordon, personal communication, (April, 1963).

T/K	Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$		Standard State Pressure = $p^\circ = 0.1\text{ MPa}$		log K _r
	C_p°	$S^\circ - (G^\circ - H^\circ(T_r))/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	
0	0	INFINITE	-8.725	424.231	INFINITE
100	29.111	176.738	-5.821	416.010	-217.301
200	29.254	196.957	-2.906	406.527	-106.028
250	29.583	203.516	-1.436	400.808	-83.744
298.15	30.089	208.768	0	395.823	-69.347
300	30.111	208.954	0.056	395.632	-68.886
350	30.757	213.643	1.577	390.461	-58.273
400	31.439	217.794	3.132	385.308	-50.316
450	32.102	221.536	4.721	380.173	-44.129
500	32.716	224.951	6.341	375.059	-39.182
600	33.761	231.012	9.667	364.891	-31.767
700	34.574	236.280	13.086	354.800	-26.475
800	35.203	240.939	16.576	344.784	-22.312
900	35.693	245.115	20.122	334.843	-19.434
1000	36.081	248.897	23.711	324.977	-16.975
1100	36.395	252.351	27.336	315.186	-14.967
1200	36.653	255.529	30.988	305.471	-13.297
1300	36.869	258.471	34.665	295.833	-11.887
1400	37.052	261.211	38.361	286.273	-10.681
1500	37.211	263.772	42.074	276.791	-9.639
1600	37.351	266.179	45.803	267.914	-8.747
1700	37.475	268.447	49.544	259.521	-7.974
1800	37.587	270.592	53.297	251.182	-7.289
1900	37.689	272.627	57.061	242.896	-6.678
2000	37.783	274.563	60.835	234.661	-6.129
2100	37.870	276.408	64.617	226.476	-5.633
2200	37.951	278.172	68.408	218.339	-5.184
2300	38.027	279.860	72.207	210.256	-4.773
2400	38.100	281.480	76.014	202.206	-4.401
2500	38.169	283.037	79.827	194.206	-4.068
2600	38.236	284.535	83.648	186.251	-3.742
2700	38.300	285.980	87.474	178.339	-3.450
2800	38.361	287.374	91.307	170.469	-3.206
2900	38.421	288.721	95.147	162.642	-3.002
3000	38.479	290.024	98.992	154.857	-2.832
3100	38.536	291.287	102.842	147.112	-2.697
3200	38.592	292.511	106.699	139.408	-2.596
3300	38.646	293.700	110.561	131.744	-2.525
3400	38.700	294.854	114.428	124.120	-2.479
3500	38.752	295.977	118.301	116.537	-2.451
3600	38.804	297.069	122.178	109.000	-2.438
3700	38.855	298.133	126.061	101.512	-2.438
3800	38.906	299.170	129.949	94.074	-2.451
3900	38.956	300.181	133.843	86.687	-2.477
4000	39.005	301.168	137.741	79.351	-2.514
4100	39.054	302.132	141.644	72.065	-2.560
4200	39.102	303.074	145.591	64.829	-2.615
4300	39.151	303.994	149.484	57.642	-2.678
4400	39.198	304.895	153.381	50.505	-2.748
4500	39.246	305.776	157.304	43.418	-2.823
4600	39.293	306.639	161.231	36.381	-2.902
4700	39.340	307.485	165.162	29.394	-2.984
4800	39.387	308.314	169.099	22.457	-3.069
4900	39.433	309.126	173.040	15.570	-3.156
5000	39.479	309.923	176.985	8.733	-3.244
5100	39.525	310.706	180.935	1.946	-3.333
5200	39.571	311.474	184.890	-4.791	-3.423
5300	39.617	312.228	188.850	-11.682	-3.514
5400	39.662	312.969	192.814	-18.617	-3.605
5500	39.708	313.697	196.782	-25.596	-3.696
5600	39.753	314.413	200.755	-32.619	-3.787
5700	39.798	315.117	204.723	-39.686	-3.878
5800	39.843	315.809	208.685	-46.799	-3.969
5900	39.888	316.491	212.640	-53.957	-4.060
6000	39.933	317.162	216.592	-61.160	-4.151

PREVIOUS: June 1963 (1 atm)

CURRENT: June 1963 (1 bar)

Beryllium Nitride (BeN)

Be₃N₂(g)

CRYSTAL(α) $M_r = 25.01158$

Beryllium Oxide, Alpha (BeO)

Be₂O₃(cr)

$S^\circ(298.15\text{ K}) = 13.770 \pm 0.21\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_m = 2373 \pm 15\text{ K}$ (α - β)
 $T_m = [2821.2 \pm 100]\text{ K}$ (β -I)
 $T_m = 2780 \pm 100\text{ K}$ (α -I)

Enthalpy of Formation

Parker¹ thoroughly reviewed the data as of 1969 and selected $-145.4 \pm 0.8\text{ kcal}\cdot\text{mol}^{-1}$. She later revised¹ this value to $-145.7 \pm 0.6\text{ kcal}\cdot\text{mol}^{-1}$ due to new HF-solution calorimetry on BeF₂(amorphous) performed by Kilday *et al.*² Values of ΔH_f° from Parker's revised analysis¹ are summarized below. We adopt -145.4 ± 0.8 , rather than the revised selection, as a compromise between the indirect results based on Be(cr) and those based on BeF₂(am). The latter depend on ΔH_f° for HF(n H₂O). Use of the JANAF ΔH_f° in place of the NBS value³ causes a change of $\pm 0.9\text{ kcal}\cdot\text{mol}^{-1}$ in the results based on BeF₂(am). Recent data for HF suggest that the change could be even larger.

Direct Determination of ΔH_f°		Indirect Determinations of ΔH_f°	
kcal·mol ⁻¹	Source	kcal·mol ⁻¹	Source
-136.2	Mielenz & Von Wartenberg (1921)	-144.9	Neumann <i>et al.</i> (1934, 1932), ΔH_f° & ΔH_f° of Be ₂ N ₂
-134.4	Moose & Parr (1924)	-141.1	Smimov & Chukreev (1958), emf data
-145.3	Neumann <i>et al.</i> (1934)	-145.7 \pm 1.5	Kilday <i>et al.</i> (1969), Thomson <i>et al.</i> (1962) ⁴
-147.3	Roth <i>et al.</i> (1938)	-145.7 \pm 1.5	Kilday <i>et al.</i> (1969), Armstrong & Coyle (1965) ^b
-143.1	Cosgrove & Snyder (1953)	-145.7 \pm 0.6	Kolesov <i>et al.</i> (1959), Bear & Turnbull (1965) ^b
		-146.2, -145.65, -145.65, -145.3 \pm 0.6	Kilday <i>et al.</i> (1959), Bear & Turnbull (1969) ^b
		-144.7(-145.6) ^c , -144.5(-145.4) ^c \pm 1.2	Kilday <i>et al.</i> (1971), Churney & Armstrong (1969) ^c

^aHCl-solution calorimetry of BeO(cr) and Be(cr). ^bHF-solution calorimetry of BeO(cr) and Be(cr). ^cHF-solution calorimetry of BeO(cr) and BeO(cr) and ΔH_f° of the latter. ^dValues in parentheses based on ΔH_f° of HF(n H₂O) from NBS³ instead of JANAF.⁴

Heat Capacity and Entropy

The adopted C_p° and S° below 298.15 K are taken from Furukawa and Reilly⁵ who measured C_p° from 16 to 370 K. The authors give a detailed comparison with the earlier data of Gmelin⁶ (5 to 75 K) and Kelley⁷ (56 to 292 K). Gmelin's results deviate by roughly +20% from 15 to 75 K and Kelley's results deviate by about +50% at 56 K, +8% at 100 K and +1% at 200 K. The deviation of Kelley are probably due to the sensitivity limit of his calorimeter and to non-standard state effects of finely powdered BeO.

The adopted C_p° above 298.15 K is from a constrained fit of the C_p° data⁵ and enthalpy data of Victor and Douglas⁸ (323 to 1173 K), Conway and Hen⁹ (2161 to 2365 K) and Shipil'rain *et al.*,¹⁰ (2023 to 2708 K). The latter data show no evidence of transition even though they extend more than 300 K above $T_m = 2373\text{ K}$. Deviations of the data⁵ from the adopted enthalpies are $< \pm 0.15\%$ above 373 K and -0.4% at 323 K. Deviations above 2000 K are -0.3 to $+0.8\%$ and -1.8 to $+0.4\%$ excluding the point at 2266 K.¹⁰ Enthalpy measurements not used in the fit deviate by -2.1 to $+2.9\%$ ¹¹ (1142 to 2697 K), -17 to $+8\%$ ¹² (2273 to 2523 K), $-2.1 \pm 0.8\%$ ¹³ (400 to 1100 K) and $+0.4$ to -0.7% ¹⁴ (363 to 1128 K). C_p° data from the cooling-rate method¹⁵ deviate by $< 2\%$ (1300 to 1700 K) but by -5% at 2000 K.

Transition Data

Refer to the β -crystal table for details.

Fusion Data

Refer to the liquid table for details.

References

- ¹V. B. Parker, J. Res. Nat. Bur. Stand. 77A, 227 (1973); U. S. Nat. Bur. Stand. Report 10004, pp. 58-81, (January, 1969).
- ²M. V. Kilday, E. J. Prosen and D. D. Wagnan, J. Res. Nat. Bur. Stand. 77A, 217 (1973).
- ³U. S. Nat. Bur. Stand. Tech. Note 270-3, 264 pp. (1968).
- ⁴JANAF Thermochemical Tables: HF(g), 12-31-68, BeF₂(cr, l), 6-30-70.
- ⁵G. T. Furukawa and M. L. Reilly, U. S. Nat. Bur. Stand. Report 9905, pp. 28-47, (July, 1968).
- ⁶E. Gmelin, Compt. Rend. 262, 1452 (1966).
- ⁷K. K. Kelley, J. Amer. Chem. Soc. 61, 1217 (1939).
- ⁸A. C. Victor and T. B. Douglas, J. Res. Nat. Bur. Stand. 67A, 325 (1963).
- ⁹J. B. Conway and R. A. Hein, Nuclconics 22 (6), 71 (1964).
- ¹⁰E. E. Shipil'rain, D. N. Kagan and L. S. Barkhatov, High Temperature (USSR) 9, 842 (1971).
- ¹¹M. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, Dokl. Akad. Nauk SSSR 131, 566 (1960).
- ¹²M. A. Greenbaum, J. Weither and M. Farber, J. Phys. Chem. 69, 4035 (1965).
- ¹³B. E. Walker, C. T. Ewing and R. R. Miller, J. Chem. Eng. Data 7, 595 (1962); B. E. Walker, personal communication, U. S. Naval Res. Lab., Washington, (April 18, 1963).
- ¹⁴E. N. Rodgina and K. Z. Gornel'skii, Russ. J. Phys. Chem. 35, 898 (1961).
- ¹⁵R. A. McDonald, F. L. Oetting and H. Prophet, CPFA Working Group on Thermochemistry, Proc. 1st Meeting, Nov., 1963, CPFA Publ. No. 44(U), pp. 213-245, (February, 1964).

TK	C_p°	Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$		$H^\circ - H^\circ(T_r)$	ΔH_f°	Standard State Pressure = $P^\circ = 0.1\text{ MPa}$		log K_r
		S°	$-(G^\circ - H^\circ(T_r))/T$			ΔG°	ΔG°	
0	0	0	INFINITE	-2435	-604.914	-604.914	INFINITE	
100	2.636	0.824	28.539	-1.771	-606.343	-597.709	312.211	
200	14.159	5.887	15.759	-2.974	-607.579	-588.573	153.719	
298.15	25.560	13.770	13.770	0	-608.354	-579.062	101.449	
300	25.744	13.928	13.770	0.047	-608.364	-578.880	100.792	
400	33.757	22.513	14.886	3.051	-608.688	-568.992	74.303	
500	38.920	30.641	17.235	6.703	-608.668	-559.065	48.405	
600	42.376	38.061	20.098	10.778	-608.440	-549.163	47.809	
700	44.823	44.786	23.152	15.144	-608.092	-539.310	40.274	
800	46.656	50.897	26.244	19.722	-607.680	-529.511	34.574	
900	48.091	56.478	29.298	24.462	-607.235	-519.767	30.166	
1000	49.262	61.607	32.276	29.331	-606.780	-510.073	26.643	
1100	50.254	66.350	35.161	34.308	-606.329	-500.424	23.763	
1200	51.116	70.760	37.946	39.377	-605.892	-490.815	21.365	
1300	51.882	74.882	40.630	44.527	-605.478	-481.243	19.337	
1400	52.580	78.753	43.216	49.751	-605.094	-471.701	17.599	
1500	53.225	82.403	45.708	55.042	-604.744	-462.185	16.095	
1600	53.827	85.857	48.111	60.394	-618.971	-452.166	14.762	
1700	54.396	89.138	50.428	65.806	-618.303	-441.761	13.574	
1800	54.944	92.262	52.666	71.273	-617.614	-431.396	12.519	
1900	55.467	95.247	54.829	76.794	-616.904	-421.069	11.576	
2000	55.974	98.105	56.922	82.366	-616.176	-410.781	10.729	
2100	56.468	100.848	58.949	87.988	-615.430	-400.530	9.963	
2200	56.948	103.486	60.914	93.659	-614.669	-390.314	9.267	
2300	57.421	106.028	62.820	99.378	-613.893	-380.133	8.633	
2373.001	57.556	107.827	64.177	105.143	-613.582	-370.000	8.053	
2400	57.881	108.482	64.672	105.143	-613.103	-369.987	7.519	
2500	58.338	110.854	66.472	110.954	-612.300	-359.873	7.027	
2600	58.789	113.151	68.224	116.810	-611.483	-349.792	6.573	
2700	59.233	115.378	69.929	122.711	-610.654	-339.743	6.153	
2800	59.676	117.540	71.590	128.657	-609.769	-329.802	5.765	
2900	60.112	119.641	73.212	134.646	-608.851	-320.219	5.406	
3000	60.547	121.687	74.794	140.679	-607.904	-311.003	5.071	
3100	60.978	123.679	76.339	146.759	-606.930	-302.152	4.752	
3200	61.404	125.622	77.849	152.874	-605.929	-293.665	4.444	
3300	61.831	127.518	79.325	159.036	-604.893	-285.532	4.152	
3400	62.254	129.370	80.770	165.240	-603.825	-277.749	3.888	
3500	62.676	131.181	82.184	171.487	-602.728	-270.317	3.648	

PREVIOUS: December, 1974

CURRENT: June 1975

Beryllium Oxide, Alpha (BeO)

Be₂O₃(cr)

Be₂O₁(cr)

Beryllium Oxide, Beta (BeO)

CRYSTAL(β)

Beryllium Oxide, Beta (β-BeO)

$M_r = 25.01158$

$\Delta_f H^\circ(298.15 \text{ K}) = [-601.659] \text{ kJ mol}^{-1}$
 $\Delta_{\text{high}} H^\circ = 6.694 \pm 1.7 \text{ kJ mol}^{-1}$
 $\Delta_{\text{low}} H^\circ = [79.057 \pm 6.3] \text{ kJ mol}^{-1}$

$\Delta_f H^\circ(298.15 \text{ K}) = H^\circ(2373 \text{ K}) - H^\circ(298.15 \text{ K})$, since the difference in enthalpy, $H^\circ(2373 \text{ K}) - H^\circ(298.15 \text{ K})$, between the α - and β -phases is zero according to the adopted functions.

Heat Capacity and Entropy
 C_p° is taken to be the same as that of BeO(α , cr). Enthalpy data for β -BeO extend from 2377 to 2501 K, a range too short for obtaining an accurate C_p° curve. The enthalpy data deviate from the adopted functions by ~ 0.2 to $\pm 1.4\%$. Other enthalpy data²⁻⁴ show no obvious transition to β -BeO; this suggests that experimental uncertainties masked the transition or that these samples failed to transform. S° is calculated in a manner analogous to that used for $\Delta_f H^\circ$.

Transition Data
 Studies of x-ray diffraction,⁵⁻⁷ optical properties,^{6,8} thermal expansion,⁹ enthalpy,¹ and decrepitation of single crystals^{8,9,15} indicate the existence of a reversible transition near 2100°C. β -BeO is tetragonal with a structure related to rutile,⁹ while α -BeO is hexagonal close-packed with a wurtzite-type structure.^{16,17}
 T_m is lower on cooling than on heating. Earlier studies gave temperature differences of about 40^{11,12}, 50¹³ and 80¹⁴, but a recent DTA study¹⁰ gave T_m values on cooling which were only $\sim 15^\circ$ below those on heating. $T_m = 2107 \pm 7^\circ \text{C}$ (IFTS-68) was proposed as a DTA standard temperature because it is reproducible and relatively unchanged by oxide impurities.¹⁰ Reported values of T_m on heating include 2100 $\pm 10^\circ \text{C}$,¹ 2107 $\pm 7^\circ \text{C}$,¹⁰ 2095¹¹, 2075 $\pm 15^\circ \text{C}$,¹² 2050-2100¹³, 2144 $\pm 40^\circ \text{C}$,¹⁴ and 2050 $\pm 25^\circ \text{C}$.⁶ We adopt 2100 $\pm 15^\circ \text{C}$.
 Reported values of $\Delta_{\text{high}} H^\circ$ include 1.35 ± 0.1 ,¹ 1.40 ± 0.25 ,¹⁰ 1.25 ± 0.25 ,¹⁴ and 0.95 ± 0.3 kcal mol⁻¹.¹³ The first value is from enthalpy data and the others are from thermal analysis. It is not clear why the transition fails to appear in two other enthalpy studies.¹³ We adopt $\Delta_{\text{high}} H^\circ = 1.60 \pm 0.4$ kcal mol⁻¹ derived from the difference between the enthalpy data for β -BeO¹ and the JANAF enthalpy for α -BeO.

Fusion Data
 Refer to the liquid table for details.

References
¹J. B. Conway and R. A. Hein, *Nuclonics* 22 (6), 71 (1964).
²E. Shpil'rain, D. N. Kagan and L. S. Barkhatov, *High Temperature (USSR)* 9, 842 (1971).
³V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, *Dokl. Akad. Nauk SSSR* 131, 566 (1960).
⁴M. A. Greenbaum, J. Weiher and M. Farber, *J. Phys. Chem.* 69, 4035 (1965).
⁵D. K. Smith, C. F. Cline and S. B. Austerman, *Acta Crystallogr.* 18, 393 (1965).
⁶D. K. Smith, C. F. Cline and V. D. Frechette, *J. Nucl. Mater.* 6, 265 (1962).
⁷T. W. Baker and P. J. Baldock, *J. Nucl. Mater.* 19, 210 (1966); *Nature* 193, 1172 (1962).
⁸C. J. Engberg and E. H. Zehms, *J. Amer. Ceram. Soc.* 42, 300 (1959).
⁹T. Sata and T. Takahashi, *Colloq. Int. Cent. Nat. Rech. Sci.*, No. 205, 331 (1972); *Yogyo Kyokai Shi* 80, 142 (1972).
¹⁰R. E. Latta, E. C. Duderstadt and R. E. Fryxell, *J. Nucl. Mater.* 35, 350 (1970).
¹¹Yu. A. Kocherzhinski, E. A. Shishkin and L. M. Yupko, *Refractories (USSR)* 1969, 314, *Ogneupory* 34 (5), 50 (1969).
¹²A. I. Kaznov and L. N. Grossman, in "Thermodynamics of Nuclear Materials 1967," pp. 25-39, Int'l. At. Energy Agency, Vienna, (1968).
¹³S. B. Austerman, U. S. At. Energy Comm. NAA-SR-7654, 14 pp. (1963); *Bull. Amer. Phys. Soc.* II 7, 28 (1962).
¹⁴S. B. Austerman, U. S. At. Energy Comm. NAA-SR-6428 (1961).
¹⁵D. K. Smith, H. W. Newkirk and J. S. Kahn, *J. Electrochem. Soc.* 111, 78 (1964).
¹⁶P. J. Baldock, W. E. Spindler and T. W. Baker, *J. Nucl. Mater.* 19, 169 (1966).

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$	
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T)]/T$	$H^\circ - H^\circ(T_r)$
J·K ⁻¹ ·mol ⁻¹		kJ·mol ⁻¹	
0			0.
100	25.560	16.591	-601.659
200	25.744	16.591	-601.669
298.15	25.744	16.591	-601.669
300	33.757	16.591	-573.032
400	38.920	16.591	-563.426
500	42.376	16.591	-553.781
600	44.823	16.591	-544.161
700	46.656	16.591	-534.590
800	48.091	16.591	-525.074
900	49.262	16.591	-515.611
1000	50.254	16.591	-506.199
1100	51.116	16.591	-496.832
1200	51.882	16.591	-487.506
1300	52.560	16.591	-478.216
1400	53.225	16.591	-468.957
1500	53.827	16.591	-459.722
1600	54.396	16.591	-449.985
1700	54.944	16.591	-439.862
1800	55.467	16.591	-429.779
1900	55.974	16.591	-419.735
2000	56.467	16.591	-409.729
2100	56.948	16.591	-399.760
2200	57.421	16.591	-389.826
2300	57.881	16.591	-379.927
2373.001	58.338	16.591	-370.063
2400	58.789	16.591	-360.232
2500	59.233	16.591	-350.433
2600	59.676	16.591	-340.666
2700	60.112	16.591	-331.032
2800	60.547	16.591	-321.527
2821.220	60.978	16.591	-312.146
2900	61.404	16.591	-302.889
3000	61.831	16.591	-293.753
3100	62.254	16.591	-284.732
3200	62.676	16.591	-275.819
3300		16.591	-267.016
3400		16.591	-258.318
3500		16.591	-249.719

--- ALPHA <---> BETA
 --- BETA <---> LIQUID

PREVIOUS: June 1971

CURRENT: December 1974

Be₂O₁(cr)

Beryllium Oxide, Beta (BeO)

BeO₂(l)

Beryllium Oxide (BeO)

M_l = 25.01158

LIQUID

Beryllium Oxide (BeO)

$$\begin{aligned} S^\circ(298.15 \text{ K}) &= [35.931] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ T_{\text{fus}} &= [2821.2 \pm 100] \text{ K} (\beta \rightarrow \text{l}) \\ T_{\text{liq}} &= 2780 \pm 100 \text{ K} (\alpha \rightarrow \text{l}) \end{aligned}$$

$$\begin{aligned} \Delta_{\text{f}}H^\circ(298.15 \text{ K}) &= [-542.705] \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_{\text{liq}}H^\circ &= [79.057 \pm 6.3] \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_{\text{fus}}H^\circ &= 84.9 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Enthalpy of Formation

$\Delta_{\text{f}}H^\circ$ is calculated from that of α -BeO by adding $\Delta_{\text{liq}}H^\circ$ and the difference in enthalpy, $H^\circ(2780 \text{ K}) - H^\circ(298.15 \text{ K})$, between the α and liquid phases.

Heat Capacity and Entropy

C_p is taken to be $19 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ based on the lower two of three enthalpy points (2867–3159 K) measured by Shipil'rain *et al.*¹ The upper two points yield $24.9 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is too large in our opinion. Earlier enthalpy data^{2,3} are inadequate for deriving C_p . Below the assumed glass transition at 1900 K, C_p is taken to be the same as that of the crystal. S° is calculated in a manner analogous to that used for $\Delta_{\text{f}}H^\circ$.

Fusion Data

Conflicting evidence suggests that the melting points of α - and β -BeO are quite uncertain. Schneider's review⁴ listed C six values (T_{fus} in K): IPTS-48, with dates in parentheses) 2410(1916), 2452(1956), 2508(1957), 2557(1920), 2570(1948) and 2573⁵. (1913). Subsequent T_{fus} values include 2430 \pm 10,⁶ 2560 \pm 10,⁶ 2444 \pm 9,² 2450 \pm 30 and 2470 \pm 30°C.⁴ The reported values fall roughly into two groups near 2450°C and 2560°C. Three enthalpy studies¹⁻³ avoided the region from 2435°C to 2547°C. Part of the conflict arises because, in most cases, the measurement of T_{fus} of BeO was only an incidental part of the study. Such values are more likely to be in error due to temperature measurement, detection of melting, impurities, volatilization and reaction with the surroundings. The actual discrepancies may be even larger than they appear, since one of the higher T_{fus} values seems to refer to α -BeO which should melt \sim 40 below β -BeO. Enthalpy data of Kandiyba *et al.*¹ suggest that their sample may have remained as α -BeO, yet they reported $T_{\text{fus}} = 2547 \pm 9^\circ\text{C}$. In contrast $T_{\text{fus}} = 2430 \pm 10^\circ\text{C}$ was found for β -BeO by Latta *et al.*³; their thermal analysis showed both T_{fus} and T_{liq} .

The conflict is epitomized by the two most recent values of T_{fus} , 2430 \pm 10°C⁶ and 2560 \pm 10°C.⁶ These studies⁶ seem to be more satisfactory than their predecessors yet at least one of them has a large bias. They agree⁶ on T_{fus} for Al₂O₃, Mo and Ta but differ in opposite directions for BeO and UO₂. Non-stoichiometry could explain the lower T_{fus} (UO₂) reported by Riley,⁵ but analogous evidence for BeO is lacking. As a compromise, we adopt $T_{\text{fus}}(\alpha) = 2507^\circ\text{C} = 2780 \text{ K}$ and calculate $T_{\text{fus}}(\beta) = 2548^\circ\text{C} = 2821.2 \text{ K}$ from $\Delta_{\text{f}}G^\circ = 0$ for BeO(β) \rightarrow BeO(l).

$\Delta_{\text{liq}}H^\circ(\alpha) = 20.3 \text{ kcal}\cdot\text{mol}^{-1}$ is calculated by difference from enthalpies (2867–3159 K) of Shipil'rain *et al.*¹ and the JANAF enthalpy for α -BeO. We assume that BeO(l) reverted to α -BeO and that β -BeO did not form during the drop calorimetry.¹ $\Delta_{\text{liq}}H^\circ(\beta) = 13.895 \text{ kcal}\cdot\text{mol}^{-1}$ is calculated from BeO(β) \rightarrow BeO(l) at the corresponding T_{liq} using the adopted tables. Enthalpy data of Greenbaum *et al.*³ gave $\Delta_{\text{liq}}H^\circ = 19.3 \text{ kcal}\cdot\text{mol}^{-1}$ (phase uncertain) even though both the crystal and liquid data have large negative bias. Ohta and Sata² derived $\Delta_{\text{liq}}H^\circ = 7.6 \pm 2.1 \text{ kcal}\cdot\text{mol}^{-1}$ from liquidus data in the binary system BeO–TiO₂. This can be discounted along with other binary data^{6,11} due to the uncertainty in T_{liq} .

Vaporization Data

The vapor over BeO is composed mainly of trimer, tetramer and individual atoms, along with minor amounts of several other molecules.

References

- ¹E. V. Shipil'rain, D. N. Kagan and L. S. Barkhatov, High Temperatures (USSR) 9, 842 (1971).
- ²V. V. Kandiyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, Dokl. Akad. Nauk SSSR 131, 566 (1960).
- ³M. A. Greenbaum, J. Weither and M. Farber, J. Phys. Chem. 69, 4035 (1965).
- ⁴S. J. Schneider, U. S. Nat. Bur. Stand. Monograph 68, 31 pp. (1963); refer to p. 8.
- ⁵R. E. Latta, E. C. Duderstadt and R. E. Fryxell, J. Nucl. Mater. 35, 350 (1970).
- ⁶B. Riley, Rev. Int. Hautes Temp. Refract. 3, 327 (1966).
- ⁷J. Kondis, J. Nucl. Mater. 14, 322 (1964).
- ⁸C. J. Engberg and E. H. Zeltins, J. Amer. Ceram. Soc. 42, 300 (1959).
- ⁹T. Ohta and T. Sata, Yogyo Kyokai Shi 82, 397 (1974).
- ¹⁰E. M. Levin, C. R. Robbins and H. F. McMurdie, "Phase Diagrams for Ceramists," 3rd ed. and 1969 Supplement, The American Ceramic Soc., Columbus, Ohio, (1964 and 1969).
- ¹¹N. A. Toropov, V. P. Barzakovskii, V. V. Lapin and N. N. Kurtseva, "Handbook of Phase Diagrams of Silicate Systems, Vol. 1, Binary Systems," 2nd revised ed. (1969), Eng. Trans. (avail. NTIS), Israel Program for Scientific Translations, Jerusalem, (1972).

T/K	C _p ^o	S ^o	-(G ^o - H ^o (T))/T	H ^o - H ^o (T)	$\Delta_{\text{f}}H^\circ$	$\Delta_{\text{f}}G^\circ$	log K _r
0				0.			
100	25.560	35.931	35.931	0.	-542.705	-520.021	91.105
200	25.744	36.089	35.931	0.047	-542.715	-519.880	90.519
300	33.757	44.675	37.047	2.051	-543.039	-520.498	66.887
400	38.920	52.802	39.396	3.051	-543.019	-504.497	52.704
500	44.376	60.222	42.259	10.778	-542.791	-496.811	43.251
600	48.823	66.948	45.313	15.144	-542.444	-489.174	36.503
700	46.656	73.058	48.405	19.762	-542.031	-481.591	31.445
800	48.091	78.639	51.459	24.452	-541.586	-474.063	27.514
900	49.262	83.768	54.337	29.331	-541.131	-466.585	24.372
1000	50.254	88.511	57.322	34.308	-540.680	-459.152	21.803
1200	51.116	92.921	60.107	39.377	-540.243	-451.760	19.665
1300	51.882	97.043	62.791	44.520	-539.830	-444.403	17.856
1400	52.580	100.914	65.377	49.751	-539.445	-437.077	16.308
1500	53.225	104.564	67.869	55.042	-539.096	-429.778	14.966
1600	53.827	108.018	70.272	60.394	-538.722	-421.975	13.776
1700	54.396	111.289	72.589	65.806	-538.353	-413.786	12.714
1800	54.944	114.423	74.827	71.273	-537.983	-405.637	11.771
1900	55.467	117.468	76.990	76.794	-537.617	-397.527	10.929
1900.001	55.467	117.468	76.990	76.794	-537.617	-397.527	10.929
1900.001	55.467	117.468	76.990	76.794	-537.617	-397.527	10.929
2000	79.496	121.486	79.114	84.743	-548.149	-389.516	10.173
2100	79.496	125.364	81.225	92.693	-545.077	-381.660	9.493
2200	79.496	129.063	83.166	100.643	-542.037	-373.950	8.879
2300	79.496	132.596	85.382	108.592	-539.036	-366.377	8.321
2400	79.496	135.980	87.921	116.541	-536.053	-358.934	7.812
2500	79.496	139.225	89.428	124.491	-533.113	-351.615	7.347
2600	79.496	142.343	91.404	132.441	-530.203	-344.412	6.919
2700	79.496	145.343	93.346	140.391	-527.326	-337.321	6.526
2800	79.496	148.234	95.255	148.340	-524.436	-330.343	6.046
2821.220	79.496	148.834	95.656	150.027	-523.000	-328.000	6.000
2900	79.496	151.024	97.131	156.290	-520.635	-320.635	5.523
3000	79.496	153.719	98.972	162.239	-518.290	-313.290	5.037
3100	79.496	156.325	100.780	167.889	-515.960	-306.000	4.584
3200	79.496	158.849	102.556	173.236	-513.650	-298.750	4.162
3300	79.496	161.295	104.299	178.288	-511.360	-291.540	3.767
3400	79.496	163.669	106.010	183.038	-509.090	-284.370	3.398
3500	79.496	165.973	107.691	187.487	-506.840	-277.240	3.051
3600	79.496	168.213	109.341	191.737	-504.610	-270.150	2.744
3700	79.496	170.391	110.962	195.787	-502.400	-263.100	2.472
3800	79.496	172.511	112.554	199.636	-500.210	-256.090	2.228
3900	79.496	174.576	114.118	203.285	-498.040	-249.120	1.984
4000	79.496	176.588	115.654	206.734	-495.890	-242.190	1.756
4100	79.496	178.551	117.165	210.083	-493.760	-235.300	1.551
4200	79.496	180.467	118.649	213.332	-491.650	-228.450	1.351
4300	79.496	182.337	120.109	216.481	-489.560	-221.640	1.190
4400	79.496	184.165	121.544	219.530	-487.490	-214.870	1.089
4500	79.496	185.952	122.955	222.479	-485.440	-208.140	0.990
4600	79.496	187.699	124.344	225.328	-483.410	-201.450	0.911
4700	79.496	189.408	125.710	228.077	-481.400	-194.800	0.841
4800	79.496	191.082	127.055	230.726	-479.410	-188.190	0.781
4900	79.496	192.721	128.378	233.275	-477.440	-181.620	0.731
5000	79.496	194.327	129.681	235.724	-475.490	-175.090	0.691

PREVIOUS: December 1971

CURRENT: December 1974

Beryllium Oxide (BeO)

BeO₂(l)

Beryllium Oxide (BeO)

$M_r = 25.01158$ Beryllium Oxide (BeO)

$Be_2O_3(cr,l)$

0 to 2373 K crystal, alpha
2373 to 2821.2 K crystal, beta
above 2821.2 K liquid

Refer to the individual tables for details.

T/K	Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa		$\log K_r$
	C_p°	$S^\circ - [C_p^\circ(T_r)/T]$	$H^\circ - H^\circ(T_r)$	$\Delta_f G^\circ$	
	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	
0	0	0	INFINITE	INFINITE	
100	2.636	0.824	-2.835	-604.914	
200	14.159	5.887	-2.771	-606.343	
298.15	25.560	13.770	-1.974	-607.579	153.719
300	25.744	13.928	0.047	-608.354	101.449
400	33.757	22.513	3.051	-608.880	100.792
500	38.970	30.641	6.703	-608.688	74.303
600	42.376	38.061	10.778	-608.568	58.405
700	44.823	44.786	15.144	-608.440	47.809
800	46.656	50.897	19.772	-608.310	40.244
900	48.091	56.478	24.462	-607.880	34.574
1000	49.262	61.607	29.331	-607.235	30.166
1100	50.254	66.350	34.308	-606.780	26.643
1200	51.116	70.760	39.377	-606.329	23.763
1300	51.882	74.882	44.527	-605.892	21.365
1400	52.580	78.753	49.751	-605.478	19.337
1500	53.225	82.403	55.042	-605.094	17.599
1600	53.827	85.857	60.394	-604.744	16.095
1700	54.396	89.138	65.806	-604.428	14.762
1800	54.944	92.262	71.273	-604.146	13.574
1900	55.467	95.247	76.794	-603.896	12.519
2000	55.974	98.105	82.366	-603.676	11.576
2100	56.467	100.848	87.988	-603.480	10.729
2200	56.948	103.486	93.659	-603.314	9.963
2300	57.421	106.028	99.378	-603.169	9.267
2373.001	57.756	107.827	103.582	-603.133	8.653
2373.001	57.758	107.849	110.276	TRANSITION	
2400	57.881	111.303	111.837	ALPHA <--> BETA	
2500	58.338	113.675	117.648	TRANSITION	
2600	58.789	115.972	123.504	ALPHA <--> BETA	
2700	59.233	118.199	129.406	TRANSITION	
2800	59.676	120.361	135.351	ALPHA <--> BETA	
2821.220	59.770	120.812	136.618	TRANSITION	
2821.220	59.496	148.834	215.676	BETA <--> LIQUID	
2900	79.496	151.024	221.939	TRANSITION	
3000	79.496	153.719	229.888	ALPHA <--> BETA	
3100	79.496	156.325	237.838	TRANSITION	
3200	79.496	158.849	245.787	ALPHA <--> BETA	
3300	79.496	161.295	253.737	TRANSITION	
3400	79.496	163.669	261.687	ALPHA <--> BETA	
3500	79.496	165.973	269.636	TRANSITION	
3600	79.496	168.213	277.586	ALPHA <--> BETA	
3700	79.496	170.391	285.535	TRANSITION	
3800	79.496	172.511	293.485	ALPHA <--> BETA	
3900	79.496	174.576	301.435	TRANSITION	
4000	79.496	176.588	309.384	ALPHA <--> BETA	
4100	79.496	178.551	317.334	TRANSITION	
4200	79.496	180.467	325.283	ALPHA <--> BETA	
4300	79.496	182.337	333.233	TRANSITION	
4400	79.496	184.165	341.183	ALPHA <--> BETA	
4500	79.496	185.952	349.132	TRANSITION	
4600	79.496	187.699	357.082	ALPHA <--> BETA	
4700	79.496	189.408	365.031	TRANSITION	
4800	79.496	191.082	372.981	ALPHA <--> BETA	
4900	79.496	192.721	380.931	TRANSITION	
5000	79.496	194.327	388.880	ALPHA <--> BETA	

PREVIOUS.

CURRENT December 1974

Beryllium Oxide (BeO)

$Be_2O_3(cr,l)$

$S^\circ(298.15 \text{ K}) = 197.625 \pm 0.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(0 \text{ K}) = 134.0 \pm 13 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15 \text{ K}) = 136.4 \pm 13 \text{ kJ}\cdot\text{mol}^{-1}$

Source	State	ϵ_r , cm ⁻¹	Electronic and Molecular Constants ($\sigma = 1$)			ω_e , cm ⁻¹	$\omega_e x_e$, cm ⁻¹
			r_e , Å	B_e , cm ⁻¹	α_e , cm ⁻¹		
1	X ¹ Σ ⁺	0.0	1.3310	1.6510	0.0190	1487.3	11.83
1-7	II	[8000]	[1.463]	[1.366]	[0.0163]	1130.8	8.2
1	A II	9234.8	1.4632	1.3661	0.0163	1144.2	8.42
4-7	Σ ⁺	[16000]	[1.362]	[1.576]	[0.015]	[1370]	[7.8]
1	B ² Σ ⁺	21197.	1.3623	1.5758	0.0154	1370.8	7.75
4	Σ ⁺	[37000]	[1.49]	[1.31]	[0.01]	[1082]	[9.]
4	Δ	[38000]	[1.49]	[1.31]	[0.01]	[1082]	[9.]
1	D ⁴ Δ	38918.	1.49	1.31	0.01	1081.5	9.1
1,4	Σ ⁺	[40000]	[1.49]	[1.31]	[0.01]	1012.2	8.4
1,4	Σ ⁻	38956.	[1.49]	[1.31]	[0.01]	[1082]	[9.]
4	Σ ⁺	[47000]	[1.49]	[1.31]	[0.01]	[1082]	[9.]

Enthalpy of Formation

We adopt $D_0^\circ = 104.2 \pm 3$ and $\Delta_f H^\circ(298.15 \text{ K}) = 32.6 \pm 3 \text{ kcal mol}^{-1}$ based on two mass-spectrometric studies,⁹ analyzed below. The adopted values correspond to the average of the two results for reaction A and also to the average for reaction B. Improved agreement between reactions A and B is due to recalculation of K_p of reaction B using the current table⁴ for BeO(α). Our analysis should be compared to the analysis of Brewer and Rosenblatt,¹⁰ using σ -functions based upon calculated levels.¹¹

The controversy over D_0° of alkaline earth oxides has been reviewed in detail.¹⁰⁻¹² Uncertainty in the electronic partition function of BeO due to triplet states now is much reduced.² Gaydon¹² derived spectroscopic values for D_0° of 91 and 111 kcal·mol⁻¹ from the X and A states, respectively. $D_0^\circ = 101 \text{ kcal mol}^{-1}$ was derived¹¹ by fitting an electro-negativity potential function to the X state.

Source	Method	Reaction ^a	T/K	ΔS Points	cal·K ⁻¹ ·mol ⁻¹	2nd law Δ _f H ^o (298.15 K), kcal·mol ⁻¹	3rd law Δ _f H ^o (298.15 K), kcal·mol ⁻¹	D ₀ ^b
⁸ Chupka (1959)	Knudsen mass spec.	A	2100-2474	8	1.6 ± 2.3	-8.4 ± 5	-11.9 ± 3	30.6
⁹ Theard (1964)	Knudsen mass spec.	A	2380	1	-	-	-15.9 ± 3	34.6
⁸ Chupka (1959)	Knudsen mass spec.	B ^b	1914-2304	6	0.7 ± 0.9	107.3 ± 2	105.9 ± 3	31.9
⁹ Theard (1964)	Knudsen mass spec.	B ^b	2380	1	-	-	104.5 ± 3	33.3

^aReactions. A) BeO(g) + O(g) = Be(g) + O₂(g); B) BeO(g) = Be(g) + O(g).

^bRecalculated as in Chupka *et al.*,⁸ assuming $P_{Be} = P_O$ and JANAF values for BeO(α) = Be(g) + O(g).

Heat Capacity and Entropy

Electronic levels (T_0) and vibrational-rotational constants of the observed states are from Rosen.¹ Field² concluded that calculations^{3-5,7} of the isoconfigurational A II - II separation should be adequate for estimating the low-lying III state. The adopted separation of 1200 cm⁻¹ is consistent with analysis³ of perturbations. We estimate Σ at 16000 cm⁻¹ by assuming that it lies 5200 ± 4000 cm⁻¹ below the isoconfigurational B state. Other predicted states and their vibrational-rotational constants are facilitated by listing the states in the isoconfigurational order of MgO.⁴ Our thermodynamic functions correspond to an "effective" ground state with $l < g < 2$ instead of $g = 3$ or 6.^{10,11} This comparison is only approximate since our functions are calculated using first-order anharmonic corrections to Q_i and Q_j in the partition function $Q = Q_e Q_v Q_r Q_t \cdot g \cdot \exp(-c_2/T)$.

Sublimation and Vaporization Data

Mass spectra⁹ at 1900-2400 K showed the vapor to consist mainly of Be, O, (BeO)₂, and (BeO)₃ with small amounts of O₂, Be₂O, BeO and other polymer of BeO. Tetramer, trimer and pentamer become dominant at higher temperatures.

References

- ¹R. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, 1970, pp. 65-6.
- ²R. W. Field, *J. Chem. Phys.* **60**, 2400 (1974).
- ³W. M. Huo, K. F. Freed and W. Klempner, *J. Chem. Phys.* **46**, 3556 (1967).
- ⁴JANAF Thermochemical Tables: BeO(α,β,g), MgO(g), CaO(g), SrO(g), BaO(g) 6-30-74.
- ⁵P. K. Pearson, S. V. O'Neil and H. F. Schaeffer, *J. Chem. Phys.* **56**, 3938 (1972); **55**, 176 (1971); *Chem. Phys. Lett.* **10**, 404 (1971).
- ⁶M. L. Sink, Ph. D. Thesis, Case Western Reserve Univ., 1972, *Diss. Abstr.* **B33**, 671 (1972).

Continued on page 428

Beryllium Oxide (BeO)

Be₂O₃(g)

T/K	C _p ^a	Enthalpy Reference Temperature = T _r = 298.15 K			H ^o - H ^o (T _r)	Δ _f H ^o	log K _r
		S ^o	-[G ^o - H ^o (T _r)]/T	-H ^o - H ^o (T _r)			
0	0	0	INFINITE	-8.688	133.984	INFINITE	
100	29.108	165.763	223.605	-5.784	127.536	-66.618	
200	29.139	185.943	200.307	-2.873	136.275	-31.550	
298.15	29.481	197.625	197.625	0	136.398	-19.275	
300	29.493	197.807	197.625	0.055	136.395	-19.277	
400	30.348	203.348	198.791	3.043	136.056	10.715	
500	31.421	213.286	201.023	6.131	135.513	102.198	
600	32.454	219.108	203.564	9.326	134.860	85.509	
700	33.345	224.179	206.155	12.617	134.133	71.340	
800	34.084	228.682	208.694	15.990	133.440	60.280	
900	34.704	232.733	211.144	19.430	132.845	51.324	
1000	35.252	236.418	213.490	22.928	132.349	43.465	
1100	35.784	239.803	215.730	26.480	131.955	36.702	
1200	36.357	242.941	217.869	30.086	131.629	30.829	
1300	37.023	245.876	219.911	33.755	131.351	25.444	
1400	37.825	248.648	221.866	37.496	131.112	20.536	
1500	38.788	251.290	223.740	41.325	130.911	16.159	
1600	39.927	253.829	225.542	45.259	130.746	12.346	
1700	41.236	256.288	227.278	49.316	130.609	8.967	
1800	42.698	258.685	228.957	53.511	130.500	6.015	
1900	44.285	261.036	230.584	57.860	130.414	3.520	
2000	45.956	263.350	232.164	62.371	130.341	1.431	
2100	47.670	265.633	233.704	67.052	130.286	0.566	
2200	49.379	267.890	235.206	71.905	130.249	0.689	
2300	51.042	270.122	236.676	76.927	130.228	0.801	
2400	52.616	272.328	238.116	82.110	130.217	0.903	
2500	54.070	274.506	239.528	87.446	130.214	0.998	
2600	55.375	276.653	240.915	92.919	130.218	1.086	
2700	56.514	278.765	242.277	98.515	130.227	1.167	
2800	57.475	280.838	243.618	104.204	130.241	1.227	
2900	58.225	282.869	244.936	110.006	130.260	1.274	
3000	58.856	284.834	246.234	115.861	130.283	1.312	
3100	59.286	286.792	247.511	121.770	130.310	1.346	
3200	59.556	288.679	248.768	127.713	130.338	1.374	
3300	59.681	290.514	250.006	133.676	130.365	1.397	
3400	59.675	292.295	251.223	139.645	130.389	1.416	
3500	59.559	294.024	252.422	145.608	130.409	1.431	
3600	59.345	295.699	253.601	151.554	130.424	1.444	
3700	59.051	297.321	254.760	157.474	130.434	1.454	
3800	58.691	298.891	255.903	163.362	130.440	1.461	
3900	58.279	300.410	257.023	169.210	130.442	1.465	
4000	57.827	301.880	258.126	175.016	130.442	1.467	
4100	57.347	303.302	259.211	180.775	130.440	1.467	
4200	56.845	304.678	260.277	186.485	130.436	1.465	
4300	56.337	306.010	261.325	192.144	130.430	1.461	
4400	55.822	307.299	262.356	197.752	130.422	1.455	
4500	55.308	308.548	263.368	203.309	130.412	1.449	
4600	54.801	309.758	264.364	208.814	130.400	1.442	
4700	54.303	310.931	265.342	214.269	130.386	1.434	
4800	53.818	312.069	266.304	219.675	130.370	1.425	
4900	53.348	313.174	267.249	225.033	130.351	1.416	
5000	52.895	314.247	268.144	230.344	130.330	1.406	
5100	52.460	315.291	269.092	235.613	130.307	1.395	
5200	52.044	316.305	269.990	240.838	130.282	1.383	
5300	51.647	317.293	270.873	246.022	130.256	1.370	
5400	51.271	318.255	271.742	251.168	130.228	1.356	
5500	50.914	319.192	272.596	256.277	130.199	1.341	
5600	50.577	320.106	273.436	261.351	130.168	1.325	
5700	50.259	320.999	274.265	266.393	130.134	1.308	
5800	49.961	321.870	275.076	271.404	130.098	1.290	
5900	49.681	322.722	275.877	276.386	130.060	1.271	
6000	49.418	323.555	276.665	281.340	130.020	1.252	

PREVIOUS: December 1974 (1 atm)

CURRENT December 1974 (1 bar)

Be₃O₄S₁(cr)

Beryllium Sulfate, Alpha (BeSO₄)

CRYSTAL(α)

Beryllium Sulfate, Alpha (α-BeSO₄)

$M_r = 105.06978$ Beryllium Sulfate, Alpha (BeSO₄)

$\Delta_f H^\circ(0 \text{ K}) = -1190.1 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15 \text{ K}) = -1200.8 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{cr}} H^\circ = [1.113] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{aq}} H^\circ = [19.552] \text{ kJ}\cdot\text{mol}^{-1}$

$S^\circ(298.15 \text{ K}) = 77.971 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{m}} = 863 \text{ K} (\alpha \rightarrow \beta)$
 $T_{\text{tr2}} = 908 \text{ K} (\beta \rightarrow \gamma)$

Enthalpy of Formation
 Bear *et al.*¹ measured the enthalpies of solution of Be(cr) and BeSO₄(cr,α) in concentrated HF and the enthalpy of reaction of H₂SO₄(aq) with BeSO₄(aq HF). Combination of these yields reaction (a) below. Taylor *et al.*² measured enthalpies of solution of Be(cr) and BeSO₄(cr,α) in H₂SO₄(aq) which yields reaction (b). Marchal³ measured the total vapor pressure of BeSO₄(cr) in the temperature range 863–1103 K. Partial pressures of SO₃(g) were calculated from Marchal's data using JANAF⁴ values for the SO₂-SO₃ equilibrium. 3rd law analysis of these data yields $\Delta_f H^\circ$ for reaction (c) as given below. This was converted to $\Delta_f H^\circ$ for α-BeSO₄ using JANAF⁴ enthalpies of transitions.

Source	Method	Reaction	7/K	$\Delta_{\text{int}} H_r$ kcal·mol ⁻¹	$\Delta_f H^\circ(298.15 \text{ K})$ kcal·mol ⁻¹
1	Calorimetric	(a) Be(cr) + H ₂ SO ₄ (109 H ₂ O) = H ₂ (g) + α-BeSO ₄	294	-74.47	-286.65 ± 0.5
2	Calorimetric	(b) Be(cr) + H ₂ SO ₄ (47.849 H ₂ O) = H ₂ (g) + α-BeSO ₄	298	-76.38	-287.55 ± 0.13
3	K_p (973–1083 K)	(c) BeSO ₄ (γ) → BeO(cr) + SO ₃ (g)	298	43.92	-286.55 ± 0.5

The adopted $\Delta_f H^\circ(298.15 \text{ K}) = -287.0 \pm 0.8$ is an average value of reaction (a) and (b). This value is for relatively finely divided crystals of BeSO₄ as was indicated by Bear *et al.*¹

Heat Capacity and Entropy
 Low temperature heat capacities (12–301 K) and high temperature enthalpies (366–864 K) were measured by Taylor, Gardner and Smith.⁵ These data were joined smoothly at 298.15 K and extrapolated graphically above 864 K. The entropy was obtained from the heat capacities using $S^\circ(12.56 \text{ K}) = 0.034 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Transition Data
 Bosik, Novoselova and Simanov⁶ observed two endothermic effects at 863–883 K and 908–913 K on the heating and cooling curves of BeSO₄(cr), thus we have adopted $T_{\text{m}}(\alpha \rightarrow \beta) = 863 \text{ K}$ and $T_{\text{tr2}}(\beta \rightarrow \gamma) = 908 \text{ K}$. $\Delta_{\text{m}} H^\circ(\alpha \rightarrow \beta) = 0.266 \text{ kcal}\cdot\text{mol}^{-1}$ was obtained from the single enthalpy point at 863.9 K observed by Taylor, Gardner and Smith.⁵ $\Delta_{\text{aq}} H^\circ(\beta \rightarrow \gamma) = 4.673 \text{ kcal}\cdot\text{mol}^{-1}$ was chosen in order to give good agreement with the equilibrium data of Marchal.³

References
¹I. J. Bear and A. G. Turnbull, *J. Phys. Chem.* **70**, 711–17 (1966).
²A. R. Taylor, Jr., B. B. Letson and D. F. Smith, U. S. Bur. Mines, Report No. 6724, 8 pp. (1966).
³G. Marchal, *J. Chim. Phys.* **22**, 502 (1925).
⁴JANAF Thermochemical Tables: SO₂(g), 6–30–61; SO₃(g), 9–30–65.
⁵A. R. Taylor, Jr., T. E. Gardner and D. F. Smith, U. S. Bur. Mines, Report No. 6240, 8 pp. (1963).
⁶I. I. Bosik, A. V. Novoselova and Yu. P. Simanov, *Russ. J. Inorg. Chem.* **6**, 1295 (1961).

7/K	C_p°	S°	$-(G^\circ - H^\circ(T))/T$	$H^\circ - H^\circ(T)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_r
0	0	0	INFINITE	-12.979	-1190.076	-1190.076	INFINITE
100	29.320	18.630	136.399	-11.777	-1195.412	-1161.311	606.607
200	60.675	48.883	85.043	-7.232	-1198.909	-1125.730	294.010
298.15	85.697	77.971	71.971	0	-1200.808	-1089.354	190.850
300	86.111	78.502	71.973	0.159	-1200.830	-1088.662	189.553
400	103.880	81.583	80.869	9.714	-1203.636	-1031.963	137.255
500	116.357	130.457	86.944	20.756	-1204.763	-1012.781	105.805
600	126.817	152.591	97.737	32.913	-1204.777	-974.366	84.826
700	137.988	172.967	107.046	46.145	-1203.793	-936.028	69.847
800	149.787	192.159	116.496	60.531	-1201.788	-897.901	58.627
900	162.046	210.506	125.928	76.120	-1251.860	-859.007	49.855
1000	174.431	228.245	135.278	92.967	-1246.475	-815.635	42.604
1100	183.088	245.296	144.510	110.864	-1240.239	-772.847	36.699
1200	189.209	261.502	151.591	129.494	-1233.452	-730.653	31.805
1300	193.543	276.877	162.487	148.643	-1226.317	-689.041	27.686
1400	196.581	291.287	171.175	168.157	-1218.980	-647.986	24.177
1500	198.656	304.925	179.642	187.925	-1211.549	-607.460	21.154
1600	200.004	317.792	187.878	207.863	-1218.639	-566.905	18.508
1700	200.706	329.941	195.861	227.903	-1210.843	-526.310	16.175
1800	200.832	341.418	203.680	248.068	-1203.693	-486.374	14.114
1900	200.852	352.276	211.189	268.068	-1195.419	-446.766	12.282
2000	200.852	362.577	218.504	288.148	-1187.825	-407.560	10.644
2100	200.832	372.376	225.599	308.231	-1180.309	-368.732	9.172
2200	200.832	381.719	232.485	328.314	-1172.870	-330.259	7.841
2300	200.832	390.646	239.169	348.397	-1165.508	-292.124	6.634

PREVIOUS: CURRENT: September 1966

Beryllium Sulfate, Alpha (BeSO₄)

CRYSTAL(β)

Beryllium Sulfate, Beta (β-BeSO₄)M_r = 63.63583Beryllium Sulfate, Beta (BeSO₄)Be₂O₄S₁(cr)

$$\Delta_f H^\circ(0 \text{ K}) = \text{Unknown}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = [-1199.695] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{cr}} H^\circ = [-1.113] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{cr}} H^\circ = [19.552] \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = [79.258] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T_{\text{m}} = 863 \text{ K } (\alpha \rightarrow \beta)$$

$$T_{\text{tr}} = 908 \text{ K } (\beta \rightarrow \gamma)$$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the alpha phase by adding $\Delta_{\text{cr}} H^\circ$, since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy

The heat capacity was assumed to be the same as that of alpha phase. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

Refer to the α -crystal table for details.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^a J·K ⁻¹ ·mol ⁻¹	S° - [G° - H°(T _r)]/T _r J·K ⁻¹ ·mol ⁻¹	H° - H°(T _r) kJ·mol ⁻¹	Δ _f G° kJ·mol ⁻¹	
0					
100					
200					
298.15	85.697	79.258	0.	-1088.624	190.722
300	86.111	79.259	0.159	-1087.935	189.426
400	103.880	82.870	9.714	-1050.464	137.177
500	116.357	90.231	20.756	-1012.312	105.755
600	126.817	99.024	32.913	-974.025	84.796
700	137.988	108.332	46.145	-935.816	69.831
800	149.787	117.782	60.531	-897.818	58.621
900	162.046	127.215	76.120	-859.052	49.858
1000	174.431	136.564	92.967	-815.809	42.613
1100	183.088	145.797	110.864	-773.149	36.714
1200	189.209	154.877	129.494	-731.084	31.823
1300	193.543	163.773	148.643	-689.601	27.708
1400	196.581	172.462	168.157	-648.675	24.202
1500	198.656	180.928	187.925	-608.277	21.182
1600	200.004	189.164	207.863	-567.851	18.538
1700	200.706	197.167	227.903	-527.485	16.208
1800	200.832	204.937	247.981	-487.577	14.149
1900	200.832	212.476	268.065	-448.098	12.319
2000	200.832	219.790	288.148	-409.020	10.683
2100	200.832	226.886	308.231	-370.321	9.211
2200	200.832	233.772	328.314	-331.976	7.882
2300	200.832	240.456	348.397	-293.970	6.676

PREVIOUS:

CURRENT: September 1966

Beryllium Sulfate, Beta (BeSO₄)Be₂O₄S₁(cr)

Beryllium Sulfate, Gamma (γ-BeSO₄)

M_r = 105.06978 Beryllium Sulfate, Gamma (BeSO₄)

CRYSTAL(γ)

Beryllium Sulfate, Gamma (γ-BeSO₄)

S°(298.15 K) = [100.784] J·K⁻¹·mol⁻¹
 T_{m1} = 863 K (α → β)
 T_{m2} = 908 K (β → γ)

Δ_fH°(298.15 K) = [-1180.143] kJ·mol⁻¹ (Unknown)
 Δ_{crd}H° = [1.113] kJ·mol⁻¹
 Δ_{crd}H° = [19.552] kJ·mol⁻¹

Enthalpy of Formation

The enthalpy of formation is calculated from that of the beta phase by adding Δ_{crd}H°, since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy

The heat capacity was assumed to be the same as that of alpha phase. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

Refer to the α-crystal table for details.

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P° = 0.1 MPa		log K _f
		S° - [G° - H°(T _r)]/T	H° - H°(T _r)	Δ _f H°	Δ _f G°	
0						
100	85.697	100.784	0.	-1180.143	-1075.491	188.422
200	86.111	101.316	0.159	-1180.166	-1074.841	187.147
298.15	86.111	101.316	0.159	-1180.166	-1074.841	187.147
300	86.111	101.316	0.159	-1180.166	-1074.841	187.147
400	103.880	128.682	9.714	-1182.991	-1039.523	135.748
500	116.357	153.270	20.756	-1184.098	-1003.523	104.837
600	126.817	175.405	32.913	-1184.113	-967.389	84.219
700	137.988	195.780	46.145	-1183.128	-931.333	69.497
800	149.787	214.973	60.531	-1181.123	-895.487	58.469
900	162.046	233.319	76.320	-1231.195	-858.874	49.848
1000	174.431	251.058	92.967	-1225.810	-817.784	42.717
1100	183.088	268.110	110.864	-1219.574	-777.277	36.910
1200	189.209	284.316	129.494	-1212.787	-737.364	32.097
1300	193.543	299.640	148.643	-1205.652	-698.033	28.047
1400	196.581	314.101	168.157	-1198.316	-659.260	24.597
1500	198.656	327.738	187.925	-1190.884	-621.016	21.626
1600	200.004	340.606	207.863	-1197.974	-582.742	19.025
1700	200.706	352.755	218.694	-1190.178	-544.528	16.731
1800	200.832	364.231	227.981	-1182.428	-506.773	14.706
1900	200.832	375.089	234.003	-1174.754	-469.446	12.906
2000	200.832	385.391	241.317	-1167.160	-432.572	11.296
2100	200.832	395.189	248.413	-1159.644	-395.975	9.849
2200	200.832	404.532	255.298	-1152.206	-359.783	8.542
2300	200.832	413.459	261.982	-1144.843	-323.930	7.357

PREVIOUS.

CURRENT: September, 1966

Beryllium Sulfate, Gamma (BeSO₄)

Be₁O₄S₁(cr)

Beryllium Tungsten Oxide (BeWO₄)

CRYSTAL

M_r = 256.85978Beryllium Tungsten Oxide (BeWO₄)Be₁O₄W₁(cr)

$S^{\circ}(298.15 \text{ K}) = [88.37 \pm 8.4] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $T_{\text{fus}} = \text{Unknown}$
 $\Delta_{\text{fus}}H^{\circ} = \text{Unknown}$
 $\Delta_{\text{fus}}H^{\circ}(0 \text{ K}) = \text{Unknown}$
 $\Delta_{\text{fus}}H^{\circ}(298.15 \text{ K}) = [-1513.4 \pm 63] \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_{\text{fus}}H^{\circ} = \text{Unknown}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_{\text{f}}H^{\circ}(\text{BeWO}_4, \text{cr}, 298.15 \text{ K}) = -361.7 \text{ kcal} \cdot \text{mol}^{-1}$, is calculated from $\Delta_{\text{f}}H^{\circ}(298.15 \text{ K}) = -17.1 \text{ kcal} \cdot \text{mol}^{-1}$ for $\text{BeO}(\text{cr}) + \text{WO}_3(\text{cr}) \rightarrow \text{BeWO}_4(\text{cr})$. The value of $\Delta_{\text{f}}H^{\circ}(298.15 \text{ K})$ is assumed to be the same as that for $\text{MgO}(\text{cr}) + \text{WO}_3(\text{cr}) \rightarrow \text{MgWO}_4(\text{cr})$, using $-143.7, -143.1, -201.5$, and $-362.3 \text{ kcal} \cdot \text{mol}^{-1}$ for the enthalpies of formation of $\text{MgO}(\text{cr})$, $\text{BeO}(\text{cr})$, $\text{WO}_3(\text{cr})$ and $\text{MgWO}_4(\text{cr})$, respectively.

Heat Capacity and Entropy

Heat capacities are estimated by comparison with those of $\text{CaWO}_4(\text{cr})$, $\text{BeO}(\text{cr})$,¹ and $\text{CaO}(\text{cr})$.²
 The entropy, $S^{\circ}(298.15 \text{ K}) = 21.12 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, is calculated from $\Delta S^{\circ}(298.15 \text{ K}) = -0.4 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\text{BeO}(\text{cr}) + \text{WO}_3(\text{cr}) \rightarrow \text{BeWO}_4(\text{cr})$. The value of $\Delta S^{\circ}(298.15 \text{ K})$ is assumed to be the same as that for $\text{MgO}(\text{cr}) + \text{WO}_3(\text{cr}) \rightarrow \text{MgWO}_4(\text{cr})$, using $6.44, 3.38, 18.14$ and $24.18 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\text{MgO}(\text{cr})$, $\text{BeO}(\text{cr})$, $\text{WO}_3(\text{cr})$ and $\text{MgWO}_4(\text{cr})$, respectively.

References

- ¹R. A. Yakovleva and T. N. Rezukhina, *Russ. J. Phys. Chem.* **34**, 390 (1960).
²JANAF Thermochemical Tables: $\text{BeO}(\text{cr})$, 9-30-65.
³K. K. Kelley, U. S. Bur. Mines. *Bull.* **584** 232 pp. (1960).

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa	
		S ^o - [G ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r)	Δ _r H ^o	Δ _r G ^o
0					
100					
200					
298.15	97.278	88.366	0	-1513.353	-1404.818
300	97.696	88.368	0.180	-1513.357	-1404.145
400	112.968	119.279	10.753	-1513.032	-1367.762
500	123.512	145.670	22.600	-1511.920	-1331.561
600	131.336	168.909	35.357	-1510.306	-1295.634
700	137.319	189.609	48.794	-1508.371	-1260.005
800	142.884	208.312	62.806	-1506.174	-1224.671
900	148.114	225.447	77.359	-1503.714	-1189.628
1000	153.009	241.307	92.417	-1500.997	-1154.873
1100	157.737	256.114	107.972	-1498.076	-1120.401
1200	162.256	270.033	123.956	-1494.906	-1086.212
1300	166.649	283.193	140.401	-1491.342	-1052.302
1400	171.126	295.708	157.791	-1487.628	-1018.667
1500	175.433	307.661	174.618	-1483.667	-985.307
1600	179.912	319.126	198.885	-1479.388	-951.693
1700	184.303	330.165	210.596	-1485.116	-917.947
1800	188.698	340.824	229.247	-1483.922	-884.498
1900	193.092	351.144	248.336	-1478.403	-851.345
2000	197.485	361.160	267.865	-1472.565	-818.492

PREVIOUS: June 1963

CURRENT: March 1967

Beryllium Tungsten Oxide (BeWO₄)Be₁O₄W₁(cr)

Be₃S₄(cr)

M_r = 41.07218 Beryllium Sulfide (BeS)

CRYSTAL

Beryllium Sulfide (BeS)

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P° = 0.1 MPa	
	C _p ^o J·K ⁻¹ ·mol ⁻¹	S° - (G° - H°(T _r))/T _r	H° - H°(T _r) kJ·mol ⁻¹	ΔG° kJ·mol ⁻¹
0				
100				
200				
298.15	34.016	37.028	0	-232.972
300	34.309	37.029	0.063	-232.964
400	42.551	38.483	3.932	-232.365
500	47.698	41.475	8.459	-231.067
600	51.045	45.060	13.405	-229.293
700	53.346	48.837	18.629	-227.834
800	55.145	52.624	24.056	-226.102
900	56.651	56.356	29.648	-223.264
1000	57.907	59.936	35.377	-219.540
1100	58.968	63.409	41.222	-207.937
1200	59.915	66.750	47.167	-200.443
1300	60.762	69.961	53.202	-188.566
1400	61.463	73.048	59.315	-187.404
1500	61.955	76.016	65.486	-178.523
1600	62.425	78.871	71.705	-170.848
1700	62.859	81.620	77.969	-162.834
1800	63.304	84.269	84.277	-154.903
1900	63.769	86.824	90.631	-147.050
2000	64.224	89.292	97.031	-139.273
2100	64.664	91.678	103.475	-131.568
2200	65.115	93.970	109.963	-123.932
2300	65.582	96.213	116.496	-116.363
2400	66.062	98.412	123.072	-108.858
2500	66.421	100.498	129.692	-101.415
2600	66.860	102.543	136.356	-94.033
2700	67.300	104.533	143.064	-86.710
2800	67.739	106.469	149.816	-79.220
2900	68.178	108.356	156.612	-71.446
3000	68.618	110.195	163.452	-63.700

S°(298.15 K) = [37.03 ± 4.2] J·K⁻¹·mol⁻¹
 T_m = 863 K
 Δ_fH°(0 K) = Unknown
 Δ_fH°(298.15 K) = -234.3 ± 8.8 kJ·mol⁻¹

Enthalpy of Formation

Von Wartenberg¹ has measured the enthalpy of solution of Be and BeS in H₂SO₄. The difference between these two enthalpies gives Δ_fH°(353 K) = -51.35 ± 2.1 kcal·mol⁻¹ for the reaction Be(cr) + H₂S(g) → BeS(cr) + H₂(g). Using auxiliary JANAF² data we calculate Δ_fH°(BeS, cr, 298.15 K) = -56.0 ± 2.1 kcal·mol⁻¹. This is in agreement with the value for the enthalpy of formation preferred by NBS.³

Heat Capacity and Entropy

No low-temperature heat capacity or high-temperature enthalpy measurements have been reported. We estimate C_p°(298.15 K) = 8.13 cal·K⁻¹·mol⁻¹ from the reaction BeO(cr, α) + MgS(cr) = BeS(cr) by assuming ΔC_p° = 0.² Comparison of this value with C_p° data for all the alkaline earth oxides and sulfides⁴ suggests that our estimate is reasonable. C_p° data above 298.15 K are estimated graphically by comparison with α- and β-BeO.²

Several methods of estimation predict that the value of S°(298.15 K) should lie near 8.85 cal·K⁻¹·mol⁻¹. A graphical comparison of the standard entropies for other alkaline-earth oxides and sulfides suggest values for S°(298.15 K) in the range 9–10 cal·K⁻¹·mol⁻¹, while additive entropy constants⁴ give 6.8 (Kelly's) and 9.3 (Latimer's) cal·K⁻¹·mol⁻¹. Literature estimates have included (in cal·K⁻¹·mol⁻¹) 7.4,² 8.0,⁶ and 8.4.⁷ We adopt S°(298.15 K) = 8.85 ± 1.0 cal·K⁻¹·mol⁻¹ based on cation increments for a series of beryllium and magnesium compounds.

Fusion Data

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

References

1. Von Wartenberg, Z. Anorg. Chem. **252**, 136 (1943).
2. JANAF Thermochemical Tables: H₂S(g), 6-30-77; H₂(g), 3-31-74; MgO(cr), 12-31-74; SrO(cr), 12-31-72; CaO(cr), 6-30-73; BaO(cr), 8-30-74; BeO(cr), 12-31-74; BaS(cr), SrS(cr), CaS(cr), and MgS(cr), 9-30-77.
3. S. Nat. Bur. Stand. Tech. Note 270-6, 119 pp. (1971).
4. D. R. Stull and H. Prophet in "The Characterization of High Temperature Vapors," J. L. Margrave, Ed., John Wiley Sons, Inc., New York, (1966).
5. V. A. Kireev, Zh. Obshch. Khim. **16**, 1569 (1946).
6. P. J. Spencer, Atomic Energy Reviews No. 4 Beryllium, International Atomic Energy Agency, Vienna, (1973).
7. M. V. H. Karapet'yants and M. L. Karapet'yants, "Thermodynamic Constants of Inorganic and Organic Compounds," Eng. Trans. by J. Schmorak, Ann Arbor, (1970).

PREVIOUS:

CURRENT: September 1977

Beryllium Sulfide (BeS)

Be₃S₄(cr)

$S^\circ(298.15\text{ K}) = 210.29 \pm 0.42\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(0\text{ K}) = [261 \pm 63]\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = [264 \pm 63]\text{ kJ}\cdot\text{mol}^{-1}$

Source	State	$\epsilon_i, \text{cm}^{-1}$	g_i	$r_e, \text{\AA}$	B_0, cm^{-1}	α_0, cm^{-1}	ω_e, cm^{-1}	ω_2, cm^{-1}
1	$X^1\Sigma^+$	0.0	1	1.7415	0.79059	0.0064	997.94	6.137
1,2	$^3\Pi$	[6600.]	6	[1.9075]	[0.6590]	[0.00605]	[762.46]	[4.12]
1	$A^1\Pi$	7842.9	2	1.9075	0.6590	0.00605	762.46	4.12
1	$^1\Delta$	[13048.4]	2	[2.000]	[0.5997]	[0.0069]	[671.6]	[5.48]
1,2	$^3\Sigma^+$	[21000.]	3	[1.8137]	[0.72894]	[0.00604]	[851.35]	[4.85]
1	$B^1\Sigma^+$	25868.6	1	1.8137	0.72894	0.00604	851.35	4.85

Enthalpy of Formation

No experimental data are available on BeS(g). We estimate $D_0(\text{BeS}, g)$ by the method of Hauge and Margrave¹ based on data involving known bond energies and force constants of the gaseous diatomic oxides and sulfides. Based on dissociation energies of the alkaline earth monoxides, taken from Srivastava,² dissociation energies of the alkaline earth sulfides and force constants calculated from JANAF data,³ we calculate $D_0(\text{BeS}, g) = 80 \pm 10\text{ kcal}\cdot\text{mol}^{-1}$. A normal linear-Birge-Spencer extrapolation of the ground state yields $D_0(\text{BeS}, g) = 115\text{ kcal}\cdot\text{mol}^{-1}$. After correcting for ionic character⁴ and for excited state products $D_0(\text{BeS}, g) = 76\text{ kcal}\cdot\text{mol}^{-1}$. These values are very uncertain. See the discussion of $\text{MgS}(g)$.⁵ We adopt $D_0(\text{BeS}, g) = 80 \pm 15\text{ kcal}\cdot\text{mol}^{-1}$. Using auxiliary JANAF data,³ we calculate $\Delta_f H^\circ(\text{BeS}, g, 298.15\text{ K}) = 63 \pm 15\text{ kcal}\cdot\text{mol}^{-1}$.

Heat Capacity and Entropy

The spectroscopic constants taken from Cheetham *et al.*⁶ are corrected to account for the natural abundances of the elements. Other low-lying electronic states and their vibrational-rotational constants are estimated in isoconfigurational groups by analogy with BeO° and from trends observed in the known states of the other alkaline-earth oxides and sulfides.³ Uncertainty in the energy and molecular constants for the estimated states may contribute as much as 2-3 cal·K⁻¹·mol⁻¹ to the entropy above 3000 K. The splitting between the $A^1\Pi$ and a $^3\Pi$ states, ~1200 cm⁻¹, is based on trends in the triplet-singlet splitting observed by Field⁷ for the alkaline-earth oxides. The Hartree-Fock calculations of Verhaegen and Richards⁸ support this. Their theoretical singlet-triplet splitting should be reasonably accurate even though the absolute energies are biased. The thermodynamic functions are calculated using first-order anharmonic corrections to Q, and Q, in the partition function $Q = Q_{el} Q_{vib} Q_{rot} Q_{trans} \exp(-c_5/T)$.

References

- R. H. Hauge and J. L. Margrave, *High Temp. Sci.* **4**, 170 (1972).
- R. D. Srivastava, *High Temp. Sci.* **8**, 225 (1976).
- JANAF Thermochemical Tables: Be(g), 9-30-61; S(g), 6-30-71; S₂(g), 12-31-65; BeO(g) and SrO(g), 6-30-74; BeO(g), MgO(g), and CaO(g), 12-31-74; MgS(g), CaS(g), SrS(g), and BaS(g), 9-30-77.
- C. J. Cheetham, W. J. M. Gissane, and R. F. Barrow, *Trans. Faraday Soc.* **61**, 1308 (1965).
- B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
- R. W. Field, *J. Chem. Phys.* **60**, 2400 (1974).
- G. Verhaegen and W. G. Richards, *Proc. Phys. Soc. (London)* **90**, 579 (1967).
- D. L. Hildenbrand, "Advances in High Temperature Chemistry," Vol. 1, L. Eyring (ed.), pp. 198-206, Academic Press, New York, (1967).

TK	Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$		Standard State Pressure = $p^\circ = 0.1\text{ MPa}$		log K _r
	C_p°	$S^\circ - (G^\circ - H^\circ(T_r))/T_r$	$H^\circ - H^\circ(T_r)$	$\Delta_f G^\circ$	
0	0	0	INFINITE	261.156	INFINITE
100	29.109	198.064	-8.780	246.831	-128.931
200	29.468	198.299	-5.872	263.335	-60.034
298.15	30.786	210.288	0	264.036	-37.363
300	30.816	210.478	0.057	263.577	-37.079
400	32.371	219.561	3.218	260.298	-25.636
500	35.626	226.926	6.521	257.571	-18.870
600	34.575	233.146	9.334	255.132	-14.405
700	35.273	238.531	13.428	252.888	-11.246
800	35.834	243.279	16.984	250.736	-8.896
900	36.363	247.530	20.594	248.648	-7.148
1000	36.960	251.391	24.259	246.622	-6.015
1100	37.713	254.947	27.901	244.712	-5.093
1200	38.688	258.269	31.784	242.938	-4.328
1300	39.917	261.423	35.737	241.284	-3.684
1400	41.409	264.433	39.801	239.750	-3.133
1500	43.124	267.338	44.026	238.327	-2.661
1600	45.017	270.180	48.432	237.000	-2.265
1700	47.016	272.969	53.033	235.762	-1.930
1800	49.044	275.714	57.836	234.609	-1.632
1900	51.023	278.419	62.840	233.532	-1.365
2000	52.883	281.084	68.037	232.530	-1.125
2100	54.566	283.706	73.411	231.593	-0.907
2200	56.030	286.279	78.943	230.726	-0.709
2300	57.292	288.797	84.609	230.000	-0.527
2400	58.209	291.255	90.384	229.400	-0.360
2500	58.829	293.647	96.242	228.900	-0.206
2600	59.365	295.967	102.159	228.498	-0.063
2700	59.825	298.214	108.112	228.176	0.079
2800	59.980	300.384	114.080	227.920	0.198
2900	59.620	302.477	120.045	227.720	0.291
3000	59.333	304.493	125.991	227.570	0.357
3100	58.975	306.433	131.907	227.468	0.400
3200	58.531	308.299	137.783	227.400	0.428
3300	58.025	310.092	143.611	227.362	0.446
3400	57.471	311.816	149.386	227.340	0.455
3500	56.890	313.474	155.105	227.330	0.456
3600	56.293	315.068	160.764	227.330	0.449
3700	55.693	316.602	166.363	227.330	0.435
3800	55.097	318.080	171.903	227.328	0.414
3900	54.512	319.503	177.386	227.322	0.388
4000	53.943	320.876	182.806	227.315	0.359
4100	53.393	322.201	188.173	227.306	0.327
4200	52.866	323.482	193.485	227.294	0.293
4300	52.363	324.720	198.746	227.279	0.257
4400	51.884	325.918	203.958	227.262	0.220
4500	51.430	327.079	209.124	227.242	0.182
4600	51.001	328.204	214.245	227.219	0.144
4700	50.597	329.297	219.325	227.193	0.106
4800	50.217	330.358	224.365	227.164	0.069
4900	49.859	331.390	229.369	227.132	0.032
5000	49.524	332.394	234.338	227.097	-0.006
5100	49.210	333.371	239.274	227.059	-0.046
5200	48.916	334.324	244.181	227.017	-0.086
5300	48.641	335.253	249.058	226.971	-0.126
5400	48.384	336.160	253.909	226.921	-0.166
5500	48.143	337.045	258.736	226.867	-0.206
5600	47.919	337.911	263.539	226.809	-0.246
5700	47.709	338.757	268.320	226.747	-0.286
5800	47.513	339.585	273.081	226.681	-0.326
5900	47.331	340.396	277.823	226.611	-0.366
6000	47.160	341.190	282.547	226.537	-0.406

PREVIOUS September 1977 (1 atm)

CURRENT September 1977 (1 bar)

Beryllium Sulfide (BeS)

$Be_1S_1(g)$

Be₂(g)

T/K	C _p ^o	S ^o - [G ^o - H ^o (T)]/T	H ^o - H ^o (T)	ΔH ^o	ΔG ^o	log K _r
0	0	INFINITE	INFINITE	631.065	631.065	INFINITE
100	37.037	167.734	-6.791	634.156	617.483	-322.540
200	34.597	194.091	-3.005	636.787	599.638	-156.609
298.15	27.492	206.410	0	637.161	581.249	-101.832
300	27.405	206.580	0.051	637.151	580.902	-101.144
400	24.295	213.975	2.614	636.030	562.294	-73.428
500	22.893	219.227	4.965	634.176	544.063	-56.838
600	22.173	223.331	7.215	631.891	526.249	-45.814
700	21.763	226.715	9.410	629.303	508.843	-37.970
800	21.509	229.603	11.572	626.472	491.825	-32.113
900	21.341	232.126	13.714	623.429	475.174	-27.978
1000	21.226	234.368	15.842	620.191	458.874	-23.969
1100	21.142	236.387	17.960	616.767	442.906	-21.032
1200	21.081	238.224	20.071	613.162	427.258	-18.598
1300	21.033	239.910	22.177	609.377	411.919	-16.551
1400	20.997	241.467	24.278	605.414	396.877	-14.808
1500	20.968	242.915	26.377	601.271	382.125	-13.307
1600	20.944	244.267	28.472	597.076	368.707	-12.037
1700	20.925	245.536	30.566	592.843	356.372	-10.950
1800	20.909	246.732	32.657	588.625	344.256	-9.990
1900	20.896	247.862	34.747	584.633	332.350	-9.137
2000	20.884	248.933	36.836	580.916	320.644	-8.374
2100	20.875	249.952	38.924	577.423	309.132	-7.689
2200	20.866	250.923	41.011	574.092	297.805	-7.071
2300	20.860	251.850	43.098	570.884	286.658	-6.510
2400	20.853	252.738	45.183	567.753	275.685	-6.000
2500	20.847	253.588	47.268	564.679	264.879	-5.534
2600	20.843	254.407	49.353	561.658	254.237	-5.108
2700	20.838	255.193	51.437	558.694	243.753	-4.716
2800	20.834	255.951	53.521	555.786	233.429	-4.347
2900	20.831	256.682	55.604	552.934	223.266	-4.000
3000	20.828	257.388	57.687	550.138	213.266	-3.666
3100	20.825	258.071	59.769	547.397	203.432	-3.347
3200	20.823	258.732	61.852	544.712	193.762	-3.040
3300	20.820	259.373	63.934	542.084	184.262	-2.744
3400	20.818	259.994	66.016	539.512	174.934	-2.458
3500	20.816	260.598	68.098	537.000	165.774	-2.181
3600	20.815	261.184	70.179	534.548	156.782	-1.913
3700	20.813	261.755	72.261	532.156	147.954	-1.654
3800	20.812	262.310	74.342	529.823	139.290	-1.403
3900	20.810	262.850	76.423	527.548	130.790	-1.159
4000	20.809	263.377	78.504	525.330	122.454	-0.922
4100	20.808	263.891	80.585	523.166	114.282	-0.692
4200	20.807	264.392	82.666	521.048	106.272	-0.467
4300	20.806	264.882	84.746	518.980	98.424	-0.246
4400	20.805	265.360	86.827	516.962	90.742	-0.028
4500	20.804	265.828	88.907	514.994	83.236	0.178
4600	20.803	266.285	90.988	513.078	75.904	0.382
4700	20.803	266.732	93.068	511.214	68.746	0.590
4800	20.802	267.170	95.148	509.402	61.762	0.801
4900	20.801	267.599	97.228	507.642	54.954	1.014
5000	20.801	268.019	99.308	505.936	48.330	1.229
5100	20.800	268.431	101.388	504.284	41.892	1.448
5200	20.799	268.835	103.468	502.686	35.634	1.671
5300	20.799	269.231	105.548	501.142	29.556	1.898
5400	20.798	269.620	107.628	499.652	23.666	2.128
5500	20.798	270.002	109.708	498.214	17.964	2.361
5600	20.798	270.377	111.788	496.828	12.450	2.597
5700	20.797	270.745	113.868	495.494	7.122	2.835
5800	20.797	271.106	115.948	494.212	1.982	3.074
5900	20.796	271.462	118.027	492.982	-3.078	3.315
6000	20.796	271.811	120.107	491.804	-8.242	3.558

CURRENT: September 1983 (1 bar)

Be₂(g)

Beryllium (Be₂)

$D_0^o = 8.535 \pm 0.879 \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_f H^o(0 \text{ K}) = 631.1 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1}$ $M_r = 18.02436$ Beryllium (Be₂)

v/	0	1	2	3	4	5	6	7	8
G(v)-G(0)	0	224	328.6	405.1	459.7	508	547.9	578.2	600.7
B(v)*	0.548	0.457	0.366	0.317	0.296	0.275	0.254	0.233	0.212
10 ⁶ × D(v)*	10.13	10.13	10.13	31.64	31.64	31.64	31.64	31.64	31.64

*Estimated as explained below.

Enthalpy of Formation

The adopted value of the ground state dissociation energy for Be₂(g), $D_0^o = 8.535 \pm 0.879 \text{ kJ}\cdot\text{mol}^{-1}$, was determined via a high level quantum mechanical calculation by Lengsfeld, *et al.*¹ Using this value and the recommended value for $\Delta_f H^o(\text{Be}, g, 0 \text{ K}) = 319.8 \text{ kJ}\cdot\text{mol}^{-1}$ from CODATA,² we calculate the adopted value of $\Delta_f H^o(\text{Be}_2, g, 0 \text{ K}) = 631.1 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1}$.

Heat Capacity and Entropy

The thermal functions were calculated using a direct summation technique analogous to the alkali dimers and diatomic halogens.¹² As in the diatomic fluorine case, the values of G(v), B, and D, were directly input into the calculation. Values of 9 bound vibrational energy levels for the Σ_g^+ ground state were determined from a high level *ab initio* quantum mechanical calculation (including full configuration interaction).³ However, a recent spectroscopic determination by Bondybe⁴ gave a value for $\Delta G_{1/2} = 224 \text{ cm}^{-1}$ which is 1.21 times larger than the corresponding value from the theoretical calculation. We therefore adopt $\Delta G_{1/2} = 224 \text{ cm}^{-1}$ and increase the rest of the theoretically determined vibrational spacings by the same factor. These scaled G(v) are given in the table above. Since the theoretical binding energy of Harrison and Handy⁵ may also be too small, we adopt the value calculated by Lengsfeld *et al.*¹ The adopted values of B, are estimated using the correlation of Calder and Ruedenberg.⁶ Since a plot of $\Delta G_{v+1/2}$ vs. v exhibits two linear regions ($0 \leq v \leq 5$ and $4 \leq v \leq 8$), the value of B_e used to estimate α_e in the $4 \leq v \leq 8$ region is reduced from 0.593 to 0.39. This is done in order to assure a smoothly decreasing B_e as v increases. The D_e parameters are determined from the estimation method of Herzberg⁶ where we use the first order D_e term only.

The rotational levels are extrapolated to high J values according to the method of Khaichunov⁷ who proposed a simpler form of Woolley's method.⁸ The rotational levels are weighted in accordance with the nuclear spin-rotation interaction⁹ as follows: even J weight = 0.625, odd J weight = 0.375. The so-called quasibound rotational levels were not included in the calculation. No suitable spectroscopic information exists for any of the excited states of Be₂. It should be noted that the inclusion of Σ_g^+ and Π_g states in the range $T_e \approx 5000 \text{ cm}^{-1}$ as proposed by Jones¹⁰ would cause our calculated thermal functions to be deficient at temperatures greater than about 2000 K.¹¹ Due to the extremely shallow well of the ground state, most Be₂ molecules will probably exist in an excited state at temperatures $T \approx 1000 \text{ K}$. The calculated $S^o(298.15 \text{ K})$ is $5.41 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ smaller than the value adopted by Glushko, *et al.*¹¹

References

- B. H. Lengsfeld III, A. D. McLean, M. Yoshimine and B. Liu, *J. Chem. Phys.* **79**, 1891 (1983).
- J. D. Cox, *J. Chem. Thermodynamics* **10**, 903 (1977).
- R. J. Harrison and N. C. Handy, *J. Chem. Phys.* **98**, 97 (1983).
- V. E. Bondybe and J. H. English, *J. Chem. Phys.* **80**, 568 (1984).
- G. V. Calder and K. Ruedenberg, *J. Chem. Phys.* **49**, 5399 (1968).
- G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, Eqn. III-123, (1950).
- H. W. Woolley, R. B. Scott, and F. G. Brickwedde, *J. Res. Nat. Bur. Stand.* **41**, 379 (1948).
- Reference 6, Chapter 5.
- V. P. Glushko, *J. Chem. Phys.* **71**, 1300 (1979).
- V. P. Glushko, V. Medvedev, *et al.*, "Thermal Constants of Substances," Volume IX, Moscow, (1979).
- JANAF Thermochemical Tables, L.J.G., 12-31-83; F.G., 6-30-82.
- See for example JANAF Thermochemical Tables, M.G., 9-30-83.

PREVIOUS:

Beryllium (Be₂)

Beryllium Chloride ((BeCl₂)₂)

IDEAL GAS

$$M_r = 159.83636$$

$$\Delta_r H^\circ(0 \text{ K}) = [-752] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H^\circ(298.15 \text{ K}) = [-749] \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = [381.47] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies	
ν , cm ⁻¹	ν , cm ⁻¹
[220] (1)	[185] (1)
[110] (1)	[100] (1)
[180] (1)	[860] (1)
[105] (1)	[300] (1)

Ground State Quantum Weight: 1

Point Group: [D_{2h}]

Bond Distances: Be-Cl = [1.7] Å;

Bond Angles: Cl-Be-Cl (in ring) = [188]°, Cl-Be-Cl = [136]°

Product of the Moments of Inertia: $I_A/I_B/I_C = [2.6276 \times 10^{-12}] \text{ g}^3 \text{ cm}^6$

$\alpha = 4$

Enthalpy of Formation

The enthalpy of formation was estimated by assuming that the concentration of dimer in equilibrium with the monomer was ~5% at 500 K as reported by Hildenbrand, Theard, Murad and Ju,¹ giving an effective $K_p = 5.5 \times 10^{-4}$ for $2\text{BeCl}_2(\text{g}) \rightarrow \text{Be}_2\text{Cl}_4(\text{g})$ at 500 K.

Heat Capacity and Entropy

The structure was assumed planar with a D_{2h} symmetry, the bond lengths were estimated from the values for BeCl₂(g), a lengthening being assumed in the ring. The frequencies were estimated using K₂Cl₂ as a basis for the ring vibrations. Two polymeric frequencies had been observed by Snelson.² These were observed in matrix isolated BeCl₂ gas and were ascribed to polymeric species on account of their warm up behavior. They are here assigned to the B_u asymmetric stretching mode and the B_u symmetric out of plane wag of the non-ring chlorines. The order of the frequencies listed above is arbitrary and not related to their species type. The principal moments of inertia are: $I_A = [18.4088 \times 10^{-39}]$, $I_B = [110.6214 \times 10^{-39}]$, and $I_C = [129.0303 \times 10^{-39}] \text{ g cm}^2$.

References

- ¹D. L. Hildenbrand, L. P. Theard, E. Murad and F. Ju, Aeronutronic Div. of Philco Corp. Report U-3068, April 1965, under contract AF 04 (611)-8523.
- ²A. Snelson, IIT Research Institute, Report No. IITRI-C 6013-4, May 1964, under contract No. DA-31-124-ARO (D)-111.

Beryllium Chloride ((BeCl₂)₂)Be₂Cl₄(g)

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S° - (G° - H°(T _r))/T	H° - H°(T _r)	Δ _r H°	
0	0	0	0	0	INFINITE
100	77.971	273.932	-25.305	-752.015	INFINITE
200	104.193	337.542	-20.163	-747.266	587.720
250	108.809	361.547	-10.836	-750.678	1.5118
298.15	115.368	381.475	-5.451	-749.715	152.150
300	115.517	382.189	0	-748.936	126.846
350	118.970	400.268	0.214	-748.909	126.036
400	121.557	416.331	6.080	-748.236	107.417
450	123.529	430.768	12.096	-747.650	93.463
500	125.056	443.865	18.225	-747.127	82.619
600	127.217	466.871	24.442	-746.632	73.949
700	128.625	488.593	31.063	-746.259	69.956
800	129.587	503.837	37.924	-745.982	61.684
900	130.270	519.142	45.769	-745.769	48.736
1000	130.771	534.894	54.822	-745.603	39.335
1100	131.149	548.377	65.191	-745.574	35.016
1200	131.440	560.801	76.820	-745.669	31.483
1300	131.669	572.331	89.612	-745.882	28.539
1400	131.852	583.096	103.561	-746.208	26.047
1500	132.000	593.149	118.674	-746.642	23.910
1600	132.123	594.721	134.959	-747.172	22.057
1700	132.225	596.824	152.425	-747.800	20.399
1800	132.311	600.292	171.088	-748.525	18.910
1900	132.384	605.076	190.965	-749.348	17.586
2000	132.446	611.192	212.071	-750.261	16.401
2100	132.500	618.650	234.428	-751.266	15.333
2200	132.546	627.467	258.052	-752.364	14.368
2300	132.587	637.643	282.951	-753.556	13.489
2400	132.625	649.287	309.229	-754.842	12.686
2500	132.655	662.502	336.982	-756.224	11.950
2600	132.683	677.325	366.248	-757.702	11.275
2700	132.708	693.763	397.031	-759.276	10.645
2800	132.731	711.820	429.354	-760.946	10.053
2900	132.751	731.509	463.230	-762.712	9.503
3000	132.769	752.843	498.664	-764.574	9.000
3100	132.786	775.847	535.661	-766.532	8.541
3200	132.801	800.528	574.228	-768.586	8.118
3300	132.814	826.895	614.475	-770.736	7.725
3400	132.827	854.952	656.412	-772.982	7.358
3500	132.838	884.701	700.049	-775.324	7.008
3600	132.849	916.145	745.396	-777.762	6.673
3700	132.858	949.288	792.453	-780.296	6.351
3800	132.867	984.135	841.221	-782.926	6.041
3900	132.875	1020.688	891.711	-785.652	5.741
4000	132.883	1058.945	943.932	-788.474	5.451
4100	132.890	1108.913	997.993	-791.392	5.171
4200	132.897	1160.596	1054.900	-794.406	4.900
4300	132.903	1214.001	1114.763	-797.516	4.637
4400	132.909	1269.138	1177.591	-800.722	4.383
4500	132.914	1326.009	1244.403	-804.124	4.138
4600	132.919	1384.724	1315.200	-807.722	3.901
4700	132.924	1445.293	1390.000	-811.516	3.671
4800	132.928	1507.726	1468.812	-815.506	3.447
4900	132.932	1572.033	1551.645	-819.691	3.228
5000	132.936	1638.215	1638.509	-824.072	3.014
5100	132.940	1706.276	1729.403	-828.649	2.805
5200	132.943	1776.219	1824.337	-833.422	2.601
5300	132.946	1848.054	1923.321	-838.391	2.402
5400	132.950	1921.791	2026.365	-843.556	2.208
5500	132.952	1997.438	2133.479	-848.917	2.019
5600	132.955	2074.995	2244.662	-854.474	1.835
5700	132.958	2154.471	2359.925	-860.227	1.656
5800	132.960	2235.876	2479.276	-866.176	1.481
5900	132.963	2319.219	2602.725	-872.321	1.311
6000	132.965	2404.509	2730.182	-878.662	1.145

PREVIOUS: June 1965 (1 atm)

CURRENT: June 1965 (1 bar)

Beryllium Chloride ((BeCl₂)₂)Be₂Cl₄(g)

Be₂F₂O(g)

Beryllium Fluoride Oxide (O(BeF₂))

IDEAL GAS

Beryllium Fluoride Oxide (O(BeF₂))

Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P° = 0.1 MPa	
T/K	C _p ^o J·K ⁻¹ ·mol ⁻¹	H° - H°(T _r) / kJ·mol ⁻¹	ΔG° / kJ·mol ⁻¹
0	0	0	0
100	47.638	-16.585	-1204.127
200	58.853	-12.725	-1204.127
300	65.225	-6.989	-1204.060
400	71.486	-3.558	-1199.485
500	76.151	0	-1192.337
600	79.915	0.141	-1182.713
700	82.987	0.406	-1171.022
800	85.463	0.618	-1157.878
900	87.441	0.791	-1143.000
1000	89.034	0.934	-1126.487
1100	90.336	1.051	-1108.555
1200	91.399	1.147	-1089.599
1300	92.266	1.225	-1069.999
1400	92.977	1.288	-1049.999
1500	93.536	1.338	-1029.999
1600	93.981	1.377	-1009.999
1700	94.331	1.406	-989.999
1800	94.599	1.426	-969.999
1900	94.791	1.439	-949.999
2000	94.913	1.446	-929.999
2100	94.971	1.448	-909.999
2200	94.981	1.448	-889.999
2300	94.951	1.446	-869.999
2400	94.881	1.442	-849.999
2500	94.781	1.436	-829.999
2600	94.651	1.428	-809.999
2700	94.491	1.418	-789.999
2800	94.301	1.406	-769.999
2900	94.081	1.393	-749.999
3000	93.831	1.378	-729.999
3100	93.551	1.362	-709.999
3200	93.241	1.344	-689.999
3300	92.901	1.324	-669.999
3400	92.531	1.302	-649.999
3500	92.131	1.278	-629.999
3600	91.701	1.253	-609.999
3700	91.241	1.227	-589.999
3800	90.751	1.200	-569.999
3900	90.231	1.171	-549.999
4000	89.681	1.141	-529.999
4100	89.101	1.110	-509.999
4200	88.491	1.078	-489.999
4300	87.851	1.045	-469.999
4400	87.181	1.011	-449.999
4500	86.481	0.976	-429.999
4600	85.751	0.940	-409.999
4700	85.001	0.903	-389.999
4800	84.221	0.865	-369.999
4900	83.411	0.826	-349.999
5000	82.571	0.786	-329.999
5100	81.701	0.745	-309.999
5200	80.801	0.703	-289.999
5300	79.871	0.660	-269.999
5400	78.911	0.616	-249.999
5500	77.921	0.571	-229.999
5600	76.901	0.525	-209.999
5700	75.851	0.478	-189.999
5800	74.771	0.430	-169.999
5900	73.661	0.381	-149.999
6000	72.521	0.331	-129.999

ΔH^o(0 K) = -1204.1 ± 21 kJ·mol⁻¹
 ΔH^o(298.15 K) = -1204.6 ± 21 kJ·mol⁻¹

S°(298.15 K) = [298.9] J·K⁻¹·mol⁻¹

Vibrational Frequencies and Degeneracies	
v, cm ⁻¹	g
[1200] (1)	[1500] (1)
[600] (1)	[900] (1)
[400] (1)	[300] (1)
[100] (1)	[300] (1)

Ground State Quantum Weight: [1]
 Point Group: [C_{2v}]
 Bond Distances: Be-O = [1.33] Å; Be-F = [1.43] Å
 Bond Angles: O-Be-F = [180]°; Be-O-Be = [150]°
 Product of the Moments of Inertia: I_AI_BI_C = [2.5549 × 10⁻¹¹⁴] g³·cm⁶

Enthalpy of Formation
 Efimenko¹ has studied mass spectrometrically the reaction BeO(cr) + BeF₂(g) → Be₂O(g) and also reported two sets of equilibrium constants. Using JANAF thermal functions, the enthalpy of reaction has been calculated from those reported equilibrium constants by the 2nd law and the 3rd law methods.

Number of Measurements	T/K	Δ _r H°(298.15K), kcal·mol ⁻¹	Drift
1st Set 13	1570-1891	41.448 ± 3.04	0.408 ± 1.726
2nd Set 21*	1872-2195	42.553 ± 0.70	0.015 ± 0.359

*There are 4 points rejected due to failure of statistical test.

A weighted average value, Δ_rH°(298.15 K) = 42.70 kcal·mol⁻¹, was chosen for the enthalpy of reaction. The enthalpy of formation Δ_rH°(Be₂O, g, 298.15 K) = 287.9 ± 5 kcal·mol⁻¹ was calculated from the selected enthalpy of reaction, using Δ_rH°(BeO, cr, 298.15 K) = 143.1 kcal·mol⁻¹ and Δ_rH°(BeF₂, g, 298.15 K) = 187.5 kcal·mol⁻¹.

Heat Capacity and Entropy

The adopted "v" shape molecular structure with nine fundamental vibrational frequencies was obtained from an estimation by Mann.² The bond distance Be-O and Be-F were estimated to be the same as those in BeO(g) and BeF₂(g), respectively. The principal moments of inertia are: I_A = 1.0103 × 10⁻³⁹, I_B = 49.7842 × 10⁻³⁹, and I_C = 50.7946 × 10⁻³⁹ g·cm².

References

- J. Efimenko, NBS Report 8186, Ch. 13 (January, 1964), refer to pp. 103-112.
- D. E. Mann, NBS Report 8186, Ch. 15 (January, 1964); refer to pp. 118-121.

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

Beryllium Fluoride Oxide (O(BeF₂))

Be₂F₂O(g)

Beryllium Oxide (Be₂O)

IDEAL GAS

M_r = 34.02376Be₂O₁(g)

$$\Delta_f H^\circ(0 \text{ K}) = -64 \pm 42 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = -63 \pm 42 \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = [220.8] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies	
ν , cm ⁻¹	g_i
[1100]	(1)
[500]	(2)
[1600]	(1)

Ground State Quantum Weight: [3] $\sigma = 2$ Point Group: D_{∞h}

Bond Distance: Be-O = [1.4] Å

Bond Angle: Be-O-Be = [180]°

Rotational Constant: B₀ = [0.477178] cm⁻¹

Enthalpy of Formation

Hildenbrand, Theard, and Ju¹ have reported the enthalpy of formation. Equilibrium constants were determined in a mass spectrometer for the reactions 2BeO(cr) → Be₂O(g) + O(g) - (1); 2BeO(g) → Be₂O(g) + O(g) - (2); and Be₂O₂(g) → Be₂O(g) + O(g) - (3). Using our own Gibbs energy functions we obtain $\Delta_f H^\circ(\text{Be}_2\text{O}, g, 298.15 \text{ K}) = 13.1, -14.5,$ and $-16.7 \text{ kcal}\cdot\text{mol}^{-1}$, all ± 10 ; the 2nd law treatment of reaction 1 gives $-18.3 \pm 10 \text{ kcal}\cdot\text{mol}^{-1}$. We adopt a median value $-15 \pm 10 \text{ kcal}\cdot\text{mol}^{-1}$.

Heat Capacity and Entropy

Buchler, Stauffer, Klemperer and Wharton² have shown Li₂O to be linear. Also Walsh³ predicted that AB₂ molecules with less than 16 bonding electrons would be linear. Thus Be₂O was taken to be linear and symmetrical, with a Be-O bond length of 1.4 Å, which is a little longer than in BeO(g). The vibrational frequencies were estimated by taking ν_2 to be larger than the stretch in BeO(g) and then calculating ν_1 from the valence force field assumption. The bending force constant was estimated as 1/20th of the stretching force constant. The two outermost electrons were considered unpaired and so gave a $^3\Sigma$ ground state.

References

- ¹D. L. Hildenbrand, L. P. Theard, and F. Ju, Ford Motor Co., Aeronautics Division, Third Quarterly Technical Report U-2231, (April-June 1963).
- ²A. Buchler, J. L. Stauffer, W. Klemperer and C. Wharton, A. D. Little, Inc., Interim Technical Report No. 5, (1963).
- ³A. D. Walsh, J. Chem. Soc. London 1953, 2269.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P° = 0.1 MPa		log K _r
	C _p	S° - (G° - H°(T _r))/T	H° - H°(T _r)	Δ _r H°	
	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	KJ·mol ⁻¹	KJ·mol ⁻¹	
0	0	0	INFINITE	INFINITE	INFINITE
100	29.748	183.340	-64.479	-64.479	-64.479
200	33.536	205.584	-63.092	-72.660	-72.660
250	38.466	218.835	-62.460	-82.559	-82.559
298.15	40.952	220.827	0	-87.581	-87.581
300	41.041	221.081	0.076	-92.388	-92.388
350	43.322	227.582	2.186	-99.572	-99.572
400	45.354	233.502	4.404	-107.510	-107.510
450	47.163	238.951	6.718	-117.387	-117.387
500	48.767	244.004	9.117	-128.444	-128.444
600	51.429	253.141	14.132	-141.964	-141.964
700	53.482	261.230	19.382	-157.327	-157.327
800	55.063	268.480	24.813	-174.502	-174.502
900	56.290	275.039	30.383	-193.506	-193.506
1000	57.250	281.021	36.062	-214.350	-214.350
1100	58.011	286.515	41.826	-237.043	-237.043
1200	58.620	291.590	47.659	-261.588	-261.588
1300	59.115	296.302	53.547	-287.988	-287.988
1400	59.520	300.698	59.479	-316.244	-316.244
1500	59.856	304.816	65.448	-346.376	-346.376
1600	60.138	308.689	71.449	-378.392	-378.392
1700	60.375	312.342	77.474	-412.308	-412.308
1800	60.577	315.799	83.522	-448.141	-448.141
1900	60.750	319.079	89.589	-485.891	-485.891
2000	60.899	322.198	95.671	-525.550	-525.550
2100	61.029	325.173	101.768	-567.112	-567.112
2200	61.142	328.015	107.877	-610.676	-610.676
2300	61.242	330.735	113.996	-656.241	-656.241
2400	61.330	333.343	120.125	-703.806	-703.806
2500	61.408	335.848	126.262	-753.371	-753.371
2600	61.478	338.258	132.406	-804.936	-804.936
2700	61.540	340.580	138.557	-858.501	-858.501
2800	61.596	342.819	144.714	-914.066	-914.066
2900	61.647	344.981	150.876	-971.631	-971.631
3000	61.692	347.072	157.043	-1031.196	-1031.196
3100	61.734	349.095	163.214	-1092.761	-1092.761
3200	61.771	351.056	169.390	-1156.326	-1156.326
3300	61.806	352.957	175.569	-1221.891	-1221.891
3400	61.837	354.803	181.751	-1289.456	-1289.456
3500	61.866	356.596	187.936	-1358.021	-1358.021
3600	61.893	358.339	194.124	-1428.586	-1428.586
3700	61.917	360.035	200.314	-1501.151	-1501.151
3800	61.940	361.687	206.507	-1575.716	-1575.716
3900	61.961	363.296	212.702	-1652.281	-1652.281
4000	61.980	364.865	310.140	-1730.846	-1730.846
4100	61.998	366.395	311.493	-1811.411	-1811.411
4200	62.015	367.890	312.818	-1894.076	-1894.076
4300	62.030	369.349	314.116	-1978.841	-1978.841
4400	62.045	370.775	315.388	-2065.706	-2065.706
4500	62.059	372.170	316.634	-2154.671	-2154.671
4600	62.071	373.534	317.856	-2245.736	-2245.736
4700	62.083	374.869	319.055	-2338.901	-2338.901
4800	62.095	376.176	320.232	-2434.166	-2434.166
4900	62.105	377.457	321.387	-2531.531	-2531.531
5000	62.115	378.711	322.521	-2630.996	-2630.996
5100	62.124	379.941	323.634	-2732.561	-2732.561
5200	62.133	381.148	324.729	-2836.226	-2836.226
5300	62.142	382.332	325.805	-2941.991	-2941.991
5400	62.149	383.495	326.862	-3049.856	-3049.856
5500	62.157	384.634	327.902	-3159.821	-3159.821
5600	62.164	385.754	328.925	-3271.886	-3271.886
5700	62.171	386.854	329.932	-3386.051	-3386.051
5800	62.177	387.935	330.923	-3502.316	-3502.316
5900	62.183	388.998	331.898	-3620.681	-3620.681
6000	62.189	390.043	343.109	-3741.146	-3741.146

PREVIOUS: September 1963 (1 atm)

CURRENT: September 1963 (1 bar)

Beryllium Oxide (Be₂O)Be₂O₁(g)

Be₂O₂(g)

Beryllium Oxide ((BeO)₂)

IDEAL GAS

Beryllium Oxide ((BeO)₂)

T/K	C _p ^o	S ^o - [C _p ^o - H ^o (T)]/T	H ^o - H ^o (T)	Δ _f H ^o	log K _f
0	0	INFINITE	INFINITE	-408.893	INFINITE
100	33.845	204.646	-8.075	-408.542	-411.575
200	40.459	229.794	-4.409	-408.242	-414.535
250	45.019	239.309	-2.273	-409.448	-415.877
298.15	49.339	247.611	0	-410.032	-417.064
300	49.499	247.917	0.091	-410.056	-417.107
350	53.618	255.862	2.671	-410.709	-418.231
400	57.274	263.266	5.445	-411.357	-419.261
450	60.456	270.200	8.391	-411.982	-420.211
500	63.197	276.715	11.484	-412.583	-421.093
600	67.555	288.643	18.033	-413.728	-422.687
700	70.753	299.310	24.956	-414.842	-424.092
800	73.124	308.970	32.156	-415.973	-425.337
900	74.910	317.641	39.561	-417.157	-426.437
1000	76.277	325.607	47.124	-418.423	-427.401
1100	77.342	332.929	54.807	-419.791	-428.233
1200	78.185	339.696	62.385	-421.278	-428.936
1300	78.861	345.982	70.438	-422.898	-429.510
1400	79.410	351.847	78.353	-424.662	-429.953
1500	79.863	357.342	86.317	-426.580	-430.265
1600	80.239	362.508	94.323	-428.652	-430.448
1700	80.555	367.384	102.363	-430.880	-430.500
1800	80.823	371.994	110.432	-433.466	-430.433
1900	81.051	376.371	118.526	-436.319	-430.168
2000	81.248	380.533	126.641	-439.467	-429.723
2100	81.419	384.501	134.775	-442.957	-429.110
2200	81.568	388.293	142.924	-446.837	-428.251
2300	81.698	391.921	151.088	-451.098	-427.178
2400	81.813	395.404	159.263	-455.843	-425.949
2500	81.915	398.743	167.450	-461.100	-424.511
2600	82.006	401.957	175.646	-466.900	-422.910
2700	82.087	405.054	183.951	-473.270	-421.100
2800	82.160	408.044	192.366	-480.250	-419.130
2900	82.226	410.925	200.883	-487.880	-417.000
3000	82.285	413.713	209.508	-496.200	-414.750
3100	82.339	416.412	218.240	-505.250	-412.400
3200	82.388	419.027	227.076	-515.050	-410.000
3300	82.432	421.562	236.017	-525.620	-407.600
3400	82.473	424.025	245.062	-536.980	-405.200
3500	82.510	426.416	254.311	-549.150	-402.800
3600	82.545	428.741	263.764	-562.150	-400.400
3700	82.576	431.003	273.421	-576.000	-398.000
3800	82.605	433.205	283.282	-590.720	-395.600
3900	82.632	435.351	293.349	-606.340	-393.200
4000	82.657	437.444	303.622	-622.880	-390.800
4100	82.681	439.485	314.101	-640.360	-388.400
4200	82.702	441.478	324.786	-658.800	-386.000
4300	82.722	443.424	335.577	-678.220	-383.600
4400	82.741	445.326	346.474	-698.640	-381.200
4500	82.759	447.186	357.477	-720.080	-378.800
4600	82.775	449.005	368.586	-742.560	-376.400
4700	82.791	450.785	379.808	-766.100	-374.000
4800	82.805	452.528	391.143	-790.720	-371.600
4900	82.819	454.236	402.591	-816.440	-369.200
5000	82.832	455.909	414.152	-843.280	-366.800
5100	82.844	457.550	425.827	-871.250	-364.400
5200	82.855	459.158	437.611	-900.380	-362.000
5300	82.866	460.737	449.501	-930.680	-359.600
5400	82.876	462.286	461.596	-962.160	-357.200
5500	82.886	463.807	473.897	-1004.840	-354.800
5600	82.895	465.300	486.404	-1058.740	-352.400
5700	82.903	466.767	499.119	-1124.880	-350.000
5800	82.912	468.209	512.042	-1204.280	-347.600
5900	82.919	469.627	525.173	-1307.940	-345.200
6000	82.927	471.020	539.513	-1436.880	-342.800

Δ_fH^o(0 K) = -409 ± 50 kJ·mol⁻¹
 Δ_fH^o(298.15 K) = -410 ± 50 kJ·mol⁻¹

S^o(298.15 K) = [247.61] J·K⁻¹·mol⁻¹

Vibrational Frequencies and Degeneracies

ν, cm ⁻¹	ν, cm ⁻¹
[1120] (1)	[460] (1)
[630] (1)	[920] (1)
[760] (1)	[1480] (1)

Ground State Quantum Weight: [1]
 Point Group: [V_h]
 Bond Distance: Be-O = [1.63] Å
 Bond Angles: Be-O-Be = [90]^o; O-Be-O = [90]^o
 Product of the Moments of Inertia: I_AI_BI_C = [3.0972 × 10⁻¹¹⁵] g³·cm⁶
 σ = 4

Enthalpy of Formation
 Chupka, Berkowitz, and Giese¹ studied the temperature dependence of the (BeO)₂ ion in a mass spectrometer and obtained a 2nd law enthalpy of vaporization of 172 ± 8 kcal·mol⁻¹ at 2150 K. No correction was made for fragmentation of higher polymers and this is reflected in the uncertainty. We adopted an enthalpy of sublimation of 178 kcal·mol⁻¹ in order to match more closely the equilibrium constant found by Chupka, *et al.*¹ However, it was not possible to alter either the enthalpy or entropy sufficiently to obtain exact agreement, the predicted pressure being too high by a factor of 20.

Heat Capacity and Entropy.
 A planar configuration was assumed which has six vibrational frequencies of the type 2A_{1g}, B_{1g}, B_{2g}, and B_{3g}. These were estimated by comparison with (LiO)₂ for which values have been calculated by White, Seshadri, Dever, Mann, and Linevsky.² It seems unlikely that any other structure than that of a ring is possible, as, in order to approach the observed equilibrium constant an even lower entropy is needed. A non-linear chain would have a higher entropy due to the change in symmetry number and the two odd electrons. A linear chain would have approximately the same entropy due to cancellation of opposite effects. The vibrational frequencies were also made as high as possible by normalizing them using B_{3g} equal to the BeO stretch in BeO(g). The bond length was taken as the sum of the covalent radii of O and Be, which is in general agreement with other polymeric structures which generally increase in bond length by 10-20% in going from monomer to polymer. The bond angle was chosen arbitrarily, however, changes in the angle would change the entropy less than 1 cal·K⁻¹·mol⁻¹. The principal moments of inertia are: I_A = 7.0589 × 10⁻³⁹, I_B = 3.9761 × 10⁻³⁹, and I_C = 11.0350 × 10⁻³⁹ g·cm².

References
¹W. A. Chupka, J. Berkowitz and C. F. Giese, *J. Chem. Phys.* **30**, 827 (1959).
²D. White, K. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, prepublication communication, (July 1963).

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

Beryllium Oxide ((BeO)₂)

Be₂O₂(g)

$$\Delta H_f^\circ(298.15 \text{ K}) = 64.190 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$T_{\text{fus}} = 1833 \text{ K}$$

$$\Delta H_f^\circ(0 \text{ K}) = [-2105 \pm 29] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^\circ(298.15 \text{ K}) = [-2117 \pm 29] \text{ kJ}\cdot\text{mol}^{-1}$$

Enthalpy of Formation

The $\Delta H_f^\circ(298.15 \text{ K})$ was estimated from the $\Delta H_f^\circ(298.15 \text{ K})$ of Mg, Ca and Ba oxides with SiO₂ given by Kelley¹ and from the $\Delta H_f^\circ(298.15 \text{ K})$ of BeO(cr) and SiO₂(cr) in the JANAF tables.² The $\Delta H_f^\circ(298.15 \text{ K}) = 0 \pm 7 \text{ kcal}\cdot\text{mol}^{-1}$ was estimated for the reaction 2BeO(cr) + SiO₂(cr) → Be₂SiO₄(cr).

Heat Capacity and Entropy

At low temperatures C_p was used from Kelley.⁴ Above 298.15 K, C_p values were estimated by summation of the component oxides using the JANAF tables,³ BeO and SiO₂. The entropy was calculated at 54.7 K using the Debye and Planck-Einstein functions D(422/T) + 2E(527/T) given by Kelley.⁴ The value of $S^\circ(54.7 \text{ K}) = 13.59 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Fusion Data

The incongruent melting point was taken from Kubaschewski and Evans.⁴

References

- ¹K. K. Kelley, U.S. Bur. Mines, RI-5901, 32 pp. (1962).
- ²JANAF Thermochemical Table, BeO(cr), 9-30-63, SiO₂(cr), 12-30-62.
- ³K. K. Kelley, J. Am. Chem. Soc., **61**, 1217 (1939).
- ⁴O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", 3rd, edition, Pergamon Press., New York, 426 pp. (1958).

T/K	C _p ^a	S ^b - [G ^c - H ^d (T)]/T	H ^d - H ^e (T)/T	Standard State Pressure = p ^o = 0.1 MPa	log K _r
	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	kJ·mol ⁻¹	
0	0	INFINITE	-12.227	-2105.003	INFINITE
100	18.794	7.470	-11.679	-2076.211	1084.501
200	60.433	33.245	-7.847	-2040.059	532.809
298.15	95.563	64.190	0	-2002.794	350.881
300	96.098	64.782	0.177	-2002.084	348.594
400	120.750	96.007	11.090	-1963.528	256.411
500	156.942	124.764	24.008	-1924.906	201.094
600	191.160	150.850	38.334	-1886.425	164.228
700	218.866	174.605	53.757	-1848.175	137.913
800	240.021	196.312	70.021	-1810.198	118.194
900	256.749	216.154	86.872	-1772.496	102.873
1000	274.054	234.324	104.120	-1735.053	90.630
1100	276.356	251.025	121.644	-1697.844	80.624
1200	278.197	266.451	139.375	-1660.841	72.985
1300	279.636	280.773	157.268	-1624.019	66.252
1400	280.916	294.134	175.298	-1587.353	59.725
1500	281.887	306.649	193.439	-1550.822	54.004
1600	282.849	318.418	211.676	-1515.353	49.406
1700	283.803	329.532	230.008	-1479.725	45.313
1800	284.749	340.065	248.436	-1443.704	41.605
1900	285.686	350.079	266.938	-1392.819	38.291
2000	286.606	359.627	285.572	-1352.061	35.312
2100	287.493	368.753	304.277	-1311.427	32.620
2200	288.380	377.496	323.071	-1270.907	30.175
2300	289.267	385.889	341.954	-1230.501	27.946
2400	290.154	393.963	360.925	-1190.202	25.904
2500	291.041	401.743	379.984	-1150.003	24.028
2600	291.928	409.253	399.133	-1109.903	22.298
2700	292.815	416.513	418.370	-1069.896	20.698
2800	293.702	423.542	437.696	-1029.882	19.222
2900	294.589	430.354	457.111	-989.856	17.872
3000	295.476	436.966	476.614	-949.822	15.593

PREVIOUS: September 1961

CURRENT: June 1965

Be₃N₂(cr)

Beryllium Nitride, Alpha (Be₃N₂)

CRYSTAL(α)

Beryllium Nitride, Alpha (α-Be₃N₂)

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
	C _p ^a	S° - [G° - H°(T _r)]/T	H° - H°(T _r)	ΔG°
0	0	INFINITE	-7.075	INFINITE
100	6.109	1.845	-580.879	INFINITE
200	35.489	14.313	-567.936	296.503
298.15	64.338	34.129	-586.429	143.852
300	64.668	34.130	-588.270	93.357
400	84.433	36.036	-588.296	532.530
500	97.512	36.974	-589.216	513.778
600	106.516	37.981	-589.325	494.891
700	111.922	38.981	-588.882	476.039
800	117.591	39.974	-588.110	457.290
900	121.043	40.952	-587.182	438.664
1000	123.612	41.917	-586.186	420.139
1100	125.520	42.859	-585.237	401.763
1200	126.922	43.779	-584.387	383.458
1300	127.926	44.680	-583.685	365.224
1400	128.616	45.564	-583.169	347.041
1500	129.047	46.433	-582.871	328.890
1600	129.269	47.288	-582.816	310.752
1700	129.319	48.130	-582.924	291.033
1800	129.366	48.959	-583.298	270.080
1900	129.411	49.777	-583.979	249.166
2000	129.452	50.583	-584.924	228.285
2100	129.490	51.377	-586.136	207.431
2200	129.526	52.159	-587.624	186.598
2300	129.559	52.931	-589.400	165.782
2400	129.588	53.694	-591.474	144.978
2473.000	129.606	54.447	-593.851	124.184
2500	129.615	55.192	-596.542	103.395
2600	129.639	56.922	-603.662	82.608
2700	129.659	58.615	-611.319	61.820
2800	129.677	60.270	-619.526	41.032
2900	129.692	61.891	-628.303	20.244
3000	129.704	63.478	-637.679	0.456

$\Delta_r H^\circ(0\text{ K}) = -580.9 \pm 1.3\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_r H^\circ(298.15\text{ K}) = -588.3 \pm 1.3\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{cr}} H^\circ = [129.3]\text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation
 Gross, Hayman, Greene and Bingham¹ have measured the enthalpy of chlorination of α-Be₃N₂ to α-BeCl₂ and the enthalpy of reaction of Be with ammonia. The chlorination reaction (A) α-Be₃N₂(cr) + 3Cl₂(g) → 3 α-BeCl₂(cr) + N₂(g) had a $\Delta_r H^\circ(298.15\text{ K}) = -210.3 \pm 0.4\text{ kcal mol}^{-1}$, which, combined with the value of $-117.1 \pm 0.4\text{ kcal}\cdot\text{mol}^{-1}$ for α-BeCl₂ reported in the same paper, yields $\Delta_r H^\circ(\alpha\text{-Be}_3\text{N}_2, \text{cr}, 298.15\text{ K}) = -141.0 \pm 1.6\text{ kcal mol}^{-1}$. Reaction (B) 3Be(cr) + 2 NH₃(g) → α-Be₃N₂(cr) + 3 H₂(g) had a $\Delta_r H^\circ(298.15\text{ K}) = -214.6 \pm 0.3\text{ kcal}\cdot\text{mol}^{-1}$, which, combined with the JANAF² value for NH₃(g), yields $\Delta_r H^\circ(\alpha\text{-Be}_3\text{N}_2, \text{cr}, 298.15\text{ K}) = -140.3 \pm 0.3\text{ kcal}\cdot\text{mol}^{-1}$. A weighted mean value of the above two determinations is adopted.

The decomposition Be₃N₂(cr) = 3 Be(g) + N₂(g) has been studied by Yates, Greenbaum and Farber³ using the torsion effusion technique. The same decomposition has also been investigated by Hoening⁴ using the Knudsen technique. An analysis of these data sets by 2nd and 3rd law methods is given below.

Source	T/K	Points	Δ _r H°(298.15 K) 2nd law	Δ _r H°(298.15 K) 3rd law	Drift cal·K ⁻¹ ·mol ⁻¹	Δ _r H°(298.15 K) kcal mol ⁻¹
1-1	1478-1592	9*	364.5 ± 5.9	374.00	6.0 ± 3.8	-139.23
1-2	1541-1652	15*	369.6 ± 8.3	376.51	4.0 ± 5.3	-141.74
1-3	1438-1661	14	347.7 ± 3.7	374.54	16.9 ± 2.4	-139.77
1-4	1450-1646	17*	366.7 ± 8.9	375.28	4.8 ± 5.7	-140.51
1-5	1473-1661	52*	358.9 ± 5.1	375.41	10.3 ± 3.3	-140.64
4-1	1767-1946	14	355.8 ± 3.3	377.77	11.9 ± 1.8	-143.00
4-2	1660-1891	10	395.0 ± 5.6	378.69	-9.1 ± 3.1	-143.92
4-3	1648-1893	10	416.9 ± 8.4	383.15	-19.5 ± 4.6	-148.38

*Points rejected due to failure of statistical test.
 The data of Yates *et al.*³ are seen to be in good agreement with the adopted $\Delta_r H^\circ(298.15\text{ K})$.

Heat Capacity and Entropy

The low temperature heat capacity of α-Be₃N₂ has been measured, 25-310 K, by Justice.⁵ These measurements are joined smoothly with the high temperature enthalpies reported by Douglas and Payne.⁶ Above 1200 K the values were smoothly extrapolated to a limiting value of $6.2\text{ cal}\cdot\text{K}^{-1}\text{ g}\cdot\text{atom}^{-1}$. The entropy at 298.15 K was calculated by integration of the low temperature data based on $S^\circ(25\text{ K}) = 0.002\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Fusion Data

Refer to the liquid table for details.

References

- ¹P. Gross, C. Hayman, P. D. Greene and J. T. Bingham, *Trans. Faraday Soc.* **62**, 2719 (1966).
- ²JANAF Thermochemical Tables, NH₃(g), 9-30-65.
- ³R. E. Yates, M. A. Greenbaum and M. Farber, *J. Phys. Chem.* **68**, 2682 (1964).
- ⁴C. L. Hoening, UCR-L-7521, (April 1964).
- ⁵B. H. Justice, The Dow Chemical Co., 1st. Quarterly Report under contract AFO4611-67-C-0009, (April 1967).
- ⁶T. B. Douglas and W. H. Payne, U. S. Nat. Bur. Stand. Report 7587, (July 1962).

PREVIOUS: September 1964

CURRENT: March 1967

Beryllium Nitride, Alpha (Be₃N₂)

Be₃N₂(cr)

Beryllium Nitride (Be₃N₂)

$$S^{\circ}(298.15 \text{ K}) = [39.457] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{fus}} = 2473 \text{ K}$$

$$\Delta H^{\circ}(298.15 \text{ K}) = [-486.979] \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{form}} H^{\circ} = [129.3] \text{ kJ} \cdot \text{mol}^{-1}$$

 $M_r = 55.04994$ Beryllium Nitride (Be₃N₂)Be₃N₂(l)log K_r

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa		log K _r
		S ^o - [G ^o - H ^o (T)]/T	H ^o - H ^o (T)/T	ΔH ^o	ΔG ^o	
0						
100						
200						
298.15	133.888	39.457	39.457	0	-486.979	75.890
300	133.888	40.285	39.459	0.248	-486.877	75.364
400	133.888	78.802	44.711	13.636	-481.931	54.272
500	133.888	108.678	54.628	27.025	-477.790	41.736
600	133.888	133.089	65.732	40.414	-474.185	33.447
700	133.888	153.728	76.857	53.803	-471.014	27.569
800	133.888	171.606	87.617	67.192	-468.225	23.189
900	133.888	187.376	97.842	80.580	-465.790	19.800
1000	133.888	201.482	107.513	93.969	-463.691	17.103
1100	133.888	214.243	116.645	107.358	-461.913	14.905
1200	133.888	225.893	125.271	120.747	-460.447	13.080
1300	133.888	236.610	133.429	134.136	-459.287	11.541
1400	133.888	246.532	141.157	147.529	-458.429	10.224
1500	133.888	255.769	148.494	160.913	-457.870	9.084
1600	133.888	264.410	155.471	174.302	-457.616	8.036
1700	133.888	272.527	162.121	187.691	-457.621	7.075
1800	133.888	280.180	168.469	201.080	-457.967	6.222
1900	133.888	287.419	174.541	214.468	-458.643	5.461
2000	133.888	294.287	180.358	227.857	-459.660	4.777
2100	133.888	300.819	185.940	241.246	-461.028	4.160
2200	133.888	307.047	191.304	254.635	-462.746	3.599
2300	133.888	312.999	196.467	268.024	-464.802	3.088
2400	133.888	318.697	201.442	281.412	-467.204	2.620
2473.000	133.888	322.709	204.963	291.186	CRYSTAL → LIQUID	---
2500	133.888	324.163	206.242	294.801	-493.682	2.190
2600	133.888	329.414	210.879	308.190	-493.235	1.793
2700	133.888	334.467	215.364	321.579	-492.861	1.426
2800	133.888	339.336	219.705	334.968	-492.543	0.738
2900	133.888	344.034	223.911	348.356	-492.277	0.140
3000	133.888	348.573	227.992	361.745	-492.061	-0.936
3100	133.888	352.964	231.953	375.134	-491.885	-1.718
3200	133.888	357.214	235.801	388.523	-491.750	-2.431
3300	133.888	361.334	239.543	401.912	-491.657	-3.099
3400	133.888	365.331	243.184	415.300	-491.602	-3.726
3500	133.888	369.212	246.730	428.689	-491.581	-4.316
3600	133.888	372.984	250.185	442.078	-491.593	-4.872
3700	133.888	376.652	253.553	455.467	-491.637	-5.396
3800	133.888	380.223	256.840	468.856	-491.713	-5.892
3900	133.888	383.701	260.048	482.244	-491.821	-6.361
4000	133.888	387.091	263.182	495.633	-491.956	-6.806

PREVIOUS: September 1964

CURRENT: March 1967

Beryllium Nitride (Be₃N₂)Be₃N₂(l)

Enthalpy of Formation

The enthalpy of formation of Be₃N₂(l) is calculated from that of the crystal by adding Δ_{form}H^o and the difference in enthalpy, H^o(2473 K) - H^o(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated to be constant and slightly greater than the maximum for Be₃N₂(cr). The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point was reported by Fichter and Brunner.¹ The enthalpy of melting is calculated on the assumption that each g-atom contributed 2.5 cal·K⁻¹·mol⁻¹ to Δ_{form}S^o.

References

¹F. Fichter and E. Brunner, Z. anorg. allgem. Chem. 93, 84 (1915).

Be₃N₂(cr,l)

M_r = 55.04994 Beryllium Nitride (Be₃N₂)

CRYSTAL(α)-LIQUID

Beryllium Nitride (Be₃N₂)

0 to 2473 K crystal, alpha
above 2473 K liquid
Refer to the individual tables for details.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ^o	S° - [G° - HF(T _r)]/T	H° - H°(T _r)	Δ _f H°	
0	0	0	INFINITE	-580.879	INFINITE
100	6.109	1.845	71.174	-583.756	296.593
200	35.489	14.313	39.125	-586.429	143.852
298.15	64.358	34.129	34.129	-588.270	93.357
300	64.668	34.578	34.130	-588.296	92.772
400	84.433	56.036	36.978	-589.216	61.292
500	97.512	76.374	42.811	-589.325	51.701
600	106.516	94.995	49.981	-588.882	41.443
700	112.922	111.922	57.640	-588.110	34.123
800	117.591	127.321	65.402	-587.172	28.642
900	121.043	141.381	73.075	-586.186	24.385
1000	123.612	154.273	80.559	-585.237	20.986
1100	125.520	166.148	87.807	-584.387	18.209
1200	126.922	177.132	94.799	-583.685	15.898
1300	127.926	187.333	101.530	-583.169	13.944
1400	128.616	196.840	108.002	-582.871	12.271
1500	129.047	205.730	114.224	-582.816	10.821
1600	129.269	214.066	120.206	-582.934	9.501
1700	129.319	221.903	125.960	-583.274	8.299
1800	129.366	229.298	131.498	-583.792	7.231
1900	129.411	236.293	136.831	-584.453	6.276
2000	129.452	242.932	141.971	-585.228	5.418
2100	129.490	249.249	146.931	-586.106	4.641
2200	129.523	255.274	151.720	-587.082	3.936
2300	129.558	261.032	156.348	-588.153	3.293
2400	129.587	266.547	160.826	-589.317	2.703
2473.000	129.606	270.430	164.004	-590.572	2.190
2473.000	133.888	322.709	164.004	CRYSTAL <- -> LIQUID TRANSITION	
2500	133.888	324.163	165.726	-493.682	-104.807
2600	133.888	329.414	171.921	-493.235	-89.261
2700	133.888	334.467	177.848	-492.861	-73.731
2800	133.888	339.336	183.529	-492.559	-59.452
2900	133.888	344.034	188.984	-492.323	-47.140
3000	133.888	348.573	194.228	-492.147	-36.556
3100	133.888	352.964	199.278	-492.025	-27.178
3200	133.888	357.214	204.148	-491.955	-18.851
3300	133.888	361.334	208.849	-491.935	-11.531
3400	133.888	365.331	213.393	-491.965	-5.276
3500	133.888	369.212	217.789	-492.045	2.816
3600	133.888	372.984	222.048	-492.175	10.872
3700	133.888	376.653	226.177	-492.355	19.396
3800	133.888	380.223	230.184	-492.585	28.426
3900	133.888	383.701	234.076	-492.865	38.061
4000	133.888	387.091	237.860	-493.195	48.306

PREVIOUS:

CURRENT: March 1967

Beryllium Nitride (Be₃N₂)

Be₃N₂(cr,l)

Beryllium Oxide ((BeO)₂)

S°(298.15 K) = [273.3] J·K⁻¹·mol⁻¹

Δ_rH°(0 K) = -1049 ± 38 kJ·mol⁻¹
 Δ_rH°(298.15 K) = -1054 ± 38 kJ·mol⁻¹

M_r = 75.03474

Beryllium Oxide ((BeO)₂)

Be₂O₃(g)

IDEAL GAS

Vibrational Frequencies and Degeneracies

v, cm ⁻¹	v, cm ⁻¹
[730] (1)	[1380] (2)
[990] (1)	[1450] (2)
[1480] (1)	[610] (2)
[1100] (1)	[320] (2)

Ground State Quantum Weight: [1]

Point Group: [D_{3h}]

Bond Distance: Be-O = [1.63] Å

Bond Angles: Be-O-Be = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [9.0703 × 10⁻¹¹⁴] g³·cm⁶

σ = [6]

Enthalpy of Formation

Chupka, Berkowitz, and Giese¹ measured the change in the intensity of the (BeO)₂ ion with temperature and obtained a 2nd law enthalpy of vaporization of 161 ± 6 kcal·mol⁻¹ at 2150 K. The uncertainty is large because of an approximate correction of 8 kcal·mol⁻¹ and the neglect of fragmentation effects. We adopted an enthalpy of sublimation at 2150 K of 163 kcal·mol⁻¹ in order to bring the equilibrium vapor pressure into agreement with that measured by Chupka *et al.*¹

Heat Capacity and Entropy

The assumed D_{3h} symmetry implies eight vibrational frequencies of the types 2A₁, A₂, A₂, 3E₁ and E₂. The frequencies were estimated by comparison with the values for the B₂O₃(O₂)₂ skeleton as given by Parsons² and the partial assignment of boroxine by Gupta and Porter.³ The bond length was taken as that in Be₂O₃(g), while the bond angle was arbitrarily taken as 120°. The principal moments of inertia are: I_A = I_B = 16.5525 × 10⁻³⁹, and I_C = 33.1050 × 10⁻³⁹ g·cm².

References

- W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.* **30**, 827 (1959).
- J. L. Parsons, *J. Chem. Phys.* **33**, 1860 (1960).
- S. K. Gupta and R. F. Porter, *J. Phys. Chem.* **67**, 1286 (1963).

T/K	C _p ^o	S ^o - (G ^o - H ^o (T))/T	H ^o - H ^o (T)	Δ _r H ^o	Δ _r G ^o	log K _r
0	0	INFINITE	0	INFINITE	-1048.871	INFINITE
100	37.082	221.244	-13.325	-1048.871	-1048.871	INFINITE
200	50.124	250.834	-9.919	-1049.940	-1049.940	546.331
250	56.935	262.750	-5.575	-1051.695	-1041.313	271.963
298.15	63.458	273.337	-2.899	-1052.982	-1038.572	216.998
300	63.706	273.731	0	-1054.368	-1035.673	181.446
350	70.315	284.051	0.118	-1054.423	-1035.306	180.306
400	76.597	293.854	3.469	-1055.921	-1032.294	154.061
450	82.418	303.217	7.144	-1057.380	-1028.818	134.350
500	87.701	312.179	11.121	-1058.758	-1025.165	118.998
600	96.611	328.989	24.610	-1060.043	-1021.362	106.701
700	103.530	344.425	44.082	-1062.350	-1013.404	88.225
800	108.857	358.612	64.632	-1064.384	-1004.004	75.000
900	112.975	371.682	85.263	-1066.249	-996.482	65.064
1000	116.187	383.758	105.930	-1067.828	-987.653	57.322
1100	118.723	394.955	124.434	-1069.112	-978.627	51.118
1200	120.750	405.376	140.892	-1071.639	-969.420	46.034
1300	122.389	415.108	155.602	-1073.359	-960.044	41.790
1400	123.730	424.229	168.024	-1073.669	-950.502	38.192
1500	124.840	432.804	178.454	-1077.818	-940.797	35.102
1600	125.766	440.892	184.985	-1080.212	-930.927	32.418
1700	126.547	448.540	188.186	-1082.417	-919.315	30.013
1800	127.210	455.793	191.041	-1084.417	-905.231	27.848
1900	127.778	462.686	193.589	-1086.212	-888.051	24.194
2000	128.268	469.253	195.844	-1087.828	-866.780	22.638
2100	128.694	475.522	197.800	-1089.288	-843.421	21.228
2200	129.065	481.517	199.467	-1090.531	-819.974	19.944
2300	129.391	487.262	200.883	-1091.585	-806.445	18.769
2400	129.679	492.775	202.058	-1092.480	-792.837	17.691
2500	129.932	498.074	202.939	-1093.250	-779.132	16.697
2600	130.162	503.175	203.547	-1093.932	-765.331	15.778
2700	130.366	508.091	203.970	-1094.560	-751.466	14.925
2800	130.549	512.835	204.316	-1095.150	-737.572	14.134
2900	130.713	517.419	204.587	-1095.718	-723.676	13.400
3000	130.862	521.853	204.784	-1096.268	-709.774	12.720
3100	130.997	526.147	204.912	-1096.800	-695.868	12.100
3200	131.120	530.307	204.975	-1097.318	-681.958	11.535
3300	131.232	534.344	204.975	-1097.825	-668.045	11.020
3400	131.335	538.263	204.912	-1098.320	-654.130	10.550
3500	131.429	542.072	204.784	-1098.800	-640.215	10.120
3600	131.516	545.775	204.644	-1099.268	-626.300	9.730
3700	131.595	549.380	204.493	-1099.725	-612.385	9.380
3800	131.669	552.890	204.331	-1100.175	-598.470	9.070
3900	131.737	556.311	204.160	-1100.620	-584.555	8.800
4000	131.800	559.647	203.984	-1101.060	-570.640	8.570
4100	131.859	562.903	203.808	-1101.495	-556.725	8.380
4200	131.914	566.081	203.623	-1101.925	-542.810	8.230
4300	131.964	569.185	203.429	-1102.350	-528.895	8.120
4400	132.012	572.220	203.226	-1102.770	-514.980	8.030
4500	132.056	575.187	203.015	-1103.185	-501.065	7.970
4600	132.098	578.090	202.797	-1103.595	-487.150	7.930
4700	132.137	580.931	202.572	-1104.000	-473.235	7.910
4800	132.173	583.714	202.341	-1104.400	-459.320	7.910
4900	132.208	586.439	202.105	-1104.795	-445.405	7.930
5000	132.240	589.111	201.864	-1105.185	-431.490	7.970
5100	132.271	591.730	201.618	-1105.570	-417.575	8.030
5200	132.299	594.298	201.367	-1105.950	-403.660	8.110
5300	132.326	596.819	201.111	-1106.325	-389.745	8.210
5400	132.352	599.292	200.850	-1106.695	-375.830	8.330
5500	132.376	601.721	200.584	-1107.060	-361.915	8.470
5600	132.399	604.106	200.313	-1107.420	-348.000	8.630
5700	132.421	606.445	200.037	-1107.775	-334.085	8.810
5800	132.442	608.735	199.756	-1108.125	-320.170	9.010
5900	132.462	611.017	199.470	-1108.470	-306.255	9.230
6000	132.480	613.244	199.179	-1108.810	-292.340	9.470

PREVIOUS: September 1963 (1 atm)

CURRENT: September 1963 (1 bar)

Beryllium Oxide ((BeO)₂)

Be₂O₃(g)

IDEAL GAS

Beryllium Oxide ((BeO)_g)

S°(298.15 K) = [302.6] J·K⁻¹·mol⁻¹

ΔH^o(0 K) = -1581 ± 50 kJ·mol⁻¹
 ΔH^o(298.15 K) = -1590 ± 50 kJ·mol⁻¹

Beryllium Oxide ((BeO)_g)

Be₃O₄(g)

Vibrational Frequencies and Degeneracies	
v, cm ⁻¹	v, cm ⁻¹
[700] (1)	[200] (2)
[850] (1)	[900] (1)
[1400] (1)	[400] (1)
[1000] (1)	[500] (1)
[800] (1)	[1150] (2)
[1000] (1)	[1200] (2)
[800] (1)	[600] (2)

Ground State Quantum Weight: [1]

Point Group: [D_{∞h}]

Bond Distance Be-O = [1.63] Å

Bond Angles, Be-O-Be = [115]°

Product of the Moments of Inertia: I_AI_BI_C = [1.1171 × 10⁻⁴⁷] g³·cm⁶

σ = [8]

Enthalpy of Formation

Chupka, Berkowitz, and Giese¹ measured the variation of intensity of the (BeO)_g ion with temperature in a mass spectrometer. They reported a 2nd law enthalpy of vaporization of 177 ± 8 kcal·mol⁻¹ at 2150 K, which included an approximate correction of 9 kcal·mol⁻¹, and this value was adopted here.

Heat Capacity and Entropy

The assumed D_{∞h} structure has 14 vibrational frequencies of the type 2A_{1g}, A_{2g}, 2B_{2g}, E_g, A_{3g}, B_{2u}, B_{1u}, and 3E_u. The frequencies were estimated by comparison with (BeO)_g and cyclobutane from Rathjens, Freeman, Gwinn, and Pitzer.² The estimated structure and frequencies gave an entropy which was in excellent agreement with the experimental enthalpy and equilibrium constant determined by Chupka *et al.*¹ The bond lengths were taken equal to those in Be₂O₂(g) and the angles were chosen so that O-Be-O was almost linear. The principal moments of inertia are I_A = I_B = 38.2258 × 10⁻⁴⁰, and I_C = 76.4515 × 10⁻⁴⁰ g·cm².

References

- ¹W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.* **30**, 827 (1959).
- ²G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.* **75**, 5634 (1953).

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P° = 0.1 MPa		log K _r
	C _p ^o	S° - [(G° - H°(T _r))/T _r]	H° - H°(T _r)	ΔH°	
0	.000	INFINITE	-16.529	-1581.354	INFINITE
100	43.449	364.943	-12.895	-1583.686	821.349
200	64.574	272.167	-7.556	-1586.479	407.477
250	77.225	287.926	-4.013	-1588.220	324.566
298.15	89.389	302.575	.000	-1589.920	270.948
300	89.844	303.129	1.66	-1546.276	269.231
350	101.591	317.876	4.956	-1591.657	229.662
400	112.062	332.140	10.303	-1593.157	199.955
450	121.155	345.877	16.140	-1594.463	176.830
500	128.942	359.056	22.397	-1595.592	158.315
600	141.187	383.708	33.937	-1597.439	130.518
700	150.034	406.173	50.522	-1598.930	102.642
800	156.507	426.652	65.865	-1600.247	95.722
900	161.327	445.377	81.768	-1601.525	84.108
1000	164.987	462.573	98.092	-1602.838	74.809
1100	167.817	478.436	114.738	-1604.314	67.194
1200	170.043	493.137	131.635	-1605.947	60.843
1300	171.821	506.821	148.732	-1607.797	55.463
1400	173.262	519.608	165.988	-1609.897	50.845
1500	174.443	531.604	183.375	-1612.275	46.838
1600	175.423	542.894	200.870	-1615.096	43.258
1700	176.245	553.555	218.455	-1617.488	40.043
1800	176.949	563.632	236.115	-1619.538	37.184
1900	177.533	573.232	253.839	-1621.457	34.623
2000	178.034	582.351	271.619	-1623.236	32.316
2100	178.464	591.049	289.446	-1624.984	30.227
2200	178.869	599.361	307.318	-1626.704	28.325
2300	179.205	607.320	325.218	-1628.404	26.588
2400	179.502	614.932	343.144	-1630.084	25.003
2500	179.765	622.286	361.117	-1631.742	23.524
2600	179.998	629.341	379.106	-1633.322	22.166
2700	180.207	636.138	397.116	-1634.849	20.907
2800	180.394	642.696	415.146	-1636.329	19.723
2900	180.563	649.029	433.194	-1637.799	18.614
3000	180.715	655.153	451.258	-1639.258	17.534
3100	180.853	661.081	469.337	-1640.708	16.476
3200	180.979	666.825	487.429	-1642.151	15.438
3300	181.093	672.395	505.532	-1643.589	14.413
3400	181.198	677.803	523.647	-1645.023	13.401
3500	181.294	683.057	541.772	-1646.453	12.401
3600	181.382	688.166	559.905	-1647.879	11.413
3700	181.463	693.136	578.048	-1649.301	10.436
3800	181.538	697.977	596.198	-1650.720	9.471
3900	181.607	702.693	614.355	-1652.135	8.517
4000	181.671	707.292	632.519	-1653.547	7.573
4100	181.731	711.779	650.689	-1654.956	6.639
4200	181.787	716.158	668.865	-1656.362	5.715
4300	181.838	720.437	687.047	-1657.766	4.801
4400	181.886	724.618	705.233	-1659.167	3.897
4500	181.931	728.706	723.424	-1660.566	3.003
4600	181.974	732.705	741.619	-1661.962	2.119
4700	182.013	736.619	759.818	-1663.356	1.245
4800	182.050	740.451	778.021	-1664.748	0.381
4900	182.085	744.205	796.228	-1666.138	-0.483
5000	182.118	747.884	814.438	-1667.525	-1.347
5100	182.149	751.491	832.652	-1668.910	-2.211
5200	182.178	755.028	850.868	-1670.292	-3.085
5300	182.205	758.499	869.087	-1671.672	-3.969
5400	182.231	761.905	887.309	-1673.050	-4.863
5500	182.256	765.249	905.533	-1674.427	-5.767
5600	182.279	768.533	923.760	-1675.802	-6.681
5700	182.301	771.759	942.000	-1677.175	-7.605
5800	182.322	774.930	960.250	-1678.547	-8.549
5900	182.342	778.047	978.454	-1679.918	-9.513
6000	182.361	781.112	996.689	-1681.288	-10.486

PREVIOUS: September 1963 (1 atm)

CURRENT: September 1963 (1 bar)

Beryllium Oxide ((BeO)_g)

Be₃O₄(g)

S°(298.15 K) = [323.28] J·K⁻¹·mol⁻¹

Δ_rH°(0 K) = -2101 ± 75 kJ·mol⁻¹
 Δ_rH°(298.15 K) = -2113 ± 75 kJ·mol⁻¹

Vibrational Frequencies and Degeneracies	
ν, cm ⁻¹	ν, cm ⁻¹
[700] (1)	[1200] (2)
[850] (1)	[600] (2)
[1400] (1)	[500] (2)
[1100] (2)	[900] (1)
[900] (2)	[200] (2)
[1000] (2)	[400] (2)
[1200] (2)	[500] (2)

Ground State Quantum Weight: [1]

Point Group: [D_{2h}]

Bond Distance: Be-O = [1.63] Å

Bond Angles: Be-O-Be = [110]°

Product of the Moments of Inertia: I_AI_BI_C = [6.9690 × 10⁻⁴²] g³ cm⁶

σ = [10]

Enthalpy of Formation

Chupka, Berkowitz, and Giese¹ measured the variation in intensity of the (BeO)₂ ion with temperature in a mass spectrometer. They calculated a 2nd law enthalpy of vaporization of 193 ± 12 kcal·mol⁻¹ at 2150 K, the uncertainty reflects the inclusion of an approximate correction of 10 kcal·mol⁻¹. This value was adopted here.

Heat Capacity and Entropy

The assumed D_{2h} structure has 14 vibrations of the type 2A₁, A₁, 3E₁, 4E₁, A₂⁺, E₁⁺, and 2E₂⁺. These were estimated by comparison with similar motions in other ring structures including (BeO)₃ and (BeO)₄. The estimated structure and frequencies gave an entropy in good agreement with the experimental enthalpy and equilibrium constant determined by Chupka *et al.*¹

The bond length was assumed to be the same as in Be₃O₃(g) and the angles were chosen so as to make O-Be-O almost linear. The principal moments of inertia are: I_A = I_B = 70.3689 × 10⁻³⁹, and I_C = 140.7378 × 10⁻³⁹ g·cm².

References

¹W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.* **30**, 827 (1959).

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
	C _p ⁰	S° - [C _p ⁰ (T _r)]/T _r	H° - H°(T _r)	Δ _r H°	
0	0	0	INFINITE	-2100.640	INFINITE
100	45.283	244.859	399.133	-2104.435	1089.271
200	77.909	285.714	332.441	-2085.343	539.256
250	95.670	305.013	325.031	-2064.746	429.064
298.15	112.018	323.278	323.278	-2042.321	357.806
300	112.622	323.973	323.280	-2041.883	355.523
350	128.074	342.516	324.709	-2029.864	302.941
400	141.704	360.528	328.067	-2017.567	263.467
450	153.478	377.916	332.646	-2005.060	232.141
500	163.529	394.621	338.014	-1992.395	208.144
600	179.296	425.909	350.095	-1966.731	171.219
700	190.665	454.448	362.996	-1940.765	144.872
800	198.973	480.478	376.079	-1914.595	125.010
900	205.156	504.288	389.021	-1888.263	109.592
1000	209.847	526.157	401.656	-1861.791	97.250
1100	213.474	546.335	413.903	-1835.180	87.145
1200	216.326	565.037	425.728	-1808.328	78.719
1300	218.603	582.445	437.121	-1781.277	71.583
1400	220.447	598.715	448.089	-1754.465	65.460
1500	221.960	613.978	458.645	-1727.232	60.148
1600	223.215	628.344	468.807	-1699.186	55.407
1700	224.267	641.909	478.504	-1671.402	51.157
1800	225.157	654.754	487.027	-1644.245	47.376
1900	225.916	666.948	497.126	-1617.978	43.991
2000	226.568	678.553	505.909	-1592.654	40.943
2100	227.132	689.621	514.396	-1567.327	38.183
2200	227.624	700.199	522.603	-1542.051	35.671
2300	228.055	710.327	530.546	-1516.869	33.377
2400	228.435	720.041	538.241	-1491.728	31.271
2500	228.771	729.373	545.701	-1466.678	29.332
2600	229.070	738.352	552.939	-1441.744	27.544
2700	229.337	747.002	559.967	-1416.936	25.880
2800	229.577	755.347	566.797	-1392.271	24.326
2900	229.792	763.407	573.438	-1367.727	22.833
3000	229.987	771.201	579.901	-1343.359	21.399
3100	230.164	778.745	586.194	-1319.114	19.999
3200	230.324	786.055	592.376	-1295.044	18.624
3300	230.471	793.145	598.305	-1271.192	17.274
3400	230.605	800.027	604.137	-1247.598	15.949
3500	230.727	806.713	609.830	-1224.191	14.637
3600	230.840	813.215	615.390	-1200.989	13.338
3700	230.944	819.541	620.822	-1177.931	12.052
3800	231.040	825.701	626.133	-1155.056	10.780
3900	231.128	831.704	631.328	-1132.394	9.522
4000	231.210	837.556	636.410	-1110.000	8.278
4100	231.287	843.266	641.386	-1087.823	7.049
4200	231.357	848.841	646.260	-1065.894	5.834
4300	231.424	854.285	651.034	-1044.152	4.633
4400	231.485	859.606	655.714	-1022.627	3.446
4500	231.543	864.809	660.303	-1001.346	2.272
4600	231.597	869.899	664.805	-980.329	1.120
4700	231.647	874.880	669.222	-959.596	0.000
4800	231.695	879.758	673.557	-939.164	-1.096
4900	231.739	884.536	677.814	-919.052	-2.209
5000	231.781	889.218	681.996	-899.289	-3.338
5100	231.821	893.808	686.104	-879.894	-4.481
5200	231.858	898.310	690.142	-860.786	-5.638
5300	231.893	902.727	694.111	-841.982	-6.808
5400	231.926	907.062	698.015	-823.499	-8.000
5500	231.958	911.317	701.854	-805.352	-9.213
5600	231.988	915.497	705.632	-787.468	-10.447
5700	232.016	919.604	709.350	-769.862	-11.703
5800	232.043	923.639	713.010	-752.559	-12.980
5900	232.068	927.606	716.614	-735.580	-14.278
6000	232.093	931.506	720.163	-718.942	-15.596

PREVIOUS: September 1963 (1 atm)

CURRENT: September 1963 (1 bar)

Beryllium Oxide ((BeO)_g)

$S^{\circ}(298.15 \text{ K}) = [343.2] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

IDEAL GAS

Beryllium Oxide ((BeO)_g)

Be₉O₆(g)

$\Delta_f H^{\circ}(0 \text{ K}) = -2645 \pm 92 \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^{\circ}(298.15 \text{ K}) = -2661 \pm 92 \text{ kJ}\cdot\text{mol}^{-1}$

Vibrational frequencies and D ₀ degeneracies ν, cm ⁻¹	ν, cm ⁻¹	D ₀ , cm ⁻¹
[700] (1)	[600] (2)	[900] (1)
[850] (1)	[750] (2)	[1100] (1)
[400] (1)	[850] (2)	[1000] (1)
[500] (1)	[850] (2)	[800] (1)
[400] (1)	[950] (2)	[1400] (1)

Ground State Quantum Weight: [1]
 Point Group: [D_{3h}]
 Bond Distance: Be-O = [1.63] Å
 Bond Angles: Be-O-Be = [110]^o
 Product of the Moments of Inertia: $I_A I_B I_C = [3.1282 \times 10^{-111}] \text{ g}^3 \text{ cm}^6$

Enthalpy of Formation

Chupka, Berkowitz, and Giese¹ measured the temperature dependence of the (BeO)_g ion in a mass spectrometer. They calculated a 2nd law enthalpy of vaporization of $203 \pm 15 \text{ kcal}\cdot\text{mol}^{-1}$ which was adopted here. The uncertainty reflects in part an approximate correction of 10 kcal·mol⁻¹ and the small observed intensities.

Heat Capacity and Entropy

The assumed symmetry D_{3h} has 20 vibrational frequencies of the type 2A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_{1g}, 4E_{2g}, A_{2u}, 2B_{1u}, 2B_{2u}, 3E_{1u}, and 2E_{2u}. The frequencies were estimated by comparison with similar motions in other ring molecules including benzene, (BeO)₃, and (BeO)₄. The assumed structure and vibrational frequencies gave an entropy in good agreement with the experimental enthalpy and equilibrium constant determined by Chupka *et al.*¹ The bond length was taken equal to that in Be₂O₃(g). The angles were chosen so that the O-Be-O angle was almost linear but with the Be-O-Be angle less than 120°. The principal moments of inertia are: I_A = I_B = 116.0793 × 10⁻³⁹, and I_C = 232.1586 × 10⁻³⁹ g·cm².

References

¹W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.* **30**, 827 (1959).

T/K	C _p ^o	S ^o - (C _p ^o - RT ²)/T	H ^o - H ^o (T _r)	Standard State Pressure = p ^o = 0.1 MPa kJ·mol ⁻¹ Δ _f H ^o	log K _r
0	0	INFINITE	0	INFINITE	INFINITE
100	50.386	253.784	-21.479	-2644.860	-2644.860
200	88.576	299.761	-17.667	-2649.997	-2623.081
250	110.694	321.887	-10.817	-2655.345	-1370.157
298.15	131.624	343.191	-5.839	-2658.293	677.535
300	132.400	344.008	0	-2661.024	538.763
350	152.248	365.937	0.244	-2662.357	449.021
400	169.665	387.432	0.428	-2663.698	446.146
450	184.604	408.302	0.578	-2665.007	379.923
500	197.270	428.426	0.711	-2666.285	330.211
600	216.981	466.236	1.019	-2667.532	291.516
700	231.084	500.802	1.404	-2668.757	260.541
800	241.334	532.364	1.761	-2669.960	214.045
900	248.936	561.249	2.094	-2671.141	180.808
1000	254.690	587.789	2.405	-2672.301	155.867
1100	259.130	612.280	2.691	-2673.446	136.459
1200	262.617	634.983	2.948	-2674.576	120.925
1300	265.398	656.117	3.181	-2675.691	108.209
1400	267.649	675.871	3.391	-2676.791	97.606
1500	269.494	694.401	3.580	-2677.876	88.629
1600	271.024	711.844	3.751	-2678.946	80.227
1700	272.309	728.315	3.907	-2679.991	72.466
1800	273.389	743.911	4.048	-2681.011	65.299
1900	274.313	758.718	4.176	-2682.006	58.629
2000	275.107	772.809	4.291	-2682.976	52.451
2100	275.795	786.248	4.395	-2683.921	46.773
2200	276.393	799.092	4.488	-2684.841	41.523
2300	276.918	811.390	4.571	-2685.736	36.645
2400	277.379	823.186	4.645	-2686.606	32.109
2500	277.788	834.518	4.711	-2687.451	27.969
2600	278.152	845.420	4.769	-2688.271	24.171
2700	278.477	855.924	4.819	-2689.076	20.687
2800	278.768	866.056	4.863	-2689.856	17.484
2900	279.030	875.843	4.901	-2690.611	14.521
3000	279.267	885.307	4.934	-2691.341	11.769
3100	279.482	894.468	4.962	-2692.046	9.214
3200	279.677	903.344	4.986	-2692.726	6.841
3300	279.853	911.953	4.995	-2693.381	4.633
3400	280.018	920.310	4.999	-2694.011	2.660
3500	280.167	928.429	4.999	-2694.616	1.824
3600	280.304	936.324	4.999	-2695.196	1.124
3700	280.430	944.005	4.999	-2695.751	0.646
3800	280.547	951.486	4.999	-2696.281	0.329
3900	280.654	958.774	4.999	-2696.786	0.181
4000	280.754	965.881	4.999	-2697.266	0.096
4100	280.847	972.815	4.999	-2697.721	0.054
4200	280.933	979.584	4.999	-2698.151	0.034
4300	281.013	986.195	4.999	-2698.556	0.021
4400	281.088	992.656	4.999	-2698.936	0.014
4500	281.158	998.974	4.999	-2699.291	0.009
4600	281.224	1005.154	4.999	-2699.621	0.006
4700	281.285	1011.203	4.999	-2699.926	0.004
4800	281.343	1017.126	4.999	-2700.206	0.003
4900	281.397	1022.927	4.999	-2700.461	0.002
5000	281.448	1028.613	4.999	-2700.691	0.001
5100	281.496	1034.187	4.999	-2700.896	0.000
5200	281.541	1039.653	4.999	-2701.076	0.000
5300	281.584	1045.016	4.999	-2701.231	0.000
5400	281.624	1050.280	4.999	-2701.371	0.000
5500	281.663	1055.448	4.999	-2701.496	0.000
5600	281.699	1060.524	4.999	-2701.606	0.000
5700	281.733	1065.510	4.999	-2701.701	0.000
5800	281.766	1070.410	4.999	-2701.781	0.000
5900	281.797	1075.227	4.999	-2701.846	0.000
6000	281.826	1079.963	4.999	-2701.896	0.000

PREVIOUS: September 1963 (1 atm)

CURRENT: September 1963 (1 bar)

Beryllium Oxide ((BeO)_g)

Be₉O₆(g)

Beryllium

Continued from page 369

- ⁹P. A. Akshin and V. P. Spiridonov, *Kristallografiya* 2, 472 (1957).
¹⁰P. A. Akshin, V. P. Spiridonov, and G. A. Sobolev, *Dokl. Akad. Nauk SSSR* 118, 1134 (1958).
¹¹A. Buchler, J. L. Stauffer, and W. Klemperer, *J. Amer. Chem. Soc.* 86, 4544 (1964).
¹²A. Snelson, *J. Phys. Chem.* 72, 250 (1968).
¹³G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, (1962).
¹⁴L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Revs.* 63, 111 (1963).
¹⁵K. S. Krasnov and V. I. Svetsov, *Izv. Vysshikh Uchebnykh Zavedenii, Khim. i Khim. Tekhnol.* 6, 167 (1963).

Continued from page 382

- ⁹K. A. Sene and R. W. Stone, *J. Phys. Chem.* 62, 453 (1958).
¹⁰A. V. Novoselova, F. Sh. Muratov, L. P. Reshetnikova and I. V. Gordlev, *Vestn. Mosk. Univ., Ser. Mat., Mekh., Astron., Fiz. Khim.* 13, No. 6, 181 (1958).
¹¹P. A. Akshin, V. P. Spiridonov and G. A. Sobolev, *Dokl. Akad. Nauk SSSR* 118, 1134 (1958), *Proc. Acad. Sci. USSR (Eng. Trans.)*, *J. Phys. Chem. Sec.* 118, 111 (1958).
¹²L. Wharton, R. A. Berg, and W. Klemperer, *J. Chem. Phys.* 39, 2023 (1963); A. Buchler, J. L. Stauffer and W. Klemperer, *J. Amer. Chem. Soc.* 86, 1554 (1964).
¹³A. Snelson, *J. Phys. Chem.* 72, 250 (1968); 70, 3208 (1966).
¹⁴A. Buchler and W. Klemperer, *J. Chem. Phys.* 29, 121 (1958).

Continued from page 392

The entropy in the present table is higher by 1.83 cal·K⁻¹·mol⁻¹ at 298.15 K and 1.76 cal·K⁻¹·mol⁻¹ at 1000 K than that proposed by Jackson,⁹ the moment of inertia as calculated by Jackson⁹ appears to be in error.

References

- ¹Y. H. Inami and F. Ju, Philco-Ford Corp., Aeronutronic Div., Report U-4307, Contract F 04611-68-C-0012, (February 1, 1968).
²Y. H. Inami and F. Ju, Philco-Ford Corp., Aeronutronic Div., Report U-4352, Contract F 06411-68-C-0012, (May 1, 1968).
³H. C. Ko, M. A. Greenbaum, and M. Farber, *J. Phys. Chem.* 71, 1815 (1967).
⁴D. L. Hildenbrand, L. P. Theard, E. Murad, and F. Ju, Philco Corp., Aeronutronic Div., Report U-3068, Contract AF 04(611)-8523, (April 1, 1965).
⁵JANAF Thermochemical Tables: Be(g), 9-30-61; BeCl(g), 9-30-66; BeO(α), BeO(β), BeO(γ), BeO(δ), BeO(ε), 12-31-74; Be₂O(g), 9-30-63; Cl(g), 6-30-72; H(g), O(g), 6-30-74; OH(g), 12-31-70; BaOH(g), CaOH(g), MgOH(g), SrOH(g), 12-31-75; BeF(g), 12-31-71; BeCl(g), 9-30-66; H₂O(g), 3-31-61.
⁶R. C. Schoonmaker, and R. F. Porter, *J. Chem. Phys.* 31, 830 (1959).
⁷J. Berkowitz, D. J. Meschi, and N. A. Chupka, *J. Chem. Phys.* 33, 533 (1960).
⁸F. E. Stafford and J. Berkowitz, *J. Chem. Phys.* 40, 2963 (1964).

Continuation of discussions of selected Be species

- ⁹D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., Report UCR-51137, Contract No. W-7405-Eng-48, (December 8, 1971).
¹⁰A. D. Walsh, *J. Chem. Soc.* 1953, 2288 (1953).
¹¹R. Acquista, S. Abramowitz, and D. R. Lide, *J. Chem. Phys.* 49, 780 (1968).
¹²R. L. Kuczowski and D. R. Lide, *J. Chem. Phys.* 44, 3131 (1966).
¹³N. Acquista and S. Abramowitz, *U. S. Nat. Bur. Stand. Report* 9903, Ch. 6 (July, 1968), refer to pp 99-111.

Continued from page 397

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

References

- ¹W. I. Stuart and G. H. Price, *J. Nucl. Mater.* 14, 417 (1964).
²W. A. Young, *J. Phys. Chem.* 64, 1003 (1960).
³L. I. Grossweiner and R. L. Seifert, *J. Amer. Chem. Soc.* 74, 2701 (1952).
⁴J. Blauer, M. A. Greenbaum, and M. Farber, *J. Phys. Chem.* 70, 973 (1966).
⁵L. Brewer and G. R. B. Elliott, UCR-1831 (1952).
⁶Morize, Roudier, and Besson, DM948.
⁷A. Baur and A. Lecocq, *Comm. Energie At. (France)*, Rapp. CEA-R2611 (1964).
⁸D. F. Hildenbrand, L. P. Theard, and F. Ju, Aeronutronic, 3rd Quarterly Technical Report No. U-2231, Contract AF 03(611)-8523, (31 July 1963).
⁹R. C. Schoonmaker and R. F. Porter, *J. Chem. Phys.* 31, 830 (1959).
¹⁰J. Berkowitz, D. J. Meschi, and W. A. Chupka, *J. Chem. Phys.* 33, 533 (1960).
¹¹F. E. Stafford and J. Berkowitz, *J. Chem. Phys.* 40, 2963 (1964).
¹²JANAF Thermochemical Tables: BeF(g), 12-31-71; Mg(OH)(g) and Be(OH)(g), 12-31-75; H₂O(g), 3-31-61.
¹³D. D. Jackson, Lawrence Livermore Laboratory, Univ. of Calif., UCR-51137, Contract No., W-7405-Eng-48, (December 8, 1971).
¹⁴M. Farber, *et al.*, Rocket Power, Inc., AFRPL-TR-66-220, (September, 1966).
¹⁵G. Verhaegen and W. G. Richards, *J. Chem. Phys.* 45, 1828 (1966).
¹⁶W. A. Chupka, J. Berkowitz and C. F. Giese, *J. Chem. Phys.* 30, 827 (1959).
¹⁷L. P. Theard and D. L. Hildenbrand, *J. Chem. Phys.* 41, 3416 (1964).
¹⁸L. Brewer and G. Rosenblatt, *Advan. High Temp. Chem.* 2, 1 (1969).
¹⁹K. Schofield, *Chem. Rev.* 67, 707 (1967).
²⁰A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall Ltd., London, 1969, pp. 236-244.
²¹B. Rai and S. N. Rai, *Indian J. Pure Appl. Phys.* 10, 401 (1972).

Continued from page 408