

Barium (Ba)

$A_r = 137.33$ Barium (Ba)

REFERENCE STATE

0 to 582.53 K crystal, alpha
582.53 to 768.13 K crystal, beta
768.13 to 1000 K crystal, gamma
1000 to 2118.599 K liquid
above 2118.599 K ideal monatomic gas

Refer to the individual tables for details.

Ba₁(ref)

Enthalpy Reference Temperature = $T_r = 298.15$ K			Standard State Pressure = $p^\circ = 0.1$ MPa		
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$ J·K ⁻¹ ·mol ⁻¹	$H^\circ - H^\circ(T_r)$ kJ·mol ⁻¹	$\Delta_f G^\circ$	log K_t
0	0	0	INFINITE	-6.912	0
100	24.301	34.083	86.220	-5.214	0
200	26.368	51.643	64.988	-2.669	0
298.15	28.096	62.475	62.475	0	0
300	28.142	62.649	62.476	0.052	0
400	33.229	71.295	63.697	3.069	0
500	43.744	79.771	65.997	6.887	0
582.530	54.400	87.232	68.471	10.929	ALPHA <--> BETA TRANSITION
582.530	32.468	87.232	68.471	10.929	TRANSITION
600	33.941	88.213	69.031	11.509	0
700	42.363	94.077	72.186	15.324	0
768.130	48.103	98.274	74.313	18.406	BETA <--> GAMMA TRANSITION
768.130	39.066	98.274	74.313	18.406	TRANSITION
800	39.066	99.863	75.299	19.651	0
900	39.066	104.464	78.289	23.557	0
1000	39.066	108.580	81.116	27.464	0
1000.000	39.066	108.580	81.116	27.464	GAMMA <--> LIQUID TRANSITION
1000.000	43.304	116.592	81.116	35.476	TRANSITION
1100	42.007	120.657	84.530	39.741	0
1200	40.878	124.262	87.693	43.883	0
1300	39.999	127.498	90.633	47.925	0
1400	39.330	130.437	93.373	51.890	0
1500	38.869	133.133	95.935	55.798	0
1600	38.618	135.633	98.339	59.670	0
1700	38.576	137.971	100.602	63.528	0
1800	38.740	140.180	102.740	67.392	0
1900	39.116	142.284	104.766	71.283	0
2000	39.706	144.304	106.693	75.223	0
2100	40.518	146.260	108.531	79.232	0
2118.599	40.692	146.618	108.863	79.987	LIQUID <--> IDEAL GAS FUGACITY = 1 bar
2118.599	30.938	212.831	108.863	220.265	TRANSITION
2200	32.665	214.029	112.732	222.853	0
2300	34.873	215.530	117.169	226.230	0
2400	37.123	217.062	121.299	229.830	0
2500	39.355	218.622	125.161	233.654	0
2600	41.512	220.208	128.786	237.698	0
2700	43.543	221.814	132.202	241.952	0
2800	45.406	223.431	135.431	246.401	0
2900	47.068	225.054	138.493	251.026	0
3000	48.509	226.675	141.406	255.807	0
3100	49.718	228.286	144.182	260.720	0
3200	50.695	229.880	146.836	265.743	0
3300	51.410	231.450	149.376	270.844	0
3400	51.931	232.992	151.813	276.012	0
3500	52.262	234.503	154.154	281.223	0
3600	52.420	235.978	156.406	286.458	0
3700	52.431	237.415	158.576	291.702	0
3800	52.319	238.812	160.669	296.940	0
3900	52.105	240.168	162.691	302.162	0
4000	51.814	241.483	164.644	307.358	0
4200	51.068	243.993	168.363	317.645	0
4400	50.234	246.350	171.855	327.776	0
4600	49.384	248.563	175.143	337.732	0
4800	48.545	250.640	178.245	347.499	0
5000	47.832	252.606	181.180	357.129	0
5200	47.194	254.465	183.963	366.608	0
5400	46.697	256.236	186.607	375.995	0
5600	46.176	257.908	189.122	385.200	0
5800	45.812	259.517	191.522	394.376	0
6000	45.369	261.036	193.810	403.351	0

PREVIOUS: December 1970 (1 atm)

CURRENT: December 1970 (1 bar)

Barium (Ba)

Ba₁(ref)

Barium, Alpha-Beta-Gamma (Ba)

 $A_f = 137.33$ CRYSTAL(α - β - γ)

Barium, Alpha-Beta-Gamma (Ba)

$$S^\circ(298.15 \text{ K}) = 62.475 \pm 0.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_m = [582.53] \text{ K } (\alpha \rightarrow \beta)$$

$$T_m = [768.13] \text{ K } (\beta \rightarrow \gamma)$$

$$T_m = 1000 \pm 3 \text{ K}$$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted values below 298.15 K are based on $C_p^\circ(18\text{--}370 \text{ K})$ of Furukawa and Ishihara¹ and $C_p^\circ(1.5\text{--}20 \text{ K})$ of Roberts.² $S^\circ(298.15 \text{ K})$ is calculated from C_p° based on an extrapolation of about 0.001 $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ below 1.5 K. We estimate that $S^\circ(298.15 \text{ K})$ is uncertain by about 0.2 $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, due mainly to possible effects of impurities. Furukawa and Ishihara¹ reported impurities (in mole %) of about 3% BaO, 1% Sr and 0.2% Ca. Further details on adjustment of the data for impurities are given in the original paper.¹

Relative enthalpies were measured by Jauch,³ Shipil'rain⁴ and Dittmars and Douglas.⁵ Earlier reviewers dismissed the anomalously high C_p° values of Jauch as due to a very impure sample. The new data confirm this decision, but at least one new study⁶ may also involve bias due to impurities. Separate portions from a common sample consisting of three Ba rods were used in the heat capacity study,¹ the enthalpy study³ and the analytical studies.^{1,5} The calorimetric data suggest variability in the impurity contents of the separate portions. The 2nd law study⁴ used Ba which was not analyzed for O or N which are the most likely contaminants. Since the premelting effect in the enthalpy at 979 K appears to be 1/4 as large in⁴ as in³, the sample of⁴ may have been more pure, however, such a conclusion would be quite speculative. Liquid enthalpies are in reasonable agreement, but the crystal enthalpies of⁴ are 4 to 20% lower than those of³. Another major difference is that⁴ suggests a single "transition" near 650 K, while³ suggests two "transitions" near 580 and 770 K. Further confusion arises because the enthalpies reported⁴ for CsF(c, l) are unreasonably large.

We tentatively adopt the smoothed C_p° of Dittmars and Douglas,⁵ pending resolution of the transition discrepancy. The following alternative functions reproduce the enthalpies of Shipil'rain⁴ and provide estimates of the possible bias in the adopted functions, Ba(α): C_p° $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 5.023 \pm 0.005657 T$ (298–650 K), $\Delta_{\alpha\beta}H^\circ = 0.345 \text{ kcal} \cdot \text{mol}^{-1}$ at 650 K; Ba(γ): C_p° $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 9.4$ (650–999.6 K), $\Delta_{\beta\gamma}H^\circ = 2.048 \text{ kcal} \cdot \text{mol}^{-1}$ at 999.6 K; Ba(δ): C_p° $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 10.0$ (999.6–1300 K). There is reasonable agreement between the alternative and adopted C_p° for Ba(δ) and Ba(γ), suggesting that the γ -phases are identical in the two studies. $C_p^\circ(\alpha)$ from the equation is a reasonable extension of the data below 298.15 K; C_p° does not show the anomalously steep rise just above 300 K which appears in the enthalpy data³ and to a lesser degree, in the C_p° data.¹ The alternative functions suggest that the adopted γ -phase entropy may be biased by about +0.6 $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (about +6% in $S^\circ(298.15 \text{ K})$ due to impurities. Dittmars and Douglas stressed the possibility of such systematic errors⁵ and estimated errors of up to 5% in C_p° and H° . Our alternative functions suggest the maximum error in $C_p^\circ(\alpha)$ may be much larger than 5%.

Transition Data

Recent data for Sr and Ca indicate that the pure metals exist in the fcc and bcc polymorphs but that impurities probably stabilize the hcp form. Although enthalpy data^{4,5} suggest a similar controversy for Ba, the pure metal is usually reported to have the bcc form at all temperatures at atmospheric pressure.^{6,9} Several high-pressure polymorphs are known.^{10–12} Earlier literature¹³ contains much evidence for a "transition" near 648 K at one atmosphere; this is consistent with new enthalpy data⁴ and could correspond to the "transition" found by Bridgman¹³ near 17 kbar at room temperature. Bridgman's "transition" is in dispute, it seems to involve a very small volume contraction^{12,14} and no obvious change in X-ray pattern.¹⁵ We speculate that these two "transitions" are identical; however, evidence for their being a property of pure Ba is inconclusive. The main support comes from the relatively small premelting effect in enthalpy.⁴ The enthalpy data⁴ are insufficient to distinguish whether the "transitions" is first or second order.

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

The adopted functions include $\Delta_{\alpha\beta}H^\circ = 0.97 \text{ cal} \cdot \text{mol}^{-1}$ at 57 K from a small-anomaly observed between 50 and 60 K.¹

Fusion and Sublimation Data

Refer to the liquid and ideal gas tables for details.

References

- ¹G. T. Furukawa and S. Ishihara, U. S. Nat. Bur. Stand., Report 10326, chap. 2, (July 1, 1970).
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- ³R. Jauch, quoted by O. Kubaschewski, Z. Elektrochem. 54, 275 (1950); Z. Metallkunde 41, 445 (1950).
- ⁴E. E. Shipil'rain and D. N. Kagan, Teplofiz. Vys. Temp. 7, 577 (1969); English transl., High Temp. 7, 525 (1969).
- ⁵D. A. Dittmars and T. B. Douglas, U. S. Nat. Bur. Stand., Report 10326, chap. 3, (July 1, 1970).

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Ba₁(cr)

Barium (Ba)

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$		Ba ₁ (cr)	
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	ΔG°	$\log K_r$
0	0	INFINITE	0	0	0
100	24.301	34.083	-6.912	0	0
200	26.368	51.643	-5.214	0	0
250	27.196	57.613	-2.669	0	0
298.15	28.096	62.475	-1.330	0	0
300	28.142	62.475	0	0	0
350	29.898	62.475	0.052	0	0
400	33.229	62.475	0.498	0	0
450	38.031	62.475	1.498	0	0
500	43.744	62.475	3.069	0	0
582.530	54.400	62.475	4.846	0	0
582.530	32.468	62.475	6.887	0	0
600	33.941	62.475	10.929	0	0
700	42.363	62.475	18.406	0	0
768.130	48.103	62.475	27.464	0	0
800	39.066	62.475	31.371	0	0
900	39.066	62.475	35.277	0	0
1000	39.066	62.475	39.184	0	0
1000.000	39.066	62.475	43.090	0	0
1100	39.066	62.475	46.997	0	0
1200	39.066	62.475	50.904	0	0
1300	39.066	62.475	54.811	0	0
1400	39.066	62.475	58.718	0	0
1500	39.066	62.475	62.625	0	0

PREVIOUS December 1970

CURRENT December 1970

Barium (Ba)

Ba₁(cr)

Ba₁(l)

Barium (Ba)

LIQUID

Barium (Ba)

Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa		log K_f	
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
0					
100					
200					
250					
298.15	28.096	66.328	66.328	0.	3.837
300	28.142	66.329	66.329	0.052	3.879
350	29.898	66.677	66.677	1.498	3.636
400	33.229	70.147	70.147	3.069	3.444
450	38.031	79.327	79.327	4.846	3.251
500	43.744	88.623	88.623	6.887	3.059
580.000	54.057	107.92	107.92	10.792	2.720
580.000	51.120	90.849	90.849	10.792	GLASS \leftrightarrow LIQUID TRANSITION
600	50.664	92.574	92.574	11.809	2.660
700	48.509	100.219	100.219	16.766	2.128
800	46.564	106.567	106.567	21.518	1.489
900	44.832	111.950	111.950	26.086	0.777
1000	43.304	116.592	116.592	30.491	0.
1000.000	43.304	116.592	116.592	30.491	GLASS \leftrightarrow LIQUID TRANSITION
1100	42.007	120.657	120.657	34.755	0.
1200	40.878	124.262	124.262	38.898	0.
1300	39.999	127.498	127.498	42.940	0.
1400	39.330	130.437	130.437	46.904	0.
1500	38.869	133.133	133.133	50.813	0.
1600	38.618	135.633	135.633	54.685	0.
1700	38.576	137.971	137.971	58.543	0.
1800	38.740	140.180	140.180	62.407	0.
1900	39.116	142.284	142.284	66.298	0.
2000	39.706	144.304	144.304	70.238	0.
2100	40.518	146.260	146.260	74.247	0.
2118.599	40.692	146.618	146.618	75.002	0.
2200	41.539	148.168	148.168	78.348	0.128
2300	42.769	150.041	150.041	82.562	0.271
2400	44.208	151.891	151.891	86.909	0.402
2500	45.857	153.728	153.728	91.410	0.522
2600	47.708	155.562	155.562	96.087	0.632
2700	49.771	157.400	157.400	100.959	0.733
2800	52.047	159.251	159.251	106.048	0.827
2900	54.536	161.120	161.120	111.376	0.914
3000	57.237	163.014	163.014	116.962	0.995
3100	60.151	164.938	164.938	122.830	1.070
3200	63.277	166.896	166.896	128.900	1.139
3300	66.616	168.894	168.894	135.493	1.204
3400	70.167	170.935	170.935	142.330	1.264
3500	73.931	173.023	173.023	149.533	1.320

PREVIOUS: December 1970

CURRENT: December 1970

Barium (Ba)

Ba₁(l)

$S^\circ(298.15 \text{ K}) = [66.328] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $T_{\text{fus}} = 1000 \pm 3 \text{ K}$

 $A_r = 137.33$

Barium (Ba)

$\Delta_f H^\circ(298.15 \text{ K}) = [4.985] \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_{\text{fus}} H^\circ = 8.012 \pm 0.62 \text{ kJ} \cdot \text{mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{\text{fus}} H^\circ$ and the difference in enthalpy, $H^\circ(1000 \text{ K}) - H^\circ(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

C_p° is based on the parabolic equation derived by Douglas and Krause¹ from enthalpy data of Dittmars and Douglas.² The enthalpy data (1003 to 1173 K) may be biased due to impurities in the sample,² however, enthalpy data (1035 to 1253 K) of Shipil'rain³ are in reasonable agreement. This suggests that the large discrepancies for Ba(cr) are partially compensated by different values of $\Delta_{\text{fus}} H^\circ$. Detailed discussions of the discrepancies and possible alternative functions are given on the crystal table. The alternative functions, derived from the possibly purer sample of Shipil'rain,³ suggest that the adopted liquid entropies may be biased by about $+0.4 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

Douglas and Krause emphasized the uncertain nature¹ of the parabolic extrapolation of C_p° from 1200 to 2000 K. The extrapolation is reasonable provided that the temperature coefficient of C_p° is not grossly biased due to effects of impurities on the observed enthalpies. Such bias seems unlikely because of the agreement in enthalpy between samples of different purity,³ and because the impurities² are present in amounts much below their solubility limits.^{2,4,5} in Ba(l). We note also that $S^\circ(2000 \text{ K})$ is not significantly changed when the parabolic fit is replaced by a two-constant fit in which C_p° approaches a constant ($8.48 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) at high temperature.

The parabolic C_p° is extrapolated to 580 K, the assumed glass transition temperature. C_p° below 580 K is taken to be the same as the crystal. $S^\circ(298.15 \text{ K})$ is calculated in a manner analogous to that of the enthalpy of formation.

Melting Data

Dittmars and Douglas² considered early melting point data and arbitrarily selected 991 K. Recent data yield higher values of $998 \pm 1^\circ \text{K}$,⁷ and $1002 \pm 1^\circ \text{K}$.^{8,10} These values represent more carefully purified samples. We adopt $1000 \pm 3 \text{ K}$ and adjust $\Delta_{\text{fus}} H^\circ$ slightly so that the result is consistent with the smoothed enthalpy² of the liquid. Alternative functions based on enthalpies of Shipil'rain³ suggest that the adopted $\Delta_{\text{fus}} H^\circ$ may be too small by about $0.15 \text{ kcal} \cdot \text{mol}^{-1}$ (see the crystal table).

Vaporization Data

$T_{\text{vap}} = 2118.599 \text{ K}$ is calculated as the temperature at which $\Delta_r G^\circ = 0$ for $\text{Ba(l)} \rightarrow \text{Ba(g)}$. $\Delta_{\text{vap}} H^\circ = 140.278 \text{ kJ} \cdot \text{mol}^{-1}$ is the difference between $\Delta_f H^\circ(\text{g})$ and $\Delta_f H^\circ(\text{l})$ at T_{vap} . Bohdanský and Schins¹¹ reported $T_{\text{vap}} = 2063 \text{ K}$ (1 atm) based on extrapolation of their vapor pressure data from 2024 K. Our calculated T_{vap} is some 60 K higher due to the entropy difference between the adopted functions and vapor pressure data¹¹ and to adoption of the mean 3rd law $\Delta_{\text{vap}} H^\circ$ rather than the apparent value at 2024 K. Refer to the ideal gas table for further details.

References

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- ²D. A. Dittmars and T. B. Douglas, U. S. Nat. Bur. Stand., Report 10326, chap. 3, (July 1, 1970).
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CRYSTAL(α - β - γ)-LIQUID

0 to 582.53 K crystal, alpha
582.53 to 768.13 K crystal, beta
768.13 to 1000 K crystal, gamma
above 1000 K liquid

Refer to the individual tables for details.

Barium (Ba)

$A_1 = 137.33$ Barium (Ba)

$Ba_1(cr,l)$

Enthalpy Reference Temperature = $T_r = 298.15$ K									
T/K	C_p°	$J \cdot K^{-1} \cdot mol^{-1}$		$J \cdot K^{-1} \cdot mol^{-1}$		$kJ \cdot mol^{-1}$		$log K_f$	
		S°	$-(G^\circ - H^\circ(T_r))/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	
0	0	0	INFINITE	-6.912	0	0	-6.912	0	
100	24.301	34.083	86.270	-5.214	0	0	-5.214	0	
200	26.368	51.643	64.988	-2.469	0	0	-2.469	0	
250	27.196	57.613	62.953	-1.530	0	0	-1.530	0	
298.15	28.096	62.475	62.475	0	0	0	0	0	
300	28.142	62.649	62.476	0.052	0	0	0.052	0	
350	29.898	67.105	62.824	1.498	0	0	1.498	0	
400	31.229	71.295	63.622	3.069	0	0	3.069	0	
450	38.031	75.475	64.706	4.846	0	0	4.846	0	
500	43.744	79.771	65.997	6.887	0	0	6.887	0	
582.530	54.400	87.232	68.471	10.929	0	0	10.929	0	
582.530	32.468	87.232	68.471	10.929	0	0	10.929	0	
600	33.941	88.213	69.031	11.509	0	0	11.509	0	
700	42.363	94.077	72.186	15.324	0	0	15.324	0	
768.130	48.103	98.274	74.313	18.406	0	0	18.406	0	
768.130	39.066	98.274	74.313	18.406	0	0	18.406	0	
800	39.066	99.863	75.299	19.651	0	0	19.651	0	
900	39.066	104.464	78.289	23.557	0	0	23.557	0	
1000	39.066	108.580	81.116	27.464	0	0	27.464	0	
1000.000	39.066	108.580	81.116	27.464	0	0	27.464	0	
1000.000	43.304	116.592	81.116	35.476	0	0	35.476	0	
1100	42.007	120.657	84.530	39.741	0	0	39.741	0	
1200	40.878	124.262	87.693	43.883	0	0	43.883	0	
1300	39.999	127.498	90.633	47.925	0	0	47.925	0	
1400	39.330	130.437	93.373	51.890	0	0	51.890	0	
1500	38.869	133.133	95.935	55.798	0	0	55.798	0	
1600	38.618	135.633	98.339	59.670	0	0	59.670	0	
1700	38.576	137.971	100.602	63.528	0	0	63.528	0	
1800	38.740	140.180	102.740	67.392	0	0	67.392	0	
1900	39.116	142.284	104.766	71.283	0	0	71.283	0	
2000	39.706	144.304	106.693	75.223	0	0	75.223	0	
2100	40.518	146.260	108.531	79.232	0	0	79.232	0	
2118.599	40.692	146.618	108.863	79.987	0	0	79.987	0	
2200	41.539	148.168	110.289	83.233	0	0	83.233	0	
2300	42.769	150.041	111.977	87.547	0	0	87.547	0	
2400	44.208	151.891	113.601	91.894	0	0	91.894	0	
2500	45.857	153.728	115.170	96.396	0	0	96.396	0	
2600	47.708	155.562	116.688	101.072	0	0	101.072	0	
2700	49.771	157.400	118.162	105.944	0	0	105.944	0	
2800	52.047	159.251	119.596	111.033	0	0	111.033	0	
2900	54.536	161.120	120.996	116.361	0	0	116.361	0	
3000	57.237	163.014	122.365	121.948	0	0	121.948	0	
3100	60.151	164.938	123.707	127.815	0	0	127.815	0	
3200	63.277	166.896	125.026	133.985	0	0	133.985	0	
3300	66.616	168.894	126.325	140.478	0	0	140.478	0	
3400	70.167	170.935	127.607	147.315	0	0	147.315	0	
3500	73.931	173.023	128.874	154.518	0	0	154.518	0	

PREVIOUS: December 1970

CURRENT: December 1970

Barium (Ba)

$Ba_1(cr,l)$

Ba(g)

Barium (Ba)

Barium (Ba)

$A_r = 137.33$ Barium (Ba)

$\Delta_f H^\circ(0 \text{ K}) = 179.8 \pm 5.0 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_f H^\circ(298.15 \text{ K}) = 179.1 \pm 5.0 \text{ kJ} \cdot \text{mol}^{-1}$

IP (Ba, g) = $42035.14 \pm 0.05 \text{ cm}^{-1}$
 $S^\circ(298.15 \text{ K}) = 170.245 \pm 0.01 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$			Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$			log K_r
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	ΔG°	
0	0	0	INFINITE	179.790	179.790	INFINITE
100	20.786	147.337	-4.119	180.170	180.170	-88.185
200	20.786	161.945	-2.040	179.704	179.704	-31.792
250	20.786	166.584	-1.001	179.404	179.404	-25.744
298.15	20.786	170.245	0	179.075	179.075	-25.744
300	20.786	170.245	0.038	179.062	179.062	-25.500
350	20.786	173.573	1.078	178.654	178.654	-21.101
400	20.786	176.353	2.117	178.123	178.123	-17.193
450	20.786	178.801	3.156	177.386	177.386	-13.159
500	20.786	180.991	4.196	176.384	176.384	-10.090
600	20.786	184.781	6.274	173.841	173.841	-6.342
700	20.786	187.985	8.353	170.104	170.104	-3.117
800	20.786	190.761	10.432	165.856	165.856	-1.469
900	20.786	193.210	12.511	160.202	160.202	-0.206
1000	20.821	195.402	14.591	153.380	153.380	-0.031
1100	20.883	197.389	16.676	145.011	145.011	0
1200	21.014	199.211	18.770	135.563	135.563	0
1300	21.251	200.901	20.882	125.033	125.033	0
1400	21.635	202.489	23.025	113.493	113.493	0
1500	22.204	204.000	25.216	100.878	100.878	0
1600	22.993	205.457	27.473	88.286	88.286	0
1700	24.024	206.881	29.822	75.732	75.732	0
1800	25.307	208.289	32.287	63.218	63.218	0
1900	26.839	209.697	34.892	50.754	50.754	0
2000	28.599	211.118	37.662	38.341	38.341	0
2100	30.556	212.560	40.618	25.978	25.978	0
2188.599	30.938	212.831	41.900	20.000	20.000	0
2200	32.665	214.029	43.778	15.530	15.530	0
2300	34.773	215.530	47.155	10.754	10.754	0
2400	37.123	217.062	50.754	6.341	6.341	0
2500	39.535	218.622	54.579	2.118	2.118	0
2600	41.512	220.208	58.623	0	0	0
2700	43.543	221.814	62.877	0	0	0
2800	45.406	223.431	67.326	0	0	0
2900	47.068	225.054	71.951	0	0	0
3000	48.509	226.675	76.732	0	0	0
3100	49.718	228.286	81.645	0	0	0
3200	50.695	229.880	86.668	0	0	0
3300	51.410	231.450	91.769	0	0	0
3400	51.931	232.992	96.936	0	0	0
3500	52.262	234.503	102.148	0	0	0
3600	52.420	235.978	107.383	0	0	0
3700	52.431	237.415	112.627	0	0	0
3800	52.319	238.812	117.865	0	0	0
3900	52.105	240.168	123.087	0	0	0
4000	51.814	241.483	128.283	0	0	0
4100	51.463	242.758	133.445	0	0	0
4200	51.068	243.993	138.570	0	0	0
4300	50.656	245.190	143.656	0	0	0
4400	50.234	246.350	148.701	0	0	0
4500	49.812	247.474	153.703	0	0	0
4600	49.384	248.563	158.657	0	0	0
4700	48.932	249.614	163.550	0	0	0
4800	48.545	250.640	168.423	0	0	0
4900	48.171	251.636	173.254	0	0	0
5000	47.832	252.606	178.054	0	0	0
5100	47.483	253.545	182.799	0	0	0
5200	47.194	254.465	187.533	0	0	0
5300	46.933	255.361	192.239	0	0	0
5400	46.697	256.236	196.920	0	0	0
5500	46.442	257.084	201.547	0	0	0
5600	46.176	257.908	206.125	0	0	0
5700	46.000	258.724	210.734	0	0	0
5800	45.812	259.517	215.301	0	0	0
5900	45.508	260.272	219.733	0	0	0
6000	45.369	261.036	224.276	0	0	0

CURRENT: December 1970 (1 bar)

PREVIOUS: December 1970 (1 atm)

Ba₁(g)

Barium (Ba)

Continued on page 358

IDEAL GAS

Electronic Levels and Quantum Weights		ϵ , cm^{-1}		g		ϵ , cm^{-1}		g	
0.0	1	22947	7	25704	3	33188	15	39765	[21]
9034.0	3	23757	9	25957	5	33837	8	39905	[36440]
9215.5	5	23068	10	26160	3	35142	10	40736	[40000]
9596.6	7	23209	1	26816	7	34649	28	40893	[20000]
11395.4	5	23480	3	28554	1	35658	20	41097	[24000]
12266.0	1	23919	5	28554	3	35893	3	42012	[25000]
12636.6	3	24192	3	30237	5	36400	55	42436	[19000]
13514.7	5	24532	5	30771	15	36974	56	43264	[39000]
18060	3	24980	7	30903	9	37425	58	35500	[42000]
22065	5	25642	1	32547	3	38031	37	37700	

Enthalpy of Formation
 $\Delta_f H^\circ$ is $\Delta_{\text{sub}} H^\circ$, $42.8 \pm 1.2 \text{ kcal} \cdot \text{mol}^{-1}$, selected from 3rd law analyses of pressure data tabulated below. The adopted value is from the recent boiling-point study of Bohdanský and Schins.¹ Except for the very scattered effusion data of Zavitsanos,⁴ the other studies differ by unusually large amounts: -2 , -6 , and $+3 \text{ kcal} \cdot \text{mol}^{-1}$. Data of Ruff and Hartmann³ are readily dismissed due to the large entropy discrepancy; their data for other metals have similar discrepancies. Data of Rudberg and Lemper² for Ca and Ba show almost identical biases, presumably due to poor effusion geometry or to impurities. A similar bias seems to exist in the effusion-resonance-fluorescence data of Hinnoy and Ohlendorf;⁵ our analysis is not tabulated below since the graphical data include large discrepancies in temperature. Hartmann and Schneider's Ba data⁶ deviate considerably more from the selected value than do their data for Li, Mg, Ca and Sr. The differences probably arise from impurity effects. Since Ba is the least volatile of the reactive metals studied,^{1,2} purification by distillation presents special problems. Even Bohdanský and Schins¹ noted that their Ba data may be biased by impurities.

Analyses of the pressure data assume that the monatomic gas is the only significant species in the vapor and that gas imperfection is negligible. Evidence supporting the unimportance of the dimer was reviewed by Douglas and Krause.⁷ Estimated bond energies for the dimers of Mg, Ca, Sr and Ba are less than $8.6 \text{ kcal} \cdot \text{mol}^{-1}$.^{13,10}

Source	Method	T/K^a	$\Delta_f H^\circ(298.15 \text{ K})$, $\text{kcal} \cdot \text{mol}^{-1}$		ΔS , $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
			2nd law	3rd law	
1	Boiling Point	1498–2027	46.7 ± 0.3	42.78 ± 0.04	2.2 ± 0.1
2	Boiling Point	1334–1421	41.4 ± 3.3	40.76 ± 0.33	0.4 ± 2.4
3	Boiling Point	1204–1404	92.6 ± 3.0	37.0 ± 6.1	43 ± 2.3
4	Effusion	1120–1210	65 ± 10	43.8 ± 1.6	18 ± 8.8
4	Torsion Effusion	1103–1216	36 ± 10	43.5 ± 1.9	-6.3 ± 8.4
5	Effusion	798–1024	43.2 ± 1.2	45.91 ± 0.77	-3.0 ± 1.3

^aTemperature adjusted to IPTS–68 assuming published values to be IPTS–48.

Heat Capacity and Entropy

Observed energy levels and quantum weights are from Moore¹¹ as modified by Garton *et al.*¹² Additional levels above the cutoffs have been reported.^{13,15} We adopt an energy-level cutoff which is about kT_{max} ($T_{\text{max}} = 6000 \text{ K}$) below each series limit. For Ba I this corresponds to omitting levels above 9s, 8p, 7d and 5f. Energies of unobserved but predicted terms¹¹ are estimated by comparison of Ca I, Sr I, Ba I and their isoelectronic ions. The most important are terms of the 5d² configuration (20000 – 25000 cm^{-1}) and those of the 5d6s² configuration (estimated at $19000 \pm 10000 \text{ cm}^{-1}$). Levels above 30000 cm^{-1} are averaged. The adopted functions are essentially identical with earlier tables up to 2000 K ; however, the entropies at 6000 K differ as follows: Hilsenrath *et al.*,¹⁶ 62.26; JANAF, 63.20; Gurvich *et al.*,¹⁷ 63.65 $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. These differences arise from different methods of cutoff and different degrees of accounting for the unobserved terms.

References

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2. H. Hartmann and R. Schneider, *Z. Anorg. Chem.* **180**, 275 (1929).
3. O. Ruff and H. Hartmann, *Z. Anorg. Chem.* **133**, 29 (1924).
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6. E. Hinnoy and W. Ohlendorf, *J. Chem. Phys.* **50**, 3005 (1969).
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Barium, Ion (Ba⁺)

IDEAL GAS

 $M_r = 137.32945$ Ba⁺(g)

IP(Ba⁺, g) = 80686.87 ± 0.05 cm⁻¹
 $S^\circ(298.15 \text{ K}) = 176.008 \pm 0.05 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H_f^\circ(0 \text{ K}) = 682.6 \pm 5.0 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = [688.126] \text{ kJ mol}^{-1}$

Electronic Levels and Quantum State	ϵ_∞ , cm ⁻¹	Weights g_i
² S _{1/2}	0.00	2
² D _{3/2}	4873.85	4
² D _{5/2}	5674.824	6
² P _{1/2}	20261.562	2
² P _{3/2}	21952.422	4
.	.	.
.	.	.
.	.	.
¹ G _{3/2}	77628	10
IP	80686.87	

Enthalpy of Formation

$\Delta H_f^\circ(\text{Ba}^+, \text{g}, 0 \text{ K})$ is calculated from $\Delta H_f^\circ(\text{Ba}, \text{g}, 0 \text{ K})$ using the spectroscopic value of IP(Ba) = 42035.14 ± 0.05 cm⁻¹ (502.8521 ± 0.0006 kJ mol⁻¹) from Moore.² The ionization limit is converted from cm⁻¹ to kJ mol⁻¹ using the factor, 1 cm⁻¹ = 0.01196266 kJ mol⁻¹, which is derived from the 1973 CODATA fundamental constants.³ Rosenstock *et al.*⁴ and Levin and Lias⁵ have summarized additional ionization and appearance potential data.

$\Delta H_f^\circ(\text{Ba}^+, \text{g}, 298.15 \text{ K})$ is calculated from $\Delta H_f^\circ(\text{Ba}, \text{g}, 0 \text{ K})$ by using IP(Ba) with JANAF¹ enthalpies, $H^\circ(0 \text{ K}) - H^\circ(298.15 \text{ K})$, for Ba(g), Ba⁺(g), and e⁻(ref). $\Delta H_f^\circ(\text{Ba} \rightarrow \text{Ba}^+ + e^-, 298.15 \text{ K})$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*⁴ $\Delta H_f^\circ(298.15 \text{ K})$ should be changed by -6.197 kJ mol⁻¹ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,^{2,6} is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first four excited states, the highest observed excited state, and the ionization potential for Ba⁺(g), all levels listed by Moore,^{2,6} as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Ba⁺(g), the thermodynamic functions are independent of the estimated missing levels (for $n = 6$), the cut-off procedure, and the inclusion of $n = 12$ levels up to 6000 K. The reported uncertainty in $S^\circ(298.15 \text{ K})$ 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 higher excited states ($n > 12$), and use of different fill and cut-off procedures.

References

- ¹JANAF Thermochemical Tables: Ba(g), 9-30-83; e⁻(ref), 3-31-82.
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- ⁵R. D. Levin and S. G. Lias, U.S. Nat. Bur. Stand., NSRDS-NBS-71, 634 pp. (1982); refer to p. 521.
- ⁶C. E. Moore, U.S. Nat. Bur. Stand., NSRDS-NBS-35, Volume III, (1970) [Reprint of NBS Circular 467, Volume III, 1958].
- ⁷J. R. Downey, Jr., The Dow Chemical Company, AFOSR-TR-78-0960, Contract No. F44620-75-1-0048, (1978).

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$				Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$		
T/K	C_p°	$S^\circ - [C_p^\circ - H^\circ(T_r)]/T_r$	$H^\circ - H^\circ(T_r)$	ΔH_f°	ΔG°	$\log K_r$
0	0	0	INFINITE	-6.197	682.643	-113.531
100	20.786	153.301	194.488	-4.119	647.772	-112.787
200	20.786	167.708	177.909	-2.040	640.991	-95.663
250	20.786	172.347	176.350	-1.001	634.127	-82.809
298.15	20.786	176.008	176.008	0	627.211	-72.805
300	20.786	176.008	176.008	0	620.275	-64.800
350	20.786	176.136	176.008	0.038	606.457	-52.797
400	20.786	179.241	176.261	1.078	592.634	-44.223
450	20.786	182.116	176.823	2.117	578.810	-37.792
500	20.787	184.564	177.550	3.156	564.973	-32.790
550	20.789	186.755	178.363	4.196	551.102	-28.787
600	20.811	190.546	180.087	6.275	538.012	-25.548
650	20.890	193.759	181.817	8.360	524.909	-22.849
700	21.081	196.560	183.488	10.457	511.777	-20.363
750	21.437	199.061	185.082	12.582	498.602	-18.003
800	21.989	201.347	186.596	14.751	485.376	-16.902
850	22.738	203.476	188.034	16.986	472.090	-15.412
900	23.660	205.493	189.406	19.305	458.741	-14.095
950	24.710	207.428	190.718	21.722	445.325	-12.923
1000	25.834	209.300	191.979	24.249	431.843	-11.872
1500	26.975	211.121	193.195	26.890	418.295	-10.925
1600	28.082	212.898	194.371	29.643	404.684	-10.066
1700	29.109	214.631	195.512	32.503	390.990	-9.412
1800	30.076	216.322	196.621	35.461	377.236	-8.840
1900	30.811	217.967	197.701	38.504	363.402	-8.314
2000	31.452	219.564	198.755	41.619	349.598	-7.829
2100	31.949	221.111	199.783	44.790	335.830	-7.380
2200	32.305	222.606	200.787	48.004	322.102	-6.963
2300	32.533	224.048	201.767	51.247	308.426	-6.576
2400	32.643	225.435	202.724	54.506	294.802	-6.215
2500	32.653	226.768	203.659	57.772	281.230	-5.877
2600	32.576	228.048	204.573	61.034	267.740	-5.561
2700	32.429	229.275	205.465	64.285	254.340	-5.265
2800	32.224	230.450	206.337	67.518	241.024	-4.986
2900	31.975	231.577	207.188	70.728	227.789	-4.724
3000	31.693	232.656	208.019	73.912	214.631	-4.477
3100	31.387	233.691	208.831	77.066	201.554	-4.244
3200	31.066	234.682	209.623	80.189	188.585	-4.023
3300	30.737	235.633	210.397	83.279	175.700	-3.814
3400	30.405	236.546	211.153	86.336	162.894	-3.616
3500	30.074	237.422	211.891	89.360	150.150	-3.428
3600	29.749	238.265	212.612	92.351	137.460	-3.249
3700	29.431	239.076	213.316	95.310	124.824	-3.079
3800	29.124	239.856	214.004	98.238	112.248	-2.917
3900	28.827	240.609	214.677	101.135	99.730	-2.762
4000	28.543	241.335	215.334	104.004	87.264	-2.614
4100	28.273	242.037	215.977	106.844	74.850	-2.472
4200	28.015	242.715	216.606	109.659	62.484	-2.337
4300	27.771	243.371	217.221	112.448	50.166	-2.207
4400	27.541	244.007	217.822	115.213	37.894	-2.083
4500	27.323	244.623	218.411	117.956	25.564	-1.963
4600	27.119	245.222	218.987	120.678	13.238	-1.849
4700	26.927	245.803	219.552	123.381	1.910	-1.738
4800	26.747	246.368	220.104	126.064	-10.404	-1.632
4900	26.579	246.918	220.646	128.730	-21.841	-1.530
5000	26.422	247.453	221.177	131.380	-33.274	-1.431
5100	26.275	247.975	221.697	134.015	-44.706	-1.336
5200	26.139	248.484	222.208	136.636	-56.136	-1.245
5300	26.012	248.980	222.708	139.243	-67.560	-1.156
5400	25.893	249.463	223.199	141.838	-78.974	-1.071
5500	25.786	249.940	223.681	144.422	-90.378	-0.988
5600	25.686	250.403	224.154	146.996	-101.774	
5700	25.593	250.857	224.618	149.560	-113.160	
5800	25.509	251.301	225.075	152.115	-124.536	
5900	25.431	251.737	225.523	154.662	-135.906	
6000	25.361	252.164	225.963	157.201	-147.274	

CURRENT, September 1983 (1 part)

PREVIOUS.

CURRENT: September 1983 (1 bar)

Barium, Ion (Ba⁺)Ba⁺(g)

Barium Bromide (BaBr)

 $M_r = 217.234$ Barium Bromide (BaBr)BaBr₂(g)

$S^\circ(298.15\text{ K}) = 270.4 \pm 0.4\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ $\Delta H_f^\circ(0\text{ K}) = -101.6 \pm 41.8\text{ kJ}\cdot\text{mol}^{-1}$ $\Delta H_f^\circ(298.15\text{ K}) = -110.6 \pm 41.8\text{ kJ}\cdot\text{mol}^{-1}$

Electronic Levels and Quantum Weights			
State	ϵ_e , cm ⁻¹	g_e	g_e
$X^1\Sigma^+$	0	2	2
$A^1\Pi$	[13000]	2	2
$B^1\Sigma$	[13500]	[4]	[4]
$C^1\Pi_{1/2}$	18650.9	2	[4]
$C_2^1\Pi_{1/2}$	19192.5	2	[2]

$\omega_e X_e = 0.42\text{ cm}^{-1}$ $\sigma = 1$
 $B_e = [0.04052]\text{ cm}^{-1}$ $\alpha_e = [0.000113]\text{ cm}^{-1}$ $r_e = [2.87]\text{ \AA}$

Enthalpy of Formation

The selected value, $\Delta H_f^\circ(0\text{ K}) = -24.3\text{ kcal mol}^{-1}$, is obtained from an analysis of spectroscopic data. Herzberg¹ suggested $D_0^\circ = 2.8\text{ eV}$ for BaBr(g) which was derived from a linear Birge-Sponer extrapolation of the ground state vibrational levels. Our adopted vibrational constants give 2.74 eV by a similar extrapolation. Based on the ionicity correction developed by Hildenbrand,² this value adjusts to 4.14 eV ($95.5\text{ kcal mol}^{-1}$) which is adopted. Gaydon³ has claimed that the spectroscopic data for BaBr(g) are insufficient to obtain a reliable extrapolation. However, our adopted value for D_0° gives $D_0^\circ(\text{BaBr}/\Delta H_f^\circ(\text{BaBr}_2)) = 0.48$ which is quite consistent with values of this ratio for other alkaline earth halide systems.⁴ $\Delta H_f^\circ(298.15\text{ K})$ corresponds to $-26.4\text{ kcal mol}^{-1}$.

Ionic model calculations^{5,6} have led to D_0° values of 4.9 eV^5 and 3.76 eV^6 . The latter result is believed to represent a minimum value. Two other experimental values, which bracket the selected value, have been reported. Flame studies⁷ gave $D_0^\circ = 3.79\text{ eV}$, and chemiluminescence⁸ from reaction of Ba atoms with Br₂ gave a lower limit to D_0° of 4.54 eV . We assign an uncertainty of $\pm 10\text{ kcal mol}^{-1}$ to $\Delta H_f^\circ(0\text{ K})$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous BaBr₂⁹ with $r_e(\text{BaBr})/r_e(\text{BaBr}_2) = 0.96$. This value for the ratio is calculated from bond lengths⁴ for several other alkaline earth halide systems. Two other estimates^{5,6} of r_e agree with the adopted value to within 0.05 \AA . The rotational constant is calculated from the estimated value for r_e . The value of α_e is obtained from a Morse potential function.

The vibrational constants are taken from the compilation of Rosen¹⁰ and are corrected for the natural isotopic abundances of the elements. The observed electronic levels for BaBr(g) are from Rosen.¹⁰ Also included are A, B, G, and H states. Their energies are estimated by analogy with those for SrBr(g).⁵

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Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$									
T/K	C_p°	S°	$-[G^\circ - H^\circ(T)]/T$	$H^\circ - H^\circ(T_r)$	ΔH_f°	ΔG°	$\log K_r$	Standard State Pressure = $p^\circ = 0.1\text{ MPa}$	
0	0.	0.	INFINITE	-10.200	-101.621	-101.621	INFINITE		
100	231.368	302.718	0.	-7.135	-101.651	-118.687	61.996		
200	36.304	255.748	273.762	-3.603	-103.114	-135.193	35.309		
250	36.742	263.900	271.003	-1.776	-104.033	-143.109	29.901		
298.15	36.996	270.395	270.395	0.	-110.587	-149.888	26.260		
300	37.004	270.624	270.396	0.068	-110.641	-150.132	26.140		
350	37.177	276.342	270.847	1.923	-116.558	-155.829	23.256		
400	37.300	281.315	271.852	3.785	-127.181	-159.970	20.890		
450	37.394	285.714	273.152	5.653	-128.011	-164.022	19.039		
500	37.469	289.658	274.609	7.524	-129.106	-167.967	17.547		
600	37.586	296.500	277.704	11.277	-131.834	-175.474	15.276		
700	37.677	302.301	280.814	15.041	-133.755	-182.607	13.626		
800	37.736	307.337	283.822	18.812	-136.187	-189.413	12.367		
900	37.826	311.788	286.687	22.592	-138.196	-195.946	11.372		
1000	37.891	315.777	289.400	26.378	-140.204	-202.255	10.565		
1100	37.954	319.392	291.964	30.170	-150.580	-207.543	9.855		
1200	38.015	322.697	294.390	33.968	-152.819	-212.622	9.255		
1300	38.075	325.742	296.686	37.773	-154.957	-217.518	8.740		
1400	38.136	328.566	298.863	41.583	-157.016	-222.253	8.292		
1500	38.199	331.199	300.932	45.400	-159.017	-226.843	7.899		
1600	38.268	333.666	302.902	49.223	-160.981	-231.300	7.551		
1700	38.343	335.989	304.780	53.054	-162.929	-235.635	7.240		
1800	38.428	338.183	306.576	56.892	-164.882	-239.836	6.960		
1900	38.526	340.263	308.294	60.740	-166.839	-243.967	6.707		
2000	38.639	342.242	309.943	64.598	-168.833	-247.973	6.476		
2100	38.769	344.130	311.526	68.468	-170.975	-251.877	6.265		
2200	38.919	345.937	313.049	72.352	-173.2674	-255.304	5.943		
2300	39.091	347.671	314.517	76.253	-175.711	-257.437	5.619		
2400	39.286	349.338	315.934	80.171	-178.377	-260.403	5.321		
2500	39.504	350.946	317.302	84.111	-181.167	-263.245	5.046		
2600	39.746	352.500	318.626	88.073	-184.076	-265.976	4.790		
2700	40.013	354.005	319.909	92.061	-187.104	-268.600	4.551		
2800	40.304	355.466	321.153	96.076	-190.250	-271.118	4.328		
2900	40.619	356.886	322.361	100.122	-193.519	-273.626	4.118		
3000	40.956	358.268	323.535	104.201	-196.909	-276.128	3.921		
3100	41.314	359.617	324.677	108.314	-200.428	-278.625	3.735		
3200	41.693	360.935	325.789	112.464	-204.076	-281.117	3.559		
3300	42.089	362.223	326.874	116.653	-207.854	-283.601	3.392		
3400	42.502	363.486	327.932	120.883	-211.662	-286.078	3.234		
3500	42.930	364.724	328.966	125.154	-215.500	-288.548	3.083		
3600	43.372	365.940	329.976	129.469	-219.366	-291.012	2.940		
3700	43.824	367.134	330.964	133.829	-223.260	-293.476	2.803		
3800	44.286	368.309	331.932	138.234	-227.183	-295.931	2.672		
3900	44.756	369.466	332.879	142.687	-231.134	-298.378	2.547		
4000	45.231	370.605	333.808	147.186	-235.113	-300.818	2.427		
4100	45.710	371.727	334.719	151.733	-239.126	-303.251	2.312		
4200	46.191	372.835	335.614	156.328	-243.173	-305.678	2.202		
4300	46.673	373.927	336.492	160.971	-247.254	-308.098	2.096		
4400	47.154	375.006	337.355	165.662	-251.369	-310.512	1.995		
4500	47.632	376.071	338.204	170.402	-255.519	-312.921	1.897		
4600	48.106	377.123	339.038	175.189	-259.704	-315.326	1.803		
4700	48.575	378.162	339.860	180.023	-263.924	-317.726	1.712		
4800	49.037	379.190	340.668	184.903	-268.178	-320.121	1.625		
4900	49.491	380.206	341.465	189.830	-272.466	-322.512	1.541		
5000	49.937	381.210	342.250	194.801	-276.788	-324.900	1.460		
5100	50.373	382.203	343.024	199.817	-281.144	-327.285	1.381		
5200	50.798	383.186	343.786	204.876	-285.534	-329.666	1.306		
5300	51.211	384.157	344.539	209.976	-289.958	-332.042	1.233		
5400	51.612	385.118	345.282	215.117	-294.418	-334.414	1.162		
5500	52.001	386.069	346.015	220.298	-298.914	-336.782	1.093		
5600	52.376	387.009	346.738	225.517	-303.446	-339.147	1.027		
5700	52.737	387.939	347.453	230.773	-308.012	-341.508	0.963		
5800	53.084	388.860	348.159	236.064	-312.612	-343.865	0.901		
5900	53.417	389.770	348.856	241.389	-317.246	-346.218	0.841		
6000	53.735	390.670	349.546	246.747	-321.914	-348.568	0.783		

PREVIOUS: December 1974 (1 atm)

CURRENT: December 1974 (1 bar)

Barium Bromide (BaBr)

BaBr₂(g)

Barium Bromide (BaBr₂)

CRYSTAL

 $M_r = 297.138$ Barium Bromide (BaBr₂)BaBr₂(cr)

$S^\circ(298.15 \text{ K}) = [148.5 \pm 4.2] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $T_{\text{fus}} = 1130 \pm 2 \text{ K}$

$\Delta_f H^\circ(0 \text{ K}) = \text{Unknown}$
 $\Delta_f H^\circ(298.15 \text{ K}) = -757.7 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_{\text{aq}} H^\circ = 31.96 \pm 0.63 \text{ kJ} \cdot \text{mol}^{-1}$

Enthalpy of Formation

The selected value is based on results obtained from solution calorimetry performed in aqueous acid media. Ehrlich *et al.*¹ reported measurements of the enthalpies of solution of Ba(cr) and BaBr₂(cr) in HBr(555 H₂O). These results lead to $\Delta_f H^\circ(\text{BaBr}_2, \text{cr}, 298.15 \text{ K}) = -181.1 \pm 0.4 \text{ kcal} \cdot \text{mol}^{-1}$ ($-757.7 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$) when combined with the most recent thermal data^{2,3} for aqueous HBr. This value is adopted and is essentially that ($-181.0 \text{ kcal} \cdot \text{mol}^{-1}$) which has been selected by NBS.⁴

Two independent calorimetric values in $\text{kcal} \cdot \text{mol}^{-1}$ of -180.7^5 and -181.7^6 bracket our adopted value. These values are based on results of early enthalpy of solution measurements^{5,6} which are combined with $\Delta_f H^\circ(\text{Ba}^{2+}, \text{aq}, 298.15 \text{ K}) = -128.5 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta_f H^\circ(\text{Br}^-, \text{aq}, 298.15 \text{ K}) = -29.039 \pm 0.035 \text{ kcal} \cdot \text{mol}^{-1}$. Use of the newly derived value (see BaO(cr) table) for $\Delta_f H^\circ$ of $\text{Ba}^{2+}(\text{aq})$ makes these values less negative by $0.5 \text{ kcal} \cdot \text{mol}^{-1}$.

Heat Capacity and Entropy

C_p° data needed to define $S^\circ(298.15 \text{ K})$ are unavailable. The adopted value $S^\circ(298.15 \text{ K}) = 35.5 \pm 1.0 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is a compromise between several estimates. JANAF⁷ entropies for the other three barium dihalides suggest a value of $S^\circ(298.15 \text{ K})$ near $35.3 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for the bromide. Application of the Berthelot principle⁸ to the process $\text{SrBr}_2(\text{cr}) + \text{Ba}(\text{cr}) \rightarrow \text{BaBr}_2(\text{cr}) + \text{Sr}(\text{cr})$ gives $S^\circ(298.15 \text{ K}) = 36.7 \pm 1.7 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Literature estimates which were considered are (in $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) 35.0^4 , 35.5 ± 5.0^9 , and 38.10^{10} . The adopted C_p° data are obtained from JANAF curve fits of the relative enthalpies (825–1130 K) reported by Efremova and Matizien.¹¹ For 27 enthalpy points the average deviation of the fit is $\pm 0.4\%$; the maximum deviation is -1.0% at 847 K. Two points (1129 and 1130 K) are omitted from the fit, since these points presumably involve pre-melting effects. The derived value of $C_p^\circ(298.15 \text{ K}) = 18.41 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is supported by the value ($18.48 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) obtained from the process $\text{BaCl}_2(\text{cr}) + 2 \text{ KBr}(\text{cr}) \rightarrow \text{BaBr}_2(\text{cr}) + 2 \text{ KCl}(\text{cr})$ with $\Delta C_p^\circ = 0$. Relative enthalpies (487–1126 K) reported in equation form by Janz *et al.*¹² suggest a somewhat lower value ($17.8 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) for C_p° at 298.15 K. Their smoothed enthalpies show deviations from our adopted ones that are generally less than $\pm 0.3\%$ but show maximum deviations of $\pm 1.0\%$ at 500 K and 900 K. The enthalpy measurement of Dworkin and Bredig¹³ at the melting point ($T_{\text{fus}} = 1130 \text{ K}$) is roughly 1% lower than that which is adopted. The values of C_p° above T_{fus} are obtained from the adopted enthalpy equation.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{\text{sub}} H^\circ(298.15 \text{ K})$ is the difference in the values of $\Delta_f H^\circ$ for the gas and crystal at 298.15 K.

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- ¹³A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.* **67**, 697 (1963).

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$			
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\log K_r$
0					
100					
200					
250					
298.15	77.015	148.532	0.000	-757.772	129.295
300	77.053	148.533	0.143	-757.772	128.476
400	79.216	171.471	7.956	-787.455	94.687
500	81.379	189.380	15.986	-786.935	74.129
600	83.542	204.409	24.232	-787.031	60.425
700	85.701	217.449	32.694	-786.122	50.643
800	87.864	229.034	41.372	-785.523	43.313
900	90.027	239.507	50.267	-784.299	37.618
1000	92.190	249.105	59.377	-782.869	33.070
1100	94.353	257.993	68.705	-789.601	29.317
1130.000	95.002	260.540	71.545	--- CRYSTAL ---> LIQUID ---	---
1200	96.512	266.295	78.248	-787.992	26.195
1300	98.675	274.106	88.007	-786.076	23.560
1400	100.839	281.498	97.983	-783.874	21.307
1500	103.002	288.528	108.175	-781.409	19.360

PREVIOUS:

CURRENT: December 1974

Barium Bromide (BaBr₂)BaBr₂(cr)

Ba₂Br₂(l)Barium Bromide (BaBr₂)

LIQUID

Barium Bromide (BaBr₂)

$S^{\circ}(298.15\text{ K}) = [172.108] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 1130 \pm 2 \text{ K}$
 $\Delta_f H^{\circ}(298.15\text{ K}) = [-730.193] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{sub}} H^{\circ} = 31.96 \pm 0.63 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

$\Delta_f H^{\circ}$ of the liquid is calculated from that of the crystal by adding $\Delta_{\text{sub}} H^{\circ}$ and the difference in enthalpy, $H^{\circ}(1130\text{ K}) - H^{\circ}(298.15\text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

C_p° for the liquid is taken equal to $25.06 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ above the assumed glass transition temperature of 800 K. The constant value of C_p° is derived from a curve fit of the relative enthalpies (1134–1963 K) reported by Efremova and Matizena.¹ For 11 enthalpy points the average deviation of the fit is $\pm 0.3\%$, the maximum deviation occurs at 1386 K and amounts to -0.7% . Our adopted value for C_p° is supported by the enthalpy measurements of Dworkin and Bredig² who found $C_p^{\circ}(l) = 25.6 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. A considerably higher value ($31 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) of $C_p^{\circ}(l)$ is obtained from yet another enthalpy study,³ however, these latter measurements extend over a relatively short temperature interval ($\sim 100\text{ K}$) above T_{fus} and are probably insufficient to accurately establish C_p° of the liquid. C_p° data below the glass transition are those of the crystal.

$S^{\circ}(298.15\text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is the value determined in two independent drop-calorimetric investigations.^{1,2} Nine other reported values for T_{fus} lie within 11 K of the adopted value. These other values are 1126 K,^{3,5} 1119 K,^{6,7} 1128 K⁸ and 1120 K.^{9–11}

$\Delta_{\text{sub}} H^{\circ}$ is calculated as the difference between JANAF values for the enthalpies of the liquid and crystal at T_{fus} . Our value for $\Delta_{\text{sub}} H^{\circ}$ is in excellent agreement with another drop-calorimetric value ($\Delta_{\text{sub}} H^{\circ} = 7.63 \text{ kcal}\cdot\text{mol}^{-1}$)² and is further supported by a value ($\Delta_{\text{sub}} H^{\circ} = 7.7 \text{ kcal}\cdot\text{mol}^{-1}$)⁴ obtained by dynamic differential calorimetry. Other published values include (in $\text{kcal}\cdot\text{mol}^{-1}$) 7.75 ± 0.08 ,¹ 7.25 ± 0.19 ,³ 7.15 ± 0.4 ,⁴ and 7.0 .⁵

Vaporization Data

T_{vap} is the temperature at which $\Delta G^{\circ} = 0$ for the process $\text{BaBr}_2(l) = \text{BaBr}_2(g)$ at $p = 1 \text{ bar}$. $\Delta_{\text{vap}} H^{\circ}$ is the corresponding difference in the $\Delta_f H^{\circ}$ values for the gas and liquid at T_{vap} . Petersen and Hutchison¹² calculated $T_{\text{vap}} = 2122 \text{ K}$ ($p = 1 \text{ atm}$) from their measured vapor pressure data which covered the range 1175–1321 K. This value is considered somewhat uncertain due to the rather long extrapolation.

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T/K	Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^{\circ} = 0.1 \text{ MPa}$		$\log K_f$
	C_p°	$S^{\circ} - [G^{\circ} - H^{\circ}(T_r)]/T$	$H^{\circ} - H^{\circ}(T_r)$	$\Delta_f G^{\circ}$	
0					
100					
200					
298.15	77.015	172.108	172.108	-730.193	125.703
300	77.053	172.585	172.109	-730.242	124.914
400	79.216	195.047	175.158	-759.926	92.323
500	81.379	212.956	180.985	-759.406	72.484
600	83.542	227.985	187.598	-759.501	59.260
700	85.701	241.025	194.319	-758.593	49.820
800	87.866	252.610	200.895	-757.994	42.747
800.000	87.866	252.610	200.895		
800.000	104.851	252.610	200.895		
900	104.851	264.959	207.340	-755.179	37.257
1000	104.851	276.007	213.664	-752.375	32.882
1100	104.851	286.000	219.793	-757.949	29.277
1130.000	104.851	288.821	221.589		
1200	104.851	295.123	225.696	-755.398	26.282
1300	104.851	303.516	231.364	-752.756	23.757
1400	104.851	311.286	236.798	-750.045	21.601
1500	104.851	318.520	242.008	-747.287	19.738
1600	104.851	325.287	247.004	-744.504	18.115
1700	104.851	331.643	251.708	-741.717	16.688
1800	104.851	337.637	256.402	-738.950	15.424
1900	104.851	343.306	260.828	-736.225	14.298
2000	104.851	348.684	265.087	-733.565	13.287
2100	104.851	353.799	269.191	-730.993	12.377
2200	104.851	358.677	273.148	-728.053	11.424
2300	104.851	363.338	276.969	-724.890	10.529
2400	104.851	367.800	280.661	-721.572	9.712
2500	104.851	372.081	284.233	-718.302	8.963
2600	104.851	376.193	287.691	-715.074	8.274
2700	104.851	380.150	291.043	-711.818	7.637
2800	104.851	383.963	294.294	-708.529	7.047
2900	104.851	387.643	297.450	-705.216	6.499
3000	104.851	391.197	300.516	-701.882	5.989

PREVIOUS:

CURRENT: December 1974

Barium Bromide (BaBr₂)Ba₂Br₂(l)

Barium Bromide (BaBr₂)

*M*_r = 297.138 Barium Bromide (BaBr₂)

CRYSTAL-LIQUID

Barium Bromide (BaBr₂)

0 to 1130 K crystal
above 1130 K liquid
Refer to the individual tables for details.

PREVIOUS.

CURRENT December 1974

Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa		log K_s	
T/K	C_p° J K ⁻¹ mol ⁻¹	$S^\circ - [G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$ kJ mol ⁻¹	ΔH°	ΔG°
0			0.000	-757.722	-738.000
100			0.143	-757.772	-737.877
200			7.956	-787.435	-725.089
250			15.986	-786.935	-709.575
298.15	77.015	148.532			
300			24.232	-787.031	-694.082
400	77.053	149.009	32.694	-786.122	-678.671
500	79.216	171.471	41.372	-785.523	-663.354
600	81.379	189.380	50.267	-784.299	-648.154
700	83.542	204.409	59.377	-782.869	-633.101
800	85.701	217.449	68.705	-789.602	-617.382
900	87.864	229.034	71.545		
1000	90.027	239.507	103.502		
1100	92.190	249.105	110.842		
1100	94.353	257.993	121.327		
1130.000	95.002	260.540	131.812		
1130.000	104.851	288.821	142.297		
1200		295.123	152.782		
1300	104.851	303.516	163.268		
1400	104.851	311.286	173.753		
1500	104.851	318.520	184.238		
1600	104.851	325.287	194.723		
1700	104.851	331.644	205.208		
1800	104.851	337.637	215.693		
1900	104.851	343.306	226.178		
2000	104.851	348.684	236.663		
2100	104.851	353.799	247.148		
2200	104.851	358.677	257.633		
2300	104.851	363.338	268.119		
2400	104.851	367.800	278.604		
2500	104.851	372.081	289.089		
2600	104.851	376.193	299.574		
2700	104.851	380.150			
2800	104.851	383.963			
2900	104.851	387.643			
3000	104.851	391.197			

CRYSTAL \leftrightarrow LIQUID TRANSITION

	-755.398	-603.794
	-752.756	-591.267
	-750.045	-578.946
	-747.287	-566.821
	-744.504	-554.881
	-741.717	-543.114
	-738.950	-531.512
	-736.225	-520.062
	-733.565	-508.754
	-730.993	-497.577
	-728.503	-481.145
	-726.178	-463.630
	-723.792	-446.248
	-721.428	-428.982
	-719.084	-411.818
	-716.757	-394.742
	-714.444	-377.745
	-712.142	-360.814
	-709.850	-343.942

Barium Bromide (BaBr₂)M_r = 297.138 Barium Bromide (BaBr₂)Ba₂Br₂(g)

$$S^{\circ}(298.15\text{ K}) = [342.1 \pm 8.4] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H^{\circ}(0\text{ K}) = -408.5 \pm 12.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^{\circ}(298.15\text{ K}) = -424.7 \pm 12.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies	
ν , cm ⁻¹	
[160] (1)	
[28] (1)	
[223] (1)	

Ground State Quantum Weight: [1]
 Point Group: C_{2v}
 Bond Distance: Ba-Br = 2.99 ± 0.03 Å
 Bond Angle: Br-Ba-Br = [150 ± 30]°
 Product of Moments of Inertia: $I_A I_B I_C = [3.718284 \times 10^{-112}] \text{ g}^2 \text{ cm}^6$

Enthalpy of Formation

The enthalpy of formation is calculated from the selected value for the enthalpy of vaporization, ($\Delta_{\text{vap}} H^{\circ}(298.15\text{ K}) = 73.04 \pm 0.24 \text{ kcal}\cdot\text{mol}^{-1}$), and the adopted value for $\Delta_f H^{\circ}(l)$. The selected value of $\Delta_{\text{vap}} H^{\circ}$ is obtained from a 3rd law analysis of the vapor pressures for the liquid (1175–1321 K) reported by Peterson and Hutchison.¹² These measurements were made by the Knudsen effusion method on a sample of anhydrous BaBr₂ which had been prepared by direct union of high purity elements. The 2nd law $\Delta_{\text{vap}} H^{\circ} = 73.7 \text{ kcal}\cdot\text{mol}^{-1}$ is in agreement with the 3rd law value; thus, the entropy deviation is small ($\Delta_{\text{vap}} S^{\circ}(2\text{nd law}) - \Delta_{\text{vap}} S^{\circ}(3\text{rd law}) = 0.5 \pm 0.8 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The dominant vapor species is assumed to be the dihalide monomer. This assumption is supported by the fact that negligible concentrations of polymeric species have been observed for some of the other alkaline-earth dihalides by use of mass spectrometry (see CaBr₂(g) table).⁹

A 3rd law analysis of a single sublimation pressure reported by Stock and Heynemann¹³ leads to $\Delta_f H^{\circ}(298.15\text{ K}) = 104.3 \text{ kcal}\cdot\text{mol}^{-1}$. This result suggests a possible uncertainty in the adopted value for $\Delta_f H^{\circ}$ of as much as ± 3 kcal·mol⁻¹. This also brings our value in agreement with the selection (−105 kcal·mol⁻¹) of NBS.⁴

Heat Capacity and Entropy

Experimental evidence which has been presented in favor of a linear or nonlinear structure for BaBr₂ is conflicting. Electron diffraction analysis by Akishin and Spiridonov⁵ showed BaBr₂ to be linear (180 ± 30°). Later studies by Klemperer *et al.*,^{6,7} using electric quadrupole deflection of molecular beams, have shown that this molecule possesses a permanent dipole moment and therefore must be bent. A simple explanation of the observed trends in the geometries of the alkaline-earth dihalides as established by the electric deflection experiments^{6,7} has been presented by Hayes,⁸ and it appears quite likely that BaBr₂ is probably bent. The bond angle is arbitrarily taken to be greater than that for BaCl₂ (100°)⁸ but less than that for BaI₂ (170°).⁸ The bond distance is taken to be that measured in the gas phase by an electron diffraction study of Akishin and Spiridonov.⁵ The principal moments of inertia are: $I_A = 228.6976 \times 10^{-39} \text{ g}\cdot\text{cm}^2$, $I_B = 221.3525 \times 10^{-39} \text{ g}\cdot\text{cm}^2$, and $I_C = 7.3451 \times 10^{-39} \text{ g}\cdot\text{cm}^2$. stretching force constant ($K = 1.117 \times 10^5 \text{ dyne/cm}$) is taken equal to that for BaBr.⁹ The ratio of the stretching to bending force constants is estimated as 125. This value for the ratio is to be compared with that for BaF₂ (93)⁹ and BaCl₂ (1199).⁹ The uncertainty in the adopted value for ν_2 is believed to be no greater than ± 20 cm⁻¹, which corresponds to roughly 1 cal·K⁻¹·mol⁻¹ in the value of $S^{\circ}(298.15\text{ K})$. Other sets¹¹⁻¹³ of estimated vibrational frequencies compare favorably with ours; the maximum deviation is 35 cm⁻¹ in ν_1 .¹¹ The ground state quantum weight of one is assigned by analogy with that for BaCl₂.⁹ Our Gibbs energy functions differ by roughly 2 cal·K⁻¹·mol⁻¹ in the range 298–2000 K from those given by Brewer *et al.*¹¹ However, their values are based on a linear structure for the bromide which now appears to be incorrect.

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Enthalpy Reference Temperature = T _r = 298.15 K									
T/K	C _p ^a	S ^b	−(G ^c − H ^c (T _r))/T	H ^c − H ^c (T _r)	Δ _f H ^c	Δ _f G ^c	log K _r	Standard State Pressure = p ^o = 0.1 MPa	
0	0	0	INFINITE	−15.255	−408.509	−408.509	INFINITE		
100	50.661	282.411	391.997	−10.929	−408.675	−438.123	221.628		
200	53.737	319.525	347.252	−5.545	−410.737	−446.430	116.700		
250	56.566	332.061	343.004	−2.736	−412.082	−455.703	93.214		
298.15	57.029	342.067	342.067	0	−424.676	−462.656	81.055		
300	57.043	342.420	342.068	0.106	−424.762	−462.891	80.597		
350	57.340	351.237	342.764	2.966	−435.999	−467.523	69.774		
400	57.536	358.908	344.313	5.838	−456.527	−469.135	61.263		
450	57.673	365.693	346.319	8.718	−457.265	−470.669	54.634		
500	57.772	371.775	348.566	11.604	−458.270	−472.107	49.321		
550	57.801	377.310	353.339	17.389	−460.827	−474.626	41.320		
600	57.880	382.352	358.133	23.183	−462.587	−476.767	35.759		
650	58.003	388.998	362.768	28.984	−464.865	−478.667	31.254		
700	58.067	395.835	367.181	34.789	−466.731	−480.280	27.875		
1000	58.092	411.934	371.357	40.597	−468.603	−481.685	23.161		
1100	58.111	417.492	375.304	46.407	−478.853	−482.083	22.892		
1200	58.125	422.549	379.033	52.219	−480.975	−482.282	20.993		
1300	58.136	427.202	382.562	58.032	−483.005	−482.308	19.379		
1400	58.145	431.511	385.906	63.846	−484.965	−482.180	17.990		
1500	58.152	435.522	389.082	69.661	−486.877	−481.915	16.782		
1600	58.158	439.276	392.103	75.477	−488.763	−481.572	15.720		
1700	58.163	442.802	394.983	81.293	−490.646	−481.012	14.780		
1800	58.167	446.126	397.732	87.109	−492.547	−480.390	13.941		
1900	58.171	449.271	400.363	92.926	−494.490	−479.662	13.187		
2000	58.174	452.255	402.884	98.743	−496.498	−478.830	12.506		
2100	58.176	455.094	405.303	104.561	−498.504	−477.896	11.887		
2200	58.178	457.800	407.628	110.378	−500.628	−476.831	11.194		
2300	58.180	460.386	409.866	116.196	−502.835	−475.644	10.533		
2400	58.182	462.862	412.023	122.015	−505.122	−474.377	9.925		
2500	58.183	465.237	414.104	127.833	−507.491	−473.043	9.363		
2600	58.185	467.520	416.115	133.651	−509.940	−471.650	8.844		
2700	58.186	469.715	418.060	139.470	−512.478	−470.211	8.361		
2800	58.187	471.832	419.943	145.288	−515.098	−468.730	7.911		
2900	58.188	473.873	421.768	151.107	−517.801	−467.205	7.490		
3000	58.189	475.846	423.537	156.926	−520.588	−465.636	7.095		
3100	58.190	477.754	425.256	162.744	−523.444	−464.021	6.724		
3200	58.190	479.602	426.925	168.564	−526.365	−462.358	6.375		
3300	58.191	481.392	428.549	174.383	−529.353	−460.645	6.045		
3400	58.191	483.129	430.129	180.202	−532.407	−458.883	5.732		
3500	58.192	484.816	431.667	186.021	−535.530	−457.073	5.436		
3600	58.192	486.456	433.167	191.840	−538.724	−455.219	5.156		
3700	58.193	488.050	434.628	197.660	−542.000	−453.325	4.888		
3800	58.193	489.602	436.055	203.479	−545.366	−451.391	4.634		
3900	58.194	491.113	437.447	209.298	−548.822	−449.420	4.391		
4000	58.194	492.587	438.807	215.118	−552.369	−447.423	4.160		
4100	58.194	494.024	440.137	220.937	−556.007	−445.398	3.938		
4200	58.195	495.426	441.436	226.757	−559.726	−443.338	3.726		
4300	58.195	496.793	442.708	232.576	−563.527	−441.243	3.523		
4400	58.195	498.133	443.953	238.396	−567.410	−439.115	3.328		
4500	58.195	499.441	445.171	244.215	−571.377	−436.956	3.141		
4600	58.196	500.720	446.365	250.035	−575.422	−434.765	2.961		
4700	58.196	501.972	447.535	255.854	−579.546	−432.543	2.789		
4800	58.196	503.197	448.682	261.674	−583.750	−430.290	2.622		
4900	58.196	504.397	449.806	267.493	−588.035	−428.006	2.462		
5000	58.196	505.573	450.913	273.313	−592.400	−425.694	2.308		
5100	58.197	506.725	451.993	279.133	−596.845	−423.357	2.159		
5200	58.197	507.855	453.057	284.952	−601.370	−420.994	2.015		
5300	58.197	508.964	454.101	290.772	−606.000	−418.608	1.876		
5400	58.197	510.052	455.127	296.592	−610.733	−416.194	1.742		
5500	58.197	511.119	456.136	302.412	−615.570	−413.753	1.612		
5600	58.197	512.168	457.127	308.231	−620.514	−411.286	1.486		
5700	58.198	513.198	458.101	314.051	−625.565	−408.794	1.364		
5800	58.198	514.210	459.060	319.871	−630.733	−406.274	1.246		
5900	58.198	515.203	460.003	325.691	−636.019	−403.728	1.132		
6000	58.198	516.183	460.932	331.510	−641.422	−401.159	1.021		

PREVIOUS: December 1974 (1 atm)

CURRENT: December 1974 (1 bar)

Barium Bromide (BaBr₂)Ba₂Br₂(g)

Barium Chloride (BaCl)

IDEAL GAS

$$M_r = 172.783$$

Barium Chloride (BaCl)

Ba₂Cl₂(g)

$$\Delta H_f^\circ(0 \text{ K}) = -140.6 \pm 12.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(298.15 \text{ K}) = -142.3 \pm 12.6 \text{ kJ mol}^{-1}$$

State	Electronic Levels and Quantum Weights	ϵ , cm ⁻¹	g	ϵ , cm ⁻¹	g
X ² Σ ⁺	0.0	2	D ² Σ ⁺	25471.5	2
A ² Π	10351.1	2	E ² Σ ⁺	27064.6	2
B ² Σ ⁺	10995.3	2	F ² Σ ⁺	29493.6	2
C ² Π	11880.0	2	G ² Σ ⁺	32511.4	2
	19062.9	2			
	19450.1	2			

$$\omega_e = 277.9 \text{ cm}^{-1}$$

$$B_e = [0.08518 \pm 0.003] \text{ cm}^{-1}$$

$$\alpha_e = [0.00035] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = [2.65 \pm 0.05] \text{ Å}$$

Enthalpy of Formation

ΔH_f° is based mainly on two sets of gas-phase equilibria measured mass spectrometrically by Hildenbrand¹ and, to a lesser extent, on the analogous data of Potter *et al.*² Analyses of the mass-spectrometric data^{1,2} are summarized below. The results from Potter *et al.*² and Zmbov³ are less negative by about 4 kcal mol⁻¹, suggesting the approximate uncertainty in ΔH_f° from the adopted ΔH_f° we derive $D_0^\circ = 106.4 \pm 3$ kcal mol⁻¹. Independent methods yield $D_0^\circ = 103 \pm 5$,⁴ ≈ 110 ,⁵ 106.8 ± 2 ,⁶ and 105 ± 6 kcal mol⁻¹.

Electron-impact data⁷ gave $D_0^\circ(\text{ClBa-Cl}) = 115.8 \pm 3.3$ kcal mol⁻¹, and we use $\Delta H_f^\circ(\text{BaCl}_2) = 219 \pm 4$ kcal mol⁻¹ to derive $D_0^\circ = 103 \pm 5$ kcal mol⁻¹. Chemiluminescence from crossed beams of Ba atoms with Cl₂ gave an approximate lower limit to D_0° of 110 kcal mol⁻¹.⁸ Flame studies⁹ gave $D_0^\circ = 106.8 \pm 2$ kcal mol⁻¹ and $D_0^\circ(\text{ClBa-Cl}) = 114 \pm 4$; we derive $D_0^\circ = 105 \pm 6$ kcal mol⁻¹ from the latter value using $\Delta H_f^\circ(\text{BaCl}_2) = 219$ kcal mol⁻¹. Ryabova⁶ considered the flames to involve BaCl₂, BaOHCl, and BaOH as well as BaCl. Schofield and Sugden¹⁰ inferred that the flames involved mainly BaCl₂ rather than BaCl as assumed in earlier flame studies. Gaydon¹¹ discounted the values derived from electronic spectra, but Hildenbrand¹ showed that ionicity corrections bring the Birge-Sponer extrapolation into reasonable agreement with D_0° .

Source	Reaction ^a	T/K	$\Delta H_f^\circ(298.15 \text{ K})$, kcal mol ⁻¹	$\Delta H_f^\circ(298.15 \text{ K})$, kcal mol ⁻¹	D_0°
(1)	A	1234-1380	3.3 ± 3.6	6.76 ± 0.8	-34.82 ± 2.2
(2)	A	1507-1702	13.0 ± 5.4	13.34 ± 1.0	-31.53 ± 2.2
(3) ^b	A	974-1052	21.8 ± 9.4	5.89 ± 1.3	-30.26 ± 2.2
(1)	B	1234-1380	10.3 ± 5.1	13.21 ± 1.1	-34.29 ± 2.6
(2)	B	1507-1702	9.7 ± 7.3	17.72 ± 1.5	-29.78 ± 2.8

^aReactions: (A) Ba(g) + BaCl₂(g) → 2BaCl(g); (B) Ba(g) + AlCl₃(g) → BaCl(g) + Al(g).

^bData given in Table 2³ are assumed to be $10^3 \times K_p$ instead of $10^4 \times K_p$.

Heat Capacity and Entropy

Electronic levels and vibrational constants are taken from the review of Rosen.⁹ The level at 10351.1 cm⁻¹ is T_0 rather than T_e . Vibrational constants are adjusted for natural isotopic abundances. B_e is calculated from r_e which is estimated by comparison of the bond lengths of MX₂(M=Mg, Ca, Sr, Ba and X=F, Cl) with those of MgCl, CaCl and MF(M=Mg, Ca, Sr, Ba). The value of α_e is estimated from the Morse potential function.

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T/K	C _p ^a	S ^b - [G ^c - H ^c (T)]/T	H ^c - H ^c (T)	ΔH ^c	ΔG ^c	log K _r
0	0	INFINITE	INFINITE	INFINITE	INFINITE	INFINITE
100	31.691	221.045	-9.878	-140.631	-140.631	INFINITE
200	35.235	244.313	-6.904	-140.812	-150.058	78.382
250	35.986	252.623	-3.526	-141.498	-159.035	41.536
298.15	36.436	258.643	-1.744	-141.864	-163.379	34.136
300	36.450	258.668	0	-142.256	-167.488	29.343
350	36.757	264.512	0.067	-142.272	-167.644	29.189
400	36.973	269.435	1.898	-142.747	-171.837	25.645
450	37.132	273.799	3.742	-143.350	-175.953	22.977
500	37.256	277.718	5.594	-144.162	-179.983	20.892
600	37.438	284.528	7.454	-145.241	-183.907	19.213
700	37.570	290.309	11.189	-147.944	-191.378	16.661
800	37.676	295.333	14.940	-149.844	-198.478	14.811
900	37.763	299.764	18.703	-152.258	-205.255	13.402
1000	37.846	303.759	22.475	-154.253	-211.760	12.290
1100	37.921	307.370	26.255	-156.247	-218.043	11.389
1200	37.995	310.673	30.044	-158.610	-223.306	10.604
1300	38.072	313.717	33.840	-160.837	-228.361	9.940
1400	38.156	316.541	37.643	-163.007	-233.235	9.371
1500	38.252	319.177	41.454	-165.107	-237.948	8.878
1600	38.364	321.649	45.275	-167.132	-242.517	8.445
1700	38.496	324.979	49.105	-169.082	-246.955	8.062
1800	38.652	328.184	52.948	-170.932	-251.273	7.721
1900	38.835	331.278	56.805	-172.698	-255.476	7.414
2000	39.046	334.275	60.679	-174.384	-259.576	7.136
2100	39.287	337.186	64.589	-176.002	-263.571	6.884
2200	39.557	340.020	68.489	-177.552	-267.467	6.653
2300	39.856	342.785	72.431	-179.032	-271.261	6.431
2400	40.183	345.488	76.402	-180.443	-274.958	6.219
2500	40.535	348.135	80.439	-181.798	-278.561	6.015
2600	40.909	350.732	84.539	-183.098	-282.077	5.819
2700	41.304	353.284	88.511	-184.348	-285.503	5.631
2800	41.716	355.793	92.472	-185.548	-288.842	5.450
2900	42.143	358.264	96.423	-186.698	-292.098	5.276
3000	42.581	360.700	100.366	-187.798	-295.269	5.109
3100	43.027	363.104	104.302	-188.846	-298.352	4.955
3200	43.478	365.477	108.232	-189.846	-301.347	4.801
3300	43.933	367.822	112.157	-190.798	-304.253	4.646
3400	44.393	370.140	116.078	-191.698	-307.077	4.491
3500	44.859	372.433	120.000	-192.548	-309.819	4.336
3600	45.287	374.703	123.915	-193.348	-312.477	4.181
3700	45.728	376.950	127.825	-194.098	-315.053	4.026
3800	46.161	379.175	131.730	-194.798	-317.547	3.871
3900	46.585	381.380	135.625	-195.448	-320.000	3.716
4000	46.998	383.564	139.510	-196.048	-322.413	3.561
4100	47.399	385.730	143.385	-196.598	-324.787	3.406
4200	47.787	387.877	147.250	-197.098	-327.121	3.251
4300	48.162	389.995	151.105	-197.548	-329.415	3.096
4400	48.523	392.084	154.950	-197.948	-331.669	2.941
4500	48.869	394.144	158.785	-198.298	-333.883	2.786
4600	49.200	396.189	162.610	-198.598	-336.057	2.631
4700	49.516	398.210	166.425	-198.848	-338.191	2.476
4800	49.817	399.206	170.230	-199.048	-340.287	2.321
4900	50.103	399.176	174.025	-199.198	-342.343	2.166
5000	50.374	399.121	177.810	-199.298	-344.359	2.011
5100	50.631	399.041	181.585	-199.348	-346.335	1.856
5200	50.873	398.937	185.350	-199.348	-348.271	1.701
5300	51.101	398.808	189.105	-199.298	-350.167	1.546
5400	51.315	398.653	192.850	-199.198	-352.023	1.391
5500	51.515	398.473	196.585	-199.048	-353.839	1.236
5600	51.703	398.269	200.310	-198.848	-355.615	1.081
5700	51.878	398.041	204.025	-198.598	-357.351	0.926
5800	52.040	397.787	207.730	-198.298	-359.047	0.771
5900	52.191	397.507	211.425	-197.948	-360.703	0.616
6000	52.331	397.191	215.110	-197.548	-362.319	0.461

PREVIOUS: December 1972 (1 atm)

CURRENT: December 1972 (1 bar)

Barium Chloride (BaCl)

Ba₂Cl₂(g)

Ba₁Cl₂(cr)

Barium Chloride (BaCl_2)

CRYSTAL(α - β)

Barium Chloride (BaCl_2)

$$\begin{aligned} \Delta_f H^\circ(\text{O K}) &= -859.17 \pm 13 \text{ (or } \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta_f H^\circ(298.15 \text{ K}) &= -838.6 \pm 13 \text{ (or } \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1} \\ T_{\text{eq}} &= 1198 \pm 1 \text{ K } (\alpha \rightarrow \beta) \\ T_{\text{eq}} &= 1235 \pm 1 \text{ K } (\beta \rightarrow \gamma) \\ \Delta_{\text{vap}} H^\circ &= 16.90 \pm 0.21 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta_{\text{sub}} H^\circ &= 15.991 \pm 0.33 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Enthalpy of Formation

ΔH_f° is from NBS Technical Note 270-6¹ and its selection was discussed in detail by Parker.² The adopted value was derived by Ehrlich *et al.*³ from their measurements of ΔH_{aq}° of BaCr and BaCl₂Cr in HCl (550 H₂O). Earlier solution data for Ba²⁺ and BaCl₂⁶ are in good agreement,⁷ but a recent study by Vorob'ev *et al.*⁷ of Ba in HCl (240 and 400 H₂O) yields $\Delta H_f^\circ = -201.8$ kcal mol⁻¹. The deviation (+3.4 kcal mol⁻¹) from the adopted value is confirmed by direct measurements⁸ of ΔH_f° and $\Delta_{aq}H^\circ$ of BaH₂Cr, yielding -202.1 kcal mol⁻¹ for BaH₂Cr (340 H₂O). All authors reported difficulties in obtaining or maintaining Ba and BaH₂ free of impurities; this provides conceivable reasons for the bias in either of the opposing results. We assign an uncertainty of ± 3 kcal mol⁻¹ to include the possibility that Vorob'ev *et al.*⁷ are correct but add an alternative of ± 0.6 kcal mol⁻¹ if their data are biased.

Parker rejected $\Delta H_f^\circ = -219.3 \text{ kcal mol}^{-1}$ obtained by direct chlorination and $\Delta H_f^\circ = -212.0 \text{ kcal mol}^{-1}$ which would be based on Maht's direct combustion.⁹ Parker noted that these more negative values are incompatible with data for BaO_2 , $\text{BaO}(\text{OH})_2$, and BaCO_3 . They are also incompatible with calorimetric data for BaH_2 noted above and equilibrium data on the tables for $\text{BaCl}_2(\text{l})$ and BaO .

Heat Capacity and Entropy

C_p° is based on adiabatic calorimetry (6–346 K) of Goodman and Westrum.¹⁰ S° is calculated from C_p° using $S^\circ(6\text{ K}) = 0.012\text{ cal K}^{-1}\text{ mol}^{-1}$. C_p° above 300 K is from constrained fitting of enthalpy data (340–1197 K for α -phase and 1201–1231 K for β -phase) measured in an ice calorimeter by Gardner and Taylor.¹¹ The sample studied at high temperatures was a portion of that used at low temperatures. Deviations of the H data¹¹ from the adopted values are $\pm 0.1\%$ for most points but show a maximum of -0.3% for two points near 400 K.

Other enthalpy studies include those of Dworkin and Bredig,¹² Janz et al.,¹³ and Gant.¹⁴ Deviations from the adopted values are about +2% for the smooth values (-1100 – 1230 K), ± 1.8 to $\pm 2.9\%$ for the equations (892 – 1235 K) of, and -1.7 to $+6.7\%$ for the data (406 – 1230 K) of Popov and Gal'chenko.¹⁵ The deviations from the adopted values are about +2% for the smooth values (-1100 – 1230 K), ± 1.8 to $\pm 2.9\%$ for the equations (892 – 1235 K) of, and -1.7 to $+6.7\%$ for the data (406 – 1230 K) of Popov and Gal'chenko.¹⁵ The deviations from the adopted values are about +2% for the smooth values (-1100 – 1230 K), ± 1.8 to $\pm 2.9\%$ for the equations (892 – 1235 K) of, and -1.7 to $+6.7\%$ for the data (406 – 1230 K) of Popov and Gal'chenko.¹⁵

Transition Data

$T_m = 1198$ K is from the enthalpy study of Gardner and Taylor.¹¹ Other enthalpy studies gave 1193¹² and 1198 K,¹³ while thermal analysis gave 1199¹⁶ and 1197 K.¹⁷ $\Delta_{\text{vap}}H^\circ$ is calculated from our adopted fits of the enthalpy data.¹¹ Published values include 4.04,¹¹ 4.10¹² and 4.15 ± 0.16 .¹³

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

References

- References
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Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa			
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$ $J \cdot K^{-1} \cdot mol^{-1}$	$H^\circ - H^\circ(T_r)$ $kJ \cdot mol^{-1}$	$\Delta_f H^\circ$	$\log K_f$
0	0.000	INFINITE	-16.707	-859.171	INFINITE
100	56.961	49.346	-13.783	-860.857	440.590
200	71.038	94.429	-7.199	-859.856	215.839
298.15	75.140	123.666	0.000	-858.557	141.959
300	75.195	124.131	0.139	-858.533	141.032
400	77.329	146.082	7.774	-857.284	103.685
500	78.857	163.505	13.585	-856.963	81.300
600	80.425	178.018	23.547	-857.255	762.428
700	82.233	190.548	31.678	-856.611	746.684
800	84.299	201.661	40.003	-856.313	730.992
900	86.624	211.721	48.546	-855.396	715.380
1000	89.471	220.988	57.345	-854.241	699.882
1100	93.531	229.692	66.480	-861.132	683.694
1198.010	100.015	237.924	75.937	ALPHA \leftrightarrow BETA TRANSITION	32.466
1198.010	123.846	252.033	92.840	-842.429	29.063
1200	123.846	252.239	93.087	----- BETA \leftrightarrow LIQUID	---
1235.000	123.846	255.799	176.915	-837.859	26.249
1300	123.846	262.152	105.472	-653.284	23.851
1400	123.846	271.330	117.856	-639.260	21.784
1500	123.846	279.874	130.241	-625.569	19.986
1600	123.846	287.867	142.625	-612.191	18.408
1700	123.846	295.375	155.010	-598.105	16.404
1800	123.846	302.454	167.595	-584.402	15.717
1900	123.846	309.150	179.779	-569.756	15.174
2000	123.846	315.503	192.164	-561.459	14.664

PREVIOUS:

CURRENT: December 1972

Barium Chloride (BaCl₂)

Ba₁Cl₂(cr)

Barium Chloride (BaCl₂)

Barium Chloride (BaCl₂)

$M_r = 208.236$

LIQUID

Barium Chloride (BaCl₂)

$S^\circ(298.15\text{ K}) = [143.518] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 1235 \pm 1 \text{ K}$
 $\Delta_f H^\circ(298.15\text{ K}) = [-832.467] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{vap}} H^\circ = 15.991 \pm 0.33 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

$\Delta_f H^\circ$ is calculated from that of the crystal by addition of $\Delta_{\text{vap}} H^\circ$ and the difference in enthalpy, $H^\circ(1235\text{ K}) - H^\circ(298.15\text{ K})$, between crystal and liquid. Independent values of $\Delta_f H^\circ$ for liquid (and crystal) may be derived from equilibrium data^{1,2} for $\text{CaO} + \text{BaCl}_2(\text{l}) \rightarrow \text{BaO} + \text{CaCl}_2(\text{l})$. Our 3rd-law analysis is summarized below; it shows that the data of Feschotte-Ostertag¹ are consistent with the adopted $\Delta_f H^\circ(\text{cr}) = -205.2 \text{ kcal}\cdot\text{mol}^{-1}$ from Ehrlich *et al.* (cf. BaCl_2 , cr), while the data of Peterson and Hinklebein² are more consistent with the alternative $\Delta_f H^\circ(\text{cr}) = -201.8 \text{ kcal}\cdot\text{mol}^{-1}$ from Vorob'ev *et al.* Both are incompatible with $\Delta_f H^\circ(\text{cr}) = -219.3$ from direct chlorination and $\Delta_f H^\circ(\text{cr}) = -212.0$ derived from Mah's $\Delta_f H^\circ$ value for $\text{BaO}(\text{cr})$.

Source	Remarks	T/K	δS $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ(298.15\text{ K})$ $\text{kcal}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ(\text{l})$ $\text{kcal}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ(\text{cr})$ $\text{kcal}\cdot\text{mol}^{-1}$
1	Direct measurement	1273	13.24 ± 1.6	-198.3 ± 2	-204.5 ± 2	
2	Indirect via SrCl_2	1273	14.12 ± 1.8	-199.1 ± 2	-205.4 ± 2	
3	Direct measurement	1173–1223	-2.5 ± 8.1	11.47 ± 0.6	-196.5 ± 1	-202.7 ± 1

Heat Capacity and Entropy

The constant $C_p^\circ = 26.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is based on enthalpy data (1238–1347 K) measured in an ice calorimeter by Gardner and Taylor.³ Deviations of the data from the adopted fit are all less than 0.05%. Smoothed enthalpies of Dworkin and Bredig⁴ deviate by +1.2% and those of Janz *et al.*⁵ by +2.7 to 2.1%. Enthalpy data of Gant⁶ deviate by +1.5%. C_p° is taken equal to that of the crystal from 298 to 800 K, the assumed glass transition. S° is calculated in a manner analogous to that used for $\Delta_f H^\circ$.

Fusion Data

T_{fus} is from the enthalpy study of Gardner and Taylor.³ Some other reported values include 1233⁴ and 1235 K⁵ from enthalpy studies and 1234⁷ and 1235 K⁸ from thermal analysis. $\Delta_{\text{vap}} H^\circ$ is obtained from the difference in the adopted enthalpy fits for liquid and β -phases. Published values include 3.82,³ 3.90⁴ and $4.13 \pm 0.12^5 \text{ kcal}\cdot\text{mol}^{-1}$.

Vaporization Data

T_{vap} is calculated as the temperature at which $\Delta_r G^\circ = 0$ for $\text{BaCl}_2(\text{l}) \rightarrow \text{BaCl}_2(\text{g})$ at $p=1$ bar. $\Delta_{\text{vap}} H^\circ$ is calculated as the corresponding $\Delta_f H^\circ$.

References

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- ⁸K. Grjotheim, H. G. Nebell and J. Krogh-Moe, Acta Chem. Scand. 22, 1159 (1968).

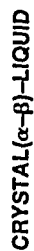
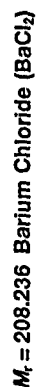
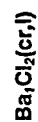
T/K	C_p°	S° $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$-[G^\circ - H^\circ(T)]/T$	Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$		
				$H^\circ - H^\circ(T)$	$\Delta_f H^\circ$	$\log K_r$
0						
100						
200						
298.15	75.140	143.518	143.518	0.000	-832.467	138.426
300	75.195	143.983	143.520	0.139	-789.857	137.526
400	77.329	165.934	146.898	7.774	-775.846	101.315
500	78.837	183.537	152.187	15.585	-762.052	79.611
600	80.425	197.869	158.624	23.547	-748.249	65.141
700	82.233	210.399	165.145	31.678	-734.491	54.808
800	84.299	221.512	171.509	40.003	-720.784	47.062
800.010	84.299	221.513	171.509	40.004		
800.010	108.784	221.513	171.509	40.004		
900	108.784	234.325	177.791	50.881	-826.972	41.051
1000	108.784	245.786	184.027	61.759	-823.737	36.260
1100	108.784	256.155	190.120	72.638	-828.885	32.317
1200	108.784	265.620	196.023	83.516	-825.911	29.043
1235.000	108.784	268.748	198.040	87.374		
1300	108.784	274.328	201.716	94.595	-822.847	26.282
1400	108.784	282.389	207.194	105.273	-819.715	23.925
1500	108.784	289.895	212.460	116.151	-816.536	21.890
1600	108.784	296.915	217.522	127.030	-813.330	20.116
1700	108.784	303.510	222.388	137.908	-810.118	18.557
1800	108.784	309.728	227.069	148.787	-806.921	17.177
1900	108.784	315.610	231.576	159.665	-803.761	15.947
2000	108.784	321.190	235.918	170.543	-800.659	14.844
2100	108.784	326.497	240.106	181.422	-797.639	13.850
2200	108.784	331.558	244.149	192.300	-794.642	12.822
2300	108.784	336.394	248.055	203.179	-791.614	11.860
2400	108.784	341.023	251.833	214.057	-788.562	10.981
2500	108.784	345.464	255.490	224.935	-785.496	10.175
2600	108.784	349.731	259.033	235.814	-782.416	9.434
2700	108.784	353.856	262.469	246.692	-779.324	8.749
2800	108.784	357.793	265.803	257.571	-776.224	8.115
2900	108.784	361.610	269.041	268.449	-773.116	7.527
3000	108.784	365.298	272.189	279.327	-770.001	6.979

PREVIOUS

CURRENT: December 1972

Barium Chloride (BaCl₂)

Barium Chloride (BaCl₂)



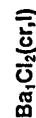
0 to 1198 K crystal, alpha
1198 to 1235 K crystal, beta
above 1235 K liquid

Refer to the individual tables for details.

T/K	Enthalpy Reference Temperature = T _r = 298.15 K			Standard State Pressure = p° = 0.1 MPa		
	C _p J·K ⁻¹ ·mol ⁻¹	S° J·K ⁻¹ ·mol ⁻¹	-(G°-H°(T _r))/T _r	H°-H°(T _r) kJ·mol ⁻¹	Δ _r H° kJ·mol ⁻¹	log K _r
0	0.000	0.000	INFINITE	-16.707	-859.171	INFINITE
90	56.961	49.346	187.175	-13.783	-860.857	440.590
200	71.038	94.429	130.426	-7.199	-859.856	215.839
298.15	75.140	123.666	123.666	0.000	-858.557	141.959
300	75.195	124.131	123.668	0.139	-858.533	141.032
400	77.329	146.082	126.646	7.774	-857.384	103.685
500	78.857	163.505	132.335	15.585	-856.963	81.300
600	80.425	178.018	138.772	23.547	-857.255	66.375
700	82.233	190.548	145.293	31.678	-856.611	55.718
800	84.299	201.661	151.657	40.003	-856.313	47.729
900	86.624	211.721	157.780	48.546	-855.396	41.520
1000	89.471	220.988	163.643	57.345	-854.241	36.558
1100	93.531	229.692	169.256	66.480	-861.132	32.466
1198.010	100.015	237.924	174.538	75.937	ALPHA <- -> BETA TRANSITION	—
1198.010	123.846	252.033	174.538	92.840	—	—
1200	123.846	252.239	174.666	93.087	-842.429	29.063
1235.000	123.846	255.799	176.915	97.422	BETA <- -> LIQUID TRANSITION	—
1235.000	108.784	268.748	176.915	113.413	—	—
1300	108.784	274.328	181.648	120.484	-822.847	26.282
1400	108.784	282.389	188.559	131.362	-819.715	23.925
1500	108.784	289.895	195.068	142.241	-816.536	21.890
1600	108.784	296.915	201.216	153.119	-813.330	20.116
1700	108.784	303.510	207.041	163.997	-810.118	18.557
1800	108.784	309.728	212.575	174.876	-806.921	17.177
1900	108.784	315.610	217.845	185.754	-803.761	15.947
2000	108.784	321.190	222.874	196.633	-800.659	14.844
2100	108.784	326.497	227.683	207.511	-797.639	13.850
2200	108.784	331.558	232.290	218.389	-794.642	12.822
2300	108.784	336.394	236.712	229.268	-791.615	11.860
2400	108.784	341.023	240.963	240.146	-788.532	10.981
2500	108.784	345.464	245.054	251.025	-785.396	10.175
2600	108.784	349.731	248.999	261.903	-782.163	9.434
2700	108.784	353.836	252.806	272.781	-778.879	8.749
2800	108.784	357.793	256.486	283.660	-775.521	8.115
2900	108.784	361.610	260.045	294.538	-772.133	7.527
3000	108.784	365.298	263.492	305.417	-768.694	6.979

PREVIOUS:

CURRENT: December 1972



Barium Chloride (BaCl₂)

IDEAL GAS

$$M_r = 208.236$$

Barium Chloride (BaCl₂)Ba₂Cl₂(g)

$$S^\circ(298.15\text{ K}) = 325.74 \pm 5.0\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(0\text{ K}) = -497.3 \pm 17(\text{or } \pm 6.7)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15\text{ K}) = -498.7 \pm 17(\text{or } \pm 6.7)\text{ kJ}\cdot\text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies ν , cm ⁻¹	
255 (1)	[36] (1) 265 (1)

Ground State Quantum Weight: [1]
 Point Group: C_{2v}
 Bond Distance: Ba-Cl = 2.82 ± 0.03 Å
 Bond Angle: Cl-Ba-Cl = [100 ± 20]°
 Product of the Moments of Inertia: $I_A I_B I_C = 1.128013 \times 10^{-112}\text{ g}\cdot\text{cm}^6$

Enthalpy of Formation

$\Delta_f H^\circ(298.15\text{ K})$ is calculated from $\Delta_f H^\circ(\text{cr})$ by addition of $\Delta_{\text{sub}} H^\circ = 86.0 \pm 1.5\text{ kcal}\cdot\text{mol}^{-1}$ derived from 3rd law analysis of the vapor-pressure equation of Hildenbrand *et al.*^{1,2} The equation¹ summarized five torsion-effusion runs (83 total points) and is reasonably consistent with five boiling pressures in the mmHg range measured by Novikov.³ Other vapor pressure data⁴⁻⁶ reviewed below are considered less reliable. $\Delta_f H^\circ(\text{g})$ is assigned alternative uncertainties to reflect the discrepancies in $\Delta_f H^\circ(\text{cr})$. Equilibria derived from flame studies⁷ yield $\Delta_f H^\circ(\text{g}) = -119.1 \pm 3$ and $\Delta_f H^\circ(\text{cr}) = -205.1 \pm 3\text{ kcal}\cdot\text{mol}^{-1}$, which confirm the adopted values by an independent path. Mass spectra⁸ at 1230 K showed that the saturated vapor consists predominantly of BaCl₂ with considerably less than 1% of dimer.

Source	Method	Points	7/K	$\Delta_{\text{sub}} H^\circ(298.15\text{ K})$, kcal·mol ⁻¹	8S
(1) ²	Torsion effusion	83 ^a	1235–1440	85.1	–0.7
(1)	Boiling Point	5	1588–1710	75.6 ± 4.2	86.30 ± 0.7
(4)	Effusion	3	1244–1277	78.5 ± 1.6	–6.4 ± 2.5
(5)	Boiling point	1	1819	85.3 ± 0.2	–5.4 ± 1.3
(6)	Static	4	1343–1487	85.4 ± 3.8	>81
(7)	Flame K_p	8	2134–2535	–9.5 ± 8.7 ^b	6.1 ± 2.7
					1.7 ± 3.7

^aPressures obtained from an equation summarizing 5 runs (83 total points).

^b $\Delta_f H^\circ$ for Ba(g) + 2 HCl(g) → BaCl₂(g) + 2 H(g) yields $\Delta_f H^\circ(298.15\text{ K}) = 119.1 \pm 3\text{ kcal}\cdot\text{mol}^{-1}$

Heat Capacity and Entropy

Vibrations ν_1 and ν_2 are the values quoted by Hildenbrand⁹ and derived from IR spectra of molecules in matrix isolation.¹⁰ The bending mode was not observed; its value was calculated¹⁰ from force-constant correlations as described for BaF₂.¹¹ Hastie *et al.*¹² assigned the bending mode to a band which they observed at 61 cm⁻¹ in argon and 62 cm⁻¹ in neon. This value would reduce S° by about 1.0 cal·K⁻¹·mol⁻¹. Our assigned uncertainty includes this possibility. Agreement is better for $\nu_1 = 255^{10}$ or 262 cm⁻¹ (in Ne)¹² and for $\nu_2 = 265 \pm 5$ (gas)¹³, 260¹⁰ or 268 cm⁻¹ (in Ne).¹² We adopt the gas-phase value¹³ for ν_2 .

Bond length is from gas-phase electron diffraction¹⁴ which also gave the bond angle 180° ± 40°. Later studies¹⁵ of electric and magnetic deflection of molecular beams revealed a permanent electric dipole moment and suggested a bond angle of the order of roughly 120°. Hastie *et al.*¹² estimated an angle of 120° ± 10° from relative intensities of ν_1 and ν_2 . The matrix spectra¹⁰ were first interpreted to give an angle of 120° but reanalysis by Hemple¹⁶ gave the angle 95.4° estimated from the three fundamentals. We adopt 100° ± 20° and note that S° changes by only 0.2 cal·K⁻¹·mol⁻¹ in the range 95° to 120°. The singlet ground state is based on magnetic deflection data.¹⁷ The principal moments of inertia are $I_A = 25.5142 \times 10^{-38}$, $I_B = 54.9471 \times 10^{-38}$, and $I_C = 80.4613 \times 10^{-38}\text{ g}\cdot\text{cm}^2$.

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Barium Chloride (BaCl₂)Ba₂Cl₂(g)

Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r	
T/K	C _p ^a	S° – (S° – H°(T _r))/T	H° – H°(T _r)	Δ _r H°	Δ _r G°
0	0	0	0	0	0
100	47.186	268.409	373.964	–14.667	–497.307
200	54.049	303.691	330.870	–10.556	–502.338
250	55.387	315.909	326.656	–5.426	–506.675
298.15	56.160	325.736	325.736	0	–508.755
300	56.183	326.083	325.737	0.104	–510.713
350	56.689	334.784	326.423	2.927	–510.787
400	57.028	342.778	327.953	5.770	–512.669
450	57.266	349.109	329.936	8.628	–514.693
500	57.439	355.152	332.161	11.496	–516.545
550	57.667	365.647	336.893	17.252	–518.305
600	57.897	374.547	341.633	23.026	–521.477
700	57.898	382.271	346.238	28.812	–524.311
800	57.861	389.096	350.646	34.603	–526.849
900	58.006	395.203	354.802	40.403	–529.135
1000	58.040	400.735	358.730	46.206	–531.216
1100	58.066	405.787	362.444	52.011	–532.293
1200	58.083	410.435	365.959	57.819	–533.173
1300	58.091	414.740	369.292	63.628	–533.882
1400	58.114	418.749	372.457	69.439	–534.439
1500	58.125	422.500	375.469	75.251	–534.860
1600	58.133	426.024	378.340	81.064	–535.155
1700	58.141	429.348	381.082	86.877	–535.228
1800	58.147	432.491	383.706	92.692	–535.335
1900	58.152	435.474	386.221	98.507	–535.405
2000	58.157	438.311	388.634	104.322	–535.371
2100	58.160	441.017	390.934	110.138	–535.255
2200	58.164	443.602	393.187	115.954	–535.076
2300	58.167	446.078	395.340	121.771	–534.842
2400	58.170	448.452	397.417	127.587	–534.558
2500	58.172	450.729	399.424	133.405	–534.228
2600	58.174	452.929	401.366	139.222	–533.857
2700	58.176	455.045	403.245	145.039	–533.448
2800	58.178	457.086	405.067	150.857	–532.998
2900	58.179	459.059	406.834	156.675	–532.511
3000	58.180	460.966	408.549	162.493	–531.979
3100	58.182	462.814	410.216	168.311	–531.406
3200	58.183	464.604	411.838	174.129	–530.794
3300	58.184	466.341	413.415	179.948	–530.148
3400	58.185	468.028	414.952	185.766	–529.468
3500	58.186	469.667	416.449	191.585	–528.746
3600	58.187	471.261	417.909	197.403	–527.985
3700	58.187	472.813	419.333	203.222	–527.190
3800	58.188	474.324	420.724	209.041	–526.362
3900	58.189	475.797	422.082	214.859	–525.506
4000	58.189	477.234	423.410	220.678	–524.612
4100	58.190	478.636	424.708	226.497	–523.681
4200	58.190	480.006	425.979	232.316	–522.720
4300	58.191	481.343	427.222	238.135	–521.735
4400	58.191	482.651	428.439	243.954	–520.728
4500	58.192	483.930	429.631	249.774	–519.704
4600	58.192	485.182	430.800	255.593	–518.666
4700	58.192	486.407	431.946	261.412	–517.615
4800	58.193	487.607	433.070	267.231	–516.545
4900	58.193	488.782	434.172	273.051	–515.458
5000	58.193	489.935	435.254	278.870	–514.357
5100	58.194	491.065	436.317	284.689	–513.243
5200	58.194	492.173	437.360	290.509	–512.116
5300	58.194	493.261	438.385	296.328	–510.978
5400	58.194	494.329	439.393	302.147	–509.829
5500	58.195	495.377	440.383	307.967	–508.670
5600	58.195	496.407	441.357	313.786	–507.492
5700	58.195	497.419	442.315	319.606	–506.305
5800	58.195	498.414	443.257	325.425	–505.108
5900	58.195	499.392	444.185	331.245	–503.908
6000	58.195	499.392	444.185	331.245	–503.908

PREVIOUS: December 1972 (1 atm)

CURRENT: December 1972 (1 bar)

Barium Fluoride (BaF)

M_r = 156.28403 Barium Fluoride (BaF)Ba₂F₂(g)

$$\Delta_f H^\circ(298.15 \text{ K}) = 246.23 \pm 0.21 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad \Delta_f H^\circ(0 \text{ K}) = -320.2 \pm 8.4 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = -322.2 \pm 8.4 \text{ kJ} \cdot \text{mol}^{-1}$$

State	Electronic Levels and Quantum Weights	ϵ , cm ⁻¹	g
X ² Σ ⁺	0	2	D ² Σ ⁺
A ² Π _{1/2}	11646.9	2	D' ² Σ ⁺
A ² Π _{3/2}	12778.2	2	F ² Σ ⁺
B ² Σ ⁺	14062.5	2	G ² Σ ⁺
C ² Π	19998.2	2	H ² Σ ⁺
	20197.2	2	

$$\omega_e x_e = 1.79 \text{ cm}^{-1}$$

$$\alpha_e = [0.00112] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = 2.152 \text{ Å}$$

Enthalpy of Formation

$\Delta_f H^\circ$ is obtained from a 3rd law analysis of K_p data for three gaseous dissociation equilibria. The K_p data were derived from observations made on the condensed phase systems BaF₂-B and BaF₂-Al¹ by the mass spectrometric-Knudsen effusion method. Results of a 2nd and 3rd law analysis of these data are given below. Also included below are results derived from two mass spectrometric studies^{2,3} of the heterogeneous reaction (D), and a value for the heat of dissociation of BaF which was determined from spectrophotometric studies^{4,5} of reaction equilibria in H₂-O₂-N₂ flames.

Source	Reaction	T/K	Points	$\Delta_f H^\circ(298.15 \text{ K})$, kcal·mol ⁻¹	2nd law	3rd law	Drift	$\Delta_f H^\circ(298.15 \text{ K})$, kcal·mol ⁻¹
1	A	1418-1512	8	-1.0	-6.6 ± 0.5	-78.0 ± 1.5	-3.8 ± 2.2	-78.0 ± 1.5
1	B	1418-1512	8	8.6	-3.5 ± 1.1	-77.3 ± 3.6	-3.5 ± 5.7	-77.3 ± 3.6
2	C	1175-1255	8	26.0	23.0 ± 0.2	-75.6 ± 3.0	-2.5 ± 0.9	-75.6 ± 3.0
2	D	1175-1255	8	-118.8	-96.4 ± 1.1	-74.9 ± 1.7	18.4 ± 3.6	-74.9 ± 1.7
3	D	1428		-103.5		-71.3 ± 3.0		-71.3 ± 3.0
4,5	E			145 ± 6		-83.3 ± 8.0		-83.3 ± 8.0



*One point rejected due to failure of a statistical test.

It is believed that the K_p data for the three homogeneous reactions (A, B, and C) are more reliable than those for the heterogeneous reaction (D) due to the need for a machine calibration constant which appears in the equilibrium expression for the latter. Ehlert *et al.*² determined this constant from vaporization experiments performed with silver contained in their Knudsen cell. Further support for this belief is provided by the large positive drift that arises in the 3rd law analysis of these K_p 's. Also, it is felt that the results obtained from the flame-spectrophotometric studies^{4,5} are somewhat more uncertain than those derived from the K_p data for the three homogeneous reactions. Therefore, we choose to adopt a median value $\Delta_f H^\circ(\text{BaF, g, } 298.15 \text{ K}) = -77.0 \pm 2.0 \text{ kcal} \cdot \text{mol}^{-1}$ of the first three results. The adopted value corresponds to a dissociation energy of $D_0(\text{Ba-F}) = 137.9 \text{ kcal} \cdot \text{mol}^{-1}$ (5.98 eV).

Gaydon¹ has reported a spectroscopic value for D_0 of 3.8 eV which is considerably lower than the adopted thermochemical value. The spectroscopic value is based on a linear Birge-Sponer extrapolation of the thirteen known vibrational levels for the ground state (²Σ⁺). However, Gaydon¹ and later Hildenbrand⁶ have shown that the linear extrapolation generally underestimates D_0 when the bonding in the molecule is partially ionic. Correcting $D_0(\text{Ba-F})$ for the ionic character of BaF with the ionicity parameter suggested by Hildenbrand⁶ we obtain $D_0(\text{Ba-F}) = 6.9 \text{ eV}$ which is somewhat high. Other values for D_0 that have been reported are 5.94¹ and 5.68 eV.⁹ Both of these values were calculated from the Rittner ionic model¹⁰ for polarizable ions and show remarkably good agreement with the adopted value.

Heat Capacity and Entropy

The spectroscopic data, except for α_e , are given by Rosen¹¹ for ¹³⁸BaF. α_e is calculated from the Morse potential function. Corrections to these data to account for the natural isotopic abundances of barium were found to be negligible. The electronic states and levels are also taken from the compilation of Rosen.¹¹

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Enthalpy Reference Temperature = T _r = 298.15 K									
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	Standard State Pressure = P ^o = 0.1 MPa	log K _r			
0	0	0	INFINITE	-9.345	-320.188	INFINITE			
100	29.574	211.330	275.613	-6.428	-320.424	172.181			
200	32.669	232.752	249.349	-3.319	-321.374	88.402			
250	33.896	240.181	246.796	-1.654	-321.748	71.608			
298.15	34.748	246.228	246.228	0	-322.168	60.744			
300	34.776	246.443	246.229	0.064	-322.185	60.396			
350	35.405	251.854	246.655	1.820	-322.670	52.377			
400	35.863	256.613	247.608	3.602	-323.274	46.352			
450	36.206	260.858	248.849	5.404	-324.082	41.656			
500	36.468	264.687	250.244	7.221	-325.155	37.889			
600	36.839	271.571	253.224	10.888	-327.847	32.205			
700	37.088	277.069	256.234	14.585	-329.741	28.117			
800	37.268	282.034	259.155	18.303	-332.154	25.030			
900	37.406	286.432	261.946	22.037	-334.154	22.613			
1000	37.517	290.379	264.595	25.783	-336.159	20.688			
1100	37.611	293.959	267.105	29.540	-338.539	19.029			
1200	37.694	297.235	269.481	33.305	-340.789	17.653			
1300	37.770	300.255	271.734	37.078	-342.943	16.481			
1400	37.843	303.057	273.872	40.859	-345.022	15.471			
1500	37.917	305.671	275.906	44.647	-347.048	14.591			
1600	37.995	308.120	277.843	48.443	-349.039	13.816			
1700	38.081	310.426	279.693	52.246	-350.916	13.128			
1800	38.179	312.605	281.461	56.059	-352.697	12.514			
1900	38.292	314.673	283.155	59.883	-354.401	11.961			
2000	38.421	316.640	284.781	63.718	-356.045	11.461			
2100	38.570	318.518	286.343	67.568	-357.149	11.005			
2200	38.740	320.316	287.847	71.433	-358.849	10.461			
2300	38.933	322.042	289.296	75.316	-360.286	9.935			
2400	39.148	323.704	290.695	79.220	-361.924	9.452			
2500	39.387	325.307	292.048	83.147	-363.759	9.005			
2600	39.649	326.857	293.357	87.098	-365.782	8.592			
2700	39.934	328.358	294.626	91.077	-367.981	8.207			
2800	40.240	329.816	295.857	95.086	-370.335	7.848			
2900	40.566	331.234	297.052	99.126	-372.823	7.513			
3000	40.911	332.615	298.215	103.200	-375.421	7.198			
3100	41.273	333.962	299.346	107.309	-378.102	6.902			
3200	41.651	335.278	300.449	111.455	-380.842	6.624			
3300	42.042	336.566	301.524	115.639	-383.636	6.360			
3400	42.445	337.827	302.573	119.864	-386.482	6.111			
3500	42.859	339.063	303.598	124.129	-389.379	5.875			
3600	43.280	340.276	304.600	128.436	-392.321	5.651			
3700	43.708	341.468	305.580	132.785	-395.308	5.438			
3800	44.140	342.639	306.540	137.177	-398.367	5.235			
3900	44.575	343.792	307.481	141.613	-401.493	5.042			
4000	45.012	344.926	308.403	146.092	-404.684	4.858			
4100	45.448	346.043	309.307	150.615	-407.941	4.681			
4200	45.883	347.143	310.195	155.182	-411.264	4.513			
4300	46.315	348.228	311.067	159.792	-414.654	4.352			
4400	46.742	349.297	311.923	164.445	-418.109	4.197			
4500	47.164	350.352	312.766	169.140	-421.629	4.049			
4600	47.579	351.394	313.594	173.877	-425.213	3.906			
4700	47.986	352.421	314.409	178.656	-428.861	3.770			
4800	48.385	353.436	315.212	183.474	-432.574	3.638			
4900	48.775	354.437	316.002	188.332	-436.344	3.512			
5000	49.155	355.427	316.781	193.229	-440.169	3.390			
5100	49.524	356.404	317.548	198.163	-444.049	3.273			
5200	49.882	357.369	318.305	203.133	-447.984	3.160			
5300	50.228	358.322	319.051	208.139	-451.973	3.052			
5400	50.563	359.264	319.787	213.179	-456.016	2.946			
5500	50.884	360.195	320.513	218.251	-460.113	2.845			
5600	51.193	361.115	321.230	223.355	-464.264	2.747			
5700	51.490	362.023	321.938	228.489	-468.469	2.652			
5800	51.773	362.921	322.636	233.653	-472.729	2.561			
5900	52.043	363.809	323.327	238.844	-477.044	2.472			
6000	52.299	364.686	324.009	244.061	-481.411	2.387			

PREVIOUS: December 1972 (1 atm)

CURRENT: December 1972 (1 bar)

Barium Fluoride (BaF)

Ba₂F₂(g)

Barium Fluoride, Ion (BaF⁺)

IDEAL GAS

$$M_r = 156.327854$$



$$S^\circ(298.15\text{ K}) = [239.0 \pm 8] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_f^\circ(0\text{ K}) = 146.1 \pm 41.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(298.15\text{ K}) = 150.2 \pm 41.8 \text{ kJ mol}^{-1}$$

Electronic Levels and Quantum Weights		<i>g_i</i>
State	<i>E_i</i> , cm ⁻¹	
X ¹ Σ ⁺	0	1
a ³ Π	[9000]	6
A ¹ Π	[11000]	2
B ¹ Δ	[13000]	2
b ³ Σ ⁻	[15000]	3
A ¹ Σ ⁺	[16000]	1
B ³ Σ ⁻	[30000]	1

$$\omega_e x_e = [540] \text{ cm}^{-1}$$

$$\omega_e = [2.06] \text{ cm}^{-1}$$

$$B_e = [0.2371] \text{ cm}^{-1}$$

$$\alpha_e = [0.00122] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = [2.064] \text{ \AA}$$

Enthalpy of Formation

The appearance potential (AP) of BaF⁺ from BaF(g) has been measured spectrometrically as 4.9 eV¹ and 4.8 ± 0.3 eV.² This latter value has been confirmed by Zmbov and Margrave.³ Combining these results with ΔH^o(BaF, g, 0 K) = -76.5 ± 2.0 kcal mol⁻¹,⁴ we obtain ΔH^o(BaF⁺, g, 0 K) equal to 36.5 and 34.2 ± 9.0 kcal mol⁻¹.

Hildenbrand⁵ also reported an AP for BaF⁺ from BaF₂(g) as 13.5 ± 1.0 eV. Green *et al.*⁶ obtained an ionization efficiency curve for BaF⁺ which extrapolates (high-energy portion) to 12.9 eV at zero ion current. Assuming the process to be e⁻ + BaF₂(g) → BaF⁺(g) + F(g) + 2e⁻, we obtain ΔH^o(BaF⁺, g, 0 K) values of 101.3 ± 25 and 87.5 kcal mol⁻¹ by combining the above results with ΔH^o(BaF₂, g, 0 K) = -191.6 ± 1.5 kcal mol⁻¹ and ΔH^o(F, g, 0 K) = 18.36 ± 0.4 kcal mol⁻¹.⁴

The two lower values for ΔH^o(0 K) are preferred here, since the dissociative ionization of BaF (g) most likely involved unknown kinetic energy factors. We choose to adopt ΔH^o(BaF⁺, g, 0 K) = 35.0 ± 10.0 kcal mol⁻¹ which gives ΔH^o(BaF⁺, g, 298.15 K) = 35.9 ± 10.0 kcal mol⁻¹. The adopted heat of formation corresponds to an ionization potential for BaF(g) of 4.83 eV.

Heat Capacity and Entropy

The dissociation energy of BaF⁺(D₀^o = 145.4 kcal mol⁻¹) is slightly greater than that for BaF(D₀^o = 137.9 kcal mol⁻¹)⁴ which implies somewhat stronger bonding in the ion. Thus, one would expect the internuclear distance (*r_e*) for the ground state of BaF⁺ to be less than that for BaF. Barrow and Beale⁷ postulated from a rotational analysis of the F²Σ⁻-X¹Σ⁺ band system of SrF for SrF⁺ which was some 4% lower than that for SrF. We assume a similar decrease in *r_e* for BaF⁺ and obtain *r_e* = 2.064 Å from *r_e*(BaF) = 2.152 Å.⁴ ω_e is calculated from Badger's rule⁸ which can be written in the form ω_e = 3.159 × 10⁶(μ/*r_e*³)^{1/2}. Molecular data for CsF⁺, BaF⁺, and BaO⁺ were used to determine the constant *d_e*. The product *x_e*μ^{1/2} has been shown to be constant within a group of similar molecules by Barrow and Caunt.⁹ Since μ^{1/2}(BaF⁺) = μ^{1/2}(BaF), we assume *x_e*(BaF⁺) = *x_e*(BaF) and obtain ω_e*x_e* equal to 2.06 cm⁻¹ with our estimated value for ω_e. α_e is obtained from the other constants assuming a Morse potential function.

BaF has eight valence electrons; thus, the ground state configuration (Σ⁺) and electronic levels for the A and B states are estimated from those for the isoelectronic molecule BaS.¹⁰ By analogy with the gaseous alkaline earth oxides,¹¹ C₂ and BeS,¹² low-lying triplet states are to be expected. The two estimated triplet levels are based on those which have been observed directly in C₂,⁴ BeS,¹³ and indirectly (through perturbative effects) in BaS.¹⁰ Also included are a ¹Π state at 11,000 cm⁻¹ and a Δ state at 13,000 cm⁻¹. These levels are also estimated by analogy with those for C₂ and BeS.¹² It is believed that our adopted electronic entropies for BaF⁺ are most likely minimal values. Probable upper limits for the electronic contributions can be established by decreasing the triplet levels to 1000 cm⁻¹ (¹Π) and 5000 cm⁻¹ (³Σ) and neglecting the other excited states. This increases the entropy (in cal K⁻¹ mol⁻¹) by 3.8 and 2.1 at 2000 K and 4000 K, respectively.

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Barium Fluoride, Ion (BaF⁺)



T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P ^o = 0.1 MPa		log K _i
		S ^o - [G ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r)	ΔH ^o	ΔG ^o	
0	0	INFINITE	0	146.127		
100	29.331	204.761	-9.205			-21.298
200	31.866	225.783	-6.293			-21.135
250	33.131	233.035	-3.245			-17.392
298.15	34.073	238.955	0	150.206	121.564	-10.624
300	34.105	239.166	0.063	150.226	121.387	
350	34.931	244.480	1.787	150.749	116.538	
400	35.371	249.160	2.911	151.158	111.620	
450	35.787	253.360	4.111	151.567	106.663	
500	36.105	257.148	5.235	151.913	101.696	
600	36.557	263.773	10.755	150.668	91.843	-7.996
700	36.859	269.433	14.427	150.827	82.015	-6.120
800	37.074	274.369	18.124	150.471	72.115	-4.715
900	37.240	278.746	21.840	150.532	62.459	-3.623
1000	37.381	282.677	25.710	150.591	52.636	-2.749
1100	37.520	286.246	29.316	142.278	43.658	-2.073
1200	37.678	289.518	33.076	142.101	34.701	-1.510
1300	37.877	292.541	36.853	142.030	25.754	-1.035
1400	38.139	295.357	40.633	142.049	16.810	-0.627
1500	38.481	298.000	44.484	142.144	7.861	-0.274
1600	38.919	300.497	48.353	142.305	-1.096	0.036
1700	39.461	302.872	52.271	142.521	-10.065	0.309
1800	40.114	305.145	56.249	142.783	-19.048	0.553
1900	40.875	307.334	60.279	143.084	-28.046	0.771
2000	41.741	309.452	64.427	143.412	-37.061	0.968
2100	42.700	311.512	68.648	143.759	-46.094	1.147
2200	43.739	313.520	72.970	144.121	-55.142	1.302
2300	44.843	315.490	77.398	144.500	-64.200	1.437
2400	45.992	317.423	81.840	144.885	-73.266	1.553
2500	47.167	319.324	86.298	145.276	-82.340	1.653
2600	48.349	321.197	90.773	145.672	-91.420	1.739
2700	49.518	323.044	95.267	146.073	-100.500	1.806
2800	50.656	324.865	99.776	146.478	-109.580	1.856
2900	51.747	326.662	104.299	146.887	-118.660	1.892
3000	52.776	328.434	108.833	147.299	-127.740	1.913
3100	53.732	330.180	113.376	147.713	-136.820	1.926
3200	54.603	331.903	117.926	148.129	-145.900	1.933
3300	55.389	333.599	122.483	148.547	-154.980	1.937
3400	56.079	335.257	127.040	148.964	-164.060	1.939
3500	56.673	336.891	131.597	149.380	-173.140	1.940
3600	57.171	338.495	136.154	149.797	-182.220	1.940
3700	57.576	340.067	140.711	150.213	-191.300	1.940
3800	57.890	341.607	145.268	150.629	-200.380	1.940
3900	58.119	343.114	149.825	151.044	-209.460	1.940
4000	58.266	344.587	154.382	151.459	-218.540	1.940
4100	58.340	346.027	158.939	151.873	-227.620	1.940
4200	58.345	347.433	163.496	152.286	-236.700	1.940
4300	58.289	348.805	168.053	152.699	-245.780	1.940
4400	58.179	350.144	172.610	153.112	-254.860	1.940
4500	58.020	351.450	177.167	153.525	-263.940	1.940
4600	57.819	352.723	181.724	153.938	-273.020	1.940
4700	57.583	353.964	186.281	154.351	-282.100	1.940
4800	57.316	355.173	190.838	154.764	-291.180	1.940
4900	57.024	356.352	195.395	155.177	-300.260	1.940
5000	56.712	357.501	199.952	155.590	-309.340	1.940
5100	56.383	358.621	204.509	156.003	-318.420	1.940
5200	56.042	359.713	209.066	156.416	-327.500	1.940
5300	55.692	360.777	213.623	156.829	-336.580	1.940
5400	55.336	361.811	218.180	157.242	-345.660	1.940
5500	54.977	362.827	222.737	157.655	-354.740	1.940
5600	54.618	363.814	227.294	158.068	-363.820	1.940
5700	54.259	364.778	231.851	158.481	-372.900	1.940
5800	53.903	365.718	236.408	158.894	-381.980	1.940
5900	53.551	366.637	240.965	159.307	-391.060	1.940
6000	53.204	367.534	245.522	159.720	-400.140	1.940

PREVIOUS: December 1972 (1 atm)

CURRENT: December 1972 (1 bar)

Barium Fluoride, Ion (BaF⁺)



BaF₂(cr)Barium Fluoride (BaF₂)

CRYSTAL (α-β-γ)

Barium Fluoride (BaF₂)

$S^\circ(298.15\text{ K}) = 96.40 \pm 0.42\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_m = 1240\text{ K } (\alpha \rightarrow \beta)$
 $T_m = 1480\text{ K } (\beta \rightarrow \gamma)$
 $T_m = 1641\text{ K}$

Enthalpy of Formation

Guntz¹ measured the heat of neutralization of Ba(OH)₂(aq) with HF(aq) as $\Delta H = -34.8\text{ kcal}\cdot\text{mol}^{-1}$ at 284 K. We estimate $\Delta C_p = 106\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Ba(OH)₂ + 2HF(110 H₂O) → BaF₂(cr) + 2H₂O(l) which gives $\Delta_f H^\circ(298.15\text{ K}) = -33.4\text{ kcal}\cdot\text{mol}^{-1}$. This leads to $\Delta_f H^\circ(298.15\text{ K}) = -288.3\text{ kcal}\cdot\text{mol}^{-1}$ when combined with auxiliary data.^{3,4,5} Petersen⁶ investigated the same reaction but with HF-200 H₂O and found that 16% of the BaF₂ remained dissolved. After correcting for incomplete precipitation his final result was $\Delta_f H^\circ(298.15\text{ K}) = -33.92\text{ kcal}\cdot\text{mol}^{-1}$ which gives $\Delta_f H^\circ(298.15\text{ K}) = -288.2\text{ kcal}\cdot\text{mol}^{-1}$.

In the same study, Petersen⁶ measured the heat of precipitation of BaF₂ from BaCl₂(aq) with AgF(aq) as $\Delta_f H^\circ(292\text{ K}) = -35.02\text{ kcal}\cdot\text{mol}^{-1}$. We estimate $\Delta C_p = 108\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for 2 (AgF-200 H₂O) + BaCl₂ 400 H₂O → BaF₂(cr) + 2AgCl(cr) which gives $\Delta_f H^\circ(292.15\text{ K}) = -34.4\text{ kcal}\cdot\text{mol}^{-1}$. Using auxiliary data,^{4,7} we obtain $\Delta_f H^\circ(298.15\text{ K}) = -288.4\text{ kcal}\cdot\text{mol}^{-1}$. Petersen⁶ also reported the heat of solution of BaF₂ as $\Delta_{\text{sol}} H^\circ = 1.88\text{ kcal}\cdot\text{mol}^{-1}$. From this result, we obtain $\Delta_f H^\circ(298.15\text{ K}) = -290.3\text{ kcal}\cdot\text{mol}^{-1}$. Stephen and Stephen⁹ have selected a "best" value for the solubility of BaF₂ of 1.614 g/l at 298.15 K which corresponds to $K_{\text{sp}} = 3.1196 \times 10^{-6}$. Using $\Delta G^\circ(\text{Ba}^{2+}, \text{aq}, 298.15\text{ K}) = -134.02^\circ$ and $\Delta G^\circ(\text{F}^-, \text{aq}, 298.15\text{ K}) = -66.96\text{ kcal}\cdot\text{mol}^{-1}$, we calculate $\Delta G^\circ(298.15\text{ K}) = -275.45\text{ kcal}\cdot\text{mol}^{-1}$. Based on the adopted functions, $\Delta_f H^\circ(298.15\text{ K}) = -287.5\text{ kcal}\cdot\text{mol}^{-1}$.

Two equilibrium studies^{8,11} have also been reported. 2nd and 3rd law analyses of these data are given below.

Source	Reaction	T/K	No. of Points	1st law	2nd law	3rd law	Drift	$\Delta_f H^\circ(298.15\text{ K})$ cal·K ⁻¹ ·mol ⁻¹
Domangem ¹⁰	A	1173–1373	3	41.0	62.5 ± 3.4	16.9 ± 1.0	-267.3	
Hood and Woykski ¹¹	B	477–1033	9	5.9	5.8 ± 1.0	-0.1 ± 0.1	-279.8	
Reaction: (A) BaF ₂ (cr) + H ₂ O(g) → 2 HF(g) + BaO(cr) (B) HF(g) + 0.5 BaCl ₂ (cr) → HCl(g) + 0.5 BaF ₂ (cr)								

The large discrepancy which arises in the $\Delta_f H^\circ$ values obtained from the equilibrium and calorimetric results is not well understood. Domangem¹⁰ has measured similar equilibria for CoF₂, MgF₂, and CaF₂ which are very consistent with JANAF heats of formation. Very recently, Finch *et al.*¹² attempted to determine the heat of precipitation of BaF₂ from BaCl₂(aq) by dissolving a slight excess of NaF. X-ray diffraction studies of the precipitate showed the formation of BaClF and Ba₂ClF₂ along with BaF₂. We believe the equilibrium results of Hood and Woykski¹¹ may have been influenced by the formation of mixed halides. Also, it seems quite likely that the calorimetric results of Petersen⁶ on the precipitation of BaF₂ from BaCl₂(aq) with AgF(aq) would be similarly influenced. We adopt $\Delta_f H^\circ(298.15\text{ K}) = -288.9 \pm 1.0\text{ kcal}\cdot\text{mol}^{-1}$ which is a weighted value of the calorimetric results of Guntz¹ and Petersen⁶ on the heat of neutralization of Ba(OH)₂(aq), the heat of solution of BaF₂(cr) and the K_{sp} value obtained from the solubility data of Stephen and Stephen.⁹ Barany *et al.*⁸ determined the heat of solution of BaO(cr) in HF(aq), which contained some dissolved silica, as $\Delta H^\circ = -73.04\text{ kcal}\cdot\text{mol}^{-1}$. We assume this value refers to the reaction BaO(cr) + 2 HF-4.41 H₂O → BaF₂(cr) + H₂O(l), and we calculate $\Delta_f H^\circ(298.15\text{ K}) = -290.2 \pm 2.0\text{ kcal}\cdot\text{mol}^{-1}$ with $\Delta_f H^\circ(\text{BaO}, \text{cr}, 298.15\text{ K}) = -132.3\text{ kcal}\cdot\text{mol}^{-1}$. These results substantiate our adopted $\Delta_f H^\circ$ value.

Heat Capacity and Entropy

C_p below 298 K is based on the low temperature (14–300 K) heat capacities of Pitzer *et al.*¹³ These data show an unusual leveling off of C_p above 274 K, and values in the range 274–300 K are obtained by graphical extrapolation of their low temperature data. $S^\circ(298.15\text{ K})$ is based on the adopted C_p 's with $S^\circ(15\text{ K}) = 0.09\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Relative enthalpies have been reported by Efremova and Matizzen (757–2053 K)¹⁴ and Krestovnikov and Karetnikov (288–1273 K).¹⁵ The enthalpy data of Efremova and Matizzen¹⁴ indicated the existence of a second order phase transition at 1240 K. We adopt their smoothed C_p data for 800–1480 K. C_p 's below 800 K are estimated graphically by comparison with those for BaCl₂, CaF₂, and SrF₂. C_p (BaF₂, γ) are based on a JANAF curve fit of their relative enthalpies (1482–1596 K). The rapid rise in the enthalpy near the melting point is assumed to be due to premelting, and these points were not used in the fit. The maximum deviation of our adopted functions from those in the fit is 0.5%. Kelley¹⁶ analyzed the enthalpy data of Krestovnikov and Karetnikov.¹⁵ His smoothed enthalpies are consistently 2–3% higher than those adopted. No second order phase transition was observed. These data are judged to be less reliable and are not used in our evaluation.

Transition Data

The transition temperatures are those reported by Efremova and Matizzen.¹⁴ We assume the transition at 1240 K is of the second order type, since no discontinuity appears in their enthalpy data at this temperature. The heat of the β-γ transition is calculated as the difference between the adopted enthalpies for these two phases at 1480 K.

Continued on page 358

Barium Fluoride (BaF₂)Ba₂F₂(cr)

PREVIOUS:

CURRENT: December 1972

Barium Fluoride (BaF ₂)			Barium Fluoride (BaF ₂)			Ba ₁ F ₂ (l)		
$M_r = 175.326806$			$M_r = 175.326806$			$M_r = 175.326806$		
$S^\circ(298.15\text{ K}) = [121.254] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$			$S^\circ(298.15\text{ K}) = [121.254] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$			$S^\circ(298.15\text{ K}) = [121.254] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		
$T_{\text{fus}} = 1641\text{ K}$			$T_{\text{fus}} = 1641\text{ K}$			$T_{\text{fus}} = 1641\text{ K}$		
$\Delta_f H^\circ(298.15\text{ K}) = [-1171.294] \text{ kJ}\cdot\text{mol}^{-1}$			$\Delta_f H^\circ(298.15\text{ K}) = [-1171.294] \text{ kJ}\cdot\text{mol}^{-1}$			$\Delta_f H^\circ(298.15\text{ K}) = [-1171.294] \text{ kJ}\cdot\text{mol}^{-1}$		
$\Delta_{\text{fus}} H^\circ = 23.359 \pm 0.628 \text{ kJ}\cdot\text{mol}^{-1}$			$\Delta_{\text{fus}} H^\circ = 23.359 \pm 0.628 \text{ kJ}\cdot\text{mol}^{-1}$			$\Delta_{\text{fus}} H^\circ = 23.359 \pm 0.628 \text{ kJ}\cdot\text{mol}^{-1}$		
Enthalpy of Formation			Enthalpy of Formation			Enthalpy of Formation		
The enthalpy of formation of the liquid is calculated from that of the crystal by addition of $\Delta_{\text{fus}} H^\circ$ the difference in enthalpy, $H^\circ(1641\text{ K}) - H^\circ(298.15\text{ K})$, between the crystal and liquid.			The enthalpy of formation of the liquid is calculated from that of the crystal by addition of $\Delta_{\text{fus}} H^\circ$ the difference in enthalpy, $H^\circ(1641\text{ K}) - H^\circ(298.15\text{ K})$, between the crystal and liquid.			The enthalpy of formation of the liquid is calculated from that of the crystal by addition of $\Delta_{\text{fus}} H^\circ$ the difference in enthalpy, $H^\circ(1641\text{ K}) - H^\circ(298.15\text{ K})$, between the crystal and liquid.		
Heat Capacity and Entropy			Heat Capacity and Entropy			Heat Capacity and Entropy		
A glass transition is assumed at 1100 K below which C_p° follows that of the crystal. C_p° is assumed constant in the temperature range 1100–3500 K and is based on a JANAF curve fit of the relative enthalpies of Efremova and Matizen ¹ for the liquid (1641–1900 K). Some scatter was observed in these data at the higher temperatures, and these points were not included in the fit. The maximum deviation of the observed enthalpies which were used in the fit from those adopted is 0.29%.			A glass transition is assumed at 1100 K below which C_p° follows that of the crystal. C_p° is assumed constant in the temperature range 1100–3500 K and is based on a JANAF curve fit of the relative enthalpies of Efremova and Matizen ¹ for the liquid (1641–1900 K). Some scatter was observed in these data at the higher temperatures, and these points were not included in the fit. The maximum deviation of the observed enthalpies which were used in the fit from those adopted is 0.29%.			A glass transition is assumed at 1100 K below which C_p° follows that of the crystal. C_p° is assumed constant in the temperature range 1100–3500 K and is based on a JANAF curve fit of the relative enthalpies of Efremova and Matizen ¹ for the liquid (1641–1900 K). Some scatter was observed in these data at the higher temperatures, and these points were not included in the fit. The maximum deviation of the observed enthalpies which were used in the fit from those adopted is 0.29%.		
$S^\circ(298.15\text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.			$S^\circ(298.15\text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.			$S^\circ(298.15\text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.		
Fusion Data			Fusion Data			Fusion Data		
T_{fus} is the value selected by Efremova and Matizen ¹ from their relative enthalpy data. These data show premelting starting near 1620 K and complete melting occurring at 1646 K. Other values for T_{fus} that have been reported are 1627, ² 1628, ³ 1627, ⁴ 1617, ⁵ and 1593 K. ⁶ The selected T_{fus} was obtained from measurements made on samples of BaF ₂ contained in steel and molybdenum capsules. There were no indications of any reaction between the sample and container. Three of the lower values given above were determined from measurements on BaF ₂ contained in either graphite ^{1,4} or tantalum ⁵ crucibles. It has now been established by mass spectroscopy ⁷ that the alkaline earth difluorides can be appreciably reduced by these materials near 1400 K. Thus, we prefer the higher value.			T_{fus} is the value selected by Efremova and Matizen ¹ from their relative enthalpy data. These data show premelting starting near 1620 K and complete melting occurring at 1646 K. Other values for T_{fus} that have been reported are 1627, ² 1628, ³ 1627, ⁴ 1617, ⁵ and 1593 K. ⁶ The selected T_{fus} was obtained from measurements made on samples of BaF ₂ contained in steel and molybdenum capsules. There were no indications of any reaction between the sample and container. Three of the lower values given above were determined from measurements on BaF ₂ contained in either graphite ^{1,4} or tantalum ⁵ crucibles. It has now been established by mass spectroscopy ⁷ that the alkaline earth difluorides can be appreciably reduced by these materials near 1400 K. Thus, we prefer the higher value.			T_{fus} is the value selected by Efremova and Matizen ¹ from their relative enthalpy data. These data show premelting starting near 1620 K and complete melting occurring at 1646 K. Other values for T_{fus} that have been reported are 1627, ² 1628, ³ 1627, ⁴ 1617, ⁵ and 1593 K. ⁶ The selected T_{fus} was obtained from measurements made on samples of BaF ₂ contained in steel and molybdenum capsules. There were no indications of any reaction between the sample and container. Three of the lower values given above were determined from measurements on BaF ₂ contained in either graphite ^{1,4} or tantalum ⁵ crucibles. It has now been established by mass spectroscopy ⁷ that the alkaline earth difluorides can be appreciably reduced by these materials near 1400 K. Thus, we prefer the higher value.		
$\Delta_{\text{fus}} H^\circ$ is obtained as the difference in the adopted functions for the liquid and crystal at T_{fus} .			$\Delta_{\text{fus}} H^\circ$ is obtained as the difference in the adopted functions for the liquid and crystal at T_{fus} .			$\Delta_{\text{fus}} H^\circ$ is obtained as the difference in the adopted functions for the liquid and crystal at T_{fus} .		
Vaporization Data			Vaporization Data			Vaporization Data		
T_{vap} is the calculated temperature at which $\Delta G^\circ = 0$ for BaF ₂ (l) → BaF ₂ (g). $\Delta_{\text{vap}} H^\circ$ is calculated from the difference in $\Delta_f H^\circ(T_{\text{vap}})$ for the gas and liquid. Ruff and Le Boucher ⁸ derived $T_{\text{vap}} = 2533\text{ K}$ and $\Delta_{\text{vap}} H^\circ = 69.8 \text{ kcal}\cdot\text{mol}^{-1}$ from an analysis of their vapor pressures (1960–2206 K).			T_{vap} is the calculated temperature at which $\Delta G^\circ = 0$ for BaF ₂ (l) → BaF ₂ (g). $\Delta_{\text{vap}} H^\circ$ is calculated from the difference in $\Delta_f H^\circ(T_{\text{vap}})$ for the gas and liquid. Ruff and Le Boucher ⁸ derived $T_{\text{vap}} = 2533\text{ K}$ and $\Delta_{\text{vap}} H^\circ = 69.8 \text{ kcal}\cdot\text{mol}^{-1}$ from an analysis of their vapor pressures (1960–2206 K).			T_{vap} is the calculated temperature at which $\Delta G^\circ = 0$ for BaF ₂ (l) → BaF ₂ (g). $\Delta_{\text{vap}} H^\circ$ is calculated from the difference in $\Delta_f H^\circ(T_{\text{vap}})$ for the gas and liquid. Ruff and Le Boucher ⁸ derived $T_{\text{vap}} = 2533\text{ K}$ and $\Delta_{\text{vap}} H^\circ = 69.8 \text{ kcal}\cdot\text{mol}^{-1}$ from an analysis of their vapor pressures (1960–2206 K).		
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Barium Fluoride (BaF₂)

IDEAL GAS

$$M_r = 175.326806$$

Barium Fluoride (BaF₂)Ba₁F₂(g)

$$S^\circ(298.15 \text{ K}) = 301.30 \pm 2.09 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad \Delta_f H^\circ(0 \text{ K}) = -801.7 \pm 6.3 \text{ kJ} \cdot \text{mol}^{-1} \quad \Delta_f H^\circ(298.15 \text{ K}) = -803.7 \pm 6.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Vibrational Frequencies, ν/cm^{-1} and Degeneracies	
413(1)	390(1)

Ground State Quantum Weight: 1 $\sigma = 2$
 Point Group: C_{2v}
 Bond Distance: Ba-F = $2.32 \pm 0.03 \text{ \AA}$
 Bond Angle: F-Ba-F = 95°
 Product of Moments of Inertia: $I_A I_B I_C = [6.858791 \times 10^{-114}] \text{ g}^3 \cdot \text{cm}^6$

Enthalpy of Formation

$\Delta_f H^\circ(\text{BaF}_2, \text{g}, 298.15 \text{ K}) = -192.1 \pm 1.5 \text{ kcal} \cdot \text{mol}^{-1}$ ($-803.7 \pm 6.3 \text{ kJ} \cdot \text{mol}^{-1}$) is obtained from that of the crystal by addition of $\Delta_{\text{sub}} H^\circ = 96.83 \pm 0.50 \text{ kcal} \cdot \text{mol}^{-1}$. The selected $\Delta_{\text{sub}} H^\circ$ is based on an analysis of six sets of vapor pressure data.¹⁻⁵ The results of our analysis are given below. A weighted value of these six results is adopted.

Source	Method	T/K	Data Points	$\Delta_{\text{sub}} H^\circ(298.15 \text{ K})$, kcal·mol ⁻¹	Drift	$\Delta_f H^\circ(298.15 \text{ K})$, kcal·mol ⁻¹
Ruff and Le Boucher ¹	Dynamic B.P.	2061-2206	9	97.0 ^a	86.79 ± 0.88^a	-4.9 ± 0.8
Green <i>et al.</i> ²	Knudsen-Mass Spec.	1232-1503	20	96.5	98.17 ± 0.45	1.2 ± 0.6
Bautista and Margrave ³	Langmuir	1130-1250	10 ^b	96.4	97.68 ± 0.19	1.1 ± 0.9
Hart and Searcy ⁴	Torsion-Effusion	1261-1548	49 ^c	93.2	96.12 ± 0.68	2.1 ± 0.7
Hart and Searcy ⁴	Torsion-Langmuir	1315-1492	25 ^d	93.7	96.47 ± 0.38	2.0 ± 0.8
Hildenbrand <i>et al.</i> ⁵	Torsion-Effusion	1265-1550	Equation	94.2	94.74 ± 0.13	0.4

^a $\Delta_{\text{sub}} H^\circ$, ^b2^b, ^c4^c, and ^d3^d points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The bond length is taken from the high-temperature electron diffraction studies of Akishin and Spiridonov.⁶ Although Akishin and Spiridonov⁶ interpreted their results in terms of a linear configuration for BaF₂, recent electric-deflection experiments⁷ and matrix isolation infrared studies^{8,9} clearly indicate that BaF₂ is bent. Calder *et al.*⁸ estimated the bond angle as 100° from the changes in the bond angles with mass of the central atom for other alkaline earth difluorides. Baikov¹⁰ estimated the angle as 115° . We prefer a slightly lower value (95°) than these, since there are indications that other heavy metal halides have bond angles below 100° . For example, bond angles for PbF₂ and PbCl₂ have been reported as 90^{11} and $96 \pm 3^\circ$ ¹², respectively.

The symmetric (ν_1) and antisymmetric (ν_3) stretching frequencies are those observed by Calder *et al.*⁸ in their study of infrared spectra of BaF₂ trapped in a krypton matrix. Other matrix frequencies in excellent agreement with the adopted ones have been reported by Snelson.⁹ Further confirmation of the adopted ν_1 is provided by observations of Baikov.¹⁰ He reported $\nu_1 = 415 \pm 7 \text{ cm}^{-1}$, which was observed in the infrared spectra of BaF₂ vapor at 1950 K. The bending frequency (ν_2) is that estimated by Calder *et al.*⁸ This value is considerably less than that observed by Baikov¹⁰ ($\nu_2 = 100 \text{ cm}^{-1}$). However, only the high frequency portion of this rather broad band was recorded. We have used our adopted frequencies in a valence bond calculation with the result $k/(k \cdot \text{Å})^2 = 11.8$. This ratio of the stretching to bending force constants appears quite reasonable in comparison with those for other alkaline earth difluorides.¹⁴ Also, our adopted frequencies give thermodynamic functions which show good compatibility with the vapor pressure data (see Enthalpy of Formation section).

The principal moments of inertia are: $I_A = 30.6016 \times 10^{-39}$, $I_B = 18.4604 \times 10^{-39}$, and $I_C = 12.1412 \times 10^{-39} \text{ g} \cdot \text{cm}^2$.

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Barium Fluoride (BaF₂)Ba₁F₂(g)

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$		log K_r	
T/K	C_p°	S°	$H^\circ - H^\circ(T_r)/T$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
0	0	0	INFINITE	-13.649	-801.659
100	42.748	248.473	346.341	-9.787	-806.804
200	50.089	280.512	308.118	-5.121	-810.853
250	52.332	291.947	302.175	-2.557	-812.732
298.15	53.780	301.297	301.297	0	-814.489
300	53.826	301.630	301.298	0.000	-814.556
350	54.840	310.008	301.957	2.818	-816.074
400	55.551	317.380	303.434	5.579	-818.055
450	56.064	323.954	305.355	8.370	-819.711
500	56.444	329.882	307.516	11.183	-821.280
600	56.957	340.222	312.130	16.855	-824.081
700	57.276	349.027	316.788	22.568	-826.557
800	57.487	356.690	321.307	28.307	-828.742
900	57.634	363.470	325.622	34.065	-830.680
1000	57.740	369.548	329.716	39.852	-832.417
1100	57.819	375.055	333.592	45.610	-833.150
1200	57.879	380.089	337.260	51.395	-833.686
1300	57.924	384.772	340.735	57.185	-834.051
1400	57.964	389.018	344.032	62.980	-834.262
1500	57.994	393.018	347.166	68.778	-834.324
1600	58.019	396.762	350.150	74.579	-834.280
1700	58.040	400.280	352.997	80.382	-834.107
1800	58.057	403.598	355.716	86.186	-833.821
1900	58.072	406.737	358.320	91.993	-833.428
2000	58.084	409.716	360.816	97.801	-832.930
2100	58.095	412.550	363.212	103.610	-832.330
2200	58.104	415.253	365.517	109.420	-831.635
2300	58.113	417.836	367.736	115.231	-830.845
2400	58.120	420.310	369.875	121.042	-830.000
2500	58.126	422.682	371.941	126.854	-829.113
2600	58.132	424.962	373.967	132.667	-828.186
2700	58.137	427.156	375.867	138.481	-827.218
2800	58.141	429.271	377.737	144.295	-826.208
2900	58.145	431.311	379.549	150.109	-825.154
3000	58.149	433.282	381.308	155.924	-824.059
3100	58.152	435.189	383.015	161.739	-822.925
3200	58.155	437.035	384.675	167.554	-821.754
3300	58.158	438.825	386.288	173.370	-820.546
3400	58.160	440.561	387.859	179.186	-819.300
3500	58.163	442.247	389.389	185.002	-818.018
3600	58.165	443.885	390.880	190.818	-816.699
3700	58.167	445.479	392.335	196.635	-815.346
3800	58.168	447.030	393.754	202.452	-813.959
3900	58.170	448.541	395.139	208.268	-812.538
4000	58.172	450.014	396.493	214.086	-811.084
4100	58.173	451.451	397.816	219.903	-809.599
4200	58.174	452.852	399.110	225.720	-808.074
4300	58.176	454.221	400.375	231.538	-806.500
4400	58.177	455.559	401.614	237.355	-804.874
4500	58.178	456.866	402.828	243.173	-803.200
4600	58.179	458.145	404.016	248.991	-801.486
4700	58.180	459.396	405.181	254.809	-799.732
4800	58.181	460.621	406.324	260.627	-797.939
4900	58.182	461.821	407.443	266.445	-796.097
5000	58.182	462.996	408.544	272.263	-794.216
5100	58.183	464.148	409.622	278.081	-792.288
5200	58.184	465.278	410.672	283.900	-790.316
5300	58.184	466.386	411.723	289.718	-788.300
5400	58.185	467.474	412.745	295.536	-786.246
5500	58.185	468.542	413.750	301.355	-784.154
5600	58.186	469.590	414.738	307.174	-782.022
5700	58.186	470.620	415.709	312.992	-779.850
5800	58.187	471.632	416.664	318.811	-777.638
5900	58.187	472.626	417.605	324.630	-775.377
6000	58.188	473.604	418.530	330.448	-773.073

PREVIOUS December 1972 (a atm)

CURRENT

December 1972 (1 bar)

BaH₂O₂(g)

Barium Hydroxide (BaOH)

IDEAL GAS

Barium Hydroxide (BaOH)

Enthalpy Reference Temperature = T _r = 298.15 K					Standard State Pressure = p° = 0.1 MPa				
T/K	C _p ^a	S°	-(G°-H°(T _r))/T	H°-H°(T _r)	ΔH°	ΔG°	log K _r		
0	0	0	INFINITE	-9.799	-221.752	-221.752	INFINITE		
90	30.847	211.167	289.791	-7.862	-223.465	-227.472	118.819		
200	40.469	235.500	256.974	-4.295	-225.245	-230.727	60.262		
250	43.984	244.931	253.644	-2.178	-225.894	-232.020	48.478		
298.15	46.356	252.893	252.893	0	-226.440	-233.150	40.847		
300	46.432	253.180	252.894	0.086	-226.460	-233.191	40.602		
350	48.141	260.474	253.466	2.453	-227.003	-234.271	34.963		
400	49.361	266.986	254.757	4.892	-227.610	-235.269	30.723		
450	50.257	272.854	256.447	7.383	-228.384	-236.182	27.415		
500	50.937	278.186	258.358	9.914	-229.396	-236.997	24.759		
600	51.916	287.565	262.466	15.060	-231.917	-238.270	20.743		
700	52.641	295.625	266.641	20.289	-233.599	-239.207	17.850		
800	53.266	302.695	270.715	25.585	-235.775	-239.854	15.661		
900	53.855	309.003	274.625	30.941	-237.515	-240.259	13.944		
1000	54.427	314.707	278.352	36.355	-239.241	-240.471	12.561		
1100	54.983	319.921	281.898	41.826	-240.930	-239.691	11.382		
1200	55.519	324.728	285.269	47.351	-242.551	-238.730	10.392		
1300	56.029	329.192	288.478	52.929	-244.107	-237.612	9.547		
1400	56.512	333.363	291.537	58.556	-245.793	-236.358	8.819		
1500	56.968	337.277	294.457	64.230	-247.552	-234.983	8.183		
1600	57.398	340.968	297.250	69.949	-249.365	-233.499	7.623		
1700	57.807	344.460	299.925	75.709	-251.244	-231.915	7.126		
1800	58.199	347.775	302.492	81.509	-253.184	-230.237	6.681		
1900	58.578	350.932	304.959	87.348	-255.182	-228.471	6.281		
2000	58.951	353.946	307.334	93.225	-257.240	-226.619	5.919		
2100	59.320	356.831	309.622	99.138	-259.362	-224.683	5.589		
2200	59.689	359.599	311.832	105.089	-261.547	-222.678	5.159		
2300	60.063	362.261	313.967	111.076	-263.793	-220.618	4.738		
2400	60.442	364.825	316.033	117.102	-266.100	-218.508	4.351		
2500	60.828	367.300	318.034	123.165	-268.468	-216.354	3.993		
2600	61.223	369.694	319.975	129.268	-270.896	-214.166	3.662		
2700	61.627	372.012	321.860	135.410	-273.383	-211.943	3.354		
2800	62.040	374.260	323.691	141.593	-275.928	-209.688	3.067		
2900	62.460	376.445	325.473	147.818	-278.532	-207.408	2.798		
3000	62.888	378.570	327.208	154.086	-281.196	-205.106	2.545		
3100	63.321	380.639	328.898	160.396	-283.919	-202.786	2.308		
3200	63.759	382.656	330.547	166.750	-286.698	-200.446	2.084		
3300	64.200	384.623	332.156	173.148	-289.532	-198.089	1.872		
3400	64.642	386.548	333.727	179.590	-292.420	-195.716	1.672		
3500	65.083	388.428	335.263	186.076	-295.362	-193.329	1.481		
3600	65.522	390.268	336.766	192.607	-298.358	-190.928	1.301		
3700	65.957	392.069	338.236	199.181	-301.408	-188.513	1.129		
3800	66.386	393.833	339.676	205.798	-304.512	-186.085	0.965		
3900	66.807	395.563	341.087	212.458	-307.670	-183.646	0.809		
4000	67.220	397.260	342.470	219.159	-310.882	-181.196	0.660		
4100	67.622	398.925	343.827	225.901	-314.148	-178.736	0.517		
4200	68.013	400.559	345.158	232.683	-317.468	-176.266	0.380		
4300	68.391	402.164	346.465	239.503	-320.842	-173.786	0.249		
4400	68.755	403.740	347.749	246.361	-324.270	-171.296	0.123		
4500	69.104	405.289	349.011	253.254	-327.752	-168.796	0.002		
4600	69.438	406.812	350.251	260.181	-331.288	-166.286	-0.114		
4700	69.756	408.309	351.470	267.141	-334.868	-163.766	-0.226		
4800	70.057	409.780	352.610	274.132	-338.492	-161.236	-0.333		
4900	70.342	411.228	353.850	281.152	-342.160	-158.696	-0.437		
5000	70.610	412.652	355.012	288.200	-345.872	-156.146	-0.536		
5100	70.860	414.052	356.156	295.273	-349.628	-153.586	-0.633		
5200	71.093	415.431	357.282	302.371	-353.428	-151.016	-0.726		
5300	71.309	416.787	358.392	309.491	-357.272	-148.436	-0.816		
5400	71.509	418.122	359.486	316.632	-361.160	-145.846	-0.902		
5500	71.691	419.436	360.564	323.793	-365.092	-143.246	-0.986		
5600	71.857	420.729	361.627	330.970	-369.068	-140.636	-1.067		
5700	72.007	422.002	362.675	338.163	-373.088	-138.016	-1.146		
5800	72.142	423.256	363.709	345.371	-377.152	-135.386	-1.222		
5900	72.261	424.490	364.729	352.591	-381.260	-132.746	-1.296		
6000	72.366	425.705	365.735	359.823	-385.412	-130.096	-1.368		

PREVIOUS: December 1975 (1 atm)

CURRENT: December 1975 (1 bar)

BaH₂O₂(g)

Barium Hydroxide (BaOH)

$S^{\circ}(298.15\text{ K}) = [252.9 \pm 8]\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$				$\Delta_f H^{\circ}(0\text{ K}) = -221.75 \pm 29.3\text{ kJ}\cdot\text{mol}^{-1}$				$\Delta_f H^{\circ}(298.15\text{ K}) = -226.44 \pm 29.3\text{ kJ}\cdot\text{mol}^{-1}$			

Barium Hydroxide, Ion (BaOH⁺)

IDEAL GAS

$$M_r = 154.336791$$

$$S^\circ(298.15\text{ K}) = [247.26 \pm 8.4] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(0\text{ K}) = 269.36 \pm 62.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15\text{ K}) = 270.90 \pm 62.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Vibrational Frequencies and Degeneracies
 ν, cm^{-1}

[460] (1)
[430] (2)
[3650] (1)

Ground State Quantum Weight: [1] $\sigma = [1]$

Point Group: [C_{2v}]

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

Bond Angle: Ba-O-H = [180]°

Rotational Constant: B₀ = [0.222053] cm⁻¹

Enthalpy of Formation

The ionization potential of BaOH(g) was deduced by Kelly and Padley¹ to be 5.25 ± 0.1 eV. These authors quantitatively examined the total positive ion concentrations produced from Ba aqueous salt additives in fuel rich, premixed H₂ + O₂ + N₂ flames. Using current JANAF auxiliary data,² we recalculate the ionization potential to be 5.36 eV.

Jensen³ determined the enthalpy of reaction $\Delta_f H^\circ = 6 \pm 10 \text{ kcal}\cdot\text{mol}^{-1}$ for Ba(g) + OH(g) = BaOH⁺(g) + e⁻ in atmospheric pressure H₂ + O₂ + N₂ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for BaOH⁺. The value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data,² we derive an ionization potential of 4.83 eV, which is not in good agreement with the value derived from the data of Kelly and Padley.¹

We adopt an ionization potential of 5.09 eV (117.38 kcal·mol⁻¹) which is an average of the above two studies.^{1,3} This leads to $\Delta_f H^\circ(0\text{ K}) = 64.38 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(298.15\text{ K}) = 64.75 \text{ kcal}\cdot\text{mol}^{-1}$ for BaOH⁺(g). We assign an uncertainty of $\pm 15 \text{ kcal}\cdot\text{mol}^{-1}$.

For comparison, the ionization potential of BaRg(g) is 4.83 eV² while that of Ba(g) is 5.21 eV.⁴

The average of these two values is very close to the ionization potential adopted for BaOH⁺.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.^{2,3,6,7} In addition, Walsh⁸ had predicted the BAH molecules (H = hydrogen atom) with ten or less valence electrons (BaOH⁺ has eight valence electrons) will be linear in their ground state. The molecule BaOH⁺ is isoelectronic with CsOH.

The bond dissociation energy for BaOH⁺ ($D_0^\circ = 108.2 \text{ kcal}\cdot\text{mol}^{-1}$)² for the process BaOH⁺(g) = Ba(g) + OH(g) is nearly the same as that for BaOH ($D_0^\circ = 105.3 \text{ kcal}\cdot\text{mol}^{-1}$).² This suggests that the bonding in these two molecules is quite similar. Thus, the bond distances are assumed to be the same as those adopted for BaOH(g).² The vibrational frequencies are assumed to be similar to those adopted for BaOH(g).²

The ground state quantum weight is assumed to be the same as that of CsOH(g).²

References

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Barium Hydroxide, Ion (BaOH⁺)Ba₁H₁O₁O₁(g)

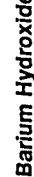
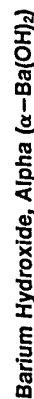
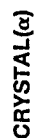
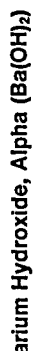
$$\text{Enthalpy Reference Temperature} = T_r = 298.15 \text{ K}$$

T/K	C _p ^a	S ^b - [C _p - R ln(T _r)]/T	H ^c - H ^d (T _r)	Δ _f H ^e	Standard State Pressure = p ^o = 0.1 MPa	log K _r
0	0	0	INFINITE	-10.823	269.364	
100	30.902	205.415	284.269	-7.885		
200	40.603	229.824	251.356	-4.306		
250	44.104	239.283	248.018	-2.184		
298.15	46.458	247.265	0	0	270.897	-45.483
300	46.533	247.552	0.086	0.086		-45.190
350	48.225	254.860	2.477	2.477		-38.445
400	49.450	261.383	2.493	2.493		-33.378
450	50.315	267.258	2.502	2.502		-29.431
500	50.986	272.596	2.527	2.527		-26.272
600	51.952	281.983	2.585	2.585		-21.538
700	52.668	290.047	2.610	2.610		-18.156
800	53.287	297.121	2.651	2.651		-15.618
900	53.872	303.431	2.690	2.690		-13.644
1000	54.440	309.137	2.724	2.724		-12.062
1100	54.994	314.351	2.763	2.763		-10.805
1200	55.526	319.159	2.797	2.797		-9.757
1300	56.031	323.624	2.828	2.828		-8.870
1400	56.505	327.794	2.857	2.857		-8.109
1500	56.945	331.707	2.886	2.886		-7.448
1600	57.351	335.396	2.913	2.913		-6.869
1700	57.723	338.884	2.938	2.938		-6.357
1800	58.064	342.193	2.962	2.962		-5.901
1900	58.373	345.341	2.985	2.985		-5.492
2000	58.658	348.343	3.017	3.017		-5.124
2100	58.917	351.211	3.043	3.043		-4.790
2200	59.152	353.957	3.064	3.064		-4.461
2300	59.366	356.591	3.083	3.083		-4.137
2400	59.562	359.122	3.100	3.100		-3.817
2500	59.740	361.557	3.114	3.114		-3.492
2600	59.903	363.903	3.126	3.126		-3.162
2700	60.053	366.167	3.136	3.136		-2.837
2800	60.190	368.354	3.145	3.145		-2.507
2900	60.316	370.468	3.153	3.153		-2.172
3000	60.432	372.515	3.159	3.159		-1.832
3100	60.539	374.498	3.164	3.164		-1.487
3200	60.637	376.422	3.168	3.168		-1.137
3300	60.726	378.289	3.171	3.171		-0.782
3400	60.813	380.103	3.173	3.173		-0.422
3500	60.891	381.867	3.175	3.175		-0.057
3600	60.964	383.584	3.176	3.176		0.312
3700	61.032	385.255	3.177	3.177		0.677
3800	61.094	386.883	3.178	3.178		1.039
3900	61.153	388.471	3.179	3.179		1.398
4000	61.208	390.020	3.180	3.180		1.753
4100	61.259	391.532	3.181	3.181		2.104
4200	61.307	393.009	3.182	3.182		2.451
4300	61.352	394.452	3.183	3.183		2.794
4400	61.395	395.863	3.184	3.184		3.133
4500	61.434	397.243	3.185	3.185		3.468
4600	61.472	398.594	3.186	3.186		3.800
4700	61.507	399.916	3.187	3.187		4.129
4800	61.540	401.211	3.188	3.188		4.455
4900	61.571	402.481	3.189	3.189		4.778
5000	61.601	403.725	3.190	3.190		5.098
5100	61.629	404.945	3.191	3.191		5.414
5200	61.655	406.142	3.192	3.192		5.726
5300	61.680	407.317	3.193	3.193		6.034
5400	61.704	408.470	3.194	3.194		6.338
5500	61.727	409.602	3.195	3.195		6.638
5600	61.748	410.715	3.196	3.196		6.934
5700	61.768	411.808	3.197	3.197		7.226
5800	61.788	412.882	3.198	3.198		7.514
5900	61.806	413.939	3.199	3.199		7.798
6000	61.824	414.977	3.200	3.200		8.078

PREVIOUS: June 1976 (1 atm)

CURRENT: June 1976 (1 bar)

Barium Hydroxide, Ion (BaOH⁺)Ba₁H₁O₁O₁(g)



Enthalpy Reference Temperature = T _r = 298.15 K				Standard State Pressure = p° = 0.1 MPa			
T/K	C _p ^o	S ^o - [G° - H°(T _r)]/T	H° - H°(T _r)	Δ _f H°	Δ _f G°	log K _r	
0							
90							
200							
250							
298.15	101.629	107.110	107.110	-946.295	-859.476	150.577	
300	101.797	107.740	107.112	-946.267	-859.438	149.554	
400	112.633	138.679	111.257	-942.380	-830.099	108.400	
500	118.658	164.520	119.399	-942.589	-801.748	83.758	
600	122.717	186.510	128.797	-941.231	-773.693	67.356	
681.150	126.022	202.280	136.628	---	CRYSTAL <--> LIQUID	---	
700	126.775	205.731	138.443	-938.765	-745.972	55.665	
800	130.834	222.924	147.947	-936.501	-718.575	46.918	
900	134.892	238.569	157.159	-933.501	-691.511	40.134	
1000	138.951	252.991	166.030	-930.182	-664.799	34.726	

Δ_fH°(0 K) = Unknown
 Δ_fH°(298.15 K) = [-946.30] kJ·mol⁻¹
 Δ_{sub}H° = 16.74 ± 1.26 kJ·mol⁻¹
 Δ_{cr}H° = Unknown

Enthalpy of Formation

The adopted Δ_fH°(298.15 K) = -226.17 ± 1.5 kcal·mol⁻¹ is obtained from the enthalpy of formation of the liquid¹ minus the enthalpy of fusion and the enthalpy difference of the liquid and the crystal between the melting point and 298.15 K. Using auxiliary data,² our 2nd and 3rd law analysis of the dissociation pressure equation of Kondakov *et al.*² for the reaction Ba(OH)₂(cr) = BaO(cr) + H₂O(g) is given below.

T/K	Δ _f H°(298.15 K), kcal·mol ⁻¹	3rd law	Drift	Δ _f H°(298.15 K) kcal·mol ⁻¹
559-682	46.4	38.04 ± 1.63	-13.5 ± 0.2	-226.84 ± 2

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

Heat Capacity and Entropy

The heat capacities at 298.15 K and above are derived from the drop-ice-calorimeter enthalpy measurements of Powers and Blalock,³ 425-681 K) combined with a graphical comparison of the heat capacities of Mg(OH)₂(cr) and Ca(OH)₂(cr).¹ From the information referenced in the Transition Data Section below, it is concluded that the α-form is maintained on cooling to 273.15 K. This JANAF Table is a single-phase alpha-crystal table.

The adopted entropy, S°(298.15 K) = [25.6 ± 2] cal·K⁻¹·mol⁻¹, is calculated from Kelley's additive entropy constants for cations and anions.⁵

Fusion Data

Seward⁶ determined a melting point of 408 ± 1°C and a cryoscopic enthalpy of fusion of 3400 ± 100 cal·mol⁻¹. Powers and Blalock³ chose a melting point of 395°C where they found Δ_{sub}H° = 24 cal/g (4113 cal·mol⁻¹) by drop calorimetry. However, their enthalpy measurements show a possible melting range of 395 to 421°C. (At the adopted temperature of melting, 408°C, our smoothing of Powers and Blalock's experimental enthalpies¹ leads to Δ_{sub}H° = 4051 cal·mol⁻¹.) Kondakov *et al.* observed barium hydroxide to melt at 682 K (ca. 409°C) while investigating the dissociation pressures of the crystal and liquid states. Michaud^{7,8} determined a melting point of 409 ± 1°C and a cryoscopic enthalpy of fusion of 3720 ± 200 cal·mol⁻¹.⁸ From a consideration of all of these data, a melting point of 681.15 ± 1 K (408 ± 1°C) and a enthalpy of fusion of 4000 ± 300 cal·mol⁻¹ are adopted.

Transition Data

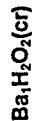
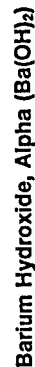
Michaud has observed a β to α crystal transition, on heating anhydrous barium dihydroxide, at 250°C⁷ and at 246°C⁸ by both thermal and dilatometric techniques. In the absence of water vapor, the high temperature α-form is maintained on cooling to room temperature.⁷ This "metastable" state has been confirmed by others.^{9,10} This present JANAF Table considers only the α-form. A transition temperature of 521 ± 2 K (248 ± 2°C) is adopted.

References

- JANAF Thermochemical Tables: Ba(OH)₂(l), 12-31-75; BaO(cr), 6-30-74; H₂O(g), 3-31-61; Mg(OH)₂(cr), 12-31-75; Ca(OH)₂(cr), 12-31-75.
- B. V. Kondakov, P. V. Kovtunenkov, and A. A. Bundel, Zh. Fiz. Khim. 38, 190 (1964).
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- R. P. Seward, J. Am. Chem. Soc. 67, 1189 (1945).
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- P. Buck and H. Baernighausen, Acta Crystallogr., Sect. B 24, 1705 (1968).
- H. D. Lutz, R. Heider, and R. A. Becker, Z. Naturforsch. B 24, 1657 (1969).

PREVIOUS:

CURRENT: December 1975



BaH₂O₂(l)Barium Hydroxide (Ba(OH)₂) $M_r = 171.34468$

LIQUID

Barium Hydroxide (Ba(OH)₂)

$S^\circ(298.15 \text{ K}) = [123.357] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $T_{\text{fus}} = 681.15 \pm 1 \text{ K}$
 $\Delta_f H^\circ(298.15 \text{ K}) = [-934.123] \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_{\text{ion}} H^\circ = [6.74 \pm 1.26] \text{ kJ} \cdot \text{mol}^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H^\circ(298.15 \text{ K}) = -223.26 \pm 1.0 \text{ kcal} \cdot \text{mol}^{-1}$ is the average of values derived from the 3rd law analysis of dissociation pressure measurements of Tamari and Shiomu¹ and of Kondakov *et al.*² Auxiliary data used in the analysis are from the JANAF Thermochemical Tables.³ Johnston⁴ has also determined pressures for the dissociation reaction $\text{Ba(OH)}_2(\text{l}) = \text{BaO}(\text{cr}) + \text{H}_2\text{O}(\text{g})$.

Source	No. of Points	T/K	$\Delta_f H^\circ(298.15 \text{ K})$, kcal·mol ⁻¹	2nd law	3rd law	Drift	$\Delta_f H^\circ(298.15 \text{ K})$, kcal·mol ⁻¹
Tamari and Shiomu ¹	7	788–1018		32.1	34.56 ± 0.48	2.8 ± 0.5	-223.35 ± 1
Kondakov <i>et al.</i> ²	Equation	682–993		34.0	34.37 ± 0.21	0.4	-223.17 ± 0.7
Johnston ⁴	11	918–1263		34.4	33.86 ± 0.38	-0.5 ± 0.5	-222.66 ± 0.9

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

Heat Capacity and Entropy

C_p° is based on the enthalpy measurements of Powers and Blalock⁵ and is assumed constant at $33.7 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ over the range of 450 to 1600 K. A glass transition is assumed at 450 K below which C_p° is that of the alpha crystal. The entropy at 298.15 K is derived from the value adopted for the alpha crystal.

Decomposition Data

T_{dec} is calculated as the temperature at which $\Delta_r G^\circ = 0$ for the reaction $\text{Ba(OH)}_2(\text{l}) = \text{BaO}(\text{cr}) + \text{H}_2\text{O}(\text{g})$.

References

- ¹S. Tamari and K. Shiomu, Z. physik. Chem. A171, 221 (1935).
- ²B. V. Kondakov, P. V. Kovtunen, and A. A. Bundel, Zh. Fiz. Khim. 38, 190 (1964).
- ³JANAF Thermochemical Tables: BaO(cr), 6–30–74; H₂O(g), 3–31–61.
- ⁴J. Johnston, Z. physik. Chem. 62, 330 (1908).
- ⁵W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm., ORNL-1653 (1954).

Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$		log K_f	
T/K	C_p°	S°	$-[G^\circ - H^\circ(T)]/T$	$H^\circ - H^\circ(T)$	$\Delta_f G^\circ$
0					
90					
200					
250					
298.15	101.629	123.357	123.357	0.000	-934.123
300	101.797	123.359	123.359	0.188	-852.148
400	112.633	154.926	127.504	10.969	-934.095
450.010	116.065	168.404	131.312	16.692	-932.208
450.010	141.001	168.404	131.312	16.692	GLASS $\leftarrow \rightarrow$ LIQUID
500	141.001	183.256	135.776	23.740	TRANSITION
600	141.001	208.964	145.896	37.841	-929.236
681.150	141.001	226.850	154.498	49.283	-925.847
700	141.001	230.699	156.498	51.941	CRYSTAL $\leftarrow \rightarrow$ LIQUID
800	141.001	249.527	166.976	66.041	-921.754
900	141.001	266.135	177.090	80.141	-918.270
1000	141.001	280.991	186.750	94.241	-914.457
1100	141.001	294.430	195.938	108.341	-910.729
1200	141.001	306.698	204.664	122.441	-907.454
1300	141.001	317.984	212.953	136.541	-904.586
1400	141.001	328.434	220.833	150.641	-902.068
1500	141.001	338.162	228.334	164.741	-900.411
1600	141.001	347.262	235.486	178.841	-898.759
1700	141.001	355.810	242.315	192.941	-897.102
1800	141.001	363.869	248.846	207.041	-895.446
1900	141.001	371.493	255.102	221.142	-893.790
2000	141.001	378.725	261.104	235.242	-892.134

PREVIOUS:

CURRENT: December 1975

Barium Hydroxide (Ba(OH)₂)BaH₂O₂(l)

Barium Hydroxide (Ba(OH)₂)

M_r = 171.34468 Barium Hydroxide (Ba(OH)₂)

Ba₁H₂O₂(cr,l)

0 to 681.15 K crystal, alpha*
above 681.15 K liquid

*A low temperature beta form does exist but is not included in this table. T_m(β → α) = 521 ± 2 K.

Refer to the individual tables for details.

Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa			
T/K	C _p J·K ⁻¹ ·mol ⁻¹	S° J·K ⁻¹ ·mol ⁻¹	-(G°-H°(T _r))/T	H°-H°(T _r) kJ·mol ⁻¹	Δ _r G° kJ·mol ⁻¹
0					log K _t
100					
200					
250					
298.15	101.629	107.110	107.110	0.000	-859.476 150.577
300	101.797	107.740	107.112	0.188	-858.938 149.554
400	112.653	138.679	111.257	10.969	-830.059 108.400
500	118.658	164.520	119.399	22.560	-801.748 83.758
600	122.717	186.510	128.797	34.628	-773.693 67.356
681.150	126.022	202.280	136.628	44.719	CRYSTAL <--> LIQUID
681.150	141.001	226.850	136.628	61.455	TRANSITION
700	141.001	230.699	139.110	-921.754	-746.439 55.700
800	141.001	249.527	151.761	-918.270	-721.627 46.117
900	141.001	266.135	163.565	-914.457	-697.277 40.469
1000	141.001	280.991	174.578	-910.729	-673.346 33.172
1100	141.001	294.430	184.872	-915.454	-648.965 30.817
1200	141.001	306.698	194.521	-912.123	-624.886 27.201
1300	141.001	317.984	203.590	-908.769	-601.085 24.152
1400	141.001	328.434	212.138	-905.411	-577.543 21.548
1500	141.001	338.162	220.219	-902.068	-554.241 19.300
1600	141.001	347.262	227.878	-898.759	-531.161 17.341
1700	141.001	355.810	235.155	-895.502	-508.286 15.618
1800	141.001	363.869	242.084	-892.316	-485.601 14.092
1900	141.001	371.493	248.696	-889.219	-463.090 12.731
2000	141.001	378.725	255.018	-886.231	-440.740 11.511

PREVIOUS:

CURRENT December 1975

Barium Hydroxide (Ba(OH)₂)

Ba₁H₂O₂(cr,l)

Barium Hydroxide (Ba(OH)₂)

IDEAL GAS

$$M_r = 171.34468$$

Barium Hydroxide (Ba(OH)₂)BaH₂O₂(g)

$$S^\circ(298.15\text{ K}) = [315.0 \pm 12.6] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_f^\circ(0\text{ K}) = -619.09 \pm 37.7 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(298.15\text{ K}) = -626.56 \pm 37.7 \text{ kJ mol}^{-1}$$

Vibrational Frequencies and Degeneracies ν , cm ⁻¹	
[413] (1)	[3650] (2)
[64] (1)	[431] (4)
[390] (1)	

Ground State Quantum Weight: [1]

Point Group: [C_{2v}]

Bond Distances: Ba-O = [2.34] Å; O-H = [0.96] Å

Bond Angles: O-Ba-O = [95]°; Ba-O-H = [180]°

Product of the Moments of Inertia: $I_A I_B I_C = [6.366076 \times 10^{-114}] \text{ g}^3 \text{ cm}^6$

Enthalpy of Formation

The adopted $\Delta H_f^\circ(298.15\text{ K}) = -149.75 \pm 9.0 \text{ kcal mol}^{-1}$ is derived from the Knudsen-cell mass-spectrometric equilibrium study of Newbury.¹ Tabulated below are the results of a 2nd and 3rd law analysis of this study,¹ the Knudsen-cell mass-spectrometric work of Stafford and Berkowitz,² and the flame-spectral work of Cotton and Jenkins.³

Source	Rxn No.	No. of Points	T/K	$\Delta H_f^\circ(298.15\text{ K})$, kcal mol ⁻¹	2nd law	3rd law	Drift	$\Delta H_f^\circ(298.15\text{ K})$, kcal mol ⁻¹	D_0° , kcal mol ⁻¹
Stafford and Berkowitz ²	A	24 ^a	1485–1727	56.4	45.37 ± 1.82	-6.7 ± 1.7	-143.43 ± 2.5	203.3	
Newbury ¹	A	44 ^a	1428–1899	39.0	39.05 ± 0.17	0.0 ± 0.1	-149.75 ± 0.7	209.6	
Cotton and Jenkin ³	B	2	1570–1800	8.1	23.04 ± 2.98	8.8 ± 0.0	-153.96 ± 4.0	213.8	

Reactions: A) BaO(cr) + H₂O(g) = Ba(OH)₂(g) B) Ba(g) + 2H₂O(g) = Ba(OH)₂(g) + 2H(g)

a. Two points rejected by a statistical test.

b. D_0° is the dissociation energy for the reaction Ba(OH)₂(g) = Ba(g) + 2OH(g).

In addition to the three investigations above, dissociation energies (D_0° as defined in the table above) have been derived from flame spectra by Ryabova and Gurvich⁵ and by Sugden and Schofield.⁶ Ryabova and Gurvich⁵ believed the dominant reaction to be Ba(g) + H₂O(g) = BaOH(g) + H(g), but they also considered the possibility that the reaction Ba(g) + 2H₂O(g) = Ba(OH)₂(g) + 2H(g) was dominant and derived $D_0^\circ = 205 \pm 20 \text{ kcal mol}^{-1}$. Sugden and Schofield⁶ considered the dihydroxide to be the dominant product and derived $D_0^\circ = 229 \pm 12 \text{ kcal mol}^{-1}$. Cotton and Jenkins³ found both BaOH and Ba(OH)₂ to be present and obtained recalculated D_0° values of 208 and 212 kcal mol⁻¹, respectively.

The 3rd law analysis of the data of Cotton and Jenkins³ above combined with current JANAF Thermochemical Table data⁴ leads to $D_0^\circ = 213.8 \text{ kcal mol}^{-1}$ which is 0.8 kcal mol⁻¹ higher than the 213 kcal mol⁻¹ derived by Cotton and Jenkins.³ Applying this difference to the values of Ryabova and Gurvich⁵ and of Sugden and Schofield⁶ as recalculated by Cotton and Jenkins³ gives $D_0^\circ = 208.8$ and 212.8 kcal mol⁻¹, respectively.

The average of the dissociation energies from the flame-spectral measurements (208.8, 212.8, and 213.8) and the dissociation energy from the Knudsen-cell mass-spectrometric work of Stafford and Berkowitz (203.3) is 209.7 kcal mol⁻¹ which happens to be in agreement with the 209.6 kcal mol⁻¹ calculated from Newbury's data.

$\Delta H_f^\circ(298.15\text{ K}) = -149.75 \pm 9.0 \text{ kcal mol}^{-1}$ is adopted because of the excellent agreement in the 2nd and 3rd law enthalpies of reaction from Newbury's data¹ and because of the larger uncertainty associated with dissociation energies derived from flame spectra.

The enthalpy of dissociation listed by Jackson⁹ leads to $\Delta H_f^\circ(298.15\text{ K}) = -151.22 \text{ kcal mol}^{-1}$. Another recent compilation¹⁰ lists $\Delta H_f^\circ(298.15\text{ K}) = -140 \text{ kcal mol}^{-1}$.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized.^{2,7-9} The O-Ba-O bond angle is assumed to be the same as the F-Ba-F bond angle,⁴ the Ba-O-H bond angle is considered to be linear as in BaOH.⁴ The Ba-O bond distance is estimated to be slightly larger, 0.02 Å, than the Ba-F distance in BaF₂⁴ after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O-H bond distance is taken to be the same as in water.⁴ The vibrational frequencies are assumed to be the same as in BaF₂⁴ (O-Ba-O symmetrical and asymmetrical stretch, and bend) and as in BaOH⁴ (O-H stretch and Ba-O-H bend). The principal moments of inertia are: $I_A = 29.8004 \times 10^{-39}$, $I_B = 17.7971 \times 10^{-39}$, and $I_C = 12.0033 \times 10^{-39} \text{ g cm}^2$.

Continued on page 359

Barium Hydroxide (Ba(OH)₂)BaH₂O₂(g)

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$		Standard State Pressure = $p^\circ = 0.1\text{ MPa}$		log K_r	
T/K	C_p°	$S^\circ - [C_p^\circ - R \ln(T/T_r)]/T$	$H^\circ - [H^\circ(T_r) - RT_r \ln(T/T_r)]$	ΔH_f°	ΔG_f°
0	0	0	0	-619.094	-619.094
100	45.351	248.363	-16.594	-616.816	-616.816
200	65.873	286.310	-12.690	-609.699	-609.699
250	72.732	301.794	-10.94	-605.700	-605.700
298.15	77.256	315.016	0	-601.731	-601.731
300	77.399	315.494	0.143	-601.731	-601.731
350	80.612	327.681	4.098	-597.376	-597.376
400	82.884	338.602	8.189	-593.116	-593.116
450	84.542	348.465	12.376	-588.795	-588.795
500	85.798	357.440	16.636	-584.399	-584.399
600	87.607	373.254	25.312	-575.322	-575.322
700	88.958	384.863	34.143	-565.991	-565.991
800	90.141	398.820	43.098	-556.443	-556.443
900	91.271	409.503	52.169	-546.718	-546.718
1000	92.380	419.177	61.352	-536.860	-536.860
1100	93.465	428.033	70.644	-526.064	-526.064
1200	94.510	436.210	80.044	-515.137	-515.137
1300	95.510	443.815	89.545	-504.100	-504.100
1400	96.447	450.928	99.144	-492.972	-492.972
1500	97.319	457.612	108.833	-481.765	-481.765
1600	98.124	463.919	118.605	-470.488	-470.488
1700	98.864	469.890	128.455	-459.148	-459.148
1800	99.540	475.561	138.376	-447.750	-447.750
1900	100.158	480.959	148.361	-436.297	-436.297
2000	100.721	486.111	158.406	-424.788	-424.788
2100	101.234	491.038	168.504	-413.224	-413.224
2200	101.702	495.759	178.651	-396.228	-396.228
2300	102.128	500.289	188.843	-379.594	-379.594
2400	102.517	504.644	199.075	-359.709	-359.709
2500	102.873	508.836	209.345	-341.597	-341.597
2600	103.198	512.877	219.649	-323.042	-323.042
2700	103.495	516.778	229.984	-304.634	-304.634
2800	103.768	520.547	240.347	-286.169	-286.169
2900	104.019	524.192	250.731	-267.641	-267.641
3000	104.250	527.723	261.150	-249.044	-249.044
3100	104.465	531.145	271.586	-230.377	-230.377
3200	104.659	534.464	282.042	-211.638	-211.638
3300	104.841	537.688	292.517	-192.825	-192.825
3400	105.009	540.820	303.010	-173.936	-173.936
3500	105.165	543.866	313.519	-154.973	-154.973
3600	105.309	546.831	324.043	-135.936	-135.936
3700	105.444	549.718	334.580	-116.826	-116.826
3800	105.569	552.532	345.131	-97.643	-97.643
3900	105.686	555.275	355.694	-78.390	-78.390
4000	105.796	557.953	366.268	-59.071	-59.071
4100	105.898	560.566	376.853	-39.684	-39.684
4200	105.993	563.119	387.447	-20.233	-20.233
4300	106.083	565.614	398.051	-0.718	-0.718
4400	106.167	568.054	408.664	18.855	18.855
4500	106.246	570.441	419.285	38.488	38.488
4600	106.321	572.777	429.913	58.176	58.176
4700	106.391	575.064	440.530	77.919	77.919
4800	106.457	577.305	451.191	97.718	97.718
4900	106.519	579.501	461.840	117.568	117.568
5000	106.578	581.653	472.455	137.469	137.469
5100	106.634	583.764	483.155	157.417	157.417
5200	106.687	585.835	493.821	177.414	177.414
5300	106.736	587.868	504.462	197.461	197.461
5400	106.784	589.864	515.169	217.552	217.552
5500	106.829	591.823	525.849	237.684	237.684
5600	106.872	593.749	536.534	257.860	257.860
5700	106.912	595.641	547.223	278.083	278.083
5800	106.951	597.500	557.902	298.348	298.348
5900	106.988	599.329	568.614	318.635	318.635
6000	107.023	601.127	579.514	338.985	338.985

PREVIOUS: December 1975 (1 atm)

CURRENT: December 1975 (1 bar)

Barium Iodide (BaI)

 $M_r = 264.345$ Barium Iodide (BaI)BaI₂(g)

$$S^\circ(298.15\text{ K}) = 278.74 \pm 0.21 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad \Delta_f H^\circ(0\text{ K}) = -39.29 \pm 84 \text{ kJ}\cdot\text{mol}^{-1} \quad \Delta_f H^\circ(298.15\text{ K}) = -42.42 \pm 84 \text{ kJ}\cdot\text{mol}^{-1}$$

Electronic Levels and Quantum Weights	
State	g_i
X[¹ S _g]	0
C[¹ H]	17816.3
D[³ P]	18568.8
E[³ S _g]	25764.4
E[³ S _g]	26753.3

$$\omega_e = 152.2 \text{ cm}^{-1} \quad \omega_e x_e = 0.29 \text{ cm}^{-1} \quad \sigma = 1 \quad \alpha_e = [0.0000591] \text{ cm}^{-1} \quad r_e = [3.20] \text{ \AA}$$

Enthalpy of Formation

The adopted $\Delta_f H^\circ(0\text{ K}) = -39.29 \pm 20 \text{ kcal}\cdot\text{mol}^{-1}$ is calculated from $D_0^\circ = 3.37 \text{ eV}$ (77.7 kcal mol⁻¹) calculated by a linear Birge-Sponer extrapolation of $\omega_e x_e$ data¹ with a correction for the ionic character of the molecule as described by Hildenbrand.² Other values, in kcal·mol⁻¹, are 55³ predicted from a correlation of binding energies of Group II and Group III diatomic hydrides and halides, 71.7⁴ as a lower bound from a consideration of ionic bonding forces and 66⁵ derived as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. $D_0^\circ = 77.7 \text{ kcal}\cdot\text{mol}^{-1}$ is adopted because the ratio of $D_0^\circ(\text{BaI})/\Delta_f H^\circ(\text{BaI}_2) = 0.47$ which is nearly the same as the ratio of 0.46 found for a series of mono- and difluorides⁶ and for other alkaline earth halides systems.⁷

$$\Delta_f H^\circ(298.15\text{ K}) = -10.14 \pm 20 \text{ kcal}\cdot\text{mol}^{-1} \text{ is calculated from the adopted } \Delta_f H^\circ(0\text{ K}) = -39.29 \pm 20 \text{ kcal}\cdot\text{mol}^{-1}.$$

Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen.¹ The adopted value of $r_e = 3.20 \text{ \AA}$ was estimated by Margrave³ and is also the bond distance in BaI₂(g).⁷ B_e is calculated from the adopted r_e ; α_e is calculated assuming a Morse potential function.

The electronic levels and their probable designation are those given by Rosen.¹

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⁸JANAF Thermochemical Tables; refer to all alkaline earth halide tables.

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 _f H°	
0	0.	INFINITE	INFINITE	-39.287	INFINITE
100	34.820	239.050	311.435	-7.239	-39.368
200	36.747	263.961	282.130	-3.634	-39.677
250	37.046	272.196	279.349	-1.788	-39.759
298.15	37.221	278.737	278.737	0.	-41.582
300	37.227	278.967	278.738	0.069	-41.582
350	37.349	284.716	279.192	1.933	-41.582
400	37.439	289.709	280.201	3.803	-41.582
450	37.510	294.123	281.507	5.677	-41.582
500	37.569	298.078	282.970	7.554	-41.582
600	37.666	304.937	286.077	11.316	-41.582
700	37.747	310.749	289.197	15.087	-41.582
800	37.820	315.794	292.213	18.865	-41.582
900	37.887	320.253	295.086	22.650	-41.582
1000	37.952	324.248	297.806	26.442	-41.582
1100	38.015	327.868	300.376	30.241	-41.582
1200	38.076	331.178	302.807	34.045	-41.582
1300	38.137	334.229	305.109	37.856	-41.582
1400	38.197	337.057	307.291	41.673	-41.582
1500	38.256	339.694	309.364	45.495	-41.582
1600	38.315	342.165	311.338	49.324	-41.582
1700	38.374	344.490	313.220	53.158	-41.582
1800	38.433	346.685	315.019	56.999	-41.582
1900	38.493	348.764	316.741	60.845	-41.582
2000	38.554	350.740	318.392	64.697	-41.582
2100	38.616	352.623	319.977	68.556	-41.582
2200	38.680	354.421	321.502	72.421	-41.582
2300	38.746	356.142	322.971	76.292	-41.582
2400	38.816	357.792	324.388	80.170	-41.582
2500	38.889	359.378	325.756	84.055	-41.582
2600	38.963	360.905	327.079	87.948	-41.582
2700	39.031	362.377	328.359	91.849	-41.582
2800	39.100	363.799	329.600	95.758	-41.582
2900	39.236	365.174	330.803	99.677	-41.582
3000	39.339	366.506	331.971	103.606	-41.582
3100	39.450	367.798	333.106	107.545	-41.582
3200	39.568	369.052	334.209	111.496	-41.582
3300	39.693	370.272	335.284	115.459	-41.582
3400	39.832	371.459	336.330	119.436	-41.582
3500	39.977	372.615	337.351	123.426	-41.582
3600	40.130	373.744	338.346	127.431	-41.582
3700	40.293	374.845	339.318	131.452	-41.582
3800	40.465	375.922	340.267	135.490	-41.582
3900	40.646	376.976	341.195	139.546	-41.582
4000	40.835	378.007	342.102	143.620	-41.582
4100	41.033	379.018	342.990	147.713	-41.582
4200	41.239	380.009	343.860	151.826	-41.582
4300	41.453	380.982	344.712	155.961	-41.582
4400	41.674	381.937	345.547	160.117	-41.582
4500	41.902	382.876	346.366	164.296	-41.582
4600	42.137	383.800	347.170	168.498	-41.582
4700	42.377	384.709	347.959	172.724	-41.582
4800	42.623	385.603	348.734	176.974	-41.582
4900	42.874	386.485	349.495	181.248	-41.582
5000	43.130	387.354	350.244	185.549	-41.582
5100	43.389	388.210	350.980	189.874	-41.582
5200	43.651	389.055	351.704	194.226	-41.582
5300	43.916	389.889	352.417	198.605	-41.582
5400	44.184	390.713	353.118	203.010	-41.582
5500	44.452	391.526	353.809	207.442	-41.582
5600	44.722	392.329	354.490	211.900	-41.582
5700	44.992	393.123	355.161	216.386	-41.582
5800	45.262	393.908	355.822	220.899	-41.582
5900	45.532	394.684	356.474	225.438	-41.582
6000	45.800	395.452	357.117	230.005	-41.582

PREVIOUS: June 1974 (1 atm)

CURRENT: June 1974 (1 bar)

Barium Iodide (BaI)

BaI₂(g)

Barium Iodide (BaI₂)

Barium Iodide (BaI₂)

$M_r = 391.139$

CRYSTAL

Barium Iodide (BaI₂)

$S^\circ(298.15\text{ K}) = 165.14 \pm 0.4\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 984 \pm 2\text{ K}$
 $\Delta_f H^\circ(0\text{ K}) = -604.5 \pm 3.3\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = -605.4 \pm 3.3\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{sub}} H^\circ = 26.53 \pm 0.54\text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

Ehrlich, Peik, and Koch¹ derived $\Delta_f H^\circ(\text{BaI}_2, \text{cr}, 298.15\text{ K}) = -144.7 \pm 0.4\text{ kcal}\cdot\text{mol}^{-1}$ from enthalpy of solution measurements of Ba(cr) and BaI₂(cr) in 0.1 N HI. An auxiliary HI enthalpy of solution value, $-13.22\text{ kcal}\cdot\text{mol}^{-1}$, calculated from data in reference² was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA key value of $\Delta_f H^\circ(\text{I}^-, \text{aq}, 298.15\text{ K}) = -13.60\text{ kcal}\cdot\text{mol}^{-1}$ in the $\Delta_f H^\circ(\text{HI}, \text{aq}, 298.15\text{ K})$ table, so that the above derived enthalpy of formation of BaI₂(cr) will be approximately $-145.1\text{ kcal}\cdot\text{mol}^{-1}$.

Combining $\Delta_f H^\circ(\text{Ba}^{+2}, \text{aq}, 298.15\text{ K}) = -128.5\text{ kcal}\cdot\text{mol}^{-1}$, selected by Parker,⁴ with the CODATA value for $\text{I}^-(\text{aq})$ ¹ gives $\Delta_f H^\circ(\text{BaI}_2, \text{aq}, 298.15\text{ K}) = -155.7\text{ kcal}\cdot\text{mol}^{-1}$. Further combination with the enthalpy of solution, $-10.98\text{ kcal}\cdot\text{mol}^{-1}$,¹¹ gives $\Delta_f H^\circ(\text{BaI}_2, \text{cr}, 298.15\text{ K}) = -144.7\text{ kcal}\cdot\text{mol}^{-1}$. This enthalpy of solution value was based on several sets of data, one of which was that of Ehrlich *et al.*^{1,11} We adopt $-144.7 \pm 0.8\text{ kcal}\cdot\text{mol}^{-1}$ ($-605.425 \pm 3.347\text{ kJ}\cdot\text{mol}^{-1}$) because of the correlation of $\Delta_f H^\circ(\text{Ba}^{+2}, \text{aq}, 298.15\text{ K})$ with the evaluation of data for several barium compounds.⁴ See also the updated discussion in the enthalpy of formation section for BaO(cr).¹²

Heat Capacity and Entropy

$C_p^\circ(13.08\text{--}300.17\text{ K})$ has been measured by Paukov, Khriplovich, and Smirnova.⁶ Our T° extrapolation agrees with their $S^\circ(13) = 0.619\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $H^\circ(13\text{ K}) - H^\circ(0\text{ K}) = 6.01\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and our smoothing and integration of their C_p° data agrees with their $S^\circ(298.15\text{ K}) = 39.47 \pm 0.1\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is adopted.

The low-temperature heat capacities join smoothly with a linear extrapolation from $C_p^\circ(298.15\text{ K}) = 18.52\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to Dworkin and Bredig's reported C_p° of $21.8\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at the adopted T_{fus} of 984 K .⁷ This gives $H^\circ(984\text{ K}) - H^\circ(298.15\text{ K}) = 13.83\text{ kcal}\cdot\text{mol}^{-1}$, in fair agreement with Dworkin and Bredig's drop calorimeter value of $13.9\text{ kcal}\cdot\text{mol}^{-1}$.⁷

Fusion Data

Dworkin and Bredig⁷ report $\Delta_{\text{fus}} H^\circ = 6.34\text{ kcal}\cdot\text{mol}^{-1}$ ($\pm 2\%$) at T_{fus} of 984 K from drop calorimetry; Emmons and Loeffelholz⁸ found $6.050\text{ kcal}\cdot\text{mol}^{-1}$ ($\pm 5\%$) at a reported T_{fus} of 981 K by high temperature cryoscopy. Hutchison⁹ determined T_{fus} to be 983 K , while Kubaschewski *et al.*¹⁰ listed 985 K . We adopt $\Delta_{\text{fus}} H^\circ = 6.34 \pm 0.13\text{ kcal}\cdot\text{mol}^{-1}$ and $T_{\text{fus}} = 984 \pm 2\text{ K}$.

Sublimation Data

$\Delta_{\text{sub}} H^\circ(298.15\text{ K})$ is calculated as the difference between the enthalpies of formation of the ideal gas and the crystal at 298.15 K .

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T/K	C_p°	Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$		Standard State Pressure = $p^\circ = 0.1\text{ MPa}$		log K_1
		$S^\circ - (G^\circ - H^\circ(T_r))/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	
0	0.000	0.000	INFINITE	-604.544	-604.544	INFINITE
100	68.952	84.559	232.338	-604.841	-603.789	315.387
200	75.228	134.767	172.276	-605.042	-602.675	157.403
298.15	77.488	165.142	0.000	-605.425	-601.407	105.364
300	77.530	165.622	0.143	-605.434	-601.382	104.710
400	79.238	188.201	7.997	-622.236	-599.374	78.270
500	81.546	206.166	16.051	-666.196	-589.434	61.578
600	83.513	221.207	24.304	-666.319	-574.057	49.976
700	85.521	234.231	32.756	-665.450	-558.758	41.695
800	87.529	245.782	41.408	-664.904	-543.545	35.490
900	89.538	256.207	50.262	-663.747	-528.443	30.670
984.000	91.211	264.271	57.853	---	CRYSTAL \leftarrow \rightarrow LIQUID	---
1000	91.546	265.743	59.314	-662.403	-513.479	26.821
1100	93.617	274.566	68.573	-669.237	-497.840	23.640
1200	95.653	282.799	78.036	-667.748	-482.322	20.995
1300	97.653	290.535	87.702	-665.980	-466.940	18.762
1400	99.617	297.844	97.566	-663.968	-451.703	16.853
1500	101.546	304.783	107.624	-661.745	-436.618	15.204

PREVIOUS:

CURRENT: June 1974

Barium Iodide (BaI₂)

Barium Iodide (BaI₂)

Barium Iodide (BaI₂)Barium Iodide (BaI₂)BaI₂(l)

$S^\circ(298.15\text{ K}) = [183.669] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 984 \pm 2 \text{ K}$

$\Delta_f H^\circ(298.15\text{ K}) = [-585.884] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{liq}} H^\circ = 26.53 \pm 0.54 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

$\Delta_f H^\circ(\text{BaI}_2, \text{l}, 298.15\text{ K})$ is calculated from that of the crystal by adding $\Delta_{\text{liq}} H^\circ$ and the difference in enthalpy, $H^\circ(984\text{ K}) - H^\circ(298.15\text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid heat capacity near the melting point, $27.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, was determined by Dworkin and Bredig¹ from drop calorimetric measurements. This value is adopted and assumed constant over a 700–2800 K range. A glass transition is assumed at 700 K below which the heat capacity is that of the crystal.

$S^\circ(298.15\text{ K})$ is calculated in a manner similar to that used for the enthalpy of formation.

Vaporization Data

The temperature at which $\Delta G^\circ = 0$ for the reaction $\text{BaI}_2(\text{l}) = \text{BaI}_2(\text{g})$ is the adopted T_{vap} . Peterson and Hutchison² have extrapolated Knudsen effusion cell measurements in the 1154–1301 K range to obtain a normal boiling point (1 atm) of 2300 K.

$\Delta_{\text{vap}} H^\circ(T_{\text{vap}})$ is the calculated difference between the enthalpies of formation of the ideal gas and the liquid at T_{vap} . Refer to the ideal gas table for details.

References

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T/K	C _p ^a	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
		J·K ⁻¹ ·mol ⁻¹	S° - (G° - H°(T _r))/T	H° - H°(T _r)	Δ _r H°	
0						
200						
298.15	71.488	183.669	183.669	0.000	-585.884	102.908
300	71.530	183.671	183.671	0.143	-585.893	102.275
400	79.538	206.728	186.736	7.997	-587.244	76.686
500	81.546	224.693	192.590	16.031	-579.156	60.504
600	83.513	239.733	199.227	24.304	-565.632	49.243
699.990	85.521	252.756	205.963	32.754		
699.990	112.968	252.756	205.963	32.754		
700	112.968	252.758	205.964	32.756		
800	112.968	267.842	212.777	44.032	-645.910	41.205
900	112.968	281.148	219.649	55.349	-642.719	35.194
984.000	112.968	291.228	225.536	64.838	-639.119	30.543
1000	112.968	293.051	226.405	66.646		
1100	112.968	303.818	237.960	77.943	-635.530	-513.914
1200	112.968	313.647	249.281	89.240	-640.325	-501.106
1300	112.968	322.689	255.354	100.536	-637.003	-488.593
1400	112.968	331.061	251.180	111.833	-633.605	-476.363
1500	112.968	338.855	256.768	123.130	-630.159	-464.399
1600	112.968	346.146	262.129	134.427	-626.698	-452.680
1700	112.968	352.995	267.275	145.724	-623.251	-441.191
1800	112.968	359.452	272.218	157.020	-619.848	-429.917
1900	112.968	365.559	276.972	168.317	-616.516	-418.841
2000	112.968	371.354	281.547	179.614	-613.281	-407.948
2100	112.968	376.866	285.956	190.911	-610.164	-397.222
2200	112.968	382.121	290.208	202.208	-607.184	-386.649
2300	112.968	387.143	294.315	213.504	-604.379	-376.839
2400	112.968	391.950	298.283	224.801	-740.384	-353.962
2500	112.968	396.562	302.123	236.098	-737.157	-337.231
2600	112.968	400.993	305.841	247.395	-734.189	-320.629
2700	112.968	405.256	309.445	258.692	-731.462	-304.141
2800	112.968	409.365	312.940	269.988	-728.956	-287.754
					-716.644	-271.456

PREVIOUS:

CURRENT: June 1974

Barium Iodide (BaI₂)BaI₂(l)

Barium Iodide (BaI₂)

CRYSTAL-LIQUID

0 to 984 K crystal
above 984 K liquid
Refer to the individual tables for details.

M_r = 391.139 Barium Iodide (BaI₂)

BaI₂(cr,l)

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$					Standard State Pressure = $p^\circ = 0.1\text{ MPa}$			
T/K	C_p°	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		$H^\circ - H^\circ(T_r)$	$\text{kJ}\cdot\text{mol}^{-1}$		$\log K_f$	
		S°	$S^\circ - [C_p^\circ - (H^\circ(T_r))/T]$		ΔH°	ΔG°		
0	0.000	0.000	INFINITE	-19.230	-604.544	-604.544	INFINITE	
100	68.952	84.559	232.338	-14.778	-604.841	-603.789	315.387	
200	75.228	134.767	172.276	-7.502	-603.042	-602.675	157.403	
298.15	77.488	165.142	165.142	0.000	-605.425	-601.407	105.364	
300	77.530	165.622	165.144	0.143	-605.434	-601.382	104.710	
400	79.538	188.201	168.209	7.997	-622.236	-599.374	78.270	
500	81.546	206.166	174.063	16.051	-666.196	-589.434	61.578	
600	83.513	221.207	180.700	24.304	-666.319	-574.057	49.976	
700	85.521	234.231	187.437	32.756	-665.450	-558.258	41.695	
800	87.529	245.782	194.022	41.408	-664.904	-543.545	35.490	
900	89.538	256.207	200.361	50.262	-663.747	-528.443	30.670	
984.000	91.211	264.271	205.477	57.853				
984.000	112.968	291.228	205.477	84.380				
1000	112.968	293.051	206.863	86.187	-635.530	-513.913	26.844	
1100	112.968	303.818	215.196	97.484	-640.325	-501.105	23.796	
1200	112.968	313.647	222.996	108.781	-637.003	-488.595	21.268	
1300	112.968	322.689	230.332	120.078	-633.604	-476.365	19.141	
1400	112.968	331.061	237.222	131.374	-630.159	-464.399	17.327	
1500	112.968	338.855	243.741	142.671	-626.698	-452.679	15.764	
1600	112.968	346.146	249.916	153.968	-623.251	-441.191	14.403	
1700	112.968	352.995	255.780	165.265	-619.848	-429.916	13.210	
1800	112.968	359.452	261.362	176.562	-616.516	-418.841	12.154	
1900	112.968	365.559	266.687	187.858	-613.280	-407.947	11.215	
2000	112.968	371.354	271.776	199.155	-610.163	-397.222	10.374	
2100	112.968	376.866	276.650	210.452	-607.184	-386.648	9.617	
2200	112.968	382.121	281.326	221.749	-604.379	-376.839	8.805	
2300	112.968	387.143	285.818	233.046	-601.634	-367.861	8.039	
2400	112.968	391.950	290.141	244.342	-600.046	-359.231	7.340	
2500	112.968	396.562	294.306	255.639	-598.518	-350.929	6.699	
2600	112.968	400.993	298.325	266.936	-597.046	-342.941	6.110	
2700	112.968	405.256	302.207	278.233	-595.628	-335.254	5.567	
2800	112.968	409.365	305.961	289.530	-594.256	-327.856	5.064	

PREVIOUS: CURRENT June 1974

Barium Iodide (BaI₂)

BaI₂(cr,l)

Barium Iodide (BaI₂)

IDEAL GAS

M_r = 391.139 Barium Iodide (BaI₂)BaI₂(g)

$S^\circ(298.15\text{ K}) = [348.14 \pm 8.4] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ $\Delta_f H^\circ(0\text{ K}) = -298.5 \pm 16.7 \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_f H^\circ(298.15\text{ K}) = -302.9 \pm 16.7 \text{ kJ}\cdot\text{mol}^{-1}$

Vibrational Frequencies and Degeneracies	
ν , cm ⁻¹	
[111] (1)	
[26] (1)	
[185] (1)	

Ground State Quantum Weight: [1]

Point Group: C_{2v}Bond Distance: Ba-I = $3.20 \pm 0.03 \text{ \AA}$ Bond Angle: I-Ba-I = 170° Product of Moments of Inertia: $I_A I_B I_C = 2.117174 \times 10^{-112} \text{ g}^3\cdot\text{cm}^6$ $\sigma = 2$

Enthalpy of Formation

Winchell¹ has reported $\Delta_f H$, ΔG , and ΔS for the vaporization of BaI₂(l) at 1150 K derived from a mass spectrometric Knudsen effusion cell investigation (28 unpublished points in the range of 1019–1278 K). The spectra showed no evidence of BaI₂ polymers; also it was concluded that BaI₂(l) = BaI₂(g) is the important vaporization. Peterson and Hutchison^{2,3} used a weight loss Knudsen effusion technique to observe vapor pressure at 18 temperatures in the range of 1154–1301 K. Their enthalpy of vaporization, $53.6 \pm 1.3 \text{ kcal}\cdot\text{mol}^{-1}$, is in good agreement with Winchell's value, $54 \pm 4 \text{ kcal}\cdot\text{mol}^{-1}$.

Source	No. of Points	$\Delta_f H^\circ(298.15\text{ K})$, kcal·mol ⁻¹	Drift
Winchell ¹	3 ^a	1019–1278	62.16
Peterson and Hutchison ²	18 ^b	1154–1301	64.35 ± 1.5
			67.61 ± 0.5
			5.1
			2.6 ± 1.2

^aΔG calculated at 1019 K and 1278 K from ΔH, ΔG, and ΔS values given at 1150 K to permit use of 2nd law.

^bone point rejected by statistical tests.

We select $\Delta_f H^\circ(298.15\text{ K}) = 67.6 \pm 3 \text{ kcal}\cdot\text{mol}^{-1}$ and combine this with $\Delta_f H^\circ(0, 298.15\text{ K}) = -140.029 \pm 0.9 \text{ kcal}\cdot\text{mol}^{-1}$ to give the adopted $\Delta_f H^\circ(g, 298.15\text{ K}) = -72.4 \pm 4 \text{ kcal}\cdot\text{mol}^{-1}$.

Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from the work of Akishin *et al.*⁴ who also judged the bond angle to be $180 \pm 20^\circ$. The later electric deflection study of Buechler *et al.*⁵ showed that all of the barium dihalide molecules are bent. Noting the trend in the magnitude of the bond angle in the alkaline earth-halide series, we have assumed a bond angle of 170° . The principal moments of inertia are: $I_A = 429.4543 \times 10^{-39}$, $I_B = 428.3033 \times 10^{-39}$, and $I_C = 1.1510 \times 10^{-39} \text{ g}\cdot\text{cm}^2$.

In estimating the vibrational frequencies, the stretching force constants for gaseous BaF₂, BaCl₂, and BaI₂ are calculated from their vibrational frequencies⁶ using the valence force model. The trend in the ratio $k(\text{monohalide})/k(\text{dihalide})$ indicates that $k(\text{BaI})/k(\text{BaI}_2) = 1$ is a reasonable approximation, an approximation used by Brewer *et al.*⁷ The stretching force constant for BaI(g) is calculated from the ground state vibrational frequency given by Rosen.⁸ The bending force constant is assumed to be 0.01 times the stretching force constant.⁷ The adopted vibrational frequencies are calculated from these estimated force constants. Other estimates for ν_1 , ν_2 , and ν_3 where a linear molecule was assumed, are 109, 26, 184⁷ and 106, 37, 178.⁹

We assign an uncertainty of $\pm 2 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to the entropy to allow for error in the estimation of bond angle and of the vibrational frequencies.

References

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- ²J. F. Hutchison, U. S. At. Energy Comm. IS-T-50, (1965).
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- ⁹K. S. Krasnov and V. I. Svetsov, Izv. Vyshtikh Uchebn. Zavedeni, Khim. i Klim. Tekhnol. 6, 167 (1963).

Enthalpy Reference Temperature = T _r = 298.15 K									
T/K	C _p ^a	S ^b - [G° - H°(T _r)]/T	H° - H°(T _r)	Δ _r H°	Δ _r G°	log K _r	Standard State Pressure = p° = 0.1 MPa		
0	0	0	INFINITE	-15.651	-298.463	INFINITE			
100	52.981	287.151	398.518	-11.137	-298.697	166.056			
200	56.623	325.343	353.375	-5.606	-300.643	87.856			
250	57.165	338.042	349.083	-2.760	-301.764	72.126			
298.15	57.463	348.139	348.139	0	-302.972	61.925			
300	57.472	348.494	348.494	0.106	-302.988	61.598			
350	57.641	357.369	348.840	2.983	-304.348	51.047			
400	57.785	365.077	350.399	5.871	-304.777	48.284			
450	57.871	371.888	352.415	8.763	-304.777	43.594			
500	57.933	377.989	354.673	11.658	-304.777	39.410			
600	58.014	388.559	359.466	17.456	-304.777	32.979			
700	58.063	397.506	364.278	23.260	-304.777	28.359			
800	58.096	405.262	368.977	29.068	-304.777	24.875			
900	58.118	412.106	373.352	34.879	-304.777	22.149			
1000	58.135	418.230	377.539	40.691	-304.777	19.958			
1100	58.145	423.771	381.494	46.505	-304.777	18.117			
1200	58.154	428.831	385.231	52.320	-304.777	16.575			
1300	58.161	433.486	388.766	58.136	-304.777	15.262			
1400	58.166	437.796	392.116	63.952	-304.777	14.131			
1500	58.171	441.810	395.297	69.769	-304.777	13.146			
1600	58.174	445.564	398.322	75.586	-304.777	12.280			
1700	58.177	449.091	401.266	81.404	-304.777	11.511			
1800	58.180	452.416	403.960	87.222	-304.777	10.825			
1900	58.182	455.562	406.594	93.040	-304.777	10.207			
2000	58.184	458.546	409.117	98.858	-304.777	9.648			
2100	58.186	461.385	411.539	104.677	-304.777	9.139			
2200	58.187	464.092	413.867	110.495	-304.777	8.546			
2300	58.188	466.679	416.107	116.314	-304.777	7.974			
2400	58.189	469.155	418.266	122.133	-304.777	7.448			
2500	58.190	471.530	420.350	127.952	-304.777	6.963			
2600	58.191	473.813	422.362	133.771	-304.777	6.512			
2700	58.192	476.009	424.309	139.590	-304.777	6.093			
2800	58.192	478.125	426.199	145.409	-304.777	5.701			
2900	58.193	480.167	428.019	151.229	-304.777	5.334			
3000	58.193	482.140	429.791	157.048	-304.777	4.990			
3100	58.194	484.048	431.510	162.867	-304.777	4.666			
3200	58.194	485.896	433.181	168.687	-304.777	4.361			
3300	58.195	487.687	434.806	174.506	-304.777	4.072			
3400	58.195	489.424	436.387	180.326	-304.777	3.798			
3500	58.195	491.111	437.926	186.145	-304.777	3.535			
3600	58.196	492.750	439.427	191.965	-304.777	3.292			
3700	58.196	494.345	440.890	197.784	-304.777	3.057			
3800	58.196	495.897	442.317	203.604	-304.777	2.833			
3900	58.196	497.408	443.710	209.423	-304.777	2.620			
4000	58.197	498.882	445.071	215.243	-304.777	2.416			
4100	58.197	500.319	446.404	221.063	-304.777	2.221			
4200	58.197	501.721	447.702	226.882	-304.777	2.034			
4300	58.197	503.091	448.974	232.702	-304.777	1.855			
4400	58.197	504.429	450.219	238.522	-304.777	1.683			
4500	58.198	505.736	451.438	244.342	-304.777	1.518			
4600	58.198	507.016	452.633	250.161	-304.777	1.360			
4700	58.198	508.267	453.801	255.981	-304.777	1.207			
4800	58.198	509.492	454.951	261.801	-304.777	1.061			
4900	58.198	510.692	456.076	267.621	-304.777	0.920			
5000	58.198	511.868	457.180	273.441	-304.777	0.784			
5100	58.198	513.021	458.264	279.260	-304.777	0.652			
5200	58.198	514.151	459.328	285.080	-304.777	0.526			
5300	58.198	515.259	460.373	290.900	-304.777	0.403			
5400	58.199	516.347	461.399	296.720	-304.777	0.285			
5500	58.199	517.415	462.408	302.540	-304.777	0.171			
5600	58.199	518.464	463.400	308.360	-304.777	0.061			
5700	58.199	519.494	464.375	314.180	-304.777	0.046			
5800	58.199	520.506	465.334	319.999	-304.777	-0.150			
5900	58.199	521.501	466.277	325.819	-304.777	-0.250			
6000	58.199	522.479	467.206	331.639	-304.777	-0.347			

PREVIOUS: June 1974 (1 atm)

CURRENT: June 1974 (1 bar)

Barium Iodide (BaI₂)BaI₂(g)

Barium Oxide (BaO)

CRYSTAL

$$M_r = 153.3294$$

Barium Oxide (BaO)

BaO₂(cr)

$$\Delta_f H^\circ(298.15 \text{ K}) = -546.8 \pm 2.1 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = -548.1 \pm 2.1 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{ox}} H^\circ = [59] \text{ kJ} \cdot \text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = 72.069 \pm 0.38 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{fus}} = 2286 \pm 15 \text{ K}$$

Enthalpy of Formation

$\Delta_f H^\circ$ is rounded from $-130.98 \pm 0.47 \text{ kcal} \cdot \text{mol}^{-1}$ derived by Fitzgibbon *et al.*¹ from calorimetric reactions of HCl(aq) with Ba(cr) and BaO(cr). Combination of their two reactions yields $\Delta_f H^\circ(298.15 \text{ K}) = -62.66 \pm 0.47 \text{ kcal} \cdot \text{mol}^{-1}$ for Ba(cr) + H₂O(l) → BaO(cr) + H₂(g). Although the resulting $\Delta_f H^\circ$ is 1.3 kcal·mol⁻¹ less negative than that of NBS Technical Note 270-6,² it confirms Parker's selection² of key values for BaO and BaCl₂ from calorimetry involving aqueous HCl³⁻⁵ instead of discrepant values derived from other reactions.⁶⁻⁸ Earlier HCl calorimetry gave $\Delta_f H^\circ(\text{BaO}, \text{cr}) = -132.0^{+2.2}_{-2.2}$ and $-132.1 \text{ kcal} \cdot \text{mol}^{-1}$.^{4,5} The new value¹ is preferred since both reactions were run in the same calorimeter on samples that were well characterized. The latter is particularly important since impurities were a major problem in studies of BaO^{3, 4, 9-14} and Ba₂O³⁻⁷.

Direct measurements of $\Delta_f H^\circ$ of Ba(cr) by Mah⁶ gave $-139.06 \pm 0.7 \text{ kcal} \cdot \text{mol}^{-1}$. Combustion studies of Fitzgibbon *et al.*¹ suggest that the negative bias of 8 kcal·mol⁻¹ was due to partial dissolution of the crucible lining (MgO) in molten BaO formed in the combustion. Dissolution was eliminated in combustions on sintered MgO disks, but large amounts of BaO₂ were formed both in this case and with the use of BaO crucibles.¹ This led the authors¹ to dismiss combustion calorimetry in favor of solution calorimetry. Parker² noted earlier that the combustion result was incompatible with data for BaCl₂(aq), Ba(OH)₂(aq and cr), BaO₂(cr) and BaCO₃(cr); also a similar discrepancy existed for SrO(cr). We find that the combustion value is incompatible with equilibrium data¹⁹ for BaCl₂(l and g).

$\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$ and $\Delta_f H^\circ(\text{Ba}^{2+}, \text{aq})$ deserve an updated discussion. We combine $\Delta_f H^\circ = -127.95 \pm 0.41 \text{ kcal} \cdot \text{mol}^{-1}$ for Ba(cr) + 2HCl(54.3 H₂O) = H₂(g) + BaCl₂ [in 149.9 HCl (55.0 H₂O)] with $\Delta_f H^\circ(\text{HCl}, 54.3 \text{ H}_2\text{O}) = -39.52 \pm 0.02 \text{ kcal} \cdot \text{mol}^{-1}$ ¹⁶ and $\Delta_{\text{ox}} H^\circ = -2.09 \pm 0.2 \text{ kcal} \cdot \text{mol}^{-1}$ ¹⁷ to give $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) = -204.9 \pm 0.5 \text{ kcal} \cdot \text{mol}^{-1}$. This confirms the JANAF¹⁹ $\Delta_f H^\circ(\text{BaCl}_2)$ of $-205.2 \text{ kcal} \cdot \text{mol}^{-1}$ based on the selection of Parker²; the alternative uncertainty of $\pm 0.6 \text{ kcal} \cdot \text{mol}^{-1}$ should now be used instead of $\pm 3 \text{ kcal} \cdot \text{mol}^{-1}$.¹⁹ The new $\Delta_f H^\circ$ for BaCl₂ yields $\Delta_f H^\circ(\text{Ba}^{2+}, \text{aq}) = -128.0 \pm 0.6 \text{ kcal} \cdot \text{mol}^{-1}$, assuming $\Delta_{\text{ox}} H^\circ(\text{BaCl}_2, \text{cr}) = -3.0 \pm 0.2 \text{ kcal} \cdot \text{mol}^{-1}$ (many references) and $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -39.933 \pm 0.021 \text{ kcal} \cdot \text{mol}^{-1}$.¹⁶ This is consistent with Parker's selection of $\Delta_f H^\circ(\text{Ba}^{2+}, \text{aq}) = -128.5 \text{ kcal} \cdot \text{mol}^{-1}$.²

Heat Capacity and Entropy

C_p° is based on data (1.4–310 K) of Gmelin¹² who reported smoothed values only in the range 4 to 300 K. Based on Gmelin's graphs, we have corrected several typographical errors and resmoothed C_p° above 240 K where the scatter increases rapidly. The entropy is obtained by integration of our adopted C_p° using $S^\circ = 0.0015 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at 4 K. The value $S^\circ = 15.75 \pm 0.02 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ reported by Gmelin¹² corresponds to neither 273.15 K nor 298.15 K and must be erroneous. C_p° data (56–299 K) of Anderson¹⁵ differ by $\pm 1.6\%$ but average about 1.0% higher from 150 to 260 K.

C_p° above 300 K is from constrained fitting of enthalpy data (391–1299 K) of Lander.¹⁴ This calorimetry is subject to bias from a calibration based on Pt and from impurities in the two samples. Information is insufficient to assess the bias due to minor changes in the enthalpy of Pt.¹⁵ We apply crude corrections to the observed enthalpies for 27 mole % SrO in one sample and for about 2.8 mole % SiO₂ in the other sample. Deviations from the adopted curve are $\pm 0.9\%$ (first sample) and $\pm 1.0\%$ (second sample) except for -2.0% at 421 K.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{\text{sub}} H^\circ$ is calculated as the difference in $\Delta_f H^\circ$ between gas and crystal.

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Barium Oxide (BaO)

BaO₂(cr)

T/K	C _p ^a	S ^b	- (G ^c - H ^c (T))/T	Standard State Pressure = p ^d = 0.1 MPa		
				H ^c - H ^c (T)	Δ _f H ^c	log K _r
0	0.000	0.000	INFINITE	-9.983	-546.833	INFINITE
100	31.941	27.501	111.119	-8.582	-539.039	181.565
200	43.493	53.898	76.289	-4.478	-548.479	138.313
298.15	47.279	72.069	72.069	0.000	-548.104	91.169
300	47.329	72.362	72.070	0.088	-548.096	90.577
400	49.898	86.347	73.960	4.955	-547.731	66.727
500	51.785	97.694	77.607	10.044	-547.990	52.420
600	53.220	107.267	81.773	15.296	-548.939	42.870
700	54.396	115.581	86.021	20.678	-548.999	36.044
800	55.405	122.892	90.186	26.169	-549.503	30.920
900	56.312	129.471	94.186	31.756	-549.526	26.934
1000	57.153	135.448	98.018	37.429	-549.490	23.744
1100	57.948	140.932	101.674	43.185	-557.766	21.096
1200	58.706	146.007	105.159	49.018	-557.850	18.889
1300	59.442	150.735	108.485	54.925	-557.776	17.021
1400	60.162	155.167	111.563	60.905	-557.567	15.420
1500	60.869	159.342	114.704	66.957	-557.244	14.034
1600	61.563	163.292	117.618	73.079	-556.829	12.822
1700	62.250	167.045	120.416	79.269	-556.342	11.753
1800	62.927	170.633	123.107	85.528	-555.805	10.803
1900	63.605	174.043	125.698	91.855	-555.239	9.955
2000	64.275	177.333	128.198	98.249	-554.665	9.192
2100	64.940	180.475	130.613	104.710	-554.107	8.503
2200	65.605	183.511	132.949	111.237	-553.562	7.749
2286.000	66.177	186.038	134.899	116.904	CRYSTAL → LIQUID	---
2300	66.270	186.442	135.211	117.831	-691.803	7.034
2400	66.927	189.276	137.405	124.491	-690.669	6.380
2500	67.588	192.022	139.535	131.216	-689.705	5.779
2600	68.245	194.686	141.605	138.008	-688.906	5.225
2700	68.898	197.273	143.620	144.865	-688.261	4.713
2800	69.553	199.791	145.581	151.788	-687.756	4.237
2900	70.208	202.243	147.493	158.776	-687.372	3.795
3000	70.860	204.634	149.358	165.830	-687.088	3.382

PREVIOUS: December 1972

CURRENT: June 1974

BaO₂(l)Ba₂O₃(l)

LIQUID

Barium Oxide (BaO)

$S^{\circ}(298.15\text{ K}) = [96.553] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $T_{\text{fus}} = 2286 \pm 15 \text{ K}$

$\Delta H^{\circ}(298.15\text{ K}) = [-491.627] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{liq}}H^{\circ} = [59] \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation

ΔH° is calculated from that of the crystal by addition of $\Delta_{\text{liq}}H^{\circ}$ and the difference in enthalpy, $H^{\circ}(2286\text{ K}) - H^{\circ}(298.15\text{ K})$, between crystal and liquid.

Heat Capacity and Entropy

C_p° of the liquid is estimated as $8 \text{ cal}\cdot\text{K}^{-1}\cdot\text{g}\cdot\text{atom}^{-1}$ by comparison with other oxides. C_p° is taken from the crystal in the range 298.15 K up to the glass transition assumed at 1600 K. S° is calculated in a manner analogous to that used for ΔH° .

Fusion Data

Feex¹ obtained $T_{\text{fus}} = 2010^{\circ}\text{C}$ from a solar-furnace study using BaO as its own container. We adopt this result but increase it by 3° for conversion to IPTS-68. Foex showed that the much lower value (1918°C) of Schumacher^{2,3} probably resulted from contamination by WO₃ from tungsten supports of the sample. $\Delta_{\text{liq}}H^{\circ}$ is estimated such that $\Delta_{\text{fus}}S^{\circ}$ is $6 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Vaporization Data

Unlike the other alkaline-earth oxides, BaO(cr) vaporizes mainly to BaO(g) with traces of Ba₂O₃ and Ba₃O₄. Mass-spectrometric studies⁴ suggest that decomposition to Ba(g) and O(g) is not a major contributor even though the observed intensities of Ba⁺ are almost comparable with those of BaO⁺. T_{vap} is the calculated temperature at which $\Delta G^{\circ} = 0$ for BaO(l) = BaO(g); $\Delta_{\text{vap}}H^{\circ}$ is the corresponding difference in ΔH° .

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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	-(G ^o - H ^o (T _r))/T	H ^o - H ^o (T _r)	ΔH ^o	
0						
100						
200						
298.15	47.279	96.553	96.553	0.000	-491.627	82.553
300	47.379	96.845	96.554	0.088	-471.205	82.022
400	49.898	110.831	98.443	4.955	-464.293	60.631
500	51.785	122.178	102.090	10.044	-457.543	47.199
600	53.220	131.750	106.257	15.296	-450.649	39.232
700	54.396	140.045	110.504	20.678	-443.686	33.108
800	55.405	147.375	114.664	26.169	-436.668	28.511
900	56.312	153.954	118.670	31.756	-429.621	24.935
1000	57.153	159.931	122.502	37.429	-422.575	22.073
1100	57.948	165.416	126.157	43.185	-415.529	19.693
1200	58.706	170.491	129.643	49.018	-408.480	17.709
1300	59.442	175.219	132.969	54.925	-401.431	16.031
1400	60.162	179.650	136.146	60.905	-394.382	14.592
1500	60.869	183.825	139.187	66.957	-387.333	13.346
1600	61.563	187.776	142.102	73.079	-380.284	12.257
1600.010	61.563	187.776	142.102	73.079	-380.284	12.257
1600.010	66.944	187.776	142.102	73.079	-380.284	12.257
1700	66.944	191.834	144.909	79.773	-373.235	11.297
1800	66.944	195.661	147.623	86.468	-366.186	10.445
1900	66.944	199.280	150.248	93.162	-359.137	9.685
2000	66.944	202.714	152.786	99.856	-352.088	9.001
2100	66.944	205.980	155.242	106.551	-345.039	8.384
2200	66.944	209.094	157.619	113.245	-337.990	7.834
2286.000	66.944	211.661	159.604	119.002	-330.941	7.374
2300	66.944	212.070	159.923	119.940	-330.080	7.042
2400	66.944	214.919	162.155	126.634	-323.031	6.444
2500	66.944	217.652	164.321	133.328	-315.982	5.894
2600	66.944	220.278	166.423	140.023	-308.933	5.387
2700	66.944	222.804	168.465	146.717	-301.884	4.918
2800	66.944	225.239	170.449	153.412	-294.835	4.483
2900	66.944	227.579	172.379	160.106	-287.786	4.078
3000	66.944	229.857	174.257	166.800	-280.737	3.700
3100	66.944	232.053	176.086	173.495	-273.688	3.346
3200	66.944	234.178	177.869	180.189	-266.639	3.014
3300	66.944	236.238	179.607	186.884	-259.590	2.703
3400	66.944	238.236	181.302	193.578	-252.541	2.409
3500	66.944	240.177	182.956	200.272	-245.492	2.132
3600	66.944	242.063	184.572	206.967	-238.443	1.870
3700	66.944	243.897	186.151	213.661	-231.394	1.622
3800	66.944	245.682	187.694	220.356	-224.345	1.386
3900	66.944	247.421	189.203	227.050	-217.296	1.163
4000	66.944	249.116	190.680	233.744	-210.247	0.951
4100	66.944	250.769	192.125	240.439	-203.198	0.748
4200	66.944	252.382	193.541	247.133	-196.149	0.556
4300	66.944	253.957	194.928	253.828	-189.100	0.372
4400	66.944	255.496	196.287	260.522	-182.051	0.196
4500	66.944	257.001	197.619	267.216	-175.002	0.028
4600	66.944	258.472	198.926	273.911	-167.953	-0.133
4700	66.944	259.912	200.209	280.605	-160.904	-0.287
4800	66.944	261.321	201.467	287.300	-153.855	-0.434
4900	66.944	262.702	202.703	293.994	-146.806	-0.576
5000	66.944	264.054	203.916	300.688	-139.757	-0.712

PREVIOUS: December 1972

CURRENT: June 1974

Barium Oxide (BaO)

Ba₂O₃(l)

Barium Oxide (BaO)

CRYSTAL-LIQUID

0 to 2286 K crystal
above 2286 K liquid
Refer to the individual tables for details.

$M_r = 153.3294$ Barium Oxide (BaO)

$Ba_2O_3(cr,l)$

T/K	C_p°	Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa		$\log K_r$
		$S^\circ - [C_p^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	
0	0.000	INFINITE	INFINITE	-546.833	-546.833	INFINITE
100	31.941	27.301	111.119	-548.383	-548.383	781.545
200	43.493	53.898	76.289	-548.479	-529.582	138.313
298.15	47.279	72.069	72.069	0.000	-520.382	91.169
300	47.329	72.362	72.070	0.088	-520.210	90.577
400	49.898	86.347	73.960	4.955	-510.977	66.727
500	51.785	97.694	77.607	10.044	-501.778	52.420
600	53.220	107.267	81.773	15.296	-492.436	42.870
700	54.596	115.561	86.021	20.678	-483.025	36.044
800	55.405	122.892	90.180	26.169	-473.558	30.920
900	56.312	129.471	94.186	31.756	-464.063	26.934
1000	57.153	135.448	98.018	37.429	-454.569	23.744
1100	57.948	140.932	101.674	43.185	-444.261	21.096
1200	58.706	146.007	105.159	49.018	-433.937	18.889
1300	59.442	150.735	108.485	54.925	-423.613	17.021
1400	60.162	155.167	111.663	60.905	-413.300	15.420
1500	60.869	159.342	114.704	66.957	-403.006	14.034
1600	61.563	163.292	117.618	73.079	-392.737	12.822
1700	62.250	167.045	120.416	79.269	-382.496	11.753
1800	62.927	170.623	123.107	85.528	-372.285	10.803
1900	63.605	174.043	125.698	91.855	-362.105	9.955
2000	64.275	177.323	128.198	98.249	-351.955	9.192
2100	64.940	180.475	130.613	104.710	-341.833	8.503
2200	65.605	183.511	132.949	111.237	-326.362	7.749
2286.000	66.177	186.038	134.899	116.904	CRYSTAL <- -> LIQUID TRANSITION	
2286.000	66.944	211.661	134.899	175.480		
2300	66.944	212.070	135.367	176.417	-633.217	7.042
2400	66.944	214.919	138.623	183.111	-632.049	6.444
2500	66.944	217.652	141.750	189.806	-631.116	5.894
2600	66.944	220.278	144.701	196.500	-630.414	5.387
2700	66.944	222.804	147.547	203.194	-629.932	4.918
2800	66.944	225.239	150.278	209.889	-629.655	4.483
2900	66.944	227.588	152.904	216.583	-629.565	4.078
3000	66.944	229.857	155.432	223.278	-629.640	3.700
3100	66.944	232.053	157.868	229.972	-629.857	3.346
3200	66.944	234.178	160.220	236.666	-630.192	3.014
3300	66.944	236.238	162.497	243.361	-630.614	2.703
3400	66.944	238.236	164.691	250.055	-631.111	2.409
3500	66.944	240.177	166.820	256.750	-631.660	2.132
3600	66.944	242.063	168.884	263.444	-632.240	1.870
3700	66.944	243.897	170.887	270.138	-632.837	1.622
3800	66.944	245.682	172.832	276.833	-633.435	1.386
3900	66.944	247.421	174.722	283.527	-634.023	1.163
4000	66.944	249.116	176.561	290.222	-634.593	0.951
4100	66.944	250.769	178.351	296.916	-635.135	0.748
4200	66.944	252.382	180.094	303.610	-635.646	0.556
4300	66.944	253.957	181.794	310.305	-636.125	0.372
4400	66.944	255.496	183.451	316.999	-636.568	0.196
4500	66.944	257.001	185.069	323.694	-636.975	0.028
4600	66.944	258.472	186.649	330.388	-637.339	-0.133
4700	66.944	259.912	188.192	337.082	-637.649	-0.287
4800	66.944	261.311	189.701	343.777	-637.946	-0.434
4900	66.944	262.702	191.177	350.471	-638.206	-0.576
5000	66.944	264.034	192.621	357.166	-638.442	-0.712

PREVIOUS:

CURRENT: June 1974

Barium Oxide (BaO)

$Ba_2O_3(cr,l)$

Ba₃O₄(g)

Barium Oxide (BaO)

IDEAL GAS

Barium Oxide (BaO)

Enthalpy Reference Temperature = $T_r = 298.15$ K									
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	ΔH°	ΔG°	$\log K_r$	Standard State Pressure = $p^\circ = 0.1$ MPa	
		$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$			
0	0	0	INFINITE	INFINITE	-9.014	-121.607	INFINITE		
100	29.160	202.190	663.233	263.233	-6.104	-121.607			
200	30.735	222.767	238.400	-3.127	-122.870	-137.747			
298.15	32.897	235.457	235.457	0	-123.846	-144.839			
300	32.932	235.661	235.458	0.061	-123.865	-144.969			
400	34.443	245.359	236.770	3.435	-124.993	-151.844			
500	35.385	253.154	239.293	6.930	-126.845	-158.363			
600	36.993	259.662	242.160	10.501	-129.476	-164.410			
700	38.329	265.242	245.068	14.172	-131.298	-170.100			
800	39.479	270.121	247.901	17.776	-133.639	-175.728			
900	40.488	274.454	250.616	21.455	-135.569	-180.592			
1000	41.399	278.350	253.197	25.152	-137.510	-185.491			
1100	42.228	281.887	255.647	28.864	-139.375	-189.375			
1200	42.981	285.126	257.971	32.597	-141.023	-193.054			
1300	43.666	288.114	260.176	36.319	-142.512	-196.534			
1400	44.291	290.886	262.272	40.060	-143.854	-199.855			
1500	44.866	293.472	264.267	43.809	-145.135	-203.093			
1600	45.399	295.896	266.169	47.564	-146.368	-206.160			
1700	45.888	298.178	267.985	51.327	-147.558	-209.105			
1800	46.337	300.333	269.723	55.099	-148.707	-211.936			
1900	46.753	302.378	271.388	58.880	-149.816	-214.658			
2000	47.135	304.324	272.987	62.675	-150.892	-217.274			
2100	47.483	306.183	274.523	66.485	-151.937	-219.787			
2200	47.801	307.960	276.003	70.312	-152.952	-222.198			
2300	48.096	309.679	277.430	74.157	-153.937	-224.508			
2400	48.366	311.335	278.809	78.021	-154.892	-226.728			
2500	48.611	312.939	280.142	81.952	-155.816	-228.850			
2600	48.834	314.504	281.434	85.972	-156.708	-230.884			
2700	49.037	316.024	282.687	90.011	-157.568	-232.832			
2800	49.221	317.519	283.904	94.121	-158.397	-234.697			
2900	49.388	318.989	285.089	98.312	-159.190	-236.481			
3000	49.539	320.442	286.243	102.596	-159.946	-238.186			
3100	49.677	321.881	287.369	106.986	-160.666	-239.812			
3200	49.801	323.312	288.470	111.494	-161.351	-241.359			
3300	49.911	324.739	289.548	116.132	-162.002	-242.828			
3400	49.011	326.166	290.604	120.912	-162.618	-244.219			
3500	50.112	327.595	291.640	125.844	-163.197	-245.532			
3600	51.777	329.030	292.659	130.937	-163.738	-246.767			
3700	53.519	330.472	293.661	136.201	-164.241	-247.924			
3800	55.325	331.924	294.654	141.643	-164.707	-248.994			
3900	57.172	333.384	295.632	147.268	-165.136	-249.979			
4000	59.044	334.853	296.586	153.078	-165.528	-250.881			
4100	60.922	336.337	297.537	159.077	-165.883	-251.699			
4200	62.784	337.827	298.479	165.262	-166.202	-252.434			
4300	64.609	339.326	299.411	171.632	-166.483	-253.087			
4400	66.380	340.832	300.336	178.182	-166.727	-253.658			
4500	68.076	342.342	301.252	184.906	-166.936	-254.147			
4600	69.681	343.856	302.162	191.794	-167.107	-254.554			
4700	71.180	345.371	303.065	198.838	-167.241	-254.881			
4800	72.561	346.885	303.962	206.026	-167.339	-255.127			
4900	73.812	348.394	304.854	213.346	-167.397	-255.294			
5000	74.928	349.896	305.740	220.784	-167.417	-255.378			
5100	75.901	351.390	306.620	228.327	-167.399	-255.378			
5200	76.725	352.872	307.493	235.960	-167.341	-255.294			
5300	77.413	354.340	308.350	243.688	-167.241	-255.127			
5400	77.953	355.793	309.190	251.437	-167.097	-254.881			
5500	78.354	357.227	310.090	259.254	-166.917	-254.554			
5600	78.620	358.641	310.944	267.104	-166.699	-254.147			
5700	78.759	360.034	311.793	274.974	-166.443	-253.658			
5800	78.777	361.404	312.637	282.851	-166.149	-253.087			
5900	78.684	362.750	313.475	290.725	-165.816	-252.434			
6000	78.489	364.071	314.307	298.585	-165.443	-251.699			

PREVIOUS: June 1974 (1 atm)

CURRENT: June 1974 (1 bar)

Ba₃O₄(g)

Barium Oxide (BaO)

Continued on page 359

$S^\circ(298.15 \text{ K}) = 235.457 \pm 0.33 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $\Delta H_f^\circ(0 \text{ K}) = -121.6 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta H_f^\circ(298.15 \text{ K}) = -123.8 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$

Electronic and Molecular Constants ($\sigma = 1$)									
Source	State	$\epsilon_e, \text{cm}^{-1}$	$r_e, \text{\AA}$	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}	ω_4, cm^{-1}
1-4	X ¹ Σ^+	0.0	1.9397	0.31261	0.00139	669.81	2.054		
1	a ³ Π	17372	2.289	0.2244	0.0014	448.3	2.4		
1	A ¹ Π	17568	2.289	0.2244	0.0014	448.3	2.4		
3	X ³ Σ^+	[14000]	2 [2.133]	[0.2583]	[0.0011]	[499.7]	[1.64]		
1,62	A ¹ Σ^+	16722	2.133	0.25832	0.00107	499.7	1.64		
3	X ³ Σ^+	[22000]	[2.26]	[0.230]	[0.0011]	[480]	[2]		
3	A ¹ Δ	[24000]	"	"	"	"	"		
3	A ¹ Δ	[24000]	"	"	"	"	"		
3	X ³ Σ^+	[24000]	"	"	"	"	"		
3	X ³ Σ^+	[24000]	"	"	"	"	"		
3	X ³ Σ^+	[28000]	"	"	"	"	"		
3	X ³ Σ^+	[32000]	[2.20]	[0.243]	"	[488]	[3.6]		
2	B ¹ Π	32775	"	"	"	488	3.6		

Enthalpy of Formation

We adopt $D_0^\circ = 131.0 \pm 2 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta H_f^\circ(298.15 \text{ K}) = -29.6 \pm 2 \text{ kcal} \cdot \text{mol}^{-1}$ based on equilibria and vaporization data analyzed below. The results are in excellent agreement, even though δS varies widely. The dissociation energy is confirmed also by values of 132 ± 5 (electron impact),¹⁷ ≥ 131.4 (crossed-beam chemiluminescence),¹⁸ and $131 \text{ kcal} \cdot \text{mol}^{-1}$ (flame study, 1973).¹⁹ We have adjusted the latter value to make it roughly consistent with our Gibbs energy functions. Less reliable data were reviewed by Schofield.¹⁹ Our analysis supports the conclusions of Brewer and Rosenblatt.²⁰

Source	Method	Reaction ^a	T/K	Points	δS	$\Delta H_f^\circ(298.15 \text{ K}), \text{kcal} \cdot \text{mol}^{-1}$	$\Delta H_f^\circ(298.15 \text{ K}), D_0^\circ$
¹ Kaliff (1970)	Flame photometric	A	~2680-2860	12	19. \pm 4	-4.7 \pm 2.5	-29.6 \pm 3 131.0
² Colin (1964)	Knudsen mass spec.	B	1934-2069	3	-11. \pm 10	-6.8 \pm 2.0	-29.1 \pm 3 130.5
³ Gemenov (1972)	"	C	1423-1723	Eqn.	3.7	108.1	102.2 \pm 1.0
¹⁰ Newbury (1968)	Knudsen thermal.	C	1563-1853	17	5.9 \pm 0.9	111.8 \pm 1.5	-28.8 \pm 2 130.2
	"	C	1503-1862	45	4.2 \pm 0.5	109.2 \pm 0.8	-29.2 \pm 2 130.6
	"	C	1590-1892	11	4.8 \pm 0.2	101.7 \pm 1.1	-28.9 \pm 2 130.3
	Knudsen mass spec.	C	1481-1917	38	5.6 \pm 0.3	101.8 \pm 1.4	-29.3 \pm 2 130.8
¹¹ Inghram (1955)	"	C	1365-1910	29	6.1 \pm 0.4	102.1 \pm 1.6	-29.2 \pm 2 130.6
	"	C	1530-1758	4	-2.8 \pm 6.1	99. \pm 10	-27.8 \pm 2 129.2
¹² Shchukarev (1957)	Langmuir mass spec.	C	~1173-1473	Eqn.	93.3	101.4 \pm 0.6	-29.6 \pm 2 131.0
¹³ Novikov (1961)	Knudsen effusion	C	~1140-1470	Eqn.	-2.0	99.8 \pm 1.5	-31.2 \pm 2 132.6
¹⁴ Blewett (1939)	"	C	1526-1800	Eqn.	-0.5 \pm 2.5	103.9 \pm 4.3	-27.1 \pm 3 128.5
¹⁵ Hermans (1937)	Langmuir	C	~1200-1560	Eqn.	16.	101.8 \pm 1.6	-29.2 \pm 3 130.7
¹⁶ Claassen (1933)	"	C	1223-1475	7	-4.5 \pm 1.5	101.9 \pm 1.0	-29.1 \pm 2 130.5

^aReactions: A) Ba(g) + CO₂(g) = BaO(g) + CO(g); B) Ba(g) + SO(g) = BaO(g) + S(g); C) BaO(cr) = BaO(g).

Heat Capacity and Entropy

Electronic levels (T_e) and vibrational-rotational constants of the observed states are from Field¹ and Rosen.² The long-sought A¹ Π and A³ Π states of CaO, SrO and BaO were characterized by Field¹ using a new method for assignment of perturbations. This study resolved the long-standing controversy over low-lying electronic levels and confirmed¹ that X³ Σ^+ is the ground state.⁴ We estimate the other potentially low-lying state (X³ Σ^+) at 14000 cm⁻¹ by assuming that it lies 3000 \pm 2500 cm⁻¹ below the isoelectronic A state. Other predicted states and their vibrational-rotational constants are estimated in isoelectronic groups by comparison with BeO, MgO, CaO and SrO.⁵ Comparisons are facilitated by listing the states in the isoelectronic order of MgO.³ Our thermodynamic functions correspond to an "effective" ground state with $g = 1$ instead of $g = 6$.^{10,19} Our functions are calculated using first-order anharmonic corrections to Q_r and Q_v in the partition function $Q = Q_e Q_v Q_r \exp(-\epsilon_0/kT)$.

Barium Sulfide (BaS)

CRYSTAL

 $M_r = 169.39$ Barium Sulfide (BaS) $Ba_2Si_3(cr)$

$$S^\circ(298.15\text{ K}) = 78.4 \pm 1.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(0\text{ K}) = -462.7 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(298.15\text{ K}) = -463.6 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$$

Enthalpy of Formation

Sabatier¹ measured the enthalpy of solution of BaS in hydrochloric acid solution as $\Delta_f H^\circ(284\text{ K}) = -27.0 \pm 1.0 \text{ kcal}\cdot\text{mol}^{-1}$ for $\text{BaS}(cr) + 2\text{HCl}(100\text{ H}_2\text{O}, aq) \rightarrow \text{BaCl}_2(100\text{ H}_2\text{O}, aq) + \text{H}_2\text{S}(aq)$. We derive $\Delta_f H^\circ(298.15\text{ K}) = -111.0 \pm 2.0 \text{ kcal}\cdot\text{mol}^{-1}$ based on the following auxiliary data: $\Delta_f H^\circ(\text{HCl}-100\text{ H}_2\text{O}, aq, 298.15\text{ K}) = -39.657 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta_f H^\circ(\text{H}_2\text{S}, aq, 298.15\text{ K}) = -9.5 \text{ kcal}\cdot\text{mol}^{-1}$, and $\Delta_f H^\circ(\text{BaCl}_2-100\text{ H}_2\text{O}, aq, 298.15\text{ K}) = -207.803 \text{ kcal}\cdot\text{mol}^{-1}$. Mourtot⁴ also measured the enthalpy of solution of BaS in hydrochloric acid solution as $\Delta_f H^\circ = -27.35 \pm 1.0 \text{ kcal}\cdot\text{mol}^{-1}$ from which we calculate $\Delta_f H^\circ(298.15\text{ K}) = -110.6 \pm 2 \text{ kcal}\cdot\text{mol}^{-1}$ using the same auxiliary data. The uncertainties quoted reflect the correction to 298.15 K and the ambiguity of the exact solution composition.

Our analyses of equilibrium studies of Okuno,³ Culver and Hamdorf,⁵ Nikonov,⁶ Schenck and Hammerschmidt,⁷ and Colin *et al.*,⁹ are listed below. The calculated 3rd law $\Delta_f H^\circ(298.15\text{ K})$ may have an uncertainty of $0.5 \text{ kcal}\cdot\text{mol}^{-1}$ since the JANAF Gibbs energy functions are partially based on the estimated C_p° data (above 300 K). The enthalpy of formation of BaS(cr) derived from equilibrium studies is in good agreement with that derived from enthalpy of solution studies.¹⁴ We discount the studies of Nikonov⁶ and of Colin *et al.*⁹ More information is given in the SrS(cr) table.¹⁰

A weighted average, $\Delta_f H^\circ(\text{BaS}, cr, 298.15\text{ K}) = -110.8 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$, is adopted in the tabulation.

Source	Method	Reaction ^a	T/K	No. of Points	$\Delta_f H^\circ(298.15\text{ K})$, kcal·mol ⁻¹	$\Delta_f H^\circ(298.15\text{ K})$, kcal·mol ⁻¹
³ Okuno (1935)	Equilibrium	A	973–1173	5	0.85 ± 0.75	-6.27 ± 0.81
⁴ Culver (1955)	Equilibrium	B	1073–1373	Equation	-2.89	-7.18 ± 0.25
⁵ Nikonov (1961)	Vaporization	C	1400–1600	Equation	2.2	9.68 ± 0.75
⁶ Schenck (1933)	Equilibrium	C	1355–1399	2	-11.4	-106.38
⁷ Colin <i>et al.</i> (1964)	Mass Spec	E	1846–2120	10	-17.6 ± 7.5	-59.4 ± 15.0
						-24.2 ± 4.2
						-118.6 ± 12

^aReactions:

- A) $\text{BaSO}_4(cr) + 4\text{CO}(g) = \text{BaS}(cr) + 4\text{CO}_2(g)$
 B) $\text{BaSO}_4(cr) + 4\text{H}_2(g) = \text{BaS}(cr) + 4\text{H}_2\text{O}(g)$
 C) $\text{BaSO}_4(g) = \text{BaS}(cr)$
 D) $\text{BaSO}_4(cr) + \text{S}_2(g) = \text{BaS}(cr) + 2\text{SO}_2(g)$
 E) $\text{Ba}(g) + 2\text{S}_2(g) = \text{BaS}(cr) + 3\text{S}(g)$

Heat Capacity and Entropy

King and Weller¹¹ measured the low temperature heat capacities from 54–296 K. Their smooth values are adopted in the tabulation. The entropy, $S^\circ(298.15\text{ K}) = 18.7 \pm 0.2 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, is based on $S^\circ(51\text{ K}) = 2.60 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ as extrapolated by King and Weller using Debye and Einstein functions ($\theta_D = 159$, $\theta_E = 267$). The C_p° values above 300 K are estimated by graphical extrapolation combined with method B of Kubaschewski *et al.*¹²

Fusion Data

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

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Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$					Standard State Pressure = $p^\circ = 0.1\text{ MPa}$				
T/K	C_p°	$S^\circ - (G^\circ - H^\circ(T_r))/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_r$		
0	0.000	0.000	INFINITE	INFINITE	-462.722	-462.722	INFINITE		
100	36.317	29.938	120.037	-9.010	-463.661	-461.995	241.321		
200	46.610	59.176	82.843	-4.733	-463.571	-460.350	120.231		
298.15	49.374	78.395	78.395	0.000	-463.587	-458.776	80.376		
300	49.407	78.701	78.396	0.091	-463.590	-458.746	79.875		
400	51.128	93.153	80.355	5.119	-466.176	-457.002	59.678		
500	52.718	104.737	84.110	10.314	-468.728	-454.445	47.476		
600	54.057	114.473	88.380	15.655	-471.593	-451.302	39.289		
700	55.061	122.882	92.722	21.112	-475.298	-447.793	33.415		
800	55.982	130.296	96.965	26.665	-478.283	-444.006	28.991		
900	56.777	136.935	101.043	32.302	-480.809	-438.930	25.475		
1000	57.656	142.963	104.938	38.025	-482.849	-432.879	22.400		
1100	58.430	148.494	108.650	43.829	-484.193	-417.908	19.845		
1200	59.204	153.612	112.186	49.710	-484.341	-406.965	17.715		
1300	59.983	158.381	115.558	55.670	-483.376	-396.017	15.912		
1400	60.752	162.855	118.778	61.707	-481.172	-385.075	14.367		
1500	61.500	167.071	121.859	67.819	-477.901	-374.148	13.029		
1600	62.238	171.065	124.810	74.007	-473.534	-363.243	11.859		
1700	63.037	174.862	127.644	80.272	-467.090	-352.363	10.827		
1800	63.806	178.487	130.369	86.614	-458.588	-341.511	9.910		
1900	64.554	181.957	132.993	93.032	-448.051	-330.688	9.091		
2000	65.312	185.288	135.525	99.525	-435.498	-319.894	8.355		
2100	66.086	188.493	137.971	106.095	-420.950	-309.127	7.689		
2200	66.866	191.585	140.339	112.742	-404.947	-293.011	6.957		
2300	67.640	194.574	142.632	119.467	-387.630	-275.725	6.262		
2400	68.408	197.469	144.857	126.270	-359.468	-258.494	5.626		
2500	69.156	200.277	147.018	133.148	-320.463	-241.308	5.042		
2600	69.915	203.004	149.119	140.102	-269.609	-224.159	4.503		
2700	70.694	205.657	151.164	147.132	-208.895	-207.041	4.005		
2800	71.463	208.242	153.157	154.240	-138.304	-189.946	3.543		
2900	72.221	210.763	155.100	161.424	-67.818	-172.871	3.114		
3000	72.969	213.224	156.996	168.684	-67.418	-155.811	2.713		

PREVIOUS:

CURRENT: September 1977

Barium Sulfide (BaS)

 $Ba_2Si_3(cr)$

Barium Sulfide (BaS)

IDEAL GAS

 $M_r = 169.39$ Barium Sulfide (BaS) $Ba_2S(g)$

$S^\circ(298.15\text{ K}) = 248.861 \pm 0.42\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(0\text{ K}) = 39.55 \pm 12.6\text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = 37.78 \pm 12.6\text{ kJ}\cdot\text{mol}^{-1}$

Source		State	ϵ_n , cm^{-1}	g_n	r_n , g	B_n , cm^{-1}	Electronic and Molecular Constants ($\sigma = 1$)		ω_n , cm^{-1}	$\omega_n x_n$, cm^{-1}
1, 2	$X^1\Sigma^+$		0.0	1	2.5067	0.103160	0.000314		379.117	0.8828
3	$X^1\Sigma^+$		[12000.]	3	[2.635]	[0.09339]	[0.000713]		[294.1]	[3.075]
1, 3	$X^1\Sigma^+$		[14000.]	6	[2.88]	[0.0784]	[0.0004]		[234.8]	[0.9]
4	$X^1\Sigma^+$		[14200.]	2	[2.88]	[0.0784]	[0.0004]		[234.8]	[0.9]
5	$A^1\Sigma^+$		14450.	1	2.635	0.09339	0.000713		294.06	3.075
6	$B^1\Sigma^+$		26997.74	1	2.7468	0.08591	0.000439		253.90	0.4373

Enthalpy of Formation

The adopted value of the enthalpy of formation, $\Delta_f H^\circ(\text{BaS}, g, 298.15\text{ K}) = 9.03 \pm 3.0\text{ kcal}\cdot\text{mol}^{-1}$, is based on the Knudsen mass-spectrometric study of Colin *et al.*¹ Our reanalysis of their ion intensity data is given below. Although the large drift would suggest a larger uncertainty in the derived quantities ($\Delta_f H^\circ$, D_0°), our experience with related work on other alkaline earth sulfides and oxides by the same authors indicates that results derived from a 3rd law analysis are preferred. Our value of the enthalpy of formation is intermediate between $\Delta_f H^\circ(298.15\text{ K}) = 7.3 \pm 5\text{ kcal}\cdot\text{mol}^{-1}$ obtained by Mills⁶ (using different Gibbs energy functions) in a recent critical compilation and $\Delta_f H^\circ(298.15\text{ K}) = 12.0\text{ kcal}\cdot\text{mol}^{-1}$ preferred by NBS.⁷ Using auxiliary JANAF data,⁸ and the recommended value for D_0° (S_2 , g) = $100.69 \pm 0.01\text{ kcal}\cdot\text{mol}^{-1}$, we calculate $D_0^\circ(\text{BaS}, g) = 99.3 \pm 3\text{ kcal}\cdot\text{mol}^{-1}$. A linear Birge-Sponer extrapolation of the $X^1\Sigma^+$ ground state based on the data of Barrow *et al.*², after an ionic correction due to Hildenbrand,⁴ yields the dissociation energy of $99.8\text{ kcal}\cdot\text{mol}^{-1}$ for the products $\text{Ba}^+(S) + S(^1D)$. The $X^1\Sigma^+$ ground state cannot dissociate to ground state atoms. If the dissociation products are instead $\text{Ba}(^1D) + S(^1P)$, analogous to the work of Field *et al.*⁵ on BaO , the dissociation energy becomes $D_0^\circ = 100.4\text{ kcal}\cdot\text{mol}^{-1}$. Both of these values are uncertain due to the very long vibrational extrapolation.

Source	Method	Reaction ^a	7/K	No. of Points	$\Delta_f H^\circ(298.15\text{ K})$, $\text{kcal}\cdot\text{mol}^{-1}$	D_0° , $\text{kcal}\cdot\text{mol}^{-1}$
Colin (1964)	Mass Spec.	$A: \text{Ba}(g) + S_2(g) \rightarrow \text{BaS}(g) + S(g)$	1846–2120	10	-2.5 ± 4.9	-3.37 ± 9.8
					1.68 ± 2.5	9.03 ± 3.0

^aReaction: $A: \text{Ba}(g) + S_2(g) \rightarrow \text{BaS}(g) + S(g)$

Heat Capacity and Entropy

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

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8. JANAF Thermochemical Tables: $\text{Ba}(g)$, 12–31–70; $S_2(g)$, 12–31–65; $S(g)$, 6–30–71; $\text{BaO}(g)$, 6–30–74.

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$		Standard State Pressure = $p^\circ = 0.1\text{ MPa}$		log K_r	
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
0	0.	0.	INFINITE	39.549	INFINITE
100	30.195	212.875	-9.556	39.549	23.464
200	33.796	234.997	-6.627	40.091	-12.256
298.15	35.531	248.861	-3.414	39.117	-1.874
300	35.552	249.081	0.	37.782	-8.232
400	36.360	259.433	0.066	37.753	1.483
500	36.789	267.597	0.666	37.740	-23.599
600	37.047	274.329	1.018	29.653	-37.494
700	37.219	280.053	1.101	25.139	-50.484
800	37.342	285.032	1.473	21.691	-50.484
900	37.438	289.436	18.461	17.881	-62.824
1000	37.515	293.384	22.200	14.732	-74.630
1100	37.583	296.963	26.743	-38.543	-84.914
1200	37.643	300.236	29.702	-40.538	-89.959
1300	37.695	303.251	32.464	-50.951	-93.981
1400	37.742	306.038	35.112	-52.219	-97.792
1500	37.787	308.657	37.659	-53.596	-101.418
1600	37.831	311.105	40.187	-54.879	-104.879
1700	37.861	313.413	42.699	-56.163	-108.190
1800	37.891	315.600	45.193	-57.453	-111.366
1900	37.921	317.685	48.579	-58.747	-114.416
2000	37.951	319.681	52.386	-60.069	-117.346
2100	37.990	321.604	56.214	-61.645	-120.164
2200	40.170	323.465	60.069	-63.620	-122.875
2300	42.168	325.277	67.902	-66.693	-125.484
2400	44.168	327.051	71.904	-71.774	-128.004
2500	46.168	328.794	75.982	-78.772	-130.534
2600	48.168	330.517	80.148	-83.829	-133.063
2700	50.168	332.225	88.812	-88.829	-135.593
2800	52.168	333.926	93.340	-93.340	-138.122
2900	54.168	335.623	98.016	-98.016	-140.651
3000	56.168	337.321	102.833	-102.833	-143.180
3100	58.168	339.022	107.862	-107.862	-145.709
3200	60.168	340.728	113.050	-113.050	-148.238
3300	62.168	342.438	118.422	-118.422	-150.767
3400	64.168	344.153	123.982	-123.982	-153.296
3500	66.168	345.872	129.728	-129.728	-155.825
3600	68.168	347.592	135.657	-135.657	-158.354
3700	70.168	349.312	141.764	-141.764	-160.883
3800	72.168	351.027	148.040	-148.040	-163.412
3900	74.168	352.736	154.474	-154.474	-165.941
4000	76.168	354.436	161.054	-161.054	-168.470
4100	78.168	356.122	167.765	-167.765	-171.000
4200	80.168	357.791	174.593	-174.593	-173.529
4300	82.168	359.441	181.522	-181.522	-176.058
4400	84.168	361.069	188.534	-188.534	-178.587
4500	86.168	362.672	195.615	-195.615	-181.116
4600	88.168	364.268	202.748	-202.748	-183.645
4700	90.168	365.859	209.918	-209.918	-186.174
4800	92.168	367.441	217.110	-217.110	-188.703
4900	94.168	369.013	224.312	-224.312	-191.232
5000	96.168	370.576	231.548	-231.548	-193.761
5100	98.168	372.133	238.825	-238.825	-196.290
5200	100.168	373.684	246.145	-246.145	-198.819
5300	102.168	375.231	253.502	-253.502	-201.348
5400	104.168	376.773	260.897	-260.897	-203.877
5500	106.168	378.311	268.332	-268.332	-206.406
5600	108.168	379.845	275.807	-275.807	-208.935
5700	110.168	381.375	283.322	-283.322	-211.464
5800	112.168	382.901	290.877	-290.877	-213.993
5900	114.168	384.423	298.472	-298.472	-216.522
6000	116.168	385.941	306.107	-306.107	-219.051

PREVIOUS: September 1977 (1 atm)

CURRENT: September 1977 (1 bar)

Barium Sulfide (BaS)

 $Ba_2S(g)$

Barium

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Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

Continuation of discussions of selected Ba species

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² $\gamma_2(\text{Ba}(\text{OH})_2 \cdot 660 \text{ H}_2\text{O}) = [-60] \text{ cal-K}^{-1} \cdot \text{mol}^{-1}$; $\Phi_2(\text{HF} \cdot 110 \text{ H}_2\text{O}) = 3.7 \text{ cal-K}^{-1} \cdot \text{mol}^{-1}$; $\Phi_2(\text{AgF} \cdot 200 \text{ H}_2\text{O}) = -[3.0] \text{ cal-K}^{-1} \cdot \text{mol}^{-1}$; $\Phi_2(\text{BaCl}_2 \cdot 400 \text{ H}_2\text{O}) = [-60] \text{ cal-K}^{-1} \cdot \text{mol}^{-1}$.
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to be the same as in BaF₂.^{7, 11} The O-H stretching frequency, 3650 cm⁻¹, is estimated from the alkali hydroxide series. The bending frequency, 431 cm⁻¹, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.^{11, 15}
 The entropy in the present table is lower by 1.25 cal-K⁻¹·mol⁻¹ at 298 K and 1.77 cal-K⁻¹·mol⁻¹ at 1000 K than that proposed by Jackson,¹¹ the vibrational frequencies and electronic levels adopted here differ from those of Jackson.¹¹ The moment of inertia in Jackson¹¹ appears to be in error.

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Jackson⁹ used a different molecular configuration and different vibrational frequencies to estimate $S^{\circ}(298.15\text{ K}) = 78.045\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. We assign uncertainty of $\pm 3\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to the adopted entropy.

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