

Relative Enthalpy of Beryllium 1:1-Aluminate, $\text{BeO} \cdot \text{Al}_2\text{O}_3$, from 273 to 1173 °K. Thermodynamic Properties from 273 to 2150 °K*

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The relative enthalpy of the beryllium aluminate $\text{BeO} \cdot \text{Al}_2\text{O}_3$ was measured by "drop" calorimetry from 273 to 1173 °K. The thermodynamic properties were calculated up to 2150 °K (approximately the melting point). For this calculation, the data were extrapolated above 1173 °K and the entropy at 273 °K, previously determined at the NBS, was used.

Key Words: Beryllium aluminate, chrysoberyl, drop calorimetry, enthalpy measurements, high-temperature calorimetry, mixed oxides, specific heat, thermodynamic properties.

1. Introduction

The relative enthalpies of the oxides BeO [1]¹ and Al_2O_3 [2] have been measured from 273 to 1173 °K in this laboratory. Similar measurements on the beryllium aluminate $\text{BeO} \cdot \text{Al}_2\text{O}_3$, reported below, have recently been completed as part of a current program at the National Bureau of Standards to provide accurate thermodynamic data on the "light" elements and their compounds. Measurements on another beryllium aluminate, $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$, are reported in another paper [2a]. No other measurements of the enthalpy or heat capacity of these "mixed" oxides were found in the literature except recent heat capacity measurements on $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ from 16 to 380 °K by adiabatic calorimetry at the NBS [3, 3a]. The thermodynamic properties of these mixed oxides are of practical interest in high temperature applications such as ceramic technology, the combustion of mixed-metal systems and the interpretation of data dealing with their chemical equilibrium with water vapor [4].

The phase diagram of the $\text{BeO} \cdot \text{Al}_2\text{O}_3$ system has been investigated by a number of workers [5, 6]. Several crystalline phases have been observed in addition to BeO and Al_2O_3 (figures in parentheses are reported melting points): $3\text{BeO} \cdot \text{Al}_2\text{O}_3$ (2253 °K), $\text{BeO} \cdot \text{Al}_2\text{O}_3$ (2143° ± 10 °K), and $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ (2183° ± 10 °K). Only the last two of these melt congruently.

Of the three mixed oxides, only $\text{BeO} \cdot \text{Al}_2\text{O}_3$ has been found in nature, where it occurs contaminated with small amounts of other metal oxides as the mineral chrysoberyl. This is also apparently the only one of the three mixed oxides whose crystal structure has been investigated [7, 8]. X-ray diffraction studies have shown that the oxygen atoms in $\text{BeO} \cdot \text{Al}_2\text{O}_3$ form an approximately hexagonal-close-packed structure, in some interstices of which the metal atoms are located.

2. Experimental Procedures

2.1. Sample

The high-temperature enthalpy measurements on $\text{BeO} \cdot \text{Al}_2\text{O}_3$ reported here involve two specimens taken from the material which had been used for the low-temperature heat-capacity measurements by Furukawa and Saba [3]. The sample of which these specimens were representative parts had been prepared particularly for this work by Semi-Elements, Inc., of Saxonburg, Pa., by arc fusion of a stoichiometric mixture of high-purity powdered BeO and Al_2O_3 . The preparative procedure involved the formation of a melted mass within a relatively large charge of the mixture. Thus, the unmelted powder served as a container for the melted sample and helped to prevent contamination. The fused sample was slowly cooled to room temperature, and any unfused material adhering to the outer surface was chipped off. Then the sample was crushed and sieved, retaining only particles between 0.3 and 2.0 mm in size. Some of the particles appeared gray, presumably from traces of graphite from the electrodes used in the arc-fusion process.

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¹ Figures in brackets indicate the literature references at the end of this paper.

The sample was further characterized at the NBS by petrographic and x-ray examinations and by spectrochemical and quantitative chemical analyses described below.

The petrographic examination was performed in the Crystallography Section of the NBS. The size of the crystalline particles was found to be about 200 μ . It is thought that the original size was considerably greater than this prior to grinding the polycrystalline material for petrographic examination. The index of refraction was in agreement with that previously reported [9]. The crystals were clear but showed some growth defects and a small volume of what appeared to be voids. No impurity phases of BeO or Al₂O₃ crystals were found.

The (room temperature) x-ray diffraction pattern, produced and interpreted in the Crystal Chemistry Section of the NBS, showed several strong lines characteristic of the BeO·Al₂O₃ crystal, but no lines attributable to separate crystalline phases of BeO, Al₂O₃ or any of the other "mixed" oxides expected. A small amount of an impurity phase was observed, but neither its identity nor amount could be established by this technique.

Qualitative spectrochemical examination in the Spectrochemical Analysis Section of the NBS involved looking for the chemical elements detectable by this technique. Table 1 shows the estimated percentage limits of those elements detected.

TABLE 1. Spectrochemical analysis of the BeO·Al₂O₃ sample

Element	Percentage limit	Element	Percentage limit
Si	< 0.01	Cd	0.001-0.01
Cu	0.01-0.1	V	0.0001-0.001
Ni	0.01-0.1	Sn	< 0.001
Fe	0.001-0.01	Pb	< 0.001
Mg	0.001-0.01	Ag	< 0.0001

TABLE 2. Chemical analysis of specimens of the BeO·Al₂O₃ sample

Specimen	Percentage by weight		Molar ratio BeO/Al ₂ O ₃
	BeO	Al ₂ O ₃	
Selected.....	19.73	80.25	1.002
Random.....	19.72	80.33	1.000
Theoretical.....	19.70	80.30	1.000

Two specimens of the sample were chemically analyzed for aluminum and beryllium in the Analysis and Purification Section of the NBS. One specimen was selected to be free of the gray coloration referred to above. The other specimen, chosen randomly, represented the bulk of the sample and contained many gray particles. The specimens were first dissolved in concentrated hydrochloric acid in a sealed ampoule by heating for 24 hr at 250 to 300 °C inside a

pressurized bomb. A known mixture of BeO and Al₂O₃ was treated in the same manner as a control on the analysis. After buffering with acetate to a pH between 4.2 and 4.5, the aluminum was precipitated as the 8-hydroxyquinolate, Al(C₉H₆ON)₃, ignited to Al₂O₃, and weighed. At a pH between 8 and 9, the beryllium was precipitated as Be(OH)₂, ignited to BeO and weighed. The results of these analyses, summarized in table 2, show the sample to be highly pure. The amount of graphite impurity was considered insignificant, and no corrections were applied for impurities or deviation from the theoretical stoichiometry in processing the thermal data.

2.2. Calorimetric Apparatus and Procedure

The high-temperature enthalpy measurements were made by the "drop" method using a Bunsen ice calorimeter. The method, which has been described in detail in a previous publication [2], is as follows: The sample, enclosed in a silver container, is suspended inside a thick-walled silver pipe in a resistance furnace until it attains the constant furnace temperature. It is then dropped, with nearly free fall, into the ice calorimeter, which measures the heat given up by sample plus container in cooling to 0 °C. In order to account for the enthalpy of the container and the small but appreciable heat lost during the drop, similar measurements are made with an identical empty container over the same range of furnace temperatures. In the present case, the enthalpy data for the empty silver container were fit with an equation by the method of least squares. The empirical equation was then used to determine the container enthalpy at appropriate furnace temperatures. See table 3.

The sample containers, fabricated from 99.9% pure silver tubing of 0.015 in wall thickness, were loaded and tightly capped in an atmosphere of air in a dry-box. They were weighed directly upon removal and sealed by flame welding immediately thereafter. Measurements were made on two specimens of BeO·Al₂O₃ sealed individually in identical silver containers. One of these containers was opened after some measurements had been completed at each temperature and a small amount of specimen removed for petrographic examination. The remainder was resealed, as described above, in another silver container.

At 500 °C and below, furnace temperatures were measured with a platinum resistance thermometer and a Pt-Pt10 percent Rh thermocouple, both inserted into long holes in the wall of the silver pipe [2]. Both were calibrated by the Temperature Physics Section of the National Bureau of Standards. From 0 to 500 °C the furnace temperature was taken as that temperature indicated by the resistance thermometer. The small differences between the temperatures indicated by the resistance thermometer and the thermocouple were extrapolated to correct the thermocouple calibration above 500 °C. Temperatures above 500 °C were measured with the above thermocouple and another independently calibrated one of the same type. The two thermocouples agreed

TABLE 3. Enthalpy measurements on empty silver capsule

Furnace temperature ^a	Measured heat ^b	Mean measured heat	Smoothed ^c - mean measured heat
°K	cal	cal	cal
323.15	{ 36.88 36.62 37.19 }	36.90	-0.15
373.15	{ 74.08 74.02 73.84 }	73.98	+0.04
473.15	{ 149.87 149.33 149.80 }	149.67	+0.12
573.15	{ 227.09 226.79 227.14 }	227.01	+0.01
673.15	{ 306.43 305.62 306.12 385.99 }	306.06	-0.31
773.15	{ 385.60 386.25 386.08 }	385.98	+0.16
873.15	{ 468.25 468.40 468.20 }	468.28	+0.09
973.15	{ 552.73 552.87 552.70 }	552.77	-0.10
1073.15	{ 639.43 638.95 639.50 }	639.29	-0.01
1173.15	{ 728.31 728.28 728.62 }	728.40	+0.02

^a International Temperature Scale of 1948, as modified in 1954.

^b 1 defined cal = 4.1840 abs joule.

^c Smoothed values obtained from the following equation:

$$H_T - H_{273.15} = (0.76152)(T - 273.15) + (2.3649)10^{-5}(T - 273.15)^2 + (0.42246)10^{-7}(T - 273.15)^3 - (8.9987)(T - 273.15)/T,$$

H_T cal at T °K.

with each other within 0.2 °C above 500 °C. The resistance thermometer ice-point resistance was measured frequently and did not change.

As a check on the accuracy of the calorimeter before the present series of runs, the relative enthalpy of a standard sample of α -aluminum oxide sealed in a silver capsule was measured at 100, 500, and 900 °C. The enthalpy values so obtained agreed with previously published measurements on this same sample of aluminum oxide [2] to within 0.2 percent.

2.3. Calorimetric Results

The results of the measurements are presented in table 4. The second and third columns are observed, unsmoothed heat values for the appropriate specimens with containers. Values in parentheses correspond to measurements on specimens opened and resealed as described in section 2.2. Duplicate measurements on the same specimen at the same temperature are recorded in the table in chronological order. This is not to imply, however, that all experiments at a given temperature were completed before proceeding to the next higher temperature. On the contrary, this was deliberately avoided in order to detect possible effects of temperature history

TABLE 4. High-temperature enthalpy measurements on BeO·Al₂O₃

Temperature ^a	Gross measured heat ^b		$H_T - H_{273.15}$ of BeO·Al ₂ O ₃ ^{b,c}			
	Specimen 1 and container ^d	Specimen 2 and container ^e	Specimen 1	Specimen 2	Mean observed	Smoothed (eq 1) - mean observed
°K	cal	cal	cal mol ⁻¹	cal mol ⁻¹	cal mol ⁻¹	cal mol ⁻¹
323.15	{ 95.23 95.18 95.25 (95.36) (95.47) (95.51) (95.23) (95.41) (95.32) }	{ 97.96 97.87 97.76 97.86 97.88 97.80 }	{ 1250. 1249. 1251. (1259.) (1262.) (1263.) (1257.) (1260.) (1258.) }	{ 1262. 1260. 1258. 1260. 1260. 1259. }	1258.	-1.
373.15	{ 199.39 199.26 198.79 198.59 198.72 198.80 (199.52) (199.45) (199.37) }	{ 204.35 204.53 204.14 203.69 203.79 }	{ 2680.6 2677.8 2667.7 2663.5 2666.2 2668.0 (2696.7) (2695.2) (2693.5) }	{ 2687.2 2690.9 2682.8 2673.6 2675.6 }	2680.0	+1.2
473.15	{ 424.79 424.11 425.27 424.50 423.96 424.04 425.28 423.09 424.73 424.82 422.88 424.04 423.27 424.75 424.16 424.16 }		{ 5879.8 5865.3 5890.1 5873.6 5862.1 5863.8 5890.3 5843.5 5878.6 5880.5 5839.0 5863.8 5847.4 5879.0 5866.4 5866.4 }		5868.1	+12.9
573.15	{ 665.49 666.24 665.73 665.77 665.75 665.87 666.06 665.86 }		{ 9375.0 9391.1 9380.2 9381.0 9380.6 9383.2 9387.2 9383.0 }		9382.7	+22.1
673.15	{ 921.62 921.47 921.53 }		{ 13168. 13165. 13166. }		13166.	-16.
773.15	{ 1184.62 1184.42 1184.44 1184.30 }		{ 17072. 17068. 17069. 17066. }		17069.	-16.
873.15	{ 1454.46 1454.47 1455.20 }		{ 21084. 21084. 21100. }		21089.	-15.
973.15	{ 1729.56 1729.25 1729.05 }		{ 25163. 25157. 25152. }		25157.	+25.
1073.15	{ 2011.98 2011.68 2011.79 }		{ 29350. 29344. 29346. }		29347.	+6.
1173.15	{ 2299.10 2298.83 2299.01 }		{ 33583. 33577. 33581. }		33580.	-9.

^a International Temperature Scale of 1948, as modified in 1954.

^b One defined cal = 4.1840 abs joule.

^c Molecular weight = 126.9728.

^d Values in this column are derived from two independent sets of measurements on specimen 1. All values from the second set are enclosed in parentheses. The specimen mass corresponding to the first set was 5.9385 g. Some of this specimen was removed for analysis. The specimen mass corresponding to the second set was 5.9090 g.

^e Mass of specimen 2 = 6.1583 g.

on the sample. It was concluded that the sample remained unaffected by furnace temperature cycling in the range 0 to 1173 °K. The fourth and fifth columns give net enthalpy values for the specimens cor-

responding to the gross measured heat values of the second and third columns respectively. These values were obtained by subtracting the appropriate smoothed heat value for the empty container (table 3) from the gross measured specimen-and-container heat and expressing the result in terms of 1 mole of specimen (see footnotes to table 4 for actual specimen masses used). The sixth column gives the mean at each temperature of all observations on all specimens.

3. Treatment of the Data

3.1. Smoothing by Empirical Equation

The mean observed heat values (table 4, sixth column) were fitted by the method of least squares with an empirical equation, weighting all values equally. Some of the measurements obtained by low-temperature adiabatic calorimetry in the range 273 to 373 °K [3] were also included in the fitting process in order to obtain thermodynamic functions merging as smoothly as possible with those derived from the low-temperature data alone. The empirical equation, where H_T is the high-temperature enthalpy in cal mol⁻¹ at T °K, is as follows (σ being the standard deviation of the mean observed values from the corresponding smoothed values):

$$H_T - H_{T_0} = (-1.00242(10^{-6}(T^3 - T_0^3) + (2.65426)10^{-3}(T^2$$

$$- T_0^2) + (45.8430)(T - T_0) - (6.54908)10^3 \ln \left(\frac{T}{T_0} \right)$$

cal mol⁻¹

$$T_0 = 273.15 \text{ °K}$$

$$\sigma = 13.41 \text{ cal mol}^{-1} \quad (1)^2$$

The seventh column of table 4 gives the deviation of the mean observed values of $H_T - H_{273.15}$ from the smoothed values calculated from eq (1). While the equation does not yield values consistently within the current precision of measurement, the deviation of the mean observed values from the smoothed values is usually 0.1 percent or less, which is within the estimated absolute accuracy (see sec. 5.2).

Figure 1 shows a comparison of observed and smoothed heat capacities. The solid curve was derived by differentiating the smooth enthalpy equation (eq 1). The observed heat capacities were calculated according to the equation [10]:

$$Z_{T_m} = \frac{\Delta H}{\Delta T} - \left(\frac{\partial^2 Z}{\partial T^2} \right)_{T_m} \frac{(\Delta T)^2}{24} - \left(\frac{\partial^4 Z}{\partial T^4} \right)_{T_m} \frac{(\Delta T)^4}{1920} \dots, \quad (2)$$

where T_m is the mean temperature of the interval ΔT and Z_{T_m} is the heat capacity at T_m , corrected for curvature. ΔH is the measured enthalpy increment corre-

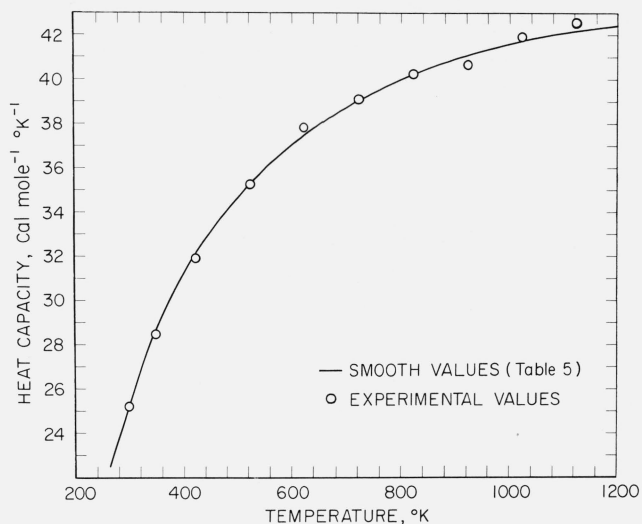


FIGURE 1. Comparison of observed and smoothed molal heat capacities for $\text{BeO} \cdot \text{Al}_2\text{O}_3$.

sponding to ΔT . Derivatives of Z with respect to T were replaced by derivatives of $\Delta H/\Delta T$ with respect to T in the computations.

3.2. Smooth Joining With Results of Low-Temperature Adiabatic Calorimetry

In order to obtain tables of thermodynamic functions merging smoothly with those derivable from the results of low-temperature adiabatic calorimetry [3], some compromise of both the low- and high-temperature heat capacity data was necessary. Since adiabatic calorimetry is believed to yield more accurate heat capacity data near room temperature (where the two sets of data were merged), more weight was given to it. Merging was accomplished by plotting the smoothed low- and high-temperature heat capacities and graphically smooth-joining them. The deviations of the smoothed low- and high-temperature heat capacities from the merged values chosen to represent the overlap range are shown in figure 2.

One measure of the extent to which the data have been compromised is a comparison of the enthalpy increment ($H_{373.15 \text{ °K}} - H_{273.15 \text{ °K}}$) determined by integrating the smoothed low-temperature heat capacity data in this range with the same quantity measured directly by drop calorimetry. The integrated value obtained from the low-temperature data [3] is 2685.4 cal/mol whereas the smoothed value obtained from the high-temperature measurements (eq 1 or table 4) is 2681.2 cal/mol. The value given by table 5, derived from the merged heat capacity, is 2685.7 cal/mol, reflecting the greater weight given the low-temperature data in the merging.

3.3. Extrapolation to Higher Temperatures

The heat capacity function derived from eq (1) was extrapolated by a straight line chosen to have a slope and value equal to those of this function at 1100 °K. (Note that eq (1) yields a negative heat capacity-

² ln designates natural logarithm.

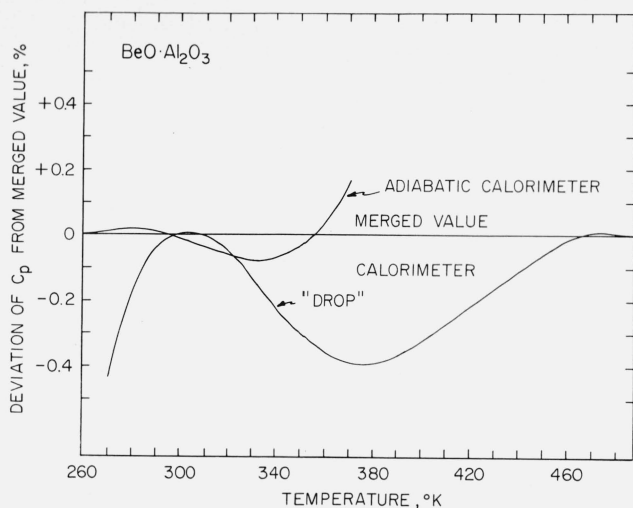


FIGURE 2. Comparison of smoothed molal heat capacity of $\text{BeO} \cdot \text{Al}_2\text{O}_3$ determined by two methods with compromise values in the region of overlap.

temperature coefficient above 1425 °K.) This method of extrapolation gives a heat capacity of $46.4 \text{ cal mol}^{-1} \text{ deg}^{-1}$ at 2150 °K. (The "additive" heat capacity, obtained by summing the individual heat capacities of BeO and Al_2O_3 from the published data [12], is $47.1 \text{ cal mol}^{-1} \text{ deg}^{-1}$, only 1.2% in excess of the above extrapolated value.) The Gibbs free energy function, $-(G_T^\circ - H_0^\circ)/T$, of interest in high-temperature equilibrium calculations, is relatively insensitive to the particular linear extrapolation used. At 2150 °K, for instance, it varies by about $0.2 \text{ cal mol}^{-1} \text{ deg}^{-1}$ for a 100 percent change in the slope of the line used to extrapolate the heat capacity.

4. Thermodynamic Functions

The smooth heat-capacity function described in section 3.2 was used as the basis for calculating the tables of thermodynamic functions (table 5 and Appendix) using well-known thermodynamic relationships. (The Appendix is a recalculation of table 5 in joules instead of calorie units; $1 \text{ cal} = 4.1840 \text{ J}$.) Differentiation and integration were performed using cubic interpolation polynomials. The following equations were derived to represent the appropriate quantities of table 5 in the indicated temperature ranges with an error not exceeding 0.01 percent.

$$H_T^\circ - H_0^\circ = (-1.00242)10^{-6}T^3 + (2.65426)10^{-3}T^2 \\ + (45.8430)T - (6.54908)10^3 \ln T \\ + 26575.2 \text{ cal mol}^{-1}; 1200 \geq T \text{ }^\circ\text{K} \geq 450 \quad (3)$$

$$H_T^\circ - H_0^\circ = (2.0524)10^{-3}T^2 + (37.575)T \\ - 10800. \text{ cal mol}^{-1}; 2150 \geq T \text{ }^\circ\text{K} \geq 1200 \quad (4)$$

TABLE 5. Thermodynamic functions for beryllium 1:1-aluminate ($\text{BeO} \cdot \text{Al}_2\text{O}_3$) solid phase

Gram molecular weight = 126.9728 g, $T \text{ }^\circ\text{K} = t \text{ }^\circ\text{C} + 273.15^\circ$

T	C_p°	$(H_T^\circ - H_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ)/T - S_0^\circ$	$-(G_T^\circ - H_0^\circ)/T - S_0^\circ$
$^\circ\text{K}$	$\text{cal deg}^{-1} \text{ mol}^{-1}$	cal mol^{-1}	$\text{cal deg}^{-1} \text{ mol}^{-1}$	$\text{cal deg}^{-1} \text{ mol}^{-1}$	cal mol^{-1}	$\text{cal deg}^{-1} \text{ mol}^{-1}$
273.15	23.174	2523.4	9.238	13.726	1225.9	4.488
275.00	23.331	2566.4	9.332	13.883	1251.4	4.551
280.00	23.749	2684.1	9.586	14.307	1321.9	4.721
285.00	24.157	2803.9	9.838	14.731	1394.5	4.893
290.00	24.556	2925.7	10.089	15.155	1469.2	5.066
295.00	24.945	3049.4	10.337	15.578	1546.0	5.241
298.15	25.185	3128.4	10.493	15.844	1595.5	5.351
300.00	25.325	3175.1	10.584	16.000	1625.0	5.417
310.00	26.071	3432.1	11.071	16.843	1789.2	5.772
320.00	26.781	3696.4	11.551	17.682	1961.8	6.131
330.00	27.457	3967.6	12.023	18.516	2142.8	6.493
340.00	28.100	4245.5	12.487	19.346	2332.1	6.859
350.00	28.706	4529.5	12.941	20.169	2529.7	7.228
360.00	29.276	4819.5	13.387	20.986	2735.5	7.599
370.00	29.810	5114.9	13.824	21.795	2949.4	7.971
373.15	29.971	5209.1	13.960	22.049	3018.4	8.089
380.00	30.309	5415.5	14.251	22.597	3171.4	8.346
390.00	30.776	5721.0	14.669	23.390	3401.3	8.721
400.00	31.214	6030.9	15.077	24.175	3639.1	9.098
425.00	32.207	6824.0	16.056	26.098	4267.7	10.042
450.00	33.093	7640.4	16.979	27.964	4943.6	10.986
475.00	33.901	8478.0	17.848	29.776	5665.4	11.927
500.00	34.643	9334.9	18.670	31.534	6431.9	12.864
550.00	35.946	11101.	20.183	34.898	8093.5	14.715
600.00	37.030	12926.	21.543	38.074	9918.6	16.531
650.00	37.948	14801.	22.771	41.075	11898.	18.305
700.00	38.730	16718.	23.883	43.917	14023.	20.034
750.00	39.401	18672.	24.896	46.612	16287.	21.716
800.00	39.979	20657.	25.821	49.174	18682.	23.353
850.00	40.478	22669.	26.669	51.613	21203.	24.944
900.00	40.908	24704.	27.448	53.939	23842.	26.491
950.00	41.278	26758.	28.167	56.161	26595.	27.995
1000.00	41.595	28830.	28.830	58.287	29456.	29.456
1050.00	41.864	30917.	29.445	60.323	32422.	30.878
1100.00	42.090	33016.	30.015	62.276	35487.	32.261
1150.00	42.295	35126.	30.544	64.151	38648.	33.607
1200.00	42.500	37246.	31.038	65.956	41901.	34.918
1250.00	42.706	39376.	31.501	67.695	45243.	36.194
1300.00	42.911	41516.	31.936	69.374	48670.	37.438
1350.00	43.116	43667.	32.346	70.997	52179.	38.651
1400.00	43.321	45828.	32.734	72.569	55769.	39.835
1450.00	43.527	47999.	33.103	74.093	59435.	40.990
1500.00	43.732	50181.	33.454	75.572	63177.	42.118
1550.00	43.937	52372.	33.789	77.009	66992.	43.221
1600.00	44.142	54574.	34.109	78.407	70877.	44.298
1650.00	44.348	56787.	34.416	79.769	74832.	45.353
1700.00	44.553	59009.	34.711	81.096	78854.	46.385
1750.00	44.758	61242.	34.995	82.390	82941.	47.395
1800.00	44.963	63485.	35.269	83.654	87092.	48.385
1850.00	45.169	65738.	35.534	84.889	91306.	49.355
1900.00	45.374	68002.	35.790	86.096	95581.	50.306
1950.00	45.579	70276.	36.039	87.277	99915.	51.238
2000.00	45.784	72560.	36.280	88.434	104308.	52.154
2050.00	45.990	74854.	36.514	89.567	108758.	53.053
2100.00	46.195	77159.	36.742	90.678	113264.	53.935
2150.00	46.400	79474.	36.964	91.767	117825.	54.803

H_0° and S_0° are, respectively, the enthalpy and entropy of the solid at 0 °K and 1 atm pressure.

^a Values below this line are extrapolations to temperatures above the measuring range.

$$C_p^\circ = (-3.00726)10^{-6}T^2 + (5.30852)10^{-3}T \\ - (6.54908)10^3T^{-1} + 45.843 \text{ cal mol}^{-1} \text{ deg}^{-1} \\ 1200 \geq T \text{ }^\circ\text{K} \geq 475 \quad (5)$$

$$C_p^\circ = (4.1048)10^{-3}T + 37.575 \text{ cal mol}^{-1} \text{ deg}^{-1}; \\ 2150 \geq T \text{ }^\circ\text{K} \geq 1200. \quad (6)$$

5. Precision and Accuracy

5.1. Precision

Random measuring errors, such as errors in temperature or mass measurement or in deviation of the sample container from the indicated furnace temperature, contribute to imprecision of the data. Also, the data-smoothing procedures used introduce additional uncertainty into the final tabulated enthalpy values (table 5). The mean unsmoothed net enthalpy of the sample (given on a molal basis in column 6, table 4) can be shown to have a standard deviation of 0.34 cal (average) for the actual sample mass involved, and this corresponds to about 7 cal mol⁻¹. The smoothing procedure leading to eq (1) introduces an additional uncertainty resulting in a standard deviation for the smoothed values of 21 cal mol⁻¹. This represents from 0.7 percent to 0.06 percent of the measured enthalpy values for BeO · Al₂O₃.

5.2. Accuracy

It is felt that the most significant systematic error was introduced in temperature measurement. Other sources considered less significant are the sample mass, the sample impurity, the calorimeter calibration factor, and differences between the heat losses during the drops of the filled and empty containers. The platinum resistance thermometer used at 500 °C and below and the Pt-Pt10 percent Rh thermocouples relied on above 500 °C were calibrated up to 1450 °C on the International Practical Temperature Scale immediately prior to the present measurements. The ice-point resistance of the resistance thermometer was checked frequently during the measurements and did not change. The resistance thermometer and thermocouples were compared in the furnace up to 500 °C. Considering these various precautions, it is felt that the temperature error at temperatures measured with the platinum resistance thermometer was insignificant. Above 500 °C, the maximum error in the enthalpy measurements due to uncertainty in the thermocouple calibrations should not exceed 0.05 percent and is probably a good deal less than this as a result of the comparison in place with the resistance thermometer and corresponding small adjustments in the thermocouple calibration.

Heat lost during the drop (significant time duration interval = approximately 0.1 sec) is a significant though small fraction of the total measured heat only at the highest temperatures. It is felt that the care used in choice of materials and design of the silver containers, and the steps taken to ensure constancy of the drop time, were adequate to eliminate the possibility of significant systematic differences between the heat loss during the drop for the full and empty containers. These containers all had the same dimensions, and the silver tubes used in their fabrication were all chosen from a single length of highly polished pure silver tubing. During the course of the experiments, no indications of oxidation on the exterior surfaces were noted.

Analyses of the sample, described in section 2.1, showed the samples to contain not only negligible amounts of impurities but also, within the errors of analysis, the stoichiometrically correct ratios of constituent elements. It is believed that the assumption of 100 percent purity for all specimens introduces negligible error into the heat measurements.³ The total error due to uncertainty of sample mass and the accepted value of the calorimeter calibration factor probably does not exceed 0.02 percent.

BeO · Al₂O₃ is stoichiometrically analogous to some mixed oxides with the spinel crystal structure and the general formula M'O · M''O₃ which have been found in recent years to show heat-capacity variations too large to be attributable to experimental error [11]. These variations have instead been assumed to be caused by disordering of metal atoms in the crystals. The question arises as to whether samples of BeO · Al₂O₃ may not also exhibit similar disorder. This suspicion is enhanced when it is realized that even if all the beryllium atoms in BeO · Al₂O₃ are in tetrahedral interstitial sites (as is generally believed, from analogy to crystalline BeO), only 1/8 of these sites are occupied.

It will be recalled that all the thermodynamic properties of BeO · Al₂O₃ recorded in the present paper are based on calorimetric measurements on specimens from a single sample. After the original preparation of the sample by cooling from the melting point (sec. 2.1), none of the specimens used was ever heated above 1173 °K. Furthermore, even though the two specimens measured at high temperatures were repeatedly cycled over various temperature intervals in the range 273 to 1173 °K, few if any irregularities in thermal values were found that do not fall within the limits of precision usually shown by this calorimetric apparatus. It is thus concluded that the results of the present paper represent to a high degree of accuracy the properties of the actual sample measured.

Nevertheless, no proof is available that this sample did not possess some fixed but arbitrary degree of "frozen-in" disorder, and for this reason the values of entropy and Gibbs free energy in table 5 and the Appendix have been expressed in terms of the excess over a residual entropy S₀^o. Furthermore, the fact that the residual entropy must be zero or positive may be of little help in deciding whether the free-energy functions of the present paper, assuming zero residual entropy, are too high or too low for use in computations of equilibria involving BeO · Al₂O₃ [4]. The calorimetry and equilibrium samples may have had different residual entropies and some consequent differences in their heat capacity and related properties.

The high temperature thermodynamic functions (table 5) necessarily include any uncertainty in the values of H₂₇₃^o and S₂₇₃^o as derived from the low temperature data, which are believed to be in error by no more than 0.1 percent [3].

³ For example, a BeO · Al₂O₃ mole ratio of 1.002 (see table 2), if neglected, would introduce into any enthalpy increment measured an error not exceeding 0.02 percent.

Considering all the above sources of error and the measurements on aluminum oxide described in section 2.2 above, it is felt that the smoothed high temperature enthalpy values derived from eq (1) can be considered to have an absolute accuracy which, because the systematic errors are negligible, can be expressed as a standard deviation, decreasing from 0.7 percent at 100 °C to 0.3 percent at 900 °C. The accuracy (expressed as standard deviation) in the values of heat capacity calculated from this equation was estimated to be 0.7–1.0 percent over the same temperature range.

The authors are indebted to several members of the staff of the National Bureau of Standards for characterizing the sample of $\text{BeO} \cdot \text{Al}_2\text{O}_3$ investigated: to A. van Valkenburg for the petrographic examination, to H. S. Peiser for the x-ray diffraction work, to Martha Darr for the spectrochemical analysis, and to T. J. Murphy for the quantitative chemical analysis.

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APPENDIX. Thermodynamic functions for beryllium 1:1-aluminate ($\text{BeO} \cdot \text{Al}_2\text{O}_3$) solid phase

Gram molecular weight = 126.9728 g, $T^\circ\text{K} = t^\circ\text{C} + 273.15^\circ$

T	C_p	$(H_T^\circ - H_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ) - TS_0^\circ$	$-(G_T^\circ - H_0^\circ)/T - S_0^\circ$
°K	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$
273.15	96.961	10558.	38.652	57.430	5129.0	18.777
275.00	97.618	10738.	39.047	58.086	5235.8	19.039
280.00	99.366	11230.	40.108	59.861	5530.7	19.753
285.00	101.07	11731.	41.163	61.635	5834.5	20.472
290.00	102.74	12241.	42.210	63.407	6147.1	21.197
295.00	104.37	12759.	43.250	65.177	6468.5	21.927
298.15	105.38	13089.	43.901	66.291	6675.6	22.390
300.00	105.96	13285.	44.282	66.945	6798.8	22.663
310.00	109.08	14360.	46.323	70.471	7485.9	24.148
320.00	112.05	15466.	48.331	73.981	8208.2	25.651
330.00	114.88	16601.	50.305	77.473	8965.5	27.168
340.00	117.57	17763.	52.244	80.943	9757.6	28.699
350.00	120.11	18951.	54.147	84.388	10584.	30.241
360.00	122.49	20165.	56.013	87.805	11445.	31.792
370.00	124.72	21401.	57.840	91.192	12340.	33.352
373.15	125.40	21795.	58.407	92.252	12629.	33.845
380.00	126.81	22659.	59.628	94.546	13269.	34.918
390.00	128.77	23937.	61.376	97.866	14231.	36.490
400.00	130.60	25233.	63.084	101.15	15226.	38.065
425.00	134.75	28551.	67.180	109.19	17856.	42.014
450.00	138.46	31967.	71.039	117.00	20684.	45.964
475.00	141.84	35472.	74.678	124.58	23704.	49.904
500.00	144.94	39057.	78.114	131.94	26911.	53.822
550.00	150.40	46445.	84.445	146.02	33863.	61.570
600.00	154.94	54082.	90.136	159.30	41499.	69.166
650.00	158.77	61927.	95.272	171.86	49781.	76.587
700.00	162.04	69950.	99.928	183.75	58674.	83.820
750.00	164.85	78124.	104.17	195.03	68146.	90.861
800.00	167.27	86428.	108.04	205.74	78167.	97.709
850.00	169.36	94845.	111.58	215.95	88712.	104.37
900.00	171.16	103360.	114.84	225.68	99755.	110.84
950.00	172.71	111957.	117.85	234.98	111273.	117.13
1000.00	174.03	120627.	120.63	243.87	123246.	123.25
1050.00	175.16	129357.	123.20	252.39	135654.	129.19
1100.00	176.10	138140.	125.58	260.56	148479.	134.98
1150.00	176.96	146966.	127.80	268.41	161705.	140.61
1200.00	177.82	155836.	129.86	275.96	175315.	146.10
1250.00	178.68	164749.	131.80	283.24	189296.	151.44
1300.00	179.54	173704.	133.62	290.26	203634.	156.64
1350.00	180.40	182702.	135.34	297.05	218318.	161.72
1400.00	181.26	191744.	136.96	303.63	233336.	166.67
1450.00	182.12	200828.	138.50	310.00	248678.	171.50
1500.00	182.97	209955.	139.97	316.19	264333.	176.22
1550.00	183.83	219126.	141.37	322.21	280294.	180.83
1600.00	184.69	228339.	142.71	328.06	296551.	185.34
1650.00	185.55	237595.	144.00	333.75	313097.	189.76
1700.00	186.41	246894.	145.23	339.30	329924.	194.07
1750.00	187.27	256236.	146.42	344.72	347025.	198.30
1800.00	188.13	265621.	147.57	350.01	364394.	202.44
1850.00	188.99	275049.	148.67	355.17	382024.	206.50
1900.00	189.84	284519.	149.75	360.23	399909.	210.48
1950.00	190.70	294033.	150.79	365.17	418045.	214.38
2000.00	191.56	303590.	151.79	370.01	436424.	218.21
2050.00	192.42	313189.	152.78	374.75	455044.	221.97
2100.00	193.28	322832.	153.73	379.39	473898.	225.67
2150.00	194.14	332517.	154.66	383.95	492982.	229.29

H_0° and S_0° are, respectively, the enthalpy and entropy of the solid at 0 °K and 1 atm. pressure.

^a Values below this line are extrapolations to temperatures above the measuring range.

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