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Relative Enthalpy of Beryllium 1:3-Aluminate, $BeO \cdot 3Al_2O_3$, from 273 to 1173 °K. Thermodynamic Properties from 273 to 2150 °K*

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The relative enthalpy of beryllium 1:3-aluminate, $BeO \cdot 3Al_2O_3$, was measured from 273 to 1173 °K. Thermodynamic properties were calculated up to 2150 °K (near the melting point) by extrapolating the present measurements and making them consistent with existing low-temperature data.

Key Words: Beryllium aluminate (1:3), drop calorimetry, enthalpy measurements, high-temperature calorimetry, mixed oxides, specific heat, thermodynamic properties.

1. Introduction

Measurements of the relative enthalpy of the beryllium aluminate $BeO \cdot 3Al_2O_3$ have recently been completed as part of a program at the National Bureau of Standards to provide accurate thermodynamic data on the "light" elements and their compounds. They complement recent measurements on $BeO \cdot Al_2O_3$ [1, 2][1] and together with similar measurements at the Bureau on BeO and Al_2O_3 [3, 4], contribute to a greater understanding of the BeO-Al_2O_3 system. The measurements will also be of value in interpreting combustion phenomena in certain mixed-metal systems.

$BeO \cdot 3Al_2O_3$ is one of the three known mixed oxides of the BeO-Al_2O_3 system [5] but is not known to occur naturally. It has been reported as melting congruently at $2183° \pm 10$ °K [6] but no structural studies of it have been found yet in the literature.

2. Experimental Procedure

2.1. Sample

Specimens used in the present measurements were taken from the same specimen as had been used in low-temperature heat capacity measurements [7]. Semi-Elements, Inc., of Saxonburg, Pa., prepared the original sample by arc fusion of part of a stoichiometric mixture of pure BeO and Al_2O_3 powders. The unfused portion served as a container and thermal insulator as the melt cooled to room temperature (cooling time approximately 3 hr) and was later removed. The fused material was crushed and sieved to collect particles between 0.3 and 2 mm in size (10 to 50 mesh). A qualitative spectrochemical examination of the sample in the Spectrochemical Analysis Section of NBS detected certain elements, the estimated percentage limits of which are given in table 1.

Many of the particles in the original sample were gray, perhaps owing to traces of carbon from the graphite electrodes used in the arc fusion process. A chemical analysis of the sample was performed in the Analysis and Purification Section of NBS. Two 0.5 g specimens were dissolved in hydrochloric acid by heating the mixture sealed in tubes at 250 °C for 16 hr. The methods of analysis were essentially the same as previously described for $BeO \cdot Al_2O_3$ [1]. The results (table 2) show the $BeO \cdot 3Al_2O_3$ sample to have the correct stoichiometric ratio of components within the precision of the analytical methods.

A petrographic examination of the sample was made in the Crystallography Section of the NBS and showed an average crystal size of 300 μ. The original material

TABLE 1. *Spectrochemical analysis of the* $BeO \cdot 3Al_2O_3$ *sample*

Element	Percentage limit	Element	Percentage limit
Fe	0.01 –0.1	Mg	0.001 –0.01
Na	0.01 –0.1	Zr	0.001 –0.01
Si	0.01 –0.1	Mn	0.0001–0.001
B	0.001–0.01	Ag	<0.0001
Ca	0.001–0.01	Cu	<0.0001

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

TABLE 2. *Chemical analysis of the* $BeO \cdot 3Al_2O_3$ *sample*

Chemical-analysis specimen	Percentage by weight		Molar ratio Al_2O_3/BeO
	Be	Al	
First	2.71[a] 2.74[a]	48.96	3.017
Second	2.72	48.93	3.004
Theoretical	2.72	48.92	3.000

[a] Duplicate aliquots.

probably contained much larger crystals prior to grinding for the examination. The crystals were clear with some voids and growth defects from too rapid cooling. There was some evidence of another phase present, possibly as much as 5 percent; however, no BeO was detected. For a discussion of the possible effect on the measured thermal values for this sample of a foreign phase present up to the extent of several percent and yet uncorrected for, see section 5.

The $BeO \cdot 3Al_2O_3$ sample was further examined by x-ray diffraction techniques in the Crystallography Section of the NBS. The observed pattern was in agreement with published values for $BeO \cdot 3Al_2O_3$ [8, 9, 10], with only very faint traces of lines characteristic of $BeO \cdot Al_2O_3$ or α–Al_2O_3. Some unidentified lines also were found. Lines characteristic of graphite, BeO, and $3BeO \cdot Al_2O_3$ were absent.

As pointed out in the paper [7] describing the low-temperature heat-capacity measurements on the same sample of $BeO \cdot 3Al_2O_3$ as that involved in this paper, certain limitations on the likely composition of the foreign phases in the sample can be deduced from the available facts. Although the optical properties of $BeO \cdot Al_2O_3$ and $BeO \cdot 3Al_2O_3$ have been found to be very similar [6, 9, 10, 11], so that it is difficult to distinguish them by this technique, there is evidence that not much of the impurity phase observed petrographically is $BeO \cdot Al_2O_3$. The presence of this phase would require either the simultaneous presence of free α-Al_2O_3 or some phase with a ratio of Al_2O_3/BeO greater than 3. However, since the x-ray examination yielded negative results for α-Al_2O_3, the suspicion is aroused that there may exist yet unidentified phases in the $BeO-Al_2O_3$ system. The work of Lang et al. [6], also points in this direction. The present sample was taken to be 100 percent $BeO \cdot 3Al_2O_3$ in processing the enthalpy data.

2.2. Calorimetric Procedure and Results

The high-temperature enthalpy measurements were made by the "drop" method using a Bunsen ice calorimeter. This method has been described in great detail in a previous publication [4] and is in all details identical to that used in the recent measurements on $BeO \cdot Al_2O_3$ [2]. The 99.9 percent pure silver specimen containers used were filled and capped in a dry box containing air. A separate series of measurements [2] on a silver container identical to the specimen containers was used as a basis for correcting measured heat values for the contribution of the specimen container. Temperatures were measured at 500 °C and below with a Pt resistance thermometer and a Pt–Pt 10 percent Rh thermocouple, both NBS-calibrated. Above 500 °C, the above thermocouple and another of identical construction were used simultaneously. The resistance thermometer was considered the more accurate indicator at and below 500 °C. Its readings were taken as the true furnace temperature and used to determine small corrections to the calibrations of the thermocouples as used in place in the apparatus.

The results of the measurements are given in table 3, the first three columns of which contain the original data with the heats slightly (less than 0.1 percent) adjusted to correspond to evenly spaced furnace temperatures. Measurements are recorded in chronological order within any single temperature grouping; however, note that temperatures were extensively mixed: measurements at 323.15 °K, for instance, were sometimes interrupted and a point at 1173.15 °K taken to confirm the independence from furnace-temperature cycling of individual runs at a given temperature. The derivation of columns four and five is described in footnote g to the table. Note that some of the data for specimen 1 were given zero weight in the final fit (starred values). These data were an average of 0.15 percent below any plausible extrapolation of the data at lower temperatures and disagreed by the same amount with measurements on specimen 2 as well as on specimen 1 resealed. The cause of this systematic deviation of this one set of measurements on specimen 1 above 773 °K is unknown. The sixth column gives the mean of all observations on all specimens with the exception noted above (starred values).

3. Treatment of the Data

3.1. Smoothing by Empirical Equation

The mean observed values (weighted equally) were fitted by the method of least squares with the following empirical equation, where T is the temperature in °K and σ is the standard deviation of the mean observed values from the equation values:

$$H_T - H_{T_0} = (4.52108)10^{-3}(T^2 - T_0^2) + (97.1098)(T - T_0)$$

$$+ (5.08769)10^6\left(\frac{1}{T} - \frac{1}{T_0}\right) - (2.75706)10^8\left(\frac{1}{T^2} - \frac{1}{T_0^2}\right)$$

cal mol^{-1} [2]

$$T_0 = 273.15\ °K$$

$$\sigma = 9.87\ \text{cal mol}^{-1} \qquad (1)$$

The deviation of observed from smoothed values (seventh column, table 3) is within the current precision of measurement.

[2] *Mole* and *mol* are hereafter to be understood as *gram mole*.

TABLE 3. *High-temperature enthalpy measurements on* $BeO \cdot 3Al_2O_3$

Furnace temperature [a]	Gross measured heat [b]		$H_T - H_{273.15}$ of $BeO \cdot 3Al_2O_3$ [b, c]			
	Specimen 1 and container [d]	Specimen 2 and container [f]	Specimen 1 [g]	Specimen 2 [g]	Mean observed	Mean observed − smoothed [h]
°K	*cal*	*cal*	*cal mol*$^{-1}$	*cal mol*$^{-1}$	*cal mol*$^{-1}$	*cal mol*$^{-1}$
	101.96	134.64	3170.0	3170.3		
	102.13	134.61	3178.3	3169.4		
	101.89	134.63	3166.6	3170.0		
		134.37		3161.6		
323.15		134.91		3179.1	3170.2	+6.8
		134.64		3170.3		
		134.57		3168.1		
		134.75		3173.9		
		134.62		3169.7		
		134.49		3165.5		
	212.33	281.75	6723.6	6727.7		
373.15	211.99	281.73	6707.0	6727.0	6722.1	−4.7
	212.43	281.48	6728.4	6719.0		
	451.73		14678.			
473.15	451.85		14684.		14680.	−7.
	451.75		14679.			
	708.35		23399.			
573.15	708.33		23398.		23396.	+9.
	708.17		23390.			
	976.14		32589.			
673.15	976.06		32585.		32584.	+10.
	975.92		32579.			
	1252.48	1685.23	42115.	42073.		
	1252.30	1685.08	42107.	42068.		
	1252.59	1684.98	42121.	42065.		
773.15	(1219.43)	1684.34	(42134.)	42044.	42095.	−13.
	(1219.67)	1685.55	(42146.)	42084.		
	(1219.23)	1685.46	(42124.)	42081.		
		1685.55		42084.		
		1685.40		42079.		
	1534.45 [e]	2071.08	*5182.5* [e]	51906.		
	1534.23	2070.99	*51814.*	51904.		
873.15	*1534.50*	2070.80	*51827.*	51897.	51906.	−4.
	(1495.67)	2070.43	(51944.)	51885.		
	(1494.97)	2070.48	(51909.)	51887.		
	(1495.10)		(51915.)			
	1824.64	2464.92	*61832.*	61932.		
	1824.82	2465.26	*61842.*	61942.		
973.15	*1824.69*	2465.13	*61836.*	61938.	61930.	+3.
	(1777.53)		(61934.)			
	(1777.18)		(61916.)			
	(1777.20)		(61917.)			
	2121.84*	2866.84	*72071.*	72143.		
	2121.74*	2866.79	*72066.*	72142.		
1073.15	(2065.63)	2866.96	(72122.)	72147.	72136.	+8.
	(2065.99)		(72140.)			
	(2065.58)		(72119.)			
	2422.96	3275.92	*82376.*	82505.		
	2423.15	3274.90	*82385.*	82472.		
	2422.78	3274.96	*82367.*	82474.		
	(2360.07)	3275.03	(82502.)	82476.		
1173.15	(2359.83)		(82490.)		82485.	−4.
	(2360.06)		(82502.)			
	(2359.10)		(82454.)			
	(2359.89)		(82493.)			
	(2359.69)		(82483.)			

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

[b] 1 Defined cal = 4.1840 abs joules.

[c] Gram molecular weight = 330.8952 g.

[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 6.8068 g. Some of this specimen was removed for analysis. The specimen mass corresponding to the second set was 6.5441 g.

[e] Starred values not included in least squares fit of data (see text).

[f] Mass of specimen 2 = 10.2170 g.

[g] These columns are derived from the first two columns respectively, by subtracting the smoothed container heat value [2] given by the following equation and converting the difference to a molar specimen basis:

$$H_T - H_{273.15} = (0.76152)(T - 273.15) + (2.3649)10^{-5}(T - 273.15)^2 + (0.42246)10^{-7}(T-273.15)^3 - (8.9987)[(T-273.15)/T] \text{ cal.}$$

This smoothed container heat value is approximately 30 percent of the specimen-plus-container value at all temperatures.

[h] The smoothed values were calculated from eq (1).

Figure 1 gives a comparison of the smoothed molal heat capacity of $BeO \cdot 3Al_2O_3$ [table 5] with high-

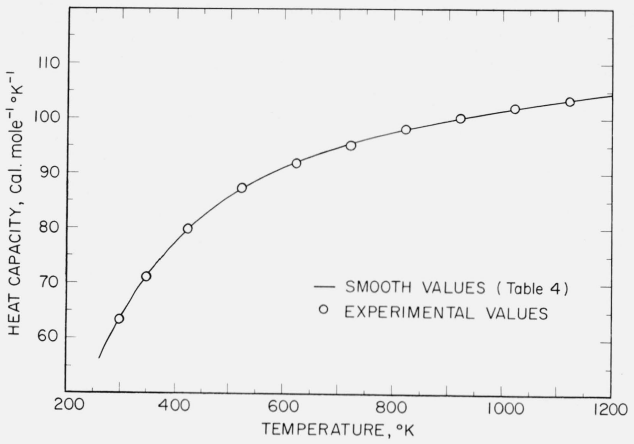

FIGURE 1. *Comparison of observed and smoothed molal heat capacity of* $BeO \cdot 3Al_2O_3$.

temperature experimental values. The latter were calculated directly from the mean unsmoothed enthalpies (sixth column, table 3), including correction for curvature of the heat capacity function according to a formula of Osborne et al., [12].

3.2. Joining High- and Low-Temperature Results; Extrapolation to Higher Temperatures

The heat capacity function obtained by differentiating eq (1) joined well with results recently available from low-temperature adiabatic calorimetry [7] on the same sample. Small adjustments to both the low- and high-temperature data were determined graphically. In this process, the low-temperature results, having been considered the more accurate, were given greater weight. Figure 2 shows the deviation in the overlapping temperature region of the heat capacity values relative to the values used in merging the two data sets. The enthalpy increment $H_{373.15°K} - H_{273.15°K}$ obtained from integration of the merged values of heat capacity is 6722. cal mol^{-1}. This compares well with the value derived from the low-temperature data (6719. cal mol^{-1}) and the high-temperature measurement (6727. cal mol^{-1}).

Equation (1), besides fitting the data well, extrapolates asymptotically (after differentiation) to a straight line of positive slope, a type of behavior frequently borne out by precise heat measurements on solids at very high temperatures. This equation was therefore chosen to extrapolate the data to 2150 °K.

4. Thermodynamic Functions

Tables of thermodynamic functions were derived in both calorie [4] and joule energy units (table 4 and appendix) from a smooth heat capacity function made up of the smoothed low-temperature results [7], the merged values (sec. 3.2) and the high-temperature values calculated from eq (1) (extrapolated to 2150 °K).

[4] 1 defined cal. = 4.1840 abs. joule.

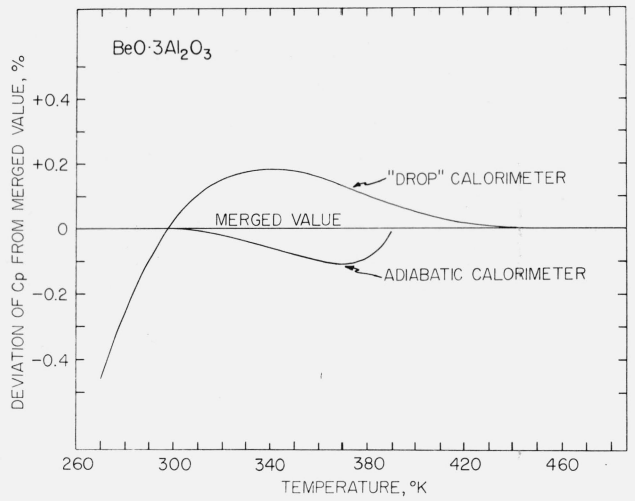

FIGURE 2. *Comparison of the smoothed values of heat capacity of* $BeO \cdot 3Al_2O_3$ *obtained by low-temperature calorimetry with values obtained by high-temperature drop calorimetry.*

The following equations were derived using constants supplied partly by the low-temperature heat capacity measurements. These equations represent the corresponding values in table 4 in the indicated temperature ranges with an error not exceeding 0.01 percent:

$$H_T - H_0 = (4.52108)10^{-3}T^2 + (97.1098)T + (5.08769)10^6 T^{-1} - (2.75706)10^8 T^{-2} - 35174.7 \text{ cal mol}^{-1}$$

$$2150 \geq T\ ^\circ\text{K} \geq 450 \qquad (2)$$

$$C_p = (9.04216)10^{-3}T - (5.08769)10^6 T^{-2} + (5.51412)10^8 T^{-3} + 97.1098 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

$$2150 \geq T\ ^\circ\text{K} \geq 450. \qquad (3)$$

5. Precision and Accuracy

The net measured heat values (fourth and fifth columns of table 3) can be shown to have a standard deviation of about 15. cal mol^{-1}. (This is equivalent to about 0.34 cal for the sample masses used.) The smoothing procedure used increases this standard deviation to 21. cal mol^{-1}, which is from 0.03 percent to 0.3 percent of the measured enthalpy values for the sample.

Systematic errors enter the measurements on $BeO \cdot 3Al_2O_3$ in the same ways as are discussed in a recent paper from this laboratory [2]. In particular, it is still likely that temperature measurement constitutes the major source of systematic error. No additional measurements on $\alpha - Al_2O_3$ were carried out prior to or during the present measurements. However, the authors believe that the results of the previous heat measurements on a standard sample of $\alpha - Al_2O_3$ [2], insofar as they are indicative of the operating state of the calorimeter, are applicable in estimating the accuracy of the present measurements.

One source of systematic error in the thermal values is the effect of the foreign phases, which, as stated in section 2.1, may amount to as much as 5 percent of the sample. However, even if perchance so much of the sample was not actually $BeO \cdot 3Al_2O_3$, the whole

TABLE 4. *Thermodynamic functions for beryllium 1:3 aluminate* $(BeO \cdot 3Al_2O_3)$ *solid phase*

Gram molecular weight = 330.8952 g, T deg K = t deg C + 273.15

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	cal deg^{-1} mol^{-1}	cal mol^{-1}	cal deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	cal mol^{-1}	cal deg^{-1} mol^{-1}
273.15	58.687	6626.1	24.258	36.611	3374.3	12.353
275.00	59.055	6735.0	24.491	37.009	3442.4	12.518
280.00	60.032	7032.8	25.117	38.082	3630.1	12.965
285.00	60.985	7335.3	25.738	39.153	3823.2	13.415
290.00	61.914	7642.6	26.354	40.221	4021.6	13.868
295.00	62.821	7954.4	26.964	41.288	4225.4	14.323
298.15	63.381	8153.2	27.346	41.958	4356.5	14.612
300.00	63.706	8270.7	27.569	42.351	4434.5	14.782
305.00	64.568	8591.4	28.169	43.411	4648.9	15.242
310.00	65.410	8916.4	28.763	44.468	4868.6	15.705
320.00	67.048	9578.8	29.934	46.571	5323.8	16.637
330.00	68.598	10257.	31.082	48.658	5800.0	17.576
340.00	70.072	10950.	32.207	50.728	6296.9	18.520
350.00	71.474	11658.	33.309	52.779	6814.5	19.470
360.00	72.808	12380.	34.388	54.812	7352.4	20.423
370.00	74.075	13114.	35.444	56.824	7910.6	21.380
373.15	74.461	13348.	35.771	57.453	8090.6	21.682
380.00	75.279	13861.	36.476	58.815	8488.8	22.339
390.00	76.420	14620.	37.486	60.786	9086.9	23.360
400.00	77.502	15389.	38.473	62.734	9704.5	24.261
425.00	79.960	17358.	40.843	67.508	11333.	26.665
450.00	82.109	19385.	43.077	72.141	13079.	29.064
475.00	84.003	21462.	45.182	76.632	14939.	31.456
500.00	85.690	23583.	47.166	80.984	16909.	33.818
550.00	88.578	27942.	50.804	89.292	21168.	38.488
600.00	90.956	32432.	54.054	97.104	25830.	43.050
650.00	92.954	37031.	56.972	104.47	30871.	47.494
700.00	94.666	41723.	59.604	111.42	36270.	51.814
750.00	96.156	46494.	61.993	118.00	42007.	56.009
800.00	97.473	51336.	64.170	124.25	48064.	60.080
850.00	98.654	56239.	66.164	130.20	54427.	64.031
900.00	99.725	61199.	67.999	135.87	61079.	67.866
950.00	100.71	66210.	69.695	141.28	68009.	71.588
1000.00	101.62	71269.	71.269	146.47	75204.	75.204
1050.00	102.47	76371.	72.734	151.45	82653.	78.717
1100.00	103.27	81515.	74.104	156.24	90346.	82.133
1150.00	104.02	86697.	75.389	160.84	98274.	85.455
[a]						
1200.00	104.74	91916.	76.597	165.29	106427.	88.690
1250.00	105.44	97171.	77.737	169.58	114800.	91.840
1300.00	106.10	102460.	78.815	173.72	123383.	94.910
1350.00	106.75	107781.	79.838	177.74	132170.	97.904
1400.00	107.37	113134.	80.810	181.63	141155.	100.82
1450.00	107.98	118518.	81.736	185.41	150331.	103.68
1500.00	108.57	123931.	82.621	189.08	159694.	106.46
1550.00	109.15	129374.	83.467	192.65	169238.	109.19
1600.00	109.72	134846.	84.279	196.13	178958.	111.85
1650.00	110.27	140346.	85.058	199.51	188849.	114.45
1700.00	110.82	145874.	85.808	202.81	198908.	117.00
1750.00	111.36	151428.	86.530	206.03	209129.	119.50
1800.00	111.90	157010.	87.228	209.18	219510.	121.95
1850.00	112.43	162618.	87.902	212.25	230046.	124.35
1900.00	112.95	168252.	88.554	215.26	240734.	126.70
1950.00	113.46	173913.	89.186	218.20	251570.	129.01
2000.00	113.98	179599.	89.799	221.08	262552.	131.28
2050.00	114.48	185310.	90.395	223.90	273677.	133.50
2100.00	114.99	191047.	90.975	226.66	284941.	135.69
2150.00	115.49	196809.	91.539	229.37	296342.	137.83

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.

sample had a stoichiometric composition very close to that of this compound (table 2); as a result, since no transition or other evidence of phase change was observed, the uncertainty in phase composition would give rise to thermal error only insofar as the heat capacities of the possible phase combinations differed from that of pure $BeO \cdot 3Al_2O_3$. The smallness of the deviations from such additivity shown later for BeO, Al_2O_3, and their known mixed oxides (table 5) suggests that the heat capacity of 5 percent of foreign phase would not be different from that of the rest of the sample by more than 2 percent, which would contribute only 0.1 percent error in the heat capacity of the sample as a whole.

TABLE 5. *Deviation of the high-temperature heat capacity of* $BeO \cdot Al_2O_3$ *and* $BeO \cdot 3Al_2O_3$ *from additivity based on mixtures of the two component oxides*

Temperature	$BeO \cdot Al_2O_3$			$BeO \cdot 3Al_2O_3$		
	Measured C_p° [b]	"Additive" C_p° [a]	ΔC_p° (Compound-mixture)	Measured C_p° [c]	"Additive" C_p° [a]	ΔC_p° (Compound-mixture)
°K	*cal mol*$^{-1}$ *deg*$^{-1}$	*cal mol*$^{-1}$ *deg*$^{-1}$	%	*cal mol*$^{-1}$ *deg*$^{-1}$	*cal mol*$^{-1}$ *deg*$^{-1}$	%
300	25.33	25.04	+0.7	63.71	62.84	+1.4
400	31.21	31.07	+0.5	77.50	77.06	+0.6
500	34.64	34.65	0.0	85.69	85.34	+0.4
600	37.03	37.00	+0.1	90.96	90.75	+0.2
700	38.73	38.64	+0.2	94.67	94.53	+0.1
800	39.98	39.86	+0.3	97.47	97.30	+0.2
900	40.91	40.80	+0.3	99.73	99.40	+0.3
1000	41.60	41.54	+0.1	101.62	101.03	+0.6
1100	42.11	42.15	−0.1	103.27	102.33	+0.9
1200	42.44	42.66	−0.5	104.74	103.38	+1.3

[a] Smoothed BeO values from reference [3]. Smoothed Al_2O_3 values from reference [4], corrected according to reference [18].
[b] Smoothed values from reference [2].
[c] From table 4.

Considering the precision of the data, the possible systematic errors and the measurements on the standard sample of $\alpha - Al_2O_3$, the authors feel that the smoothed enthalpy values derived from eq (2) can be assigned an accuracy which because the systematic errors are negligible can be expressed as a standard deviation decreasing from 0.4 percent at 100 °C to 0.3 percent at 900 °C. The corresponding accuracy (as standard deviation) in the values of heat capacity calculated from this equation should be from 0.4 percent to 0.7 percent over the same temperature range.

6. $BeO \cdot Al_2O_3$ and $BeO \cdot 3Al_2O_3$: Comparisons With Other Thermodynamic Data

6.1. Deviations of Heat Capacity from Additivity

The heat capacity of mixed-metal oxide compounds for which original heat capacity data are lacking is frequently approximated by summing individual values for the component oxides. Furukawa and Saba [1] have compared the heat capacity of $BeO \cdot Al_2O_3$ with that of an equimolar mixture of BeO and Al_2O_3. Their results show the mixed oxide to have a heat capacity from 25 percent to 1 percent in excess of the "additive" value (equimolar mixture of components) over the temperature range 10 to 380 °K. This behavior is attributed to the additional vibrational degrees of freedom present in the compound (especially at the lower temperatures). The present measurements provide a valuable extension of this comparison to higher temperatures, since accurate values of heat capacity have already been determined by the "drop" method for BeO [3] and Al_2O_3 [4, 18]. A comparison of the smoothed heat capacity of the mixed oxides $BeO \cdot Al_2O_3$ [2] and $BeO \cdot 3Al_2O_3$ (table 4) with the corresponding additive heat capacity obtained by summing existing values for the component oxides of these two compounds is presented in table 5. Columns five and seven of this table show the deviations of the molar heat capacity from additivity for the two compounds. These deviations must, of course, be considered in light of the accuracy of the data ([2] and sec. 5 of the present work). Column 5 shows a small positive deviation from additivity for $BeO \cdot Al_2O_3$ on the order of a percent near room temperature. This is in agreement with the findings of Furukawa and Saba [1]. At higher temperatures, the compound and mixture approach equality of heat capacity within the accuracy of the data. Column 7 shows, however, a definite trend in the deviation from additivity for $BeO \cdot 3Al_2O_3$. At room temperature, the heat capacity of the compound is seen to be a percent above that of the mixture, and this difference decreases with increasing temperature. This is in complete agreement with recent results of Furukawa and Saba [7] on the same compound. The high-temperature data indicate also a minimum near 700 °K in the deviation from additivity for $BeO \cdot 3Al_2O_3$.

6.2. Correlation With Heat-of-Formation and Equilibrium Data

Besides the thermodynamic functions for $BeO \cdot Al_2O_3$ and $BeO \cdot 3(Al_2O_3)$ based on heat-capacity and enthalpy measurements at the NBS reported in this paper and previously [1, 2, 7], the results of other measurements involving these two substances have been published, and all may be examined for thermodynamic interconsistency. Holm and Kleppa [13] have recently measured the heats of solution of BeO, Al_2O_3, and these two mixed oxides [5] in a molten (lead-cadmium) borate near 1000 °K, and from the results have calculated the heats of the reactions

$$BeO(c) + Al_2O_3(c) = BeO \cdot Al_2O_3(c) \qquad (4)$$

and

$$BeO(c) + 3Al_2O_3(c) = BeO \cdot 3(Al_2O_3)(c). \qquad (5)$$

Over the approximate temperature range 1600 to 1850 °K Young [14] measured equilibria involving the transpiration by water vapor of beryllium oxide from each of the same mixed oxides.

[5] Using specimens of the mixed oxides from the same samples as in the present work and that of references [1, 2, 7].

Young cited evidence indicating that the three reactions he studied are as follows:

$$BeO(c) + H_2O(g) = Be(OH)_2(g) \quad (6)$$

$$3BeO \cdot Al_2O_3(c) + 2H_2O(g) = BeO \cdot 3(Al_2O_3)(c) + 2Be(OH)_2(g) \quad (7)$$

$$BeO \cdot 3(Al_2O_3)(c) + H_2O(g) = 3Al_2O_3(c) + Be(OH)_2(g). \quad (8)$$

No one to the authors' knowledge has proved that the gaseous product of reactions (6)–(8) has a $BeO:H_2O$ ratio of 1:1, but it seems likely that this may be predominantly true in the temperature range investigated. Although spectroscopic data on $Be(OH)_2(g)$ are lacking, it is possible to estimate a set of molecular constants for the molecule which correspond to these various transpiration data [15] within their precision and interconsistency.

Nevertheless, in order to concentrate on the solid phases and avoid the uncertainties in the properties of $Be(OH)_2(g)$, Young's reactions (6)–(8) will be considered here only in the form of their linear combinations that give reactions (4) and (5). Table 6 shows the values of ΔH_0° calculated for these two reactions (a) after correcting the calorimetric heats of reaction to 0 °K by use of the enthalpy functions and (b) by combining Young's equilibrium constants with the free-energy functions, for reactions (6)–(8) averaging only the ΔH_0° values derived from equilibrium measurements above 1790 °K. Although reaction (6) was also studied by transpiration in two additional investigations [16, 17] and some of these results seem to be at least as accurate as Young's, only the latter's results for this reaction are used in the comparison here, in order to avoid possible inconsistency in various conditions, especially temperature, among the three investigations of this reaction. Furthermore, Young's precision limitations below about 1800 °K are greatly magnified percentagewise when applied to reactions (4) and (5), and hence were considered too great to justify giving weight to Second-Law values of ΔH_0° calculated from his data.

Although both methods of calculation indicate that at 0 °K $BeO \cdot Al_2O_3$ is exothermic and $BeO \cdot 3(Al_2O_3)$ is endothermic with respect to their component oxides, the two values of ΔH_0° for each compound disagree substantially, and it is natural to seek the cause. The uncertainties in the calorimetric heats of reactions (4) and (5) [13] are believed to be considerably less than the disagreements; also, the free-energy functions are very insensitive to any reasonable variation in how the heat-capacity data are extrapolated above 1200 °K [2]. One explanation quantitatively possible is that the free-energy functions may not be strictly applicable to the equilibrium data because of greater or smaller degree of disorder in the two different samples of each

TABLE 6. *Heats of formation at 0 °K of* $BeO \cdot Al_2O_3$(c) *and* $BeO \cdot 3(Al_2O_3)$(c) *from their solid component oxides, from calorimetric and equilibrium data*

Compound	Reaction No.	ΔH_0°	
		From calorimetric data	From equilibrium data
		kcal mol^{-1}	*kcal mol*$^{-1}$
$BeO \cdot Al_2O_3$	(4)	−4.1	−2.6
$BeO \cdot 3(Al_2O_3)$	(5)	+2.5	+0.2

APPENDIX. *Thermodynamic functions for beryllium 1:3 aluminate* ($BeO \cdot 3Al_2O_3$) *solid phase*

Gram molecular weight = 330.8952 g, T deg K = t deg C + 273.15

C_p°	T	C°	$(H_T^\circ - H_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$S_T^\circ - S_0^\circ$	$-(G_T^\circ - H_0^\circ) - TS_0^\circ$	$-(G_T^\circ - H_0^\circ)/T - S_0^\circ$
°K		*J deg*$^{-1}$ *mol*$^{-1}$	*J mol*$^{-1}$	*J deg*$^{-1}$ *mol*$^{-1}$	*J deg*$^{-1}$ *mol*$^{-1}$	*J mol*$^{-1}$	*J deg*$^{-1}$ *mol*$^{-1}$
273.15		245.55	27724.	101.50	153.18	14118.	51.686
275.00		247.09	28179.	102.47	154.84	14403.	52.374
280.00		251.17	29425.	105.09	159.33	15188.	54.244
285.00		255.16	30691.	107.69	163.81	15996.	56.127
290.00		259.05	31977.	110.26	168.29	16827.	58.023
295.00		262.84	33281.	112.82	172.75	17679.	59.929
298.15		265.19	34113.	114.42	175.55	18228.	61.136
300.00		266.54	34605.	115.35	177.20	18554.	61.847
305.00		270.15	35947.	117.86	181.63	19451.	63.774
310.00		273.67	37306.	120.34	186.05	20370.	65.711
320.00		280.53	40078.	125.24	194.85	22275.	69.609
330.00		287.01	42916.	130.05	203.58	24267.	73.537
340.00		293.18	45817.	134.76	212.24	26346.	77.489
350.00		299.05	48778.	139.37	220.83	28512.	81.462
360.00		304.63	51797.	143.88	229.33	30763.	85.452
370.00		309.93	54870.	148.30	237.75	33098.	89.454
373.15		311.55	55849.	149.67	240.39	33851.	90.717
380.00		314.97	57994.	152.62	246.08	35517.	93.467
390.00		319.74	61168.	156.84	254.33	38019.	97.486
400.00		324.27	64388.	160.97	262.48	40604.	101.51
425.00		334.55	72627.	170.89	282.45	47416.	111.57
450.00		343.54	81105.	180.23	301.84	54721.	121.60
475.00		351.47	89795.	189.04	320.63	62503.	131.59
500.00		358.53	98672.	197.34	338.84	70748.	141.50
550.00		370.61	116910.	212.56	373.60	88568.	161.03
600.00		380.56	135697.	226.16	406.28	108073.	180.12
650.00		388.92	154940.	238.37	437.08	129165.	198.71
700.00		396.08	174569.	249.38	466.17	151753.	216.79
750.00		402.32	194533.	259.38	493.72	175756.	234.34
800.00		407.83	214789.	268.49	519.86	201101.	251.38
850.00		412.77	235306.	276.83	544.74	227721.	267.91
900.00		417.25	256058.	284.51	568.46	255556.	283.95
950.00		421.36	277025.	291.60	591.13	284550.	299.53
1000.00		425.17	298189.	298.19	612.84	314653.	314.65
1050.00		428.72	319537.	304.32	633.67	345819.	329.35
1100.00		432.06	341057.	310.05	653.69	378007.	343.64
1150.00		435.24	362741.	315.43	672.97	411176.	357.54
1200.00		438.25	384578.	320.48	691.56	445292.	371.08
1250.00		441.15	406564.	325.25	709.51	480322.	384.26
1300.00		443.93	428691.	329.76	726.86	516233.	397.10
1350.00		446.63	450956.	334.04	743.67	552999.	409.63
1400.00		449.24	473353.	338.11	759.96	590592.	421.85
1450.00		451.78	495878.	341.98	775.77	628987.	433.78
1500.00		454.26	518529.	345.69	791.13	668161.	445.44
1550.00		456.68	541303.	349.23	806.06	708092.	456.83
1600.00		459.06	564196.	352.62	820.60	748760.	467.98
1650.00		461.39	587208.	355.88	834.76	790146.	478.88
1700.00		463.69	610335.	359.02	848.57	832230.	489.55
1750.00		465.95	633576.	362.04	862.04	874997.	500.00
1800.00		468.19	656929.	364.96	875.20	918429.	510.24
1850.00		470.39	680394.	367.78	888.06	962512.	520.28
1900.00		472.57	703968.	370.51	900.63	1007230.	530.12
1950.00		474.73	727651.	373.15	912.93	1052570.	539.78
2000.00		476.88	751441.	375.72	924.98	1098519.	549.26
2050.00		479.00	775338.	378.21	936.78	1145064.	558.57
2100.00		481.11	799341.	380.64	948.35	1192193.	567.71
2150.00		483.20	823448.	383.00	959.69	1239895.	576.70

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 above the temperature range of the measurements.

mixed oxide; however, the two discrepancies have opposite signs (table 6). If Young's data depend systematically to a small extent on gas-flow rate, which several of his data suggest, or if some solid solution of the product oxide in the reacting oxide occurred in his experiments, the equilibrium constants that were calculated for reactions (7) and (8) would be correspondingly in error. It is concluded that the available facts offer no simple explanation of the discrepancies in table 6.

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