[CONTRIBUTION FROM THE METALLURGICAL FUNDAMENTALS SECTION, METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Specific Heats at Low Temperatures of Beryllium Oxide and Beryllium Orthosilicate (Phenacite)[1]

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There are only two normal metal oxides of the second group whose specific heats at low temperatures and entropies at 298.1°K. have not been determined heretofore, beryllium oxide and radium oxide. The only silicates of this group that previously have been studied adequately are two forms of calcium silicate, although a partial investigation has been made of magnesium silicate and calcium–magnesium double silicate. The results for these silicates and for the seven oxides of the second group already investigated have been summarized by the writer.[3]

The present paper presents specific heat measurements in the temperature range 52.5 to 298.1°K. and entropy values at 298.1°K. for beryllium oxide and beryllium orthosilicate (Be_2SiO_4). This work continues a program of study of the Metallurgical Division of the Bureau of Mines.

Materials

The beryllium oxide was a Kahlbaum preparation given to this Laboratory about twelve years ago by Prof. G. S. Parks of Stanford University. It was in the form of fine powder, and analysis showed 89.3% BeO, 10.4% $CaCO_3$ and 0.33% H_2O.

To remove the calcium carbonate, the material first was treated with 1:10 hydrochloric acid until carbon dioxide evolution ceased and then filtered with suction and thoroughly washed. But little beryllium oxide was lost in this process, as it was only very slowly soluble in acid of the strength used. After drying at 900°, the beryllium oxide was kept in screw-cap bottles in a desiccator over concentrated sulfuric acid until it was placed in the calorimeter. Analysis of the purified product gave 99.6% BeO. No aluminum oxide was found with the 8-hydroxyquinoline procedure recommended by Hillebrand and Lundell.[4]

It required 66.5 g. to fill the calorimeter.

Two samples of natural beryllium orthosilicate (Phenacite) were purchased. One came from Brazil and the other from Colorado. The Brazilian sample consisted of well-crystallized particles of about 4 mm. size. After crushing and washing to remove a small amount of claylike impurity, analysis showed 99.9% Be_2SiO_4. The Colorado sample was not as well crystallized and was contaminated with mica. This material was sorted carefully and scrubbed, over 50% being discarded. Analysis of the portion used showed 99.8% Be_2SiO_4.

The entire Brazilian sample of 126.5 g. and 83.5 g. of the Colorado material were used to fill the calorimeter.

Specific Heats

The method and apparatus have been described previously.[5]

The results, expressed in defined calories (1 calorie = 4.1833 int. joules), are given in Table I and shown graphically in Fig. 1. Both substances behave normally throughout the temperature range studied.

TABLE I

SPECIFIC HEAT OF BeO (25.02 G.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
55.5	0.134	103.4	0.742	202.3	3.486
59.9	.174	111.9	0.921	212.5	3.796
64.0	.206	122.1	1.160	222.3	4.091
68.4	.246	132.1	1.422	232.6	4.405
73.2	.294	142.0	1.675	242.4	4.675
78.0	.350	152.2	1.963	252.3	4.947
81.3	.395	162.8	2.276	262.2	5.228
81.5	.396	172.5	2.568	272.4	5.489
85.7	.445	182.0	2.863	282.2	5.716
94.5	.577	192.4	3.185	288.4	5.823
				292.4	5.948

SPECIFIC HEAT OF Be_2SiO_4 (110.10 G.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.7	0.935	114.5	5.889	213.7	15.75
58.6	1.160	124.3	6.872	223.8	16.68
63.3	1.457	134.6	7.903	234.5	17.66
68.2	1.820	143.9	8.846	245.3	18.58
72.6	2.157	154.3	9.931	255.5	19.41
76.6	2.479	163.9	10.87	265.3	20.21
81.4	2.870	174.0	11.87	275.2	21.06
86.1	3.253	184.2	12.89	284.4	21.72
95.0	4.039	193.6	13.82	294.1	22.48
104.5	4.912	203.8	14.81		

The specific heat of beryllium oxide is, as would be expected, lower on a gram atom basis than that of any other metal oxide that has been studied. The measured result at 55.5°K. is only 0.134 cal. per gram formula mass. The results below 70°K. are represented adequately by the T^3 law, $C_p = 7.87 \times 10^{-7}T^3$. Up to 102°K., the results are reproduced by the Debye

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(3) Kelley, Bureau of Mines Bulletin 394, 1936, 55 pp.

(4) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 405.

(5) Millar, THIS JOURNAL, **50**, 1875 (1928); Anderson, *ibid.*, **52** 2296 (1930).

function of θ = 855, while a combination of the Debye function of θ = 855 and the Einstein function of θ = 1170 fits the results over the entire temperature range studied.

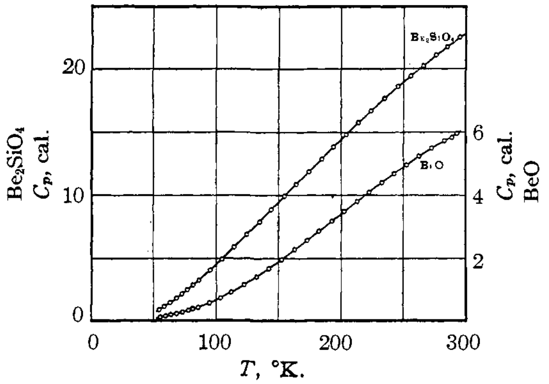

Fig. 1.—Specific heats of BeO and Be_2SiO_4 in calories per gram formula mass.

The specific heat of beryllium orthosilicate also is remarkably low, falling to 0.935 cal. per gram formula mass at 54.7°K. from a value 24 times as great, 22.48, at 294.1°K. The results for this substance throughout the temperature range studied may be represented by the function combination

$$D\left(\frac{422}{T}\right) + 2E\left(\frac{527}{T}\right) + 4E\left(\frac{1135}{T}\right)$$

Entropy Calculations

The entropies at 298.1°K., shown in Table II, were calculated in the usual manner, the portion above 53.1°K. being obtained graphically and that below 53.1°K. by extrapolation. The beryllium oxide results were extrapolated by means of the T^3 law and those for beryllium orthosilicate by the function combination $D\left(\frac{422}{T}\right) + 2E\left(\frac{527}{T}\right)$. In the latter instance, however, the contribution of the Einstein functions is virtually negligible at 53.1°K.

TABLE II

ENTROPIES AT 298.1°K.

	BeO	Be_2SiO_4
0–53.1°K. (extrapolation)	0.037	0.30
53.1–298.1°K. (graphical)	3.336	15.07
$S_{298.1}$	3.37 ± 0.05	15.4 ± 0.1

The value for beryllium oxide is about what would be expected in comparison with results for other second group oxides. The figure for beryllium orthosilicate is 2 units lower than would be computed assuming a simple additive rule involving beryllium oxide and silica. This is not unreasonable, as the substance should constitute one of the severest tests of such additivity because of the low formula mass of beryllium oxide and because of the very high degree of hardness of this silicate.

Related Thermal Data

Values for the heat of formation of beryllium oxide ranging from $\Delta H = -151{,}500$ to $\Delta H = -130{,}500$ are to be found in the literature.[6,7] Just recently Roth, Börger and Siemonsen[8] have redetermined this property and obtained $\Delta H_{293.1} = -147{,}300 \pm 600$. This value will be used here.

The entropy of formation of beryllium oxide is $\Delta S_{298.1} = -23.43$, computed from the figure for beryllium oxide in this paper and the entropies of the elements.[3] The corresponding free energy of formation is $\Delta F°_{298.1} = -140{,}320$.

Summary

Specific heat measurements of beryllium oxide and beryllium orthosilicate were made covering the temperature range 52.5 to 298.1°K.

The entropies are $S_{298.1} = 3.37 \pm 0.05$ for beryllium oxide and $S_{298.1} = 15.4 \pm 0.1$ for beryllium orthosilicate (Be_2SiO_4).

The value $\Delta F°_{298.1} = -140{,}320$ is given as the free energy of formation of beryllium oxide.

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(6) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Verlag von Julius Springer, Berlin, Vol. II, 1923, p. 1519; 1st Supplement, 1927, p. 824; 2nd Supplement, Vol. II, 1931, p. 1506; 3rd Supplement, Vol. III, 1936, p. 2761.

(7) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, pp. 112 and 338.

(8) Roth, Börger and Siemonsen, *Z. anorg. allgem. Chem.*, **239**, 321 (1938).