Heat Content and Heat Capacity of Crystalline Boron from 298° to 1700° K.

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WHEN THIS investigation was started, reliable high temperature heat content data on crystalline boron were not available. Measurements up to 1100° K. have since been published by Wise, Margrave, and Altman (*6*). This work extends the experimental range up to 1668° K.

EXPERIMENTAL

Material. The sample of crystalline boron, −4 + 20 mesh, was obtained from the United States Borax and Chemical Corp. After completion of the heat content measurements, the sample was crushed to −80 mesh in order to obtain a more representative sample for analysis. The assay by Parr bomb method with mannitol titration was 99.41% boron. Spectrographic analysis indicated: Al, 0.004 to 0.012%; Cu, 0.001 to 0.003%; Fe, 0.07 to 0.16%; Mg, 0.005 to 0.015%; Mn, 0.03 to 0.07%; and Si, 0.02 to 0.04%. Only the β-rhombohedral form was found by x-ray diffraction.

Enthalpy. A 2.539-gram portion of boron was contained in a tantalum can (8.279 grams) which was sealed in a platinum–10% rhodium capsule (13.882 grams) by arc welding under a helium pressure of 8 cm. of mercury.

The heat content, $H_T - H_{298.15}$, was measured in a copper block drop calorimeter previously described (*4*). The platinum *vs.* platinum–10% rhodium thermocouple that measured the temperature of the sample capsule in the furnace was calibrated against a similar couple standardized at the National Bureau of Standards. A few measurements of the enthalpy of α-aluminum oxide were made as a check of the accuracy of the apparatus.

RESULTS

The observed enthalpies of α-aluminum oxide are compared with values calculated from the work of Furukawa, Douglas, McCoskey, and Ginnings (*2*) in Table I.

The observed enthalpies of boron are listed in Table II. They fall between two crystalline samples measured by Wise, Margrave, and Altman (*6*), but are nearer their Sample II (also from the United States Borax and Chemical Corp.). The observed values were smoothed by the method of Shomate (*5*) using the low temperature data of Johnston, Hersh, and Kerr (*3*) as corrected by Evans, Wagman, and Prosen (*1*). The heat capacity at 298.15° K. is given as 2.65 cal. mole^{-1} deg.$^{-1}$ in both publications. However, to join the Shomate functions of the low and high temperature data smoothly, it was necessary to use $C_{p\ 298.15} = 2.67$ cal. mole^{-1} deg.$^{-1}$.

Smoothed values of heat content and heat capacity are given in Table III. The heat capacity above 1000° K. is lower than that calculated by Wise and others (*6*).

$$H_T - H_{298.15} = 4.735\,T + 6.90 \times 10^{-4}\,T^2 + 2.201 \times 10^5/T - 2211.3 \text{ cal. mole}^{-1}$$

represents the smoothed enthalpy within 0.11% between 1000° and 1700° K. and was derived by the Shomate method (*5*) to fit the high temperature portion for extrapolation purposes.

By differentiation

$$C_p = 4.735 + 1.38 \times 10^{-3}T - 2.201 \times 10^5/T^2 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

Table I. Enthalpy of α-Al_2O_3

Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1} Observed	NBS[a]	Difference	% Deviation from NBS
290.2	−1.387	−1.460	+0.073	+5.00
786.4	121.38	121.51	−0.13	−0.11
788.4	122.36	122.06	+0.30	+0.25
794.6	123.76	123.82	−0.06	−0.05
1268.3	262.64	262.51	+0.13	+0.05
1293.0	269.96	269.95	+0.01	+0.00
1303.6	273.38	273.12	+0.26	+0.10
1623.1	374.08	370.17	+3.91	+1.06
1641.3	377.51	375.72	+1.79	+0.48

[a] Equation from Reference 2.

Table II. Observed Enthalpy of Crystalline Boron

(At. Wt. Boron = 10.82)

Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}	Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}	Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}
282.8	−37.74	876.7	2700	1282.0	5165
332.7	101.2	905.7	2873	1334.3	5499
432.8	454.9	947.0	3110	1367.4	5698
575.4	1092	997.8	3414	1406.4	5972
579.4	1116	1063.1	3797	1459.6	6331
622.2	1338	1098.7	4027	1483.7	6490
660.7	1530	1148.4	4334	1539.8	6857
681.5	1656	1205.0	4673	1573.5	7079
767.0	2108	1210.8	4722	1602.1	7280
833.0	2476	1254.5	4986	1667.8	7729

Table III. Smoothed Enthalpy and Heat Capacity of Crystalline Boron

Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}	C_p, Cal. Mole^{-1} Deg.$^{-1}$	Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}	C_p, Cal. Mole^{-1} Deg.$^{-1}$
298.15	0	2.67	1000	3430	5.95
300	4.96	2.68	1100	4033	6.12
400	327.4	3.72	1200	4652	6.26
500	740.2	4.49	1300	5285	6.41
600	1218	4.99	1400	5934	6.54
700	1735	5.32	1500	6594	6.67
800	2281	5.56	1600	7268	6.79
900	2846	5.76	1700	7953	6.90

LITERATURE CITED

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