whence

$$\Delta F^0_{298.16} = -283.1 \pm 3.4 \text{ kcal.}$$

When these values are combined with our values of $H^0 - H^0_0$ at 298.16°K. for crystalline boron and for B_2O_3[19] and with that of Johnston and Walker[24] for oxygen, we obtain

$$\Delta H^0_0 = -300.5 \pm 3.4 \text{ kcal.}$$

This value is conveniently used with the tabulated free energy functions to obtain ΔF° at temperatures other than 298°K.

Free Energy of Formation of Boric Acid.—The heat of formation of boric acid from its elements can be obtained by combining equations 1, 2, 4 and 5 with the reaction

$$2H_3BO_3(\text{crystalline}) + \text{aqua} = 2H_3BO_3(\text{aqueous}) \quad (7)$$

$$\Delta H^0_{298.16} = +10.20 \pm 0.10 \text{ kcal.}^{20}$$

to give

$$B(\text{crystalline}) + 3/2H_2(\text{gas}) + 3/2O_2(\text{gas}) = H_3BO_3(\text{crystalline}) \quad (8)$$

$$\Delta H^0_{298.16} = -260.23 \pm 3.5 \text{ kcal.}$$

Using our values for the thermodynamic function of the crystalline forms of B and H_3BO_3[13] and those of Johnston and Walker[24] and of Giauque[25] for O_2 and H_2, respectively, we obtain

$$\Delta S^0_{298.16} = -100.56 \pm 0.1 \text{ e.u.}$$

$$\Delta F^0_{298.16} = -23.03 \pm 3.5 \text{ kcal.}$$

$$\Delta H^0_0 = -233.87 \pm 3.5 \text{ kcal.}$$

Free Energy of Hydration of Boric Oxide.—Equations 3 and 7 can be combined with the relationship

$$H_2O(\text{liquid}) = H_2O(\text{gas}) \quad (9)$$

$$\Delta H^0_{298.16} = +10.520 \pm 0.003 \text{ kcal.}^{26}$$

to yield

$$B_2O_3(\text{crystalline}) + 3H_2O(\text{gas}) = 2H_3BO_3(\text{crystalline}) \quad (10)$$

$$\Delta H^0_{298.16} = -45.21 \pm 0.11 \text{ kcal.}$$

$$\Delta S^0_{298.16} = -105.75 \text{ e.u.}$$

$$\Delta F^0_{298.16} = -13.68 \pm 0.1 \text{ kcal.}$$

$$\Delta H^0_0 = -16.18 \text{ kcal.}$$

Acknowledgments.—We wish to acknowledge the assistance of Mr. Nathan C. Hallett in making the runs.

Summary

Pure boron has been prepared in both the amorphous and crystalline forms in sufficient quantity to permit accurate heat capacity determinations.

Heat capacities were measured from about 16°K. to over 300°K. The data yield a value of 1.403 ± 0.005 cal. per mole per deg. for the entropy of crystalline boron at 298.16°K. and yield 1.564 ± 0.01 cal. per mole per deg. for that of amorphous boron relative to S^0_0. Tables of thermodynamic functions have been prepared for smoothed values of the temperature.

Crystalline boron satisfies the T^3 law for temperatures between 60 and 125°K. to within about 3% and satisfies the Debye equation to within about 2% when θ_D is set equal to 1219. As in the case of diamond, observed heat capacities above 125°K. are higher than those given by the T^3 law or by the Debye equation. Amorphous boron fails to fit either the T^3 law or the Debye equation, but its capacity between 50 and 75°K. corresponds roughly to a θ_D of 1102.

Low maxima are observed below 30°K. for both the amorphous and crystalline forms. The maximum for the amorphous form is somewhat higher than that of the crystalline form and occurs at a lower temperature. There may be some correlation between these maxima and the narrow 2*p* doublet that constitutes the ground state of the boron atom.

Standard free energies have been evaluated for the formation of B_2O_3 (crystalline), the formation of H_3BO_3 (crystalline), and the hydration of B_2O_3 to form the acid.

COLUMBUS 10, OHIO RECEIVED JULY 5, 1950

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[25] W. F. Giauque, THIS JOURNAL, **52**, 4816 (1930).

[26] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. E. Pitzer and F. D. Rossini, *J. Research Natl. Bur. of Standards*, **34**, 143 (1945).

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacity of Inorganic Solids. VI. The Heat Capacity of Decaborane, $B_{10}H_{14}$, from 14 to 305°K.[1]

BY EUGENE C. KERR, NATHAN C. HALLETT AND HERRICK L. JOHNSTON

Introduction

Although decaborane $B_{10}H_{14}$ has been known for many years as a by-product residue from vessels used for storage of diborane and other low molecular weight boron hydrides, no measurements of thermodynamic interest have been reported except for vapor pressure data on the solid and liquid by Stock and Pohland.[2] Kelley[3] used these data to derive the heats of fusion, sublimation and vaporization.

The present paper reports the results of measurements on the heat capacity of decaborane from 14 to 305°K.

Apparatus and Materials.—The heat capacity measurements were made in calorimeter No. 4, one of a group of seven calorimeters for the measurement of the heat capacity of solid materials. This calorimeter is identical in all respects to calorimeter No. 1 which has been described in an earlier paper.[4]

A sample of decaborane was loaned to us through the courtesy of Dr. A. L. Marshall of the General Electric Research Laboratory. Before we received the sample, it had been purified by several vacuum sublimations, the last two of which showed no change in melting point. We subjected

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] Stock and Pohland, *Ber.*, **62B**, 90 (1929).

[3] K. K. Kelley, U. S. Bureau of Mines Bull., p. 383, 1935.

[4] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

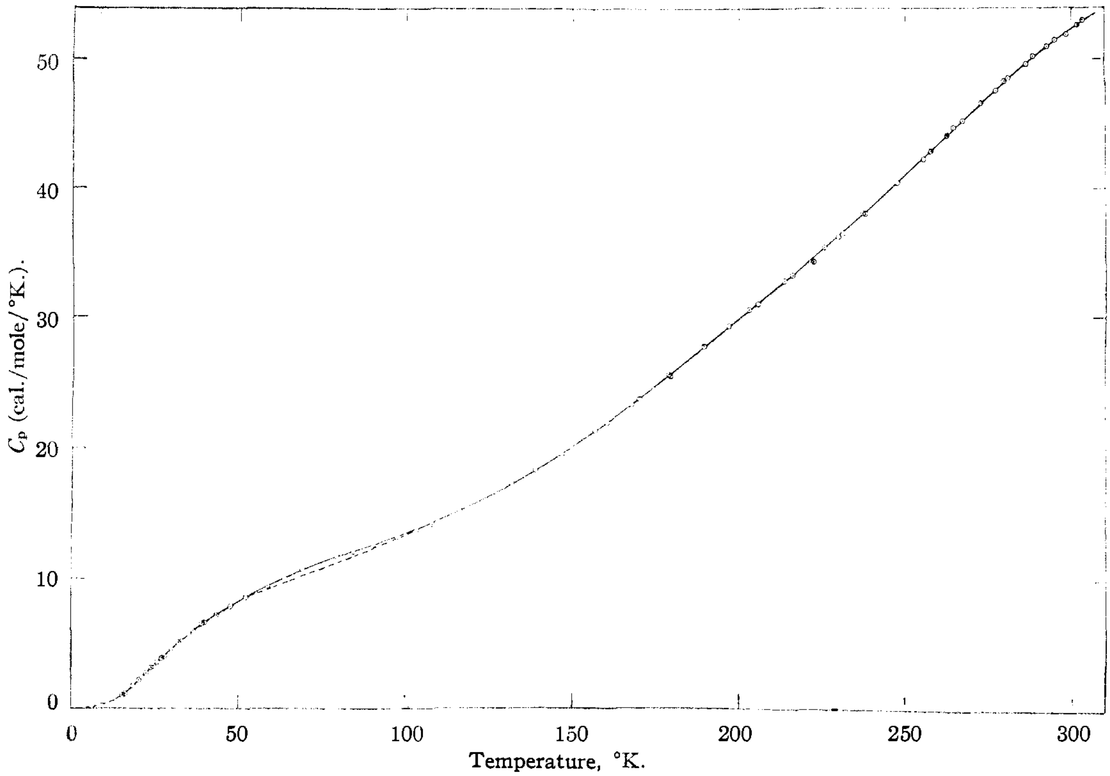

Fig. 1.—Heat capacity of decaborane ($B_{10}H_{14}$).

the sample to one more vacuum sublimation before putting it in the calorimeter. The calorimeter contained 34.3547 g. (0.28088 mole) of decaborane.

Experimental Results

The experimental heat capacity data are summarized in Table I and shown graphically in Fig. 1.

TABLE I

HEAT CAPACITY OF 0.28088 MOLE OF DECABORANE, $B_{10}H_{14}$

Mol. wt. 122.31 g., 1 cal. = 4.1833 int joules

T, °K.	C_p cal./mole/°K.	T, °K.	C_p cal./mole/°K.
15.21	1.092	138.90	18.312
16.06	1.224	146.94	19.490
18.08	1.636	157.05	21.31
18.10	1.646	160.65	21.93
20.03	2.071	168.01	23.26
20.91	2.284	170.34	23.69
22.26	2.615	179.25	25.49
23.59	3.009	179.65	25.40
24.48	3.155	189.72	27.64
25.62	3.458	197.27	29.23
27.01	3.838	203.25	30.61
27.66	4.005	205.78	31.08
29.69	4.594	213.60	32.88
29.78	4.953	216.07	33.43
31.78	5.120	221.79	34.54
32.73	5.355	222.67	34.57
34.95	5.778	230.08	36.49
36.23	6.096	231.50	36.74
39.00	6.592	237.48	38.16
39.85	6.697	238.04	38.18
43.23	7.192	247.46	40.49
47.64	7.761	255.27	42.20
52.28	8.464	257.41	42.97
64.03	10.111	262.38	43.98
69.31	10.593	264.23	44.54
74.41	11.079	272.60	46.56
79.59	11.547	276.84	47.44
84.47	11.964	279.53	48.22
90.47	12.490	280.76	48.62
97.37	13.085	286.21	49.69
103.43	13.662	288.22	50.31
108.18	14.015	292.47	51.20
116.29	15.149	294.98	51.65
131.89	17.242	298.36	52.49
		301.64	53.09

In the figure, a small hump is evident between 50 and 100°K. In order better to determine the magnitude of this hump and also to assist in extrapolating the curve below 14°K., the experimental curve was fitted to the following combination of Einstein and Debye functions

$$C_p = 2\,D\left(\frac{145}{T}\right) + 8E_1\left(\frac{358}{T}\right) + 44E_2\left(\frac{812}{T}\right) + 14E_3\left(\frac{2100}{T}\right)$$

in which the Debye θ has its usual significance as a "characteristic" temperature and the Einstein's θ are in frequency numbers for a Planck–Einstein oscillator in one degree of freedom. The coefficients of the above terms and the first approximation to the frequencies were selected from a rough estimate of the expected vibrational modes and frequencies for this molecule. In this selection, we used as a model the structure derived by Kaspar, Lucht and Harker[5] from single crystal X-ray diffraction studies.

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(5) J. S. Kaspar, C. Lucht and D. Harker, THIS JOURNAL, **70**, 881 (1948).

TABLE II

THERMODYNAMIC FUNCTIONS FOR DECABORANE, $B_{10}H_{14}$

T, °K.	C_p cal./mole/°K.	S^0 cal./°K.	$H^0 - H^0_0$ cal./mole	$(H^0 - H^0_0)/T$	$(F^0 - H^0_0)T$
14	0.810	0.270[a]	2.835[a]	0.203	0.067
25	3.350	1.352	24.714	0.989	0.363
50	8.135	5.381	176.86	3.537	2.207
75	11.135	9.300	421.08	5.614	3.686
100	13.325	12.799	726.47	7.265	5.534
125	16.30	16.074	1094.8	8.758	7.316
150	20.03	19.365	1547.5	10.317	9.048
175	24.62	22.790	2104.3	12.025	10.765
200	29.82	26.414	2784.3	13.922	12.423
225	35.30	30.241	3597.9	15.991	14.250
250	41.02	34.254	4551.3	18.205	16.049
275	47.13	38.448	5652.7	20.555	17.893
298.16	52.42	42.475	6806.9	22.830	19.645
300	52.78	42.798	6903.7	23.012	19.786

[a] Debye extrapolation: $C_p = 2D\,(145/T)$.

Since the above equation fits the experimental data to within 0.5% throughout most of the range, only that portion under the hump is shown (dotted line) in the figure. The area between the experimental curve and the Debye–Einstein curve correspond to an entropy of 0.210 e.u.

Standard thermodynamic functions have been calculated from the experimental data and are given at integral temperature values in Table II. The entropy at 298.16 is 42.48 ± 0.1 e.u.

Summary

The heat capacities of decaborane have been measured in the range 14 to 305°K. and the derived thermodynamic functions have been calculated and tabulated at integral values of the temperature over this range. The entropy at 298.16°K. is 42.48 ± 0.1 e.u.

COLUMBUS 10, OHIO RECEIVED JULY 5, 1950

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. VII. Heat Capacity and Thermodynamic Functions of Li_2O. Thermodynamics of the Li_2O–H_2O System[1]

BY HERRICK L. JOHNSTON AND THOMAS W. BAUER

Introduction

No previous measurements of the heat capacity of lithium oxide have been reported in the literature.

Apparatus and Material

The calorimetric data were obtained with our calorimeter No. 3, whose construction and operation have been described in a previous paper[2] from this Laboratory.

Relatively pure lithium hydroxide, obtained from the Metalloy Corporation of Minneapolis, was purified by recrystallization from triply distilled water. The $LiOH \cdot H_2O$ formed was decomposed to Li_2O in a nickel boat, in a stream of purified hydrogen gas, first at about 150° to LiOH and then at about 800°. Difficulty was experienced due to the extreme wetting properties of the fused LiOH. The fused material showed a tendency to creep out of the boat and attacked the monel furnace tube even in a reducing atmosphere of hydrogen. Titration with normal HCl gave a purity of 99.4% when all the base present was calculated as Li_2O. A spectroscopic analysis of the purified sample showed that some calcium was present as an impurity and that faint traces of less than 0.001% aluminum, magnesium, silicon, sodium and nickel were also present.

The lithium oxide was further purified by heat treatment in a nickel crucible at temperatures ranging from 1000 to 1300°. The crucible was supported inside a water-cooled Pyrex condenser through which hydrogen circulated, and was heated by induction heating.

Heating the sample for 3 to 5 hours increased its purity to 99.90 ± 0.10%, on the basis of an hydrochloric acid titration of Li_2O; further heating did not change the purity. Nickel contamination did not rise above 0.001%. We assumed that the 0.50% increase in purity must have represented removal of the last traces of water, and possibly CO_2, and that any remaining impurity must be CaO. After correcting for CaO, on the basis of the 99.90% Li_2O titration, the composition of the final purified sample was 99.74% Li_2O, the remaining 0.26% being CaO.

The measured values of the heat capacity were corrected for the small amount of CaO present by use of the data of Nernst and Schwers[3] and of Parks and Kelley.[4] This correction was less than 0.07%.

Results

Measurements were made with the calorimeter filled with 43.088 g. (1.4420 moles) of Li_2O and with 0.112 g. (0.0020 mole) of CaO.

The experimental values of the molal heat capacity are given in Table I in defined thermochemical calories.[5] The heat capacity of the empty calorimeter amounts to almost 90% of the total heat capacity below 30°K.

Smoothed values of the thermodynamic functions obtained by graphical means from the heat capacity are entered in Table II. The smoothed values are accurate to within 0.2% above 45°K., but might be in error as much as 2% at 20°K. The values at the lowest temperatures are less accurate than other data[6] obtained at this Laboratory, due to the very low heat capacity of Li_2O in this region. The molal entropy of Li_2O at 298.16°K. is 9.06 ± 0.03 e.u., with only 0.003 e.u. contributed by a Debye extrapolation ($\theta = 559$) below 16°K.

Thermodynamic Calculations

Third Law Check on the Entropies Through the Dissociation Pressure of LiOH.—Johnston[7]

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

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[3] W. Nernst and F. Schwers, *Sitzb. kgl. preuss. Akad. Wiss.*, 355 (1914).

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