microcrystals, m.p. 102-103° (dec.). The yield was very small (2%).

Anal. Calcd. for $C_{12}H_{10}SeO_3$: Se, 28.1; neut. equiv., 281; equiv. wt., 93.8. Found: Se, 28.7; neut. equiv., 283; equiv. wt. (iod.), 94.0; *pK*, 4.88 ($\sigma = -0.114$).[13]

The Reaction between *p*-Nitrochlorobenzene and Selenium in Sodium Ethoxide.—Five 5-g. pieces of metallic sodium were dissolved in 250 ml. of 95% ethanol, and 16 g. of dried elementary selenium was added. The mixture was stirred for 30 minutes while refluxing was maintained. Thirty-two grams of *p*-nitrochlorobenzene was dissolved in 200 ml. of hot ethanol and the solution added slowly to the sodium ethoxide–selenium mixture. Refluxing and stirring were maintained for 3 hours, at the end of which time the preparation was cooled to 5°. The solid was filtered off and treated with boiling glacial acetic acid, leaving a residue of 12 g. of elementary selenium. Cooling the acetic acid solution yielded 40 g. of orange solid. Two additional recrystallizations from glacial acetic acid yielded a product melting at 151–152°, containing no selenium. This product, presumably *p,p'*-dichloroazoxybenzene, was not affected by concentrated hydrogen peroxide or peracetic acid, but was converted by refluxing 90 minutes with concentrated nitric acid to a bright yellow compound, m.p. 135° (from ethanol).

***p*-Nitrobenzeneseleninic Acid.**—*p*-Selenocyanonitrobenzene was prepared from *p*-nitroaniline by the procedure of Bauer.[19]

To 25 ml. of 40% solution of peracetic acid in glacial acetic acid[20] was added 2.5 g. of *p*-selenocyanonitrobenzene. The mixture was heated on a hot plate, gases being vigorously evolved when the temperature reached 60–70°. After gas evolution had ceased, the solution was slowly evaporated to 15 ml. and excess 15 *N* ammonium hydroxide was added. The solution was heated to 80° and filtered, and the filtrate cooled and treated with dilute sulfuric acid, yielding a cream-colored precipitate which was filtered off, washed with cold water, and dissolved in a minimum quantity of boiling methanol. The methanolic solution was added cautiously to 250 ml. of water at 90°. Upon cooling the solution, orange-yellow crystals appeared. These were dried for an hour, then dissolved in a minimum quantity of concentrated nitric acid. The resulting solution was added to 200 ml. of boiling water, and the mixture allowed to cool. The pale yellow crystals which formed were filtered off after two days standing and were dried 3 days in a vacuum desiccator over anhydrous calcium chloride. The yield was 1.2 g. (45%), m.p. 212–213° (Behagel and Seibert report 214–215°[21]).

Anal. Calcd. for $C_6H_5SeNO_4$: neut. equiv., 234; equiv. wt., 78.0. Found: neut. equiv., 235.5; equiv. wt. (iod.), 77.4; *pK*, 4.00 ($\sigma = 0.778$).

Physical Measurements.—The dissociation constants of the acids were determined as described in our earlier communication, merely by measuring the *p*H of a half-neutralized solution of the acid and correcting for the activity coefficient of the acid anion.[2] However, these acids were difficultly soluble in warm water and were best dissolved by adding to the weighed sample 4.0 ml. of C.P. methanol, (in which they dissolve readily) diluting with 100 ml. of boiled distilled water, then titrating with standard sodium hydroxide. This procedure necessitated a correction for the effect of the added methanol on the *p*H at half-neutralization, determined by measuring the *p*H of half-neutralized solutions of benzeneseleninic acid and *p*-tolueneseleninic acid in water before and after successive known volumes of methanol were added to the solutions. In this way it was shown that the observed *p*H of these solutions containing 0.0025 mole/liter of both the arylseleninic acid and its salt rises 0.04 unit for each 5.0 ml. of methanol added to 100 ml. of solution; it was assumed that the effect of methanol on the observed *p*H of solutions of the heavier seleninic acids and their salts was roughly the same. In some determinations, the titration was omitted, and only the *p*H at half-neutralization was recorded. In the case of *p*-biphenylseleninic acid, its extremely low water solubility (2.7×10^{-4} fwt. per liter at 25°) made it more convenient to determine a *pK* value by the "partition method" described by Sherrill,[22] using the sodium salt of benzeneseleninic acid, the *pK* value for the latter acid having been previously determined.

Acknowledgments.—The authors wish to express thanks to Dr. J. Robert McCormick for valuable suggestions during the course of this work.

Summary

1. Treatment of aryllithium compounds with elementary selenium, followed by hydrolysis and air oxidation of the reaction mixture, has been found to yield symmetrically substituted diaryl diselenides.

2. Peracetic acid oxidation of *p*-selenocyanonitrobenzene yields *p*-nitrobenzeneseleninic acid.

3. The dissociation constants (as *pK*) for five additional substituted benzeneseleninic acids have been determined. Three of these fall on the ρ-σ curve constructed from previous experiments.

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[19] H. Bauer, *Ber.*, **46**, 92 (1913).

[20] Obtained as a sample from the Buffalo Electrochemical Company, Buffalo, N. Y.

[21] O. Behagel and H. Seibert, *Ber.*, **66B**, 708 (1933).

[22] M. S. Sherrill, "A Course of Laboratory Experiments in Physico-Chemical Principles," The Macmillan Co., New York, N. Y., 1924, p. 64.

LOS ANGELES, CALIFORNIA RECEIVED JULY 27, 1950

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

Low Temperature Heat Capacities of Inorganic Solids.[1] V. The Heat Capacity of Pure Elementary Boron in Both Amorphous and Crystalline Conditions between 13 and 305°K. Some Free Energies of Formation

BY HERRICK L. JOHNSTON, HERBERT N. HERSH AND EUGENE C. KERR

Introduction

Although boron was reported in 1808 by Gay Lussac and Thenard,[2] who obtained it by the action of potassium on boric acid, there have been very few preparations of the pure metal[3] up until now. Methods employed have been: (a) Reduction of the chloride or oxide by aluminum,[4] which invariably leads to heavy contamination with AlB_{12}. (b) Reduction of the oxide by magnesium, a method due to Moissan[5] who reported the preparation of small amounts of 98.3% pure boron in the amorphous condition. (c) Electrolytic reduction,[6] which has given no better than 92% boron.

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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] Gay-Lussac and Thenard, *Ann. chim.*, **68**, 169 (1808).

[3] *Cf.* Laubengayer, *J. Chem. Ed.*, **19**, 382 (1942), for a review of the subject.

[4] (a) St. Clair Deville and Wohler, *Compt. rend.*, **43**, 1088 (1856); (b) Wohler, *Ann.*, **141**, 262 (1867).

[5] (a) Moissan, *Ann. chim. phys.*, **6**, 296 (1895); (b) Cueilleron, *Ann. chim.*, **19**, 459 (1944).

[6] Andireux, *Ann. chim. phys.*, **12**, 423 (1929).

(d) Reduction of the chloride, or of the product of Moissan's method, by hydrogen in an electric arc,[7] a process reputed to have given 99.8% pure boron. (e) Reduction of the chloride or bromide by hydrogen on a hot tungsten or tantalum filament,[8] which has yielded boron of substantially 100% purity.[9] (f) Reduction of the bromide by hydrogen in a quartz tube at 800°, the means by which Kiessling[10] prepared 1- to 2-gram batches of 98.9% purity.

Reputedly pure boron can be obtained commercially, but Winslow and Liebhafsky[11] demonstrated that three such samples contained less than 80% boron, and not all of it as free metal.

Preparation of Samples of Pure Boron

Amorphous Boron.—None of the methods given above have produced boron in sufficient quantity and purity for use in accurate thermodynamic studies. Methods (e) and (f) could probably be used for this purpose, but their use would be tedious for the preparation of any moderately large quantity. To produce pure boron for calorimetric studies, we have therefore resorted to a different method, based on the reaction used by Prosen, Johnson and Yenchius,[12] to determine the heat of formation of diborane. These investigators found that diborane decomposes quantitatively to amorphous boron and hydrogen when diborane vapor, mixed with helium, is passed through a quartz tube at 700°.

Several hundred grams of pure amorphous boron have been prepared at this Laboratory by passing 99.8% pure diborane through a long quartz tube, held at about 700° by a resistance furnace. The diborane was allowed to vaporize from a steel cylinder, held at the temperature of Dry Ice, and was carried into the quartz tube by a stream of helium. Boron deposited in the tube as a finely powdered material. Figure 1 is an electron microscope photomicrograph of some of the deposit. The aggregates are composed of spherical particles that range in diameter from 0.025 to 0.500 μ.

Spectrographic analyses of the boron deposited in cooler portions of the tube indicated the presence of trace amounts of silicon, magnesium and copper. The part deposited in the hottest portion of the tube differed in appearance from that deposited in the colder portion, and was not used for fear that it might have reacted with the silica.

Crystalline Boron.—Nearly all of the methods cited in the introduction yield either amorphous or glassy boron. Laubengayer, Hurd, Newkirk and Hoard[9] obtained small crystals of pure boron in the form of needles and hexagonal plates by choosing the right conditions for deposit on a tantalum wire, and obtained X-ray patterns for both forms.

We have prepared several grams of microcrystals by a recrystallization method. Pure amorphous boron, prepared in the manner outlined above, was pressed into cylinders, 19 mm. o.d. by about 20 mm. length. These cylinders were heated, one at a time, in high vacuum to between 1700 and 1900° by means of induction heating. Figure 2 is a diagram of the water-jacketed Pyrex cell in which the heating took place. The cylinder of compressed boron rested on the tips of three tungsten wires that formed an inverted tripod and was heated by direct radiation from a surrounding cylinder of sheet tantalum, which was separately supported in such a manner as to make no contact with the boron. The tantalum cylinder was heated inductively by power supplied from a General Electric 15-kw. high frequency set, whose work coil surrounded the water-jacketed cell.

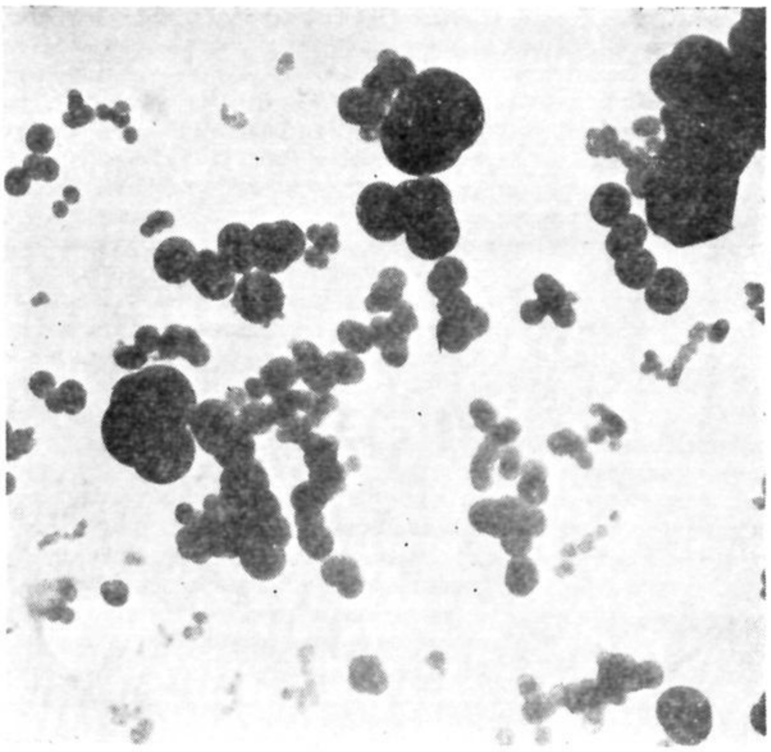

Fig. 1.—Electron micrograph of amorphous boron.

The progress of crystallization was followed by X-ray powder diffraction photographs. Boron from a heat-treated cylinder was dispersed in apiezon stopcock grease, or in amyl acetate service cement coated on the surface of a Pyrex glass capillary, and exposed to soft X-radiation. The characteristic boron lines had to be distinguished from those due to the specimen holder. Crystallization was assumed to be complete when sharp boron lines with no trace of diffuse bands were observed. The rate of crystal growth was found to depend on the degree of compactness of the compressed cylinder of boron as well as on temperature. However, ten minutes of heat treatment at 1700° was usually adequate to bring out sharp boron lines that had no accompaniment of diffuse bands even on 12-hour exposure to X-radiation. The "*d*" values obtained from the boron line spacings agreed well with those obtained by Laubengayer, Hurd, Newkirk and Hoard[9] for the needle crystals.

Although both tungsten and tantalum have extremely low vapor pressures at 1800°, and although the point of tungsten contact gave no visible evidence of alloy formation, the sides, bottom, and top of the cylinder were scraped away to minimize the possibility of contamination. Spectrographic analysis of the remainder of the cylinder indicated the same high purity as the amorphous samples had given, and indicated no trace of either tantalum or tungsten.

Experimental Data

The calorimetric data were obtained with our calorimeter No. 1, whose construction and operation have been described in a previous paper from this Laboratory.[13] Measurements were made with the calorimeter filled first with 27.520 g. (2.5434 gram atoms) of amorphous boron and later, with 33.774 g. (3.1214 gram atoms) of crystalline boron.

The experimental values of the atomic heat capacities are presented in Tables I and II and are shown graphically in Figs. 3 and 4. As was expected, the heat capacity of amorphous boron exceeded that of the crystalline form. The difference amounted to 0.208 cal. per gram-atom at 298.16°K. The experimental values of heat capacity are believed to be accurate to within 0.3% above 200°K., where the correction for the empty calorimeter amounts to about half of the total heat capacity. However they may be in error by more

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(7) Weintraub, *Ind. Eng. Chem.*, **5**, 106 (1913).

(8) (a) Warth, *Bull. Maryland Acad. Sci.*, **3**, 8 (1932); (b) Mellor, Cohen and Underwood, *Australian Chem. Inst., J. and Proc.*, **3**, 329 (1936).

(9) A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

(10) R. Kiessling, *Acta Chim. Scand.*, **2**, 702 (1948).

(11) E. H. Winslow and H. A. Liebhafsky, THIS JOURNAL, **64**, 2725 (1942).

(12) E. J. Prosen, W. H. Johnson and F. A. Yenchius, "Experimental Determination of the Heat of Formation of Diborane. Calculation of the Heat of Formation of Boric Oxide," National Bureau of Standards, ONR Tech. Rpt., Sept. 30, 1948.

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

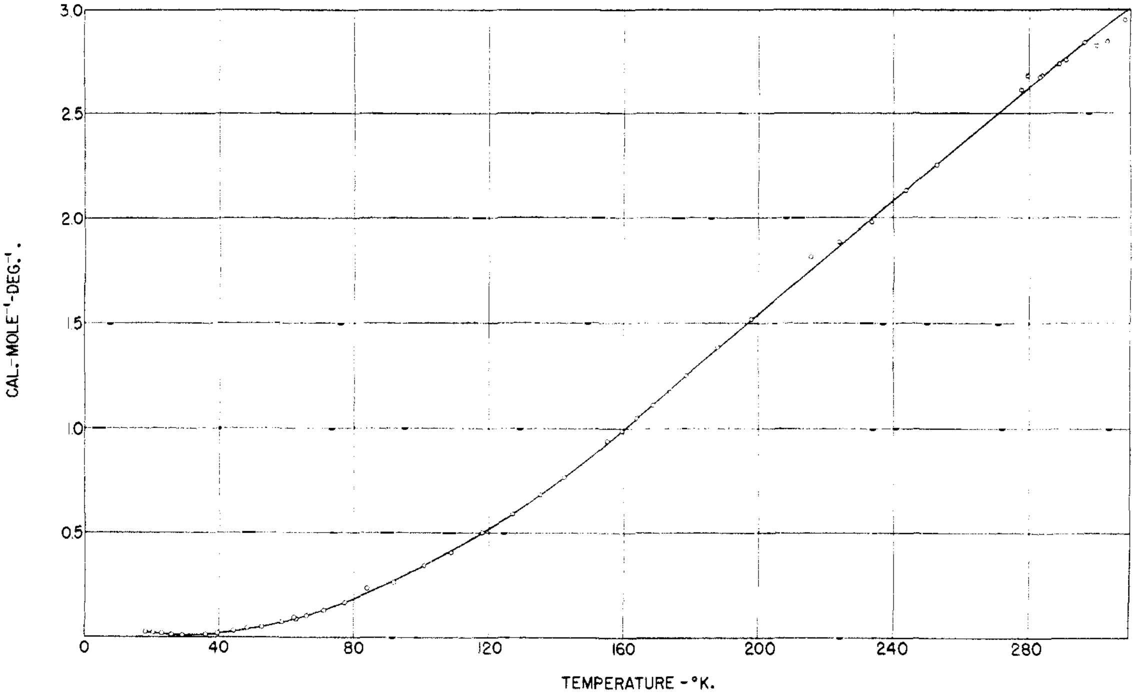

Fig. 2.—Heat capacity of boron (amorphous).

than 1% at 20°K., where the empty calorimeter contributes 70% of the total heat capacity.

TABLE I

HEAT CAPACITY OF 2.543 GRAM-ATOMS AMORPHOUS BORON, ATOMIC WEIGHT 10.82

$T_{av.}$, °K.	C_p, cal./mole/°K.	$T_{av.}$, °K.	C_p, cal./mole/°K.
18.25	0.0238	142.40	0.764
20.55	.0221	155.10	.938
23.04	.0190	159.49	.986
25.89	.0120	163.88	1.048
29.08	.0093	168.71	1.110
35.98	.0130	178.62	1.250
39.70	.0192	187.96	1.385
44.43	.0293	197.89	1.519
48.52	.0426	215.29	1.816
52.97	.0492	223.73	1.982
58.71	.0743	233.59	2.133
62.25	.0952	243.69	2.252
63.10	.0878	252.69	2.611
66.10	.1014	277.62	2.678
71.20	.1290	279.62	2.671
77.03	.1664	283.18	2.677
83.79	.2329	283.85	2.735
91.78	.260	288.97	2.754
100.83	.341	291.10	2.835
108.93	.404	296.58	2.822
118.06	.500	300.26	2.842
127.04	.590	303.26	2.842
135.43	.681	308.29	2.946

TABLE II

HEAT CAPACITY OF 31.21 GRAM-ATOMS CRYSTALLINE BORON, ATOMIC WEIGHT 10.82

$T_{av.}$, °K.	C_p, cal./mole/°K.	$T_{av.}$, °K.	C_p, cal./mole/°K.
16.90	0.0025	116.81	0.407
19.47	.0050	125.43	.496
21.89	.0075	133.00	.574
24.90	.0089	140.54	.658
27.84	.0064	147.98	.749
30.48	.0060	157.86	.876
32.74	.00517	166.08	.973
35.47	.00412	175.54	1.103
40.48	.00399	185.96	1.233
43.87	.00642	195.77	1.384
48.12	.0163	202.71	1.487
50.96	.0198	211.43	1.611
54.51	.0325	220.70	1.748
57.77	.0459	227.43	1.827
61.46	.0593	232.75	1.894
65.23	.0701	241.07	2.000
72.71	.0882	251.28	2.113
79.58	.1106	261.67	2.247
84.74	.1550	270.29	2.348
91.66	.1976	297.74	2.446
97.02	.2343	296.44	2.631
103.11	.2795	301.79	2.689
109.72	.333	303.71	2.720

Smoothed values of the thermodynamic functions were computed at 25° intervals by graphic integration of the heat capacity curves. These values are entered in Tables III and IV. The heat content, entropy and free energy entries for boron are, of course, relative to the values at absolute zero since amorphous boron must possess some entropy at 0°K. We are not now in a position to give the absolute values.

The entropy of amorphous boron at 298.16°K. was found to be 1.564 ± 0.01 cal. per mole per deg., of which only 0.01 e.u. arose from extrapolation below 17°K. This value differs significantly from the value, 1.7 ± 0.2 e.u., estimated by Kelley.[14]

The entropy of crystalline boron was found to

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(14) K. K. Kelley, THIS JOURNAL, 63, 1137 (1941).

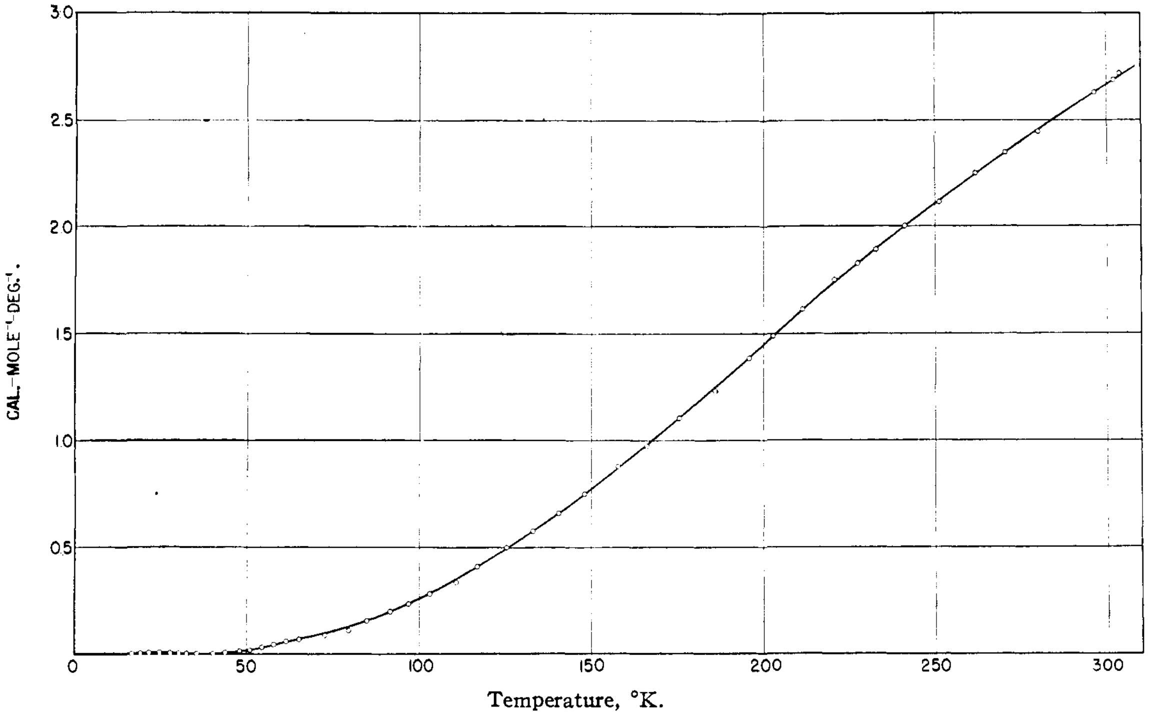

Fig. 3.—Heat capacity of crystalline boron.

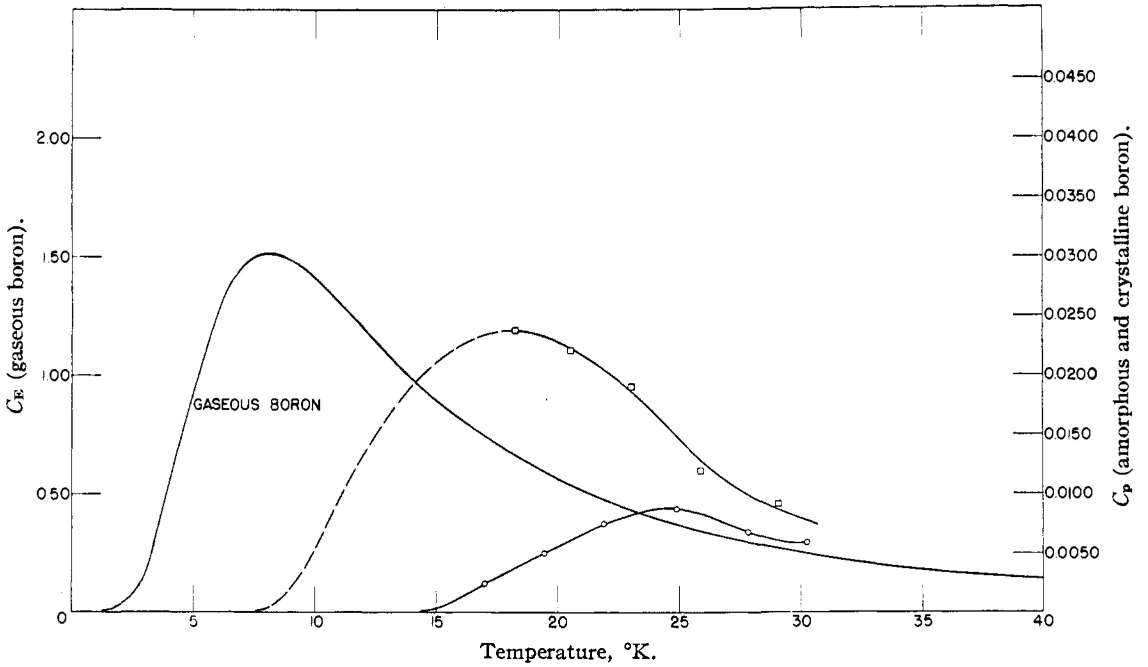

Fig. 4.—Low temperature maxima in the heat capacities of crystalline (O), amorphous (□), and gaseous boron.

be 1.420 ± 0.005 cal. per mole per deg., of which only 0.001 e.u. was extrapolated below 16°K.

Discussion

Between 60 and 150°K., the heat capacity of crystalline boron fits the Debye equation to within 2% with θ_D set equal to 1219. Between 60 and 125°, it fits the T^3 law, using a coefficient of 2.56 × 10^{-7}, to within about 3%. Above 125°, observed values are lower than those calculated by either the T^3 law or the Debye equation. This latter effect corresponds to the situation found by Pitzer[15] for diamond.

Amorphous boron fails to fit either the T^3 law or the Debye equation, which is not surprising since it is non-crystalline substance. Heat capacities between about 50 and 75°K. correspond to a θ_D' of 1102 to within about 4%, the calculated values being low at the 50° end of this range and high at the 75° end.

An interesting feature of both the crystalline

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(15) K. S. Pitzer, *J. Chem. Phys.*, **6**, 68 (1938).

TABLE III

THERMODYNAMIC FUNCTIONS OF AMORPHOUS BORON

T, °K.	C_p^0	$(H - H_0)$	$(S^0 - S_0^0)$	$\left(\frac{H^0 - H_0^0}{T}\right)$	$-\left(\frac{F^0 - H_0^0}{T}\right)$
18	0.0236	0.124	0.0121	0.0069	0.00521
25	.0145	.268	.0190	.0107	.00823
50	.0413	.757	.0313	.0151	.01620
75	.1504	2.975	.0658	.0397	.02615
100	.330	8.812	.1318	.0881	.04365
125	.572	19.99	.2306	.1600	.07063
150	.860	37.766	.3594	.2518	.1076
175	1.202	63.49	.5173	.3628	.1545
200	1.549	96.90	.7006	.4845	.2161
225	1.886	139.87	.9026	.6216	.2810
250	2.218	191.19	1.1186	.7647	.3539
275	2.550	250.81	1.3457	.9120	.4336
298.16	2.858	313.40	1.5640	1.0511	.5129
300	2.879	318.68	1.5817	1.0623	.5194

TABLE IV

THERMODYNAMIC FUNCTIONS OF CRYSTALLINE BORON

T, °K.	C_p^0	$(H^0 - H_0^0)$	S^0	$\left(\frac{H^0 - H_0^0}{T}\right)$	$-\left(\frac{F^0 - H_0^0}{T}\right)$
17	0.0024	0.0058	0.00139	0.00034	0.00105
25	.0090	.0567	.00374	.00227	.00148
50	.0183	.2265	.00832	.00453	.00528
75	.1078	1.764	.03203	.02352	.01379
100	.2563	6.139	.08136	.06139	.01997
125	.4866	15.282	.1620	.1223	.03975
150	.772	30.951	.2755	.2063	.06915
175	1.097	54.226	.4184	.3099	.1086
200	1.447	85.98	.5875	.4299	.1576
225	1.794	126.55	.7782	.5624	.2158
250	2.107	175.37	.9842	.7015	.2827
275	2.402	233.18	1.1990	.8479	.3511
298.16	2.650	291.74	1.4033	.9785	.4248
300	2.667	296.63	1.4197	.9888	.4309

and amorphous forms is the existence of a shallow maximum below 30°K. This effect is brought out in Fig. 4, which shows the fully developed maximum for the crystalline form at about 25°K. and the incomplete curve for the amorphous form. The latter curve evidently goes through a maximum in the neighborhood of 18°K. At 17°K., near the maximum in the amorphous curve, the heat capacity of crystalline boron is 0.0025 cal. per gram-atom which is almost as low as its T^3 law value of 0.0013 cal. per gram-atom, based on our data at 100°K.

As evidenced by the curves, the heat and entropy effects are somewhat larger for the amorphous than for the crystalline form. The entropy under the maximum of the crystalline curve amounts to 0.005 e.u. while that under the amorphous curve amounts to about 0.02 e.u.

Cristescu and Simon[16] observed a small maximum in the heat capacity curve of beryllium at 11°K., which they thought might be related in some manner to the behavior of the conducting electrons. Simon and Swain[17] found a much greater anomaly, of the same general appearance in lithium in the neighborhood of 100°K.

We believe that there may be some correlation between the anomalies we have observed for boron and the normal doublet P state that characterizes free boron atoms. The separation of the doublet levels is 15 wave number.[18] We have computed the electronic contributions to heat capacity that would arise in gaseous boron due to this doublet. The computed curve is entered in Fig. 5, along with those of crystalline and amorphous boron, but on a 50-fold smaller ordinate scale. A maximum occurs at 8°K. with a height of 1.5 calories. The entropy under this electronic curve amounts to 2.28 e.u. This contribution would be present for boron gas in the ideal state, but would not ordinarily be expected in the solid. However, the characteristic appearance of the curves for amorphous and crystalline boron in the same region, with only small contributions to entropy, suggests that there may be some small residual quantum effect. The position of the amorphous boron maximum in relation to crystalline boron, and its somewhat larger entropy contribution, is in line with expectation if the explanation is correct, since the disorder incident to the amorphous condition must produce slightly more resemblance to liquid or to gas.

Thermodynamic Treatment of the Data

By combining data obtained in this Laboratory on the entropies of boron, boric acid[13] and boric oxide,[19] with other available data, we are able to compute free energies of formation of B_2O_3 and of $B(OH)_3$ and the free energy of hydration of the oxide.

Free Energy of Formation of Boric Oxide.—The heats of the following reactions are known

$$2B(\text{solid, amorphous}) + 3H_2(\text{gas}) = B_2H_6(\text{gas}) \quad (1)$$
$$\Delta H_{298.16} = 6.73 \pm 0.52 \text{ kcal.}^{12}$$

$$B_2H_6(\text{gas}) + 6H_2O(\text{liquid}) = 2H_3BO_3(\text{aqueous}) + 6H_2(\text{gas}) \quad (2)$$
$$\Delta H_{298.16} = -108.1 \pm 2.9 \text{ kcal.}^{20}$$

$$2H_3BO_3(\text{aqueous}) = B_2O_3(\text{crystalline}) + 3H_2O(\text{liquid}) \quad (3)$$
$$\Delta H_{298.16} = +3.48 \pm 0.01 \text{ kcal.}^{21}$$

$$3H_2(\text{gas}) + 3/2O_2(\text{gas}) = 3H_2O(\text{liquid}) \quad (4)$$
$$\Delta H_{298.16} = -204.94 \pm 0.03 \text{ kcal.}^{22}$$

The further value

$$2B(\text{crystalline}) = 2B(\text{solid, amorphous})$$
$$\Delta H_{298.16} = 0.8 \text{ kcal.} \quad (5)$$

is selected by the National Bureau of Standards[23] on the basis of some of their unpublished work.

Equations 1 through 5 can be combined to yield

$$2B(\text{crystalline}) + 3/2O_2(\text{gas}) = B_2O_3(\text{crystalline}) \quad (6)$$
$$\Delta H^0_{298.16} = -302.0 \pm 3.4 \text{ kcal.}$$

By using our values for the entropies of crystalline boron and of B_2O_3[15] and an accurate spectroscopic value for the entropy of oxygen,[24] the entropy change for reaction 6 proves to be

$$\Delta S^0_{298.16} = -63.43 \pm 0.1 \text{ e.u.}$$

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[16] S. Cristescu and F. Simon, *Z. physik. Chem.*, **B25**, 273 (1934).

[17] F. Simon and R. C. Swain, *ibid.*, **B28**, 189 (1935).

[18] Bacher and Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., Inc., New York, N. Y., 1932, p. 63.

[19] E. C. Kerr, H. N. Hersh and H. L. Johnston, THIS JOURNAL, **72**, 4738 (1950).

[20] W. A. Roth, E. Borger and A. Bertram, *Ber.*, **70B**, 971 (1937).

[21] J. C. Southard, THIS JOURNAL, **63**, 3147 (1941).

[22] Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

[23] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards.

[24] H. L. Johnston and M. K. Walker, THIS JOURNAL, **55**, 2744 (1933).

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 $2p$ 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.

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[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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