capacity is only 7% of equipartition, and gives the appearance of a spread out hump, from about 20 to 150°K., superimposed on a normal lattice vibration curve. This effect may represent the development of the hydrogen bond disorder discussed above. If so, the entries in Table II are correct as they stand. However it is difficult to separate the contributions due to lattice vibrations from the total heat capacity for a molecule as complicated as boric acid. A decisive treatment of this matter would require a Third Law check through some reaction in which boric acid takes part. Unfortunately there are at present no reliable equilibrium data to which to apply the method.

Acknowledgment.—We wish to acknowledge the assistance of Mr. Nathan C. Hallett and Mr. Herbert N. Hersh, who assisted with measurement and calculations.

Summary

A description has been presented of one of the seven vacuum calorimeters recently constructed and assembled at The Ohio State University Cryogenic Laboratory for measurements of heat capacities of solids. These calorimeters are similar in their general features to those developed by Giauque and co-workers[2] at the University of California, and to the condensed gas calorimeter recently designed and constructed in this Laboratory.

The heat capacities of boric acid, containing less than 0.05% impurities, have been measured between 16 and 296°K. The data yield a value of 21.21 ± 0.1 calories per mole per degree for the entropy at 298.16°K. A table of thermodynamic functions has been prepared for boric acid at smoothed values of the temperature.

Disorder, due to hydrogen bonding in the layer lattice of boric acid has been discussed. This disorder, which makes an entropy contribution of 0.69 E. U., may be responsible for a spread out hump that appears to exist in the heat capacity curve between 20 and 160°K. If this is true, the disorder entropy is contained in the tabulated values derived from the heat capacities.

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

Low Temperature Heat Capacities of Inorganic Solids.[1] II. The Heat Capacity of Crystalline Boric Oxide from 17 to 300°K.

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

Introduction

Crystalline boric oxide has been known for only a relatively short time, having been first reliably reported by McCulloch[2] in 1937 and subsequently by Kracek, Morey and Merwin.[3] Low temperature heat capacity data on crystalline boric oxide have been obtained by Kelley[4] in the temperature range of 51 to 298°K.

During the present investigation, the heat capacities of the crystalline form of boric oxide have been measured in the range of 17 to 300°K., to extend the range of the earlier measurements and to better correlate the results of an extensive program of low temperature thermodynamic measurements on boron and several of its compounds. Crystalline boric oxide was studied in solid calorimeter No. 1, which has been described previously.[5]

Preparation and Purity of Crystalline Boric Oxide.—Crystalline boric oxide was prepared by one of the methods of Kracek, Morey and Merwin.[3] Boric acid, containing a maximum of 0.05% impurity, was heated for one week at 120 to 130°, after which the temperature was increased 10° per day until it remained at 200° for one day. About 40% additional boric acid (based on the original weight) was added with stirring. The resulting mixture crystallized at 200° over a period of three days. The temperature was then raised to 400° and was maintained at this level for two days under vacuum to complete the removal of water. The hard cake of finely crystalline material was crushed and screened, and finally reheated at 400° for three more days under vacuum to remove any moisture adsorbed during the crushing and screening process.

Analysis was made by hydration to boric acid and controlled drying to a constant weight. A sample of boric acid was similarly moistened and dried as a control blank. The results indicated that the boric oxide crystals were moisture free within the limits of the analytical precision, ±0.1%.

The amount of pure boric oxide used for heat capacity measurements was 69.689 g. or 1.007 moles.

Experimental Results

The experimental results are summarized in Table I and are plotted in Fig. 1 with the experimental data of Kelley.[4] There are no significant differences between the two sets of data.

Thermodynamic functions derived from the smoothed heat capacity curve are given in Table II at integral values of the temperature. The entropy at 298.16°K. is 12.87 E. U., of which 0.03 E. U. was obtained by a Debye T^3 extrapolation with θ set equal to 329. This value of the entropy at 298.16°K. differs from that given by Kelley[4] by only 0.13 E. U., and 0.08 E. U. of this figure can

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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] L. McCulloch, THIS JOURNAL, **59**, 2650 (1937).

[3] F. C. Kracek, G. W. Morey and H. E. Merwin, *Am. J. Sci.*, **35A**, 143 (1938).

[4] K. K. Kelley, THIS JOURNAL, **63**, 1137 (1941).

[5] H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 4733 (1950).

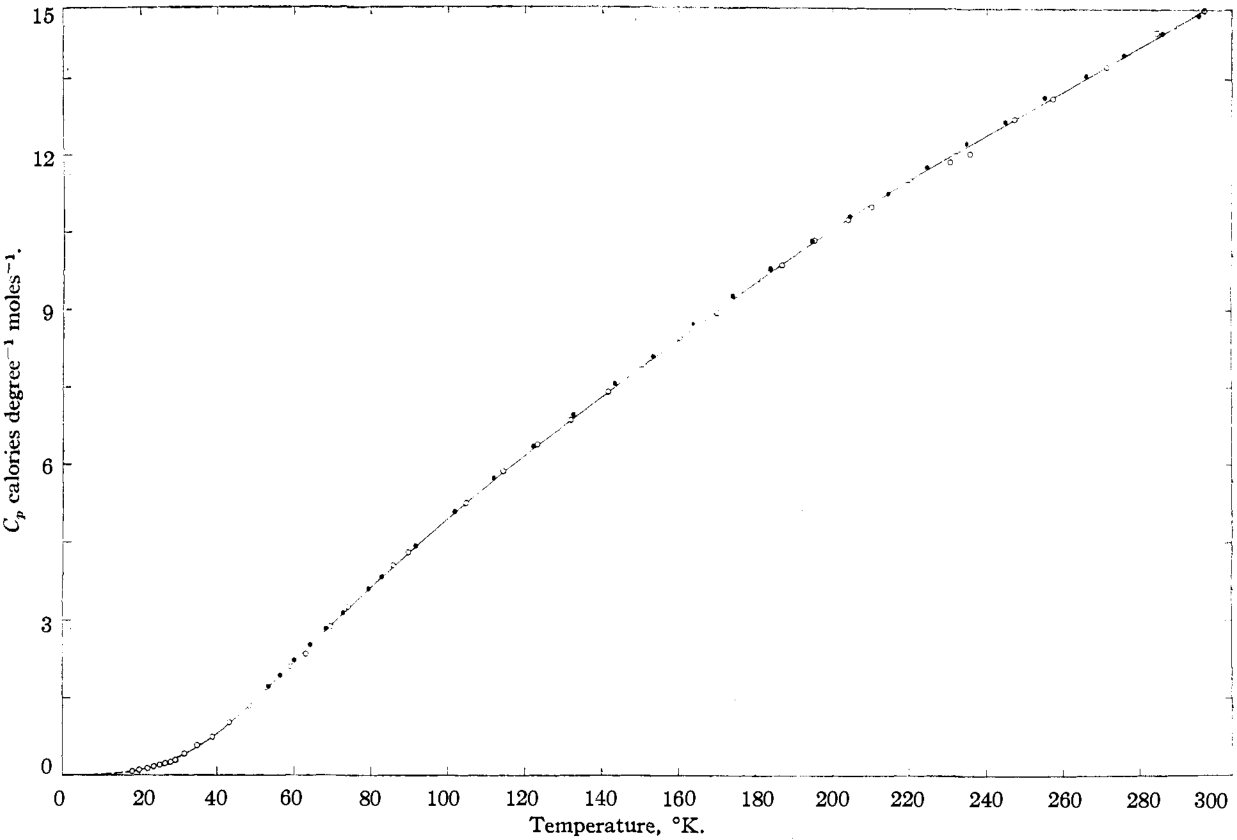

Fig. 1.—Heat capacity of boric oxide (B_2O_3): ⊙, these data; ●, K. K. Kelley.

be accounted for by the difference between Kelley's extrapolation below 53°K. and our own experiments down to 17°K.

TABLE I

HEAT CAPACITY OF BORIC OXIDE

Mean temp., °K.	T	C_p, cal./mole/deg.	Mean temp., °K.	T	C_p, cal./mole/deg.
18.08	1.857	0.0747	104.82	10.166	5.316
19.94	1.463	.1069	114.39	8.944	5.864
21.98	1.551	.1417	123.32	8.709	6.394
23.64	1.284	.1775	132.19	8.919	6.906
25.19	1.366	.2034	141.77	9.727	7.460
26.55	1.193	.2430	150.98	8.808	7.986
27.95	1.353	.2742	160.31	9.880	8.471
29.30	1.181	.3193	169.98	9.612	8.983
31.57	2.818	.4235	187.01	8.471	9.861
34.81	3.440	.5690	195.35	8.248	10.271
38.65	4.055	.7206	204.19	9.503	10.718
43.33	5.323	.968	210.32	10.461	10.995
48.48	5.062	1.325	220.39	9.791	11.45
53.53	5.058	1.733	230.55	11.084	11.89
59.10	6.062	2.137	235.87	8.603	12.14
63.20	6.255	2.429	247.38	12.640	12.74
69.72	4.345	2.825	257.32	11.89	13.11
74.23	4.617	3.226	271.10	10.744	13.80
79.58	6.038	3.548	284.00	11.761	14.41
85.90	2.965	4.039	296.60	8.764	14.98
89.71	4.544	4.318			

TABLE II

THERMODYNAMIC FUNCTIONS OF CRYSTALLINE BORIC OXIDE

Temp., °K.	C_p, cal./mole/deg.	S^0, cal./mole/deg.	$(H^0 - H_0^0)$ cal./mole	$(H^0 - H_0^0)/T$ cal./mole/deg.	$-(F^0 - H_0^0)/T$
18	0.080	0.027	0.360	0.0200	0.0067
25	0.202	.070	1.304	.0522	.0177
50	1.426	.512	18.985	.3797	.1325
75	3.277	1.443	77.95	1.0393	.4040
100	4.987	2.624	181.56	1.8156	.8082
125	6.489	3.900	325.26	2.6021	1.2981
150	7.922	5.212	505.65	3.7098	1.5019
175	9.242	6.533	720.38	4.1165	2.4167
200	10.499	7.850	967.34	4.8367	3.0137
225	11.656	9.155	1244.5	5.5313	3.6238
250	12.772	10.441	1549.9	6.1994	4.2413
275	13.935	11.712	1883.6	6.8494	4.8627
298.16	15.050	12.870	2218.3	7.4398	5.4303
300	15.137	12.976	2246.9	7.4898	5.4862

The heat capacity curve for boric oxide is quite regular. In this respect, it differs from that for boric acid. Some free energies of formation and reaction will be given in paper number IV of this series.

Acknowledgment.—We wish to acknowledge the help of Mr. Nathan C. Hallett who assisted with the runs.

Summary

The heat capacities of crystalline boric oxide have been measured from 17 to 300°K. The entropy at 298.16°K. derived from the heat capacity data is 12.87 ± 0.1 E. U. This figure is compared with the value of 13.0 ± 0.1 E. U. obtained by Kelley.[4]

The thermodynamic functions for boric oxide have been computed and tabulated for integral values of temperature.

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

Low Temperature Heat Capacities of Inorganic Solids.[1] III. Heat Capacity of Aluminum Oxide (Synthetic Sapphire) from 19 to 300°K.

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

Introduction

The first low-temperature heat capacity data reported for aluminum oxide were obtained by Parks and Kelley[2] on a sample of natural ceylon sapphire for the temperature range 90 to 295°K. Later, Simon and Swain[3] measured the heat capacity of a sample of synthetic sapphire, prepared by the Griesheim Werk of the I. G. Farbenindustrie, over the temperature range 30 to 280°K. Kelley[4] refers to some unpublished data of C. T. Anderson at the Pacific Coast Station of the Bureau of Mines. On the basis of Kelley's tables, these values must be higher than either those of Parks and Kelley or of Simon and Swain. Because of these discrepancies, and because synthetic sapphire has been recommended as a calorimetric standard by the subcommittee on Physico and Chemical Standards of the National Research Councils Committee on Physical Chemistry, we deemed it advisable to remeasure the low-temperature heat capacities of aluminum oxide.

Apparatus and Materials.—Pure aluminum oxide was obtained in the form of polished rods of synthetic sapphire, through the courtesy of the Linde Air Products Co., and was crushed in a punch press with a stainless steel die. The portion passing through a 50-mesh screen was then passed over a strong Alnico magnet several times to eliminate the danger of iron contamination of the sample through abrasion of the punch press die.[5] No analysis was made of the aluminum oxide, but Ginnings and Corruccini[6] reported that a similar sample of Linde sapphire contained 0.02% silica as the only impurity detectable spectrographically. Since silica has nearly the same heat capacity as aluminum oxide, no correction was applied for the impurity. After drying the final powdered sample to a constant weight at 110° to ensure removal of adsorbed moisture, "Solid Calorimeter No. 2," of the group of seven vacuum calorimeters described in the first paper[7] of this series, was filled with 161.744 g. (1.5867 moles) of aluminum oxide for the heat capacity measurements.

Experimental Results

Experimental heat capacities are summarized in Table I and plotted in Fig. 1 along with the superimposed data of Parks and Kelley[2] and of Simon and Swain.[3] The latter investigators reported their data in terms of heat capacities at selected integral temperatures and are not their directly observed experimental results. Their points are slightly higher than ours below 80°K. and considerably lower than ours above this temperature. The data of Parks and Kelley are somewhat higher than ours throughout their temperature range.

TABLE I

MOLAR HEAT CAPACITY OF ALUMINUM OXIDE (SYNTHETIC SAPPHIRE)

Mol. weight 101.94 g., 1.5867 moles

Mean T, °K.	ΔT	C_p, cal./mole/°K.	Mean T, °K.	ΔT	C_p, cal./mole/°K.
20.19	1.652	0.0087	97.32	6.876	2.858
21.91	1.342	.0253	103.59	5.836	3.377
23.85	1.514	.0305	111.03	7.041	3.996
25.40	1.298	.0372	117.48	6.175	4.557
26.95	1.449	.0474	123.70	6.568	5.132
28.54	1.695	.0572	130.82	7.854	5.812
30.39	2.012	.0772	138.85	8.586	6.602
32.29	1.713	.0897	146.94	7.973	7.334
34.95	3.481	.1136	154.99	8.818	8.125
38.04	2.719	.1382	164.11	9.900	8.978
40.60	2.545	.1729	173.28	8.765	9.864
42.97	2.150	.2086	181.42	8.548	10.64
45.05	2.082	.2460	189.85	9.014	11.38
46.96	1.833	.2888	199.02	9.962	12.16
48.92	2.323	.3293	208.20	9.123	12.91
51.06	2.039	.3854	216.93	8.392	13.60
54.13	4.311	.4560	225.44	9.490	14.23
58.74	5.094	.5972	234.46	8.863	14.88
63.72	5.081	.7882	243.08	8.320	15.50
69.60	6.127	1.072	251.59	9.311	16.09
75.01	4.943	1.366	260.24	8.627	16.68
79.48	4.212	1.625	269.44	9.420	17.33
84.58	6.102	1.938	278.05	8.918	17.93
85.76	6.113	2.042	285.61	10.228	18.35
91.34	5.139	2.435	294.85	9.663	18.90

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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] G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[3] F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

[4] K. K. Kelley, Contribution to the Data of Theoretical Metallurgy, Bull. No. 434, U. S. Bureau of Mines.

[5] The stainless steel from which the die was made was magnetic.

[6] D. C. Ginnings and R. J. Corruccini, *Bur. Standards J. Research*, **38**, 583 (1947).

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