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by the Griesheim Werk of the I. G. Farbenindustrie, over the temperature range 30 to 280°K. Kelley[4] refers to some unpublished data of C. T. Anderson at the Pacific Coast Station of the Bureau of Mines.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

(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).

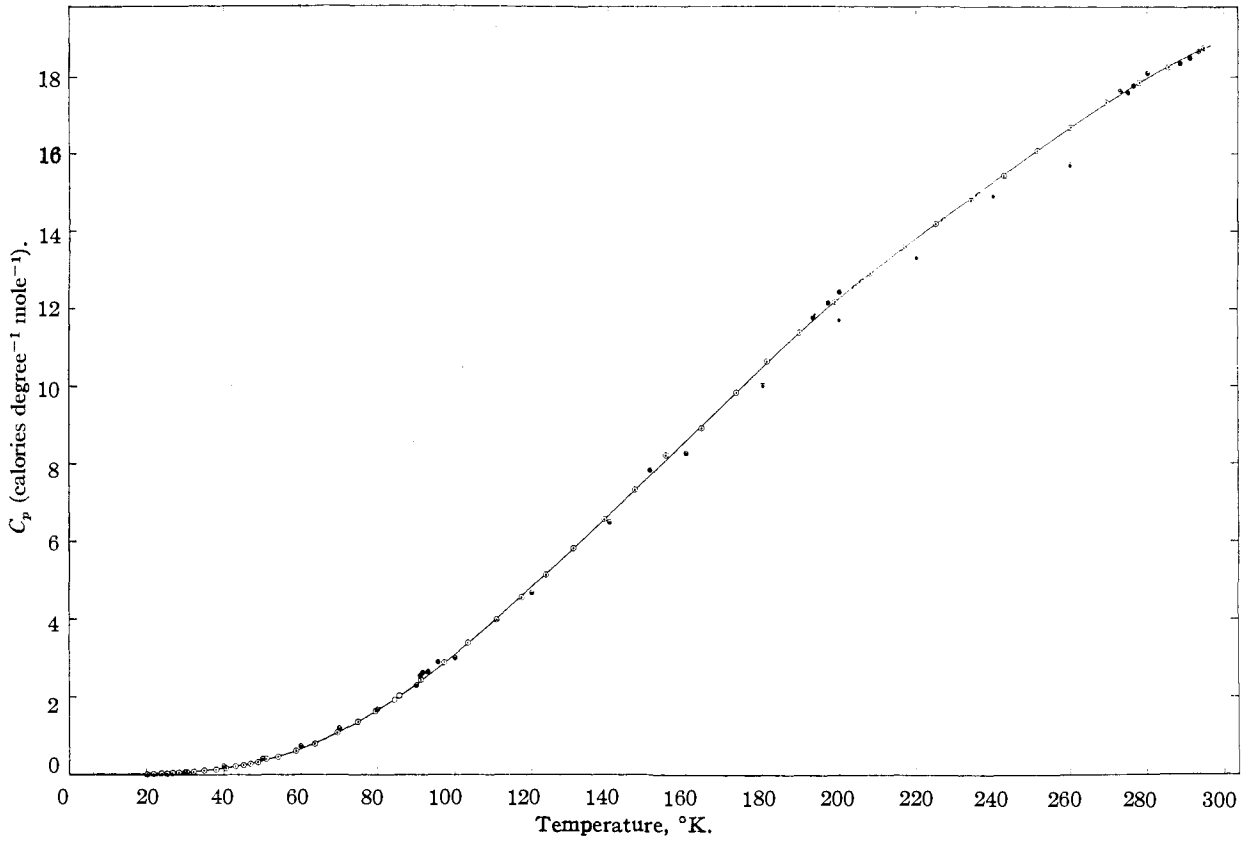

Fig. 1.—Heat capacity of aluminum oxide (synthetic sapphire): ⊙, this research; ●, Parks and Kelley; ◒, Simon and Swain; ⊕, Ginnings and Corruccini.

Two heat capacity points derived from the enthalpy–temperature data of Ginnings and Corruccini,[1] who used a drop calorimeter for measurements between 0 and 900°, are also plotted in Fig. 1. Their point at 20° fits our experimental curve almost exactly, while their point at 0° is only slightly off the curve. This small difference may only be the result of an inaccuracy in determining the slope of the enthalpy–temperature curve at its extreme lower end since our experimental curve can be extrapolated smoothly into the higher temperature curve of Ginnings and Corruccini.

TABLE II

THERMODYNAMIC FUNCTIONS FOR ALUMINUM OXIDE (SYNTHETIC SAPPHIRE)

T, °K.	C_p, cal./mole/°K.	S^0, cal./mole/°K.	$(H - H_0^0)$ cal./mole	$(H^0 - H_0^0)/T$ cal./mole/°K.	$-(F^0 - H_0^0)/T$ cal./mole/°K.
17	0.016	0.0041	0.052	0.0031	0.0010
25	.039	.0133	0.254	.0102	.0031
50	.350	.1092	4.142	.0828	.0264
75	1.358	.411	23.601	.3147	.0964
100	3.075	1.022	77.705	.7770	.2448
125	5.245	1.933	180.86	1.4469	.4865
150	7.640	3.100	341.74	2.2783	.8217
175	10.038	4.457	572.62	3.2721	1.1848
200	12.240	5.943	841.55	4.2078	1.7356
225	14.198	7.500	1172.5	5.2110	2.2891
250	15.990	9.089	1549.9	6.1997	2.8895
275	17.683	10.694	1971.2	7.1680	3.5260
298.16	19.089	12.165	2396.4	8.0373	4.1276
300	19.190	12.299	2432.6	8.1087	4.1900

Table II gives the heat capacity and derived thermodynamic functions for aluminum oxide at selected integral values of the temperature. The entropy at 298.1°K. is 12.16 E. U., of which 0.01 E. U. was contributed by the Debye T^3 extrapolation below 20°K. with θ equal to 571. Parks and Kelley[2] reported a value of 12.6 ± 0.2 E. U. based on their own data, whereas Kelley[4] obtained 12.5 ± 0.15 E. U. on the basis of the data of Parks and Kelley, of Simon and Swain, and of C. T. Anderson.

Only two of our experimental heat capacity points above 80°K. deviate from a smooth curve by more than 0.2%. We believe that the accuracy of our entropy measurements corresponds to better than 0.02 E. U.

Summary

The heat capacities of aluminum oxide (synthetic sapphire) have been measured in the temperature range 20 to 300°K., and the derived thermodynamic functions have been calculated and tabulated at integral values of the temperature over this range.

The entropy at 298.1°K. is given as 12.16 ±

0.02 E. U. as compared with the previous "best" values of 12.5 E. U. selected by Kelley on the basis of the earlier work of several other investigators.

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Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Andalusite, Kyanite, and Sillimanite

BY S. S. TODD

This paper presents low-temperature heat-capacity data and entropy values at 298.16°K. for three crystalline modifications of aluminum silicate (Al_2SiO_5), namely, andalusite, kyanite and sillimanite. The heat capacities of all three substances were studied previously by Simon and Zeidler,[1] and their data were used by Kelley[2,3] in evaluating the entropies at 298.16°K. These entropy values range from 20.7 to 27.0 E.U., the spread being 6.3 units. The magnitude of the variation appears unaccountably high, which was one of the factors justifying the present work.

Materials.—The materials used in this investigation were natural minerals from the following sources: andalusite, Standish, Maine; kyanite, Celo Mines, Burnsville, N. C.; and sillimanite, Benson Mines, N. Y. They were supplied to us by the Geophysical Laboratory of the Carnegie Institution of Washington, where they had been subjected to careful purification and microscopic examination. Subsequently, complete chemical analyses also were furnished.[4] These appear in Table I and may be compared with the theoretical composition, 62.93% Al_2O_3 and 37.07% SiO_2.

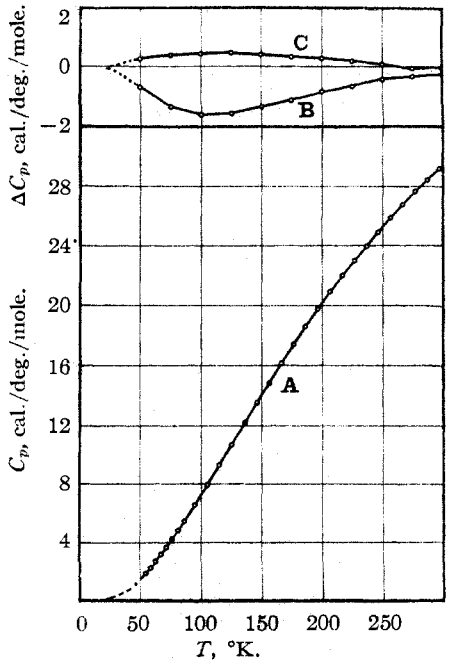

Fig. 1.—Heat capacities: curve A, C_p (andalusite); curve B, C_p (kyanite) − C_p (andalusite); curve C, C_p (sillimanite) − C_p (andalusite).

TABLE I

CHEMICAL ANALYSES (WEIGHT %, DRY BASIS)

	Andalusite	Kyanite	Sillimanite
Al_2O_3	63.15	63.20	61.80
SiO_2	36.84	36.90	36.44
TiO_2	Trace[a]	None	None
FeO	None	None	0.14
Fe_2O_3	0.11	0.10	0.98
MgO	Trace	None	0.24
CaO	0.02	0.05	0.07
MnO	Trace	None	0.04
Na_2O	None	None	Trace
K_2O	None	None	None
P_2O_5	....	....	0.28
F	....	....	0.04
Total	100.12	100.25	100.03

[a] "Trace" means < 0.01%.

According to microscopic examinations, the andalusite contained a few muscovite inclusions, the kyanite contained less than 0.2% unidentified inclusions, and the sillimanite contained less than 0.7% wagnerite inclusions. The samples were heated 4 hours at 540°, to remove moisture, before enclosing in the calorimeter.

Heat Capacities.—The heat-capacity measurements were made with previously described apparatus.[5] The results, expressed in defined calories (1 calorie = 4.1833 int. joules) per deg. per mole (162.00 g.), are listed in Table II. The masses of materials employed were 198.61 g. of andalusite, 212.19 g. of kyanite, and 207.71 g. of sillimanite. No corrections were applied for deviations of the chemical analyses from the theoretical composition. Figure 1 shows the results for andalusite plotted against temperature and also the curves for the difference in heat capacity between andalusite and kyanite and between andalusite and sillimanite. This method of plotting is more informative in this instance than a single plot of this size showing all three individual heat-capacity curves.

The heat-capacity values of Simon and Zeidler[1] deviate markedly from the present work. Thus, for andalusite their results range from 97% higher at the lower end of the common temperature range to 11% higher at the upper end of the common temperature range. Similar comparison for kyanite shows their results are from 31 to 2% higher,

(1) F. Simon and W. Zeidler, *Z. physik. Chem.*, **123**, 383 (1926).
(2) K. K. Kelley, *U. S. Bur. Mines Bull.* 350 (1932).
(3) Kelley, *ibid.*, 394 (1936); *ibid.*, 434 (1941).

(4) The author expresses his thanks to Th. G. Sahama, Professor of Geochemistry, University of Helsinki, Finland (formerly Visiting Investigator at the Geophysical Laboratory), and to L. H. Adams, Director, Geophysical Laboratory, for their kind coöperation and interest.

(5) K. K. Kelley, B. F. Naylor and C. H. Shomate, *U. S. Bureau of Mines Tech. Paper* 686 (1946).