N_2H_4, has been measured both at atmospheric and at lower pressures. In contradiction to the claim made by Eucken and Krome,[1a] the results obtained show that hydrazine is not associated in the vapor phase. This conclusion is also confirmed by electron diffraction and spectroscopic investigations.

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[CONTRIBUTION FROM THE METALLURGICAL FUNDAMENTALS SECTION, METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Specific Heats at Low Temperatures of Crystalline Boric Oxide, Boron Carbide and Silicon Carbide[1]

BY K. K. KELLEY[2]

In continuation of a program of study of the thermodynamic properties of metallurgically important substances by the Metallurgical Division of the Bureau of Mines, the specific heats of crystalline B_2O_3, B_4C, and SiC have been determined in the temperature range 51° to 298°K. Crystalline boric oxide has been known for only a relatively short time, having been reported first by McCulloch[3] in 1937 and by Kracek, Morey and Merwin[4] in 1938.[5] Crystalline B_4C in relatively pure form also is a substance of recent origin. The methods of manufacture and some of its physical properties were described by Ridgway[6] in 1934. These three substances are similar in that they have relatively low average atomic heats below room temperature and hence, it will be seen, are particularly satisfactory for study with the equipment of this Laboratory, which now enables us to reach a temperature of about 51°K.

Materials.—Crystalline boric oxide was prepared from boric acid by one of the methods of Kracek, Morey and Merwin.[4] A weighed quantity of boric acid was heated for one week at 120°, after which the temperature was raised 10° daily until the material was at 200° for one day. At this point about 40% additional boric acid (based upon the original weight) was added with stirring. The resulting mixture crystallized completely over a period of two days with the evolution of steam. The temperature was raised to 400° and maintained there for two days to complete the removal of water. The product obtained, a stony material, was crushed, screened, and reheated at 400°. Analysis showed 99.7% boric oxide. Of the remaining 0.3%, 0.1% appeared to be water, and 0.1% was accounted for by the impurities in the original boric acid. This preparation and analysis were made by Dr. G. W. Marks of this Laboratory, to whom the author expresses his appreciation. A sample of 161.5 g. was employed in the measurements, and correction was made for 0.1% water.

The B_4C was furnished by the Norton Company through the courtesy of Dr. R. R. Ridgway. This material was in granular, crystalline form and was reported to be 96% B_4C and 4% free and included graphite. The sample used for specific heat measurements contained 144.3 g. Correction for the graphite content was made in the results.

The silicon carbide (SiC) also was furnished by Dr. R. R. Ridgway of the Norton Company. This material, light green and semitransparent, was reported to be 99% silicon carbide, the principal impurity being 0.6% silicon dioxide for which correction was made in the specific heat results. A 220.4-g. sample was studied.

Apparatus.—The B_4C and silicon carbide were studied in the apparatus previously described.[7] Before the crystalline boric oxide measurements several alterations were made that should be recorded. (1) A new calorimeter of the same design and dimensions as that used previously was constructed. (2) A new heavy surrounding shield or "block" was made for us by Mr. G. F. Nelson, Head Mechanic, Department of Chemistry, University of California. This "block" is identical in design with those used in the laboratory of Prof. W. F. Giauque of the University of California. (3) The temperature scale now employed is that of the National Bureau of Standards. Through the kind coöperation of Dr. F. G. Brickwedde, copper–constantan thermocouples were calibrated for us between liquid hydrogen and room temperatures. These couples are employed in conjunction with a gold heater-resistance thermometer in exactly the manner described by Giauque and Wiebe.[8] (4) In addition, a Kinney vacuum pump of 15 cu. ft. per min. displacement has replaced the rather cumbersome combination of pumps used heretofore for evacuating the liquid and solid nitrogen. With the new pumping facilities a temperature of 51.1°K. is reached readily.

Specific Heats.

—The results, expressed in defined calories (1 calorie = 4.1833 int. joules), are

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. (Not subject to copyright.)

[2] Chemist, Metallurgical Division, Bureau of Mines.

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

[4] Kracek, Morey and Merwin, *Am. J. Sci.*, **35A**, 143 (1938).

[5] The earlier report of "crystalline B_2O_3" of Taylor and Cole, THIS JOURNAL, **56**, 1648 (1934), and *J. Am. Ceram. Soc.*, **18**, 55 (1935), is considered to be erroneous. The material they prepared melted at 294° whereas McCulloch obtained 460° and Kracek, Morey and Merwin 450° for their preparations.

[6] Ridgway, *Trans. Amer. Electrochem. Soc.*, **66**, preprint 25, 293 (1934).

[7] Millar, THIS JOURNAL, **50**, 1875 (1928); Anderson, *ibid.*, **52**, 2296 (1930).

[8] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

given in Table I and shown graphically in Fig. 1. The atomic weight values employed are: B, 10.82; Si, 28.06; C, 12.010; O, 16.0000. Normal behavior is exhibited by all three substances.

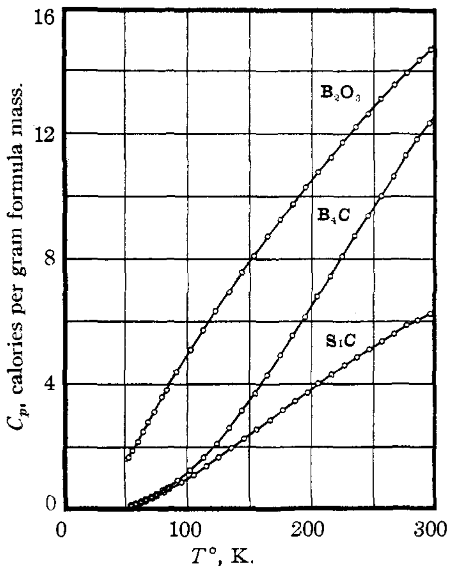

Fig. 1.—The specific heats of crystalline B_2O_3, B_4C and SiC.

The boric oxide results have been corrected for a water content of 0.1%, assuming the latter to have the specific heat of ice. The correction ranged from 0.29% at 52.9° to 0.14% at 295°. The figures for B_4C were corrected for a graphite content of 4%. This correction amounted to 10.0% at 54.5° and 0.97% at 294°. Likewise, a correction for 0.6% silicon dioxide, assuming its presence as quartz, was made in the silicon carbide results. This ranged from 3.60% at 54.3° to 0.08% at 295°. Except for the uncertainties inherent in these corrections, it is believed that the average error in the B_4C and SiC results does not exceed 0.5%, and that for the boric oxide results, with the apparatus improvements previously mentioned, the average error is nearer 0.3%.

No previous specific heat measurements have been reported for crystalline boric oxide and B_4C. Samsoen[9] and Thomas and Parks[10] have measured the specific heat of B_2O_3 glass at elevated temperatures. An extrapolation of the results of the latter workers to 298°K. indicates no difference, within the limits of experimental error, from the present result for the crystals at this temperature. At higher temperatures marked difference should, of course, become evident.

TABLE I

T	C_p	T	C_p	T	C_p
Specific Heat of Crystalline B_2O_3 (69.64 g.)					
52.9	1.695	112.0	5.751	214.5	11.26
56.3	1.922	122.2	6.363	224.3	11.76
60.1	2.204	132.6	6.980	234.9	12.25
64.3	2.521	143.2	7.602	244.7	12.66
68.4	2.825	153.2	8.127	255.1	13.14
72.7	3.142	163.7	8.756	265.6	13.58
79.4	3.613	174.0	9.276	275.7	13.96
82.7	3.838	183.8	9.779	285.6	14.39
91.5	4.415	194.5	10.32	295.1	14.72
101.8	5.115	204.3	10.80		
Specific Heat of B_4C (55.29 g.)					
54.5	0.162	112.7	1.693	214.0	7.470
58.5	.219	122.7	2.125	224.3	8.124
62.3	.278	133.0	2.631	234.5	8.784
66.2	.351	143.4	3.170	244.7	9.423
70.6	.432	153.5	3.717	254.8	10.05
75.0	.523	163.6	4.307	264.9	10.66
80.1	.638	174.1	4.939	275.3	11.33
83.6	.725	184.3	5.567	284.5	11.85
92.1	.964	194.0	6.163	294.3	12.36
102.0	1.281	204.1	6.823		
Specific Heat of SiC (40.07 g.)					
54.3	0.139	114.7	1.410	215.6	4.332
58.2	.186	124.7	1.691	225.9	4.619
62.1	.238	135.1	1.993	235.8	4.882
66.2	.303	145.2	2.284	245.6	5.141
70.6	.376	155.4	2.577	255.7	5.393
75.2	.462	165.7	2.883	265.7	5.616
80.7	.573	176.0	3.193	276.1	5.908
85.4	.674	185.6	3.467	284.8	6.084
94.9	.894	195.8	3.758	294.6	6.283
104.6	1.134	205.4	4.040		

The low-temperature specific heat of silicon carbide was investigated many years ago by Nernst and Schwers[11] (52–96.5°) and Günther[12] (53–73.5°). Their results lie in the range below 1.02 calorie, in which it is not possible to make a comparison on a chart of the scale of Fig. 1. It will suffice to say that these early data are quite scattered and fall both above and below the silicon carbide curve in Fig. 1.

Entropies.—The entropies at 298.16°K. were calculated in the usual manner. The specific heats of B_4C and silicon carbide are below 0.2 calorie per gram formula mass at the lowest temperatures studied; consequently, extrapolation was made on the basis of the T^3 law. The crystalline boric oxide specific heats are represented adequately over the entire temperature range studied by the function sum, $D\left(\frac{311}{T}\right) + E\left(\frac{480}{T}\right) + 2E\left(\frac{1086}{T}\right)$.

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[9] Samsoen, *Bull. soc. encour. ind. nat.*, 185 (1929).

[10] Thomas and Parks, *J. Phys. Chem.*, **35**, 2091 (1931).

[11] Nernst and Schwers, *Sitzb. Kg. Preuss. Akad. Wiss.*, 355 (1914).

[12] Günther, *Ann. Physik*, [4] **51**, 828 (1916).

Extrapolation below 53.1° was made by use of this combination of functions, but only the first term has much significance. The entropy results are in Table II.

TABLE II

ENTROPIES AT 298.16°K.

	B_2O_3	B_4C	SiC
0–53.1°, extrapolation	0.68	0.047	0.043
53.1–298.16°, graphical	12.36	6.427	3.905
$S_{298.16}$	13.0 ± 0.1	6.47 ± 0.07	3.95 ± 0.04

The present value of the entropy of silicon carbide is, rather fortuitously, only 0.05 unit different from that (3.90 ± 0.2)[13] calculated from the older data of Nernst and Schwers and Günther.

The entropy of crystalline boron has not yet been determined. From the result for B_4C in comparison with those for SiC and Si[13] and TaC[14] and Ta[15] it may be estimated that $S_{298.16} = 1.7 \pm 0.2$ for B. This value is suggested for us until an experimental result is available.

Related Thermal Data.—The heats of formation of crystalline boric oxide and B_4C have not been determined; consequently it is not possible to derive free-energy values for these substances, although Roth and Börger's[16] $\Delta H = -349{,}000$ for B_2O_3 glass at room temperature might be used to set an upper limit for the free energy of formation of boric oxide crystals.

Heat of formation values for silicon carbide have been reported by von Wartenberg and Schütte[17] ($\Delta H = -31{,}000 \pm 6000$), Ruff and Grieger[18] ($\Delta H = -26{,}700 \pm 2100$), Ruff and Konschak[19] ($\Delta H = -25{,}000$), and Brunner[20] ($\Delta H = -39{,}000$). If the value of Ruff and Grieger is employed, then $\Delta F^\circ_{298.16} = -26{,}100$ is calculated, the entropies[13] of silicon and graphite being, respectively, 4.50 and 1.36. However, in view of the wide discrepancies in the ΔH results but little reliance can be placed on this free energy value.

Summary

Specific heat measurements of crystalline boric oxide, boron carbide and silicon carbide were made, covering the temperature range 51 to 298°K.

The entropies at 298.16°K. are 13.0 ± 0.1 for boric oxide, 6.47 ± 0.07 for boron carbide and 3.95 ± 0.04 for silicon carbide.

The value $S_{298.16} = 1.7 \pm 0.2$ is suggested for crystalline boron.

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[13] Kelley, *Bureau of Mines Bulletin*, 394, 1936, 55 pp.

[14] Kelley, THIS JOURNAL, **62**, 818 (1940).

[15] Kelley, *J. Chem. Phys.*, **8**, 316 (1940).

[16] Roth and Börger, *Ber.*, **70B**, 48 (1937).

[17] Von Wartenberg and Schütte, *Z. anorg. Chem.*, **211**, 222 (1933).

[18] Ruff and Grieger, *ibid.*, **211**, 145 (1933).

[19] Ruff and Konschak, *Z. Elektrochem.*, **32**, 515 (1926).

[20] Brunner, *Z. anorg. allgem. Chem.*, **217**, 157 (1934).

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF HOWARD COLLEGE]

The Absorption of Oxygen by Mercaptans in Alkaline Solution[1]

BY J. XAN, E. A. WILSON, L. D. ROBERTS AND N. H. HORTON[2]

It has been known for some time that air or oxygen oxidizes sodium thioethylate in water or alcohol solution to ethyl disulfide.[3] The investigation herewith deals with the absorption of oxygen by alkaline solutions of representative aliphatic and aromatic mercaptans at several temperatures and concentrations of alkali.

The disulfides, which are insoluble in the aqueous alkali, separate as the reaction progresses. *n*-Butyl, phenyl and benzyl disulfides were identified by their physical properties. An unexpected result was found: more oxygen disappears than can be accounted for by the oxidation of the mercaptan to disulfide. This excess absorption is trifling if the alkali is weak, but rises to about 50% of the theoretical for the disulfide as the strength of the alkali is increased to 2.71. This indicates a further reaction, perhaps to a sulfonic acid, but its nature has not been determined.

It was realized from the first that the experimental method adopted, shaking a solution with a gas, is not suited to measurements of extreme accuracy, since the disappearance of the oxygen depends on the rate of diffusion as well as on the re-

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[1] Read at the Cincinnati A. C. S. meeting, April 1940. Original manuscript received May 13, 1940.

[2] We wish to express our appreciation to Dr. E. Emmet Reid, research advisor, Howard College, for his interest and helpful suggestions during the course of this investigation.

[3] P. Klason, *Ber.*, **20**, 3412 (1888).