TABLE II

EXCHANGE RESULTS FOR PEROXYACETIC ACID

Expt.	$[CH_3CO_2OH]$	$[CH_3CO_2^-]$	pH	Temp., °C.	Time, min.	% lost[c]	CH_3CO_2OH, c.p.m.	$CH_3CO_2^-$, c.p.m.	% activity as CH_3CO_2OH
C1	0.09	0.13	6	60	30	n.d.	437	5082	8.6[a]
C2	.15	.15	6	25	6 hr.	40	25	5533	0.4
C3	.15	.15	6	50	30	43	26	5330	0.5
C4	.15	.15	6	75	30	54	89	5270	1.7
C5	.25	.25	6	25	0	0	13	5055	0.3[b]
C6	.25	.25	6	25	0	0	18	5027	0.4[b]
C7	.30	.30	6	75	30	48	53	5102	1.0
C8	.30	.30	6	75	30	45	41	5138	0.8
C9	.20	.20	6	25	0	0	175	5089	3.4[b]

EXCHANGE RESULTS FOR PEROXYBENZOIC ACID

Expt.	$[C_6H_5CO_2OH]$	$[C_6H_5CO_2^-]$	pH	Temp., °C.	Time, min.	% lost[c]	$C_6H_5CO_2OH$, c.p.m.	$C_6H_5CO_2^-$, c.p.m.	% activity as $C_6H_5CO_2OH$
C10	0.030	0.03	7	50	30	n.d.	338	13280	2.5
C11	.039	.04	7	50	30	38	91	13089	0.7
C12	.076	.08	7	50	30	30	133	13099	1.0
C13	.066	.07	7	50	30	34	66	13080	0.5

[a] H_2O_2 present. [b] Sample immediately worked up without heating. [c] n.d. signifies not determined.

susceptible to attack by a polarizable nucleophile than by a basic nucleophile.[11] Thus, free-radical mechanisms for certain peroxide reactions, such as the decomposition of peroxydisulfate ion in water and as alcohol oxidation by this ion, would seem to be more reasonable than postulations of electrophilic attack on oxygen by the peroxide.

Acknowledgment.—The authors are grateful to the BECCO Division of Food Machinery and Chemical Corp. and to the Office of Ordnance Research of the U. S. Army for support.

PROVIDENCE, R. I.

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[11] J. O. Edwards, THIS JOURNAL, **76**, 1540 (1954); **78**, 1819 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Heat Capacities and Thermodynamic Properties of Crystalline and Vitreous Anhydrous Sodium Tetraborate from 6 to 350°K.

BY EDGAR F. WESTRUM, JR., AND GEORGE GRENIER

RECEIVED NOVEMBER 23, 1956

The heat capacities of crystalline and vitreous anhydrous sodium tetraborate ($Na_2B_4O_7$) have been determined from about 6 to 350°K. by adiabatic calorimetry. Values of the heat capacity and the derived thermodynamic functions have been computed and tabulated. Molal values at 298.15°K. of the heat capacity at constant pressure, entropy, enthalpy increment ($H^\circ_T - H^\circ_0$), and free energy function are: 44.64 cal./deg., 45.30 cal./deg., 7262 cal., and −20.94 cal./deg., respectively, for the crystalline modification. For the vitreous modification, the molal values at 298.15°K. of the heat capacity at constant pressure, entropy increment ($S^\circ_T - S^\circ_0$), and enthalpy increment ($H^\circ_T - H^\circ_0$), are: 44.42 cal./deg., 44.39 cal./deg., and 7127 cal., respectively.

Introduction

Despite the use of borax and related materials in ceramic technology for many centuries and their widespread utilization in current chemical technology, reliable thermodynamic data on alkali borates are relatively rare. Data in the chemical literature on the physical properties of anhydrous vitreous and crystalline sodium tetraborate[1] are concerned primarily with melting point and phase equilibrium studies[2] on the $Na_2O-B_2O_3$ systems. Although two or possibly three distinct crystallographic phases of this material exist,[2] the material prepared for this work is the α-form and is that ordinarily obtainable and commercially available. No evidence for an enantiotropic inversion between the various forms has been found,[2] despite a careful search from below 500° to the melting point. The rate of conversion of β to α is very slow and the reverse transformation has not been observed.

Experimental

Preparation and Purity of Crystalline Sodium Tetraborate.—The sodium tetraborate sample was prepared by crystallizing a dehydrated sample of analytical reagent grade sodium tetraborate decahydrate from the molten state under carefully controlled conditions.[3] Since rapid cooling or prolonged periods of heating at temperatures appreciably higher than the melting point of 742.5°[2] result in glass formation, it is essential for crystal growth that the temperature does not exceed 760° nor even remain at this value for more than ten minutes, and that a controlled rate of cooling be maintained. These conditions were achieved by heating in an electric muffle furnace. After gradually decreasing the temperature in the muffle from 750 to about 300° over ten hours, the covered platinum dish containing the sample was transferred to a desiccator containing phosphorus pent-

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(1) We use the designation sodium tetraborate to refer to the chemical composition $Na_2B_4O_7$, although a contrary usage is occasionally found (*Cf.* ref. 2).

(2) G. W. Morey and H. E. Merwin, THIS JOURNAL, **58**, 2248 (1936).

(3) L. G. Black, U. S. Patents, 2,064,337 (1936); 2,073,827 (1937).

oxide and the sample allowed to cool to room temperature without adsorption of water. The resulting white crystals were shown to be free of vitreous regions by careful examination of the sample under a polarizing microscope. X-Ray diffraction indicated the structure of the sample to be that of crystalline anhydrous sodium tetraborate.

Determination of water was made by loss in weight on fusion.[4] Although it is reported by Morey and Merwin[2] that both the crystalline material at 300° and the molten tetraborate will take up water in humid weather, this is lost upon crystallization of the compound under anhydrous conditions. The method as employed here was, therefore, efficacious and indicated 0.01 ± 0.01% water. The application of Karl Fischer reagent is unsatisfactory because complicating reactions are involved with borates. The Na_2O content of the sample was determined by carefully evaporating a hydrochloric acid solution of sample to dryness and titrating the residual chloride with standardized silver nitrate solution using dichlorofluorescein as an indicator.[4] The B_2O_3 content of the sample was obtained by first neutralizing a sample of the metaborate with hydrochloric acid, then adding mannitol and titrating the boric acid potentiometrically.[5] The per cent. by weight of Na_2O was 30.79 ± 0.01% (theoretical, 30.80%), that of B_2O_3 was 69.18 ± 0.03% (theoretical, 69.20%).[6] The material is, therefore, stoichiometric, anhydrous sodium tetraborate, $Na_2B_4O_7$. The mass of the crystalline calorimetric sample was 79.671 g. (*in vacuo*).

Preparation and Purity of Vitreous Sodium Tetraborate.—The vitreous sodium tetraborate was prepared from the same reagent as the crystalline sample. The dehydrated sample was heated to 820° for 30 minutes to ensure glass formation on subsequent cooling. The glass was annealed for 15 minutes at 420° and cooled in an anhydrous atmosphere.

Analytical data (by methods identical to those used for the crystalline preparation) on the vitreous material[6] indicated: water, 0.0 ± 0.01%; Na_2O, 30.79 ± 0.01% (theoretical, 30.80%); B_2O_3, 69.21 ± 0.03% (theoretical, 69.20%), in good accord with theory. The completely vitreous nature of the sample was established by X-ray diffraction. The mass of the calorimetric sample, consisting of fragments of 2 to 5 mesh, was 112.644 g. (*in vacuo*).

Cryogenic Technique.—The Mark I adiabatic cryostat,[7] calorimeter W-9,[8] and method of measurement[7] have been described. The calorimeter was loaded in a dry-box. After evacuation, 2.0 cm. of helium gas at 300°K. was added to aid in the establishment of thermal equilibrium with the sample. Temperatures and temperature increments were determined with a capsule-type platinum resistance thermometer (Laboratory Designation A-3) contained within the entrant well of the calorimeter. It had been previously calibrated against the temperature scale of the National Bureau of Standards above 10°K.[9] Below this temperature a provisional scale was employed.[8] The temperature scale is considered to accord with the thermodynamic temperature scale within 0.1° from 4 to 10°K., within 0.03° from 14 to 90°K. and within 0.05° above 90°K. The ice point was taken to be 273.15°K. Calibrated instruments were used in the determination of experimental quantities including the time interval of the energy input. The over-all accuracy of our heat capacity determinations was established by measuring the heat capacity of pure benzoic acid made available by the National Bureau of Standards in conjunction with the program of the Calorimetry Conference.[10] Excellent agreement with published values[11,12] was obtained.

Results

The experimental values of the heat capacity of crystalline and vitreous sodium tetraborate are presented in Table I. Since these data are presented in chronological sequence, the temperature increments employed in the individual determinations may usually be inferred from the differences between adjacent mean temperatures. Small corrections have been made for the finite temperature increments and for the slight differences in the amounts of helium and solder in the measurements on the empty and on the loaded calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules and the molecular weight of $Na_2B_4O_7$ as 201.262 g.

TABLE I

THE MOLAL HEAT CAPACITY OF ANHYDROUS SODIUM TETRABORATE (IN CALORIES PER DEGREE)

T, °K.	*C*p	*T*, °K.	*C*p	*T*, °K.	*C*p
		Crystalline			
Series I		55.32	8.746	257.40	40.32
		61.01	10.11	266.90	41.36
5.82	0.0154	67.36	11.59	276.50	42.36
6.60	.0188	74.48	13.15	286.39	43.41
7.81	.0298	81.61	14.70	296.65	44.47
9.07	.0550	89.18	16.27	306.88	45.52
10.21	.0890	97.84	17.89	317.02	46.53
11.50	.144	107.29	19.60	327.09	47.51
12.92	.226	117.03	21.28	337.30	48.48
14.37	.328	126.62	22.91	347.69	49.33
15.92	.460	135.89	24.38		
17.52	.623	144.71	25.73	Series II	
19.21	.843	153.70	27.08		
21.03	1.097	162.66	28.38	253.26	39.78
23.02	1.430	172.08	29.70	262.55	40.81
25.23	1.824	181.88	31.03	271.91	41.88
27.73	2.289	191.80	32.34	281.41	42.89
30.61	2.882	201.60	33.60	291.36	43.92
33.80	3.591	211.13	34.83	301.61	44.99
37.25	4.380	220.53	35.99	311.91	46.02
41.09	5.296	229.84	37.12	322.22	47.00
45.45	6.346	238.94	38.17	333.05	48.02
50.18	7.506	248.07	39.22	343.97	49.06
		Vitreous			
5.31	0.0147	41.92	5.361	177.49	29.77
6.68	.0269	46.13	6.326	186.79	31.05
8.09	.0569	51.00	7.445	196.08	32.30
9.22	.0985	56.39	8.694	205.13	33.49
10.32	.150	62.26	10.00	214.14	34.66
11.54	.217	68.55	11.38	223.13	35.80
12.82	.305	75.01	12.72	232.21	36.92
14.13	.411	81.43	14.08	241.51	38.06
15.59	.549	88.06	15.41	250.99	39.18
17.21	.724	95.20	16.73	260.78	40.36
19.01	.947	103.03	18.14	270.61	41.42
21.08	1.231	111.83	19.67	280.35	42.49
23.41	1.598	121.62	21.33	290.09	43.56
25.95	2.030	131.54	22.94	300.00	44.60
28.71	2.543	140.88	24.42	310.30	45.68
31.69	3.137	149.95	25.79	320.84	46.77
34.85	3.794	159.04	27.14	331.13	47.74
38.23	4.540	168.25	28.48	343.63	48.92

The molal heat capacity and the thermodynamic functions derived from the numerical quadrature

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[4] H. Menzel and H. Schulz, *Z. anorg. Chem.*, **245**, 157 (1940); **251**, 167 (1943); E. Rimbach, *Ber.*, **26**, 164 (1893); W. Ramsay and E. Aston, *Chem. News*, **66**, 92 (1892).

[5] H. V. A. Briscoe, P. L. Robinson and G. E. Stephenson, *J. Chem. Soc.*, **127**, 150 (1925).

[6] The analyses of the final calorimetric samples were performed by Lynn J. Kirby.

[7] E. F. Westrum, Jr., and A. F. Beale, Jr., to be published.

[8] E. Greenberg and E. F. Westrum, Jr., THIS JOURNAL, **78**, 4526 (1956).

[9] H. J. Hoge and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **22**, 351 (1939).

[10] D. C. Ginnings and G. T. Furukawa, THIS JOURNAL, **75**, 522 (1953).

[11] G. T. Furukawa, R. E. McCoskey and G. J. King, *J. Research Natl. Bur. Standards*, **47**, 256 (1951).

[12] D. W. Osborne, E. F. Westrum, Jr., and H. R. Lohr, THIS JOURNAL, **77**, 2737 (1955).

of the heat capacity of these substances are listed at rounded temperatures in Tables II and III.

TABLE II

MOLAL THERMODYNAMIC PROPERTIES OF CRYSTALLINE SODIUM TETRABORATE

T, °K.	Cp, cal./deg.	$S°$, cal./deg.	$(H° - H°_0)$, cal.	$-(F° - H°_0)/T$, cal./deg.
5	0.012	0.004	0.014	0.001
10	.081	.027	0.202	.007
15	.379	.108	1.255	.024
20	.949	.288	4.449	.066
25	1.781	.585	11.19	.138
30	2.751	0.993	22.46	0.244
35	3.861	1.499	38.96	.386
40	5.036	2.091	61.17	.562
45	6.238	2.753	89.34	.768
50	7.462	3.474	123.57	1.003
60	9.870	5.047	210.22	1.543
70	12.18	6.744	320.60	2.164
80	14.35	8.512	453.26	2.846
90	16.38	10.322	607.1	3.576
100	18.29	12.149	780.6	4.343
110	20.08	13.976	972.5	5.135
120	21.79	15.797	1181.9	5.948
130	23.43	17.607	1408.1	6.776
140	25.00	19.401	1650.3	7.613
150	26.53	21.178	1908.0	8.458
160	27.99	22.938	2180.6	9.309
170	29.41	24.678	2467.6	10.163
180	30.77	26.399	2768.6	11.018
190	32.10	28.097	3083.0	11.871
200	33.40	29.777	3410.5	12.725
210	34.68	31.438	3750.9	13.576
220	35.93	33.080	4104.0	14.425
230	37.12	34.705	4469.4	15.273
240	38.29	36.310	4846.5	16.117
250	39.43	37.896	5235.1	16.956
260	40.57	39.463	5635.1	17.789
270	41.67	41.016	6046.3	18.622
280	42.75	42.552	6468.4	19.451
290	43.79	44.070	6901.1	20.273
300	44.83	45.572	7344.2	21.091
350	49.65	52.850	9708.1	25.112
273.15	42.01	41.504	6178.6	18.885
298.15	44.64	45.296	7261.9	20.940

The heat capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of 0.1% above 25°K., 1% at 14°K., increasing to 5% at 5°K. The heat capacity was extrapolated below 10°K. with a Debye function. The effect of nuclear spin and isotope mixing is not included in the entropy and free energy function. The estimated probable errors in the entropy, enthalpy and free energy functions are 0.1% above 100°K., but in order to make the tables internally consistent and to permit accurate interpolation, some of the values are given to one more figure than is justified by the estimated probable error.

Since the third law of thermodynamics may not be assumed valid for the vitreous phase, only the entropy and enthalpy increments are tabulated.

TABLE III

MOLAL THERMODYNAMIC PROPERTIES OF VITREOUS SODIUM TETRABORATE

T, °K.	Cp, cal./deg.	$(S° - S°_0)$, cal./deg.	$(H° - H°_0)$, cal.
5	0.013	0.004	0.016
10	.134	.044	0.334
15	.490	.158	1.795
20	1.078	.375	5.635
25	1.866	.697	12.92
30	2.795	1.117	24.51
35	3.828	1.625	41.04
40	4.933	2.207	62.93
45	6.063	2.853	90.40
50	7.220	3.552	123.61
60	9.499	5.072	207.30
70	11.69	6.702	313.32
80	13.78	8.400	440.64
90	15.77	10.138	588.5
100	17.60	11.895	755.4
110	19.36	13.655	940.1
120	21.06	15.413	1142.2
130	22.70	17.163	1361.1
140	24.28	18.903	1596.0
150	25.80	20.631	1846.4
160	27.29	22.343	2111.8
170	28.70	24.041	2391.8
180	30.11	25.721	2686.0
190	31.48	27.387	2993.9
200	32.82	29.036	3315.4
210	34.12	30.668	3650.1
220	35.40	32.285	3997.7
230	36.65	33.887	4357.9
240	37.87	35.471	4730.5
250	39.07	37.042	5115.2
260	40.23	38.597	5511.7
270	41.36	40.136	5916.6
280	42.46	41.660	6338.7
290	43.54	43.169	6768.7
300	44.61	44.663	7209.5
350	49.50	51.918	9565.2
273.15	41.71	40.620	6050.9
298.15	44.42	44.391	7127.6

Formulas for the extrapolation of the molal thermodynamic functions to temperatures above 350°K. are derived by the method described by Shomate[13] using 300°K. as the base temperature. The equations for crystalline sodium tetraborate (in cal. deg.$^{-1}$ mole^{-1}) are

$$C_p = 21.83 + 0.0850T - 2.250 \times 10^5\ T^{-2},$$

$$(H° - H°_0)/T = 21.83 + 0.0425T + 2.250 \times 10^5\ T^{-2} - 3779.8\ T^{-1}$$

and

$$S° = 50.27 \log T + 0.0850T + 1.125 \times 10^5\ T^{-2} - 105.70$$

Those for vitreous sodium tetraborate in the same units are

$$C_p = 27.83 + 0.0270T - 4.320 \times 10^5\ T^{-2},$$

$$(H° - H°_0)/T = 27.83 + 0.0360T + 4.320 \times 10^5\ T^{-2} - 5819.5\ T^{-1}$$

and

$$S° - S°_0 = 64.09 \log T + 0.0720T + 2.160 \times 10^5\ T^{-2} - 137.96$$

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[13] C. H. Shomate, *J. Phys. Chem.*, **58**, 368 (1954).

These equations should be used with caution above 350°K. as they represent an approximation justified only by the absence of experimental determinations. However, no evidence for thermal transformations or anomalies was detected by Morey and Merwin[2] by thermal analysis between 350°K. and the melting point.

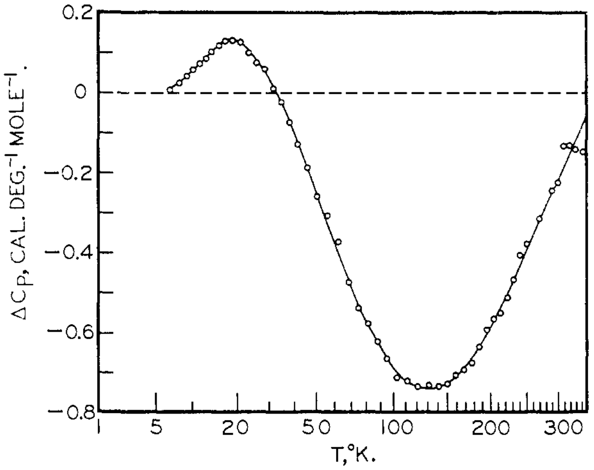

Fig. 1.—Deviation of the experimental measurements on vitreous $Na_2B_4O_7$ from those of crystalline $Na_2B_4O_7$ ($\Delta C_p = C_p$ (vit.) $-$ C_p (cryst)).

It is striking that the heat capacity of the crystals exceeds that of the vitreous material at all temperatures above 35°K., as may be seen clearly in the deviation plot, Fig. 1. This contrasts with data on other crystalline–vitreous pairs. For example, the heat capacity of quartz rises above that of vitreous silica only at about 210°K.[14] Moreover, the heat capacity of crystalline boron trioxide[14] exceeds the heat capacity of vitreous boron trioxide only at temperatures above 300°K.

From the heats of solution in nitric acid of Na_2O, B_2O_3 and two forms of $Na_2B_4O_7$[15] and the heats of formation of Na_2O and B_2O_3,[16] the heats of formation of crystalline and vitreous $Na_2B_4O_7$ are calculated as -786.4 ± 3 and -781.5 ± 3 kcal. mole^{-1}, respectively, at 25°. The present measurements together with entropy data on the elements[16,17] permit the evaluation of the free energy of formation of crystalline $Na_2B_4O_7$ as -739.7 ± 3 kcal. mole^{-1} at 25°. It is not possible to evaluate the zero-point entropy of the vitreous material; however, for the devitrification reaction, $\Delta H^{\circ}_{0^{\circ}\mathrm{K.}} = -4.99$ kcal. mole^{-1}.

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(14) Edgar F. Westrum, Jr., to be published.

(15) L. Shartsis and W. Capps, *J. Am. Ceram. Soc.*, **37**, 27 (1954).

(16) "Contributions to the Data of Theoretical Metallurgy. XII. Heats and Free Energies of Formation of Inorganic Oxides," Bulletin No. 542, Bureau of Mines, U. S. Govt. Printing Office, Washington, D. C., 1954.

(17) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular No. 500, U. S. Govt. Printing Office, Washington, D. C., (1950).

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Low Temperature Heat Capacity and Thermodynamic Properties of Sodium Methoxide

BY GEORGE GRENIER AND EDGAR F. WESTRUM, JR.

RECEIVED DECEMBER 26, 1956

Heat capacities of sodium methoxide were measured from 5 to 345°K. The heat capacity curve follows the normal sigmoid shape with the exception of a small hump of undetermined origin near 34°K. involving an excess entropy of about 0.43 cal. mole^{-1} deg.$^{-1}$ Molal values of the heat capacity at constant pressure, the entropy, the enthalpy increment ($H° - H_0°$), and the free energy function are: 16.60 ± 0.02 cal. deg.$^{-1}$, 26.43 ± 0.05 cal. deg.$^{-1}$, 3374 ± 6 cal., and -15.12 ± 0.03 cal. deg.$^{-1}$, respectively, at 298.16°K.

Sodium methoxide has long been used as a laboratory reagent in the preparation of important organic intermediates. Since 1944 it has been commercially available and currently is widely used on a large scale in the manufacture of certain pharmaceuticals, dyestuffs and other important organics. There is, therefore, considerable technological interest in accurate thermal properties of this material. No previous measurements of the heat capacity of sodium methoxide have been reported in the literature.

Preparation and Purity of Sodium Methoxide.—The reaction of sodium metal with methyl alcohol to yield sodium methoxide and hydrogen was performed in a closed Pyrex vacuum system in a nitrogen atmosphere purified by passage over hot copper to remove oxygen, over potassium hydroxide pellets to remove acid, and through two phosphorus pentoxide columns to remove the remaining traces of water. Analytical reagent grade methyl alcohol (ketone, aldehyde and organic acid content to pass ACS test) was purified by refluxing for 24 hours over magnesium methoxide[1] followed by subsequent fractional distillation in the nitrogen atmosphere directly into a storage bulb connected to the reaction vessel. About 60 g. of sodium metal (99.95% purity) was cut under xylene into one-cm. cubes with fresh metallic surfaces and quickly transferred into a cylindrical receiver 4 cm. diam. by 25 cm. in length. This receiver communicated with the spherical one-liter reaction vessel below it through a coaxial Pyrex capillary tube of 0.9 mm. internal diameter and 4 cm. length. After evacuation of the sodium for 20 hours (while the alcohol was refluxing), the sodium was fused to permit possible slag to float to the surface.

Five hundred ml. of methanol was added to the reaction vessel, and molten sodium was then injected under a slight

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(1) A. I. Vogel, "Practical Organic Chemistry," 2nd Edition, Longmans, Green, New York, N. Y., 1951.