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

The Heat Capacity and Thermodynamic Functions of Sodium Metaborate from 5 to 350° K.

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The heat capacity of anhydrous sodium metaborate ($NaBO_2$) has been determined from about 6 to 350°K.; no evidence of anomalous behavior was detected. Values of the derived thermodynamic functions are given at rounded temperatures together with the smoothed heat capacity data. Molal values of the heat capacity at constant pressure, entropy, enthalpy increment and free energy function at 298.16°K. are: 15.76 cal./deg., 17.57 cal./deg., 2780 cal., and −8.25 cal./deg., respectively.

Introduction

Anhydrous sodium metaborate ($NaBO_2$) is a hygroscopic crystalline solid which melts at about 966° to a viscous liquid which does not yield a vitreous phase. Data from the chemical literature on the physical properties of anhydrous sodium metaborate pertain almost exclusively to phase equilibria in the Na_2O–B_2O_3 system,[1] melting points and optical properties,[1,2] sublimation pressures,[3] and structural studies and densities based on fragmentary X-ray diffraction data.[2–4]

The heat capacity of sodium metaborate was determined to permit the calculation of entropy, enthalpy and free-energy function for use in chemical thermodynamics.

Experimental

Preparation of Anhydrous Sodium Metaborate.—A pure sodium metaborate tetrahydrate (sold by Eastman Kodak Co. under the trade name of "Kodalk") was used as the starting material. Removal of a trace of calcium and further purification of the material was accomplished by recrystallization from distilled water. Most of the water of hydration was removed by evacuation at 25° for three days; then the sample was heated to 100° and evacuation was continued with a high-speed diffusion pump. It is essential that almost all the water be removed before the substance is placed in the furnace because the evolution of water vapor causes a large increase in volume of the sample. The dried sample was placed in a platinum dish and was heated gradually in a furnace to above 966°, the melting point of anhydrous sodium metaborate. The material was allowed to cool gradually to 200°, then it was transferred from the furnace to a desiccator containing P_2O_5. White crystals of acicular habit were formed during the slow cooling. The best crystals from the various batches were removed in a dry box, combined, fused and recrystallized slowly to ensure purity, homogeneity and good crystal development of the calorimetric samples.

No water was detected within a 0.01% limit upon loss in weight on fusion.[5] The usual application of Karl Fischer reagent is unsatisfactory because complicating reactions are involved with borates. The Na_2O content was determined by carefully evaporating a hydrochloric acid solution of the sample to dryness and titrating the residual chloride with standardized silver nitrate solution using dichlorofluorescein as an indicator.[5,6] 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.[7] The per cent. by weight of Na_2O was 47.11 ± 0.20% (theoretical Na_2O, 47.09%); that of B_2O_3 was 52.91 ± 0.13% (theoretical B_2O_3, 52.91%).[8] The material, therefore, is stoichiometric, anhydrous sodium metaborate. It was handled and loaded into the calorimeter in a dry box.

Cryogenic Technique.—The adiabatic Mark I cryostat,[9] W-9 calorimeter,[10] and method of operation[9] have been described previously.

The calorimeter was loaded in a dry box and after evacuation 2.0 cm. of helium gas was added at 25° to aid in the establishment of thermal equilibrium.

Temperatures were measured with a capsule-type platinum resistance thermometer (laboratory designation A-3) contained in a re-entrant well in the calorimeter. The thermometer was calibrated on the temperature scale of the National Bureau of Standards,[11] from 10 to 373°K. Below 10°K., the scale was obtained by fitting the equation[11] $R = A + BT^2 + CT^5$ to the resistance at the boiling point of helium and to the resistance and dR/dT at 10°K. It is believed that our temperature scale agrees with the thermodynamic scale within 0.1° from 4 to 14°K., within 0.03° from 14 to 90°K., and within 0.05° from 90 to 373°K.

The thermometer resistance and the power input were measured with a calibrated White double-potentiometer, calibrated resistances and a calibrated standard cell. An electric timer operated by a calibrated tuning fork and amplifier was automatically started at the beginning of the heating period and stopped at the end.

Results

The original experimental values of the molal heat capacity of sodium metaborate at the mean temperature of the runs are given in Table I. Since these are listed in chronological sequence, the individual temperature increments of the runs may usually be inferred from the difference in adjacent mean temperatures. Small corrections have been made for these finite temperature increments and for the slight differences in the amounts of helium and solder in the measurements on the empty and on the full calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The ice point is taken to be 273.16°K., and the gram molecular weight of sodium metaborate ($NaBO_2$) as 65.811 g. A calorimetric sample of 133.638 g. was employed for these determinations.

The molal heat capacity and the thermodynamic functions derived from the heat capacity are listed at rounded temperatures in Table II. These heat

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

[2] S. S. Cole, S. R. Scholes and C. R. Amberg, *J. Am. Ceram. Soc.*, **18**, 58 (1935); S. S. Cole, N. W. Taylor and S. R. Scholes, *ibid.*, **18**, 79 (1935).

[3] S. S. Cole and N. W. Taylor, *ibid.*, **18**, 82 (1935).

[4] Ssü-Mien Fang, *ibid.*, **20**, 214 (1937); S. S. Cole, S. R. Scholes and C. R. Amberg, *ibid.*, **20**, 215 (1937).

[5] H. Menzel and H. Schulz, *Z. anorg. Chem.*, **245**, 157 (1940); **251**, 167 (1943).

[6] W. Ramsay and E. Aston, *Chem. News*, **66**, 92 (1892); E. Rimbach, *Ber.*, **26**, 164 (1893).

[7] H. V. A. Briscoe, P. L. Robinson and G. E. Stephenson, *J. Chem. Soc.*, **127**, 150 (1925); E. T. Wherry and W. H. Chapin, THIS JOURNAL, **30**, 1691 (1908); L. V. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **2**, 358 (1930).

[8] The analyses were performed by Lynn J. Kirby.

[9] Edgar F. Westrum, Jr., and A. F. Beale, Jr., to be published.

[10] E. Greenberg and E. F. Westrum, Jr., THIS JOURNAL, **78**, 4256 (1956).

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

TABLE I

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

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
5.48	0.003	45.57	2.405	177.16	11.88
6.68	.005	50.72	2.997	187.21	12.28
7.83	.010	55.96	3.598	197.36	12.66
9.08	.017	60.88	4.152	207.75	13.02
10.38	.027	64.98	4.604	215.06	13.28
11.72	.040	71.20	5.244	225.14	13.62
13.06	.057	77.18	5.839	235.23	13.94
14.40	.078	77.94	5.908	245.47	14.27
15.74	.105	84.46	6.515	255.80	14.58
17.14	.139	91.34	7.099	265.98	14.88
18.69	.185	99.00	7.674	276.10	15.16
20.53	.253	107.29	8.257	286.16	15.45
22.74	.354	115.59	8.796	296.22	15.71
25.15	.487	123.94	9.310	306.34	15.99
27.64	.652	132.48	9.797	316.45	16.24
30.36	.859	140.98	10.25	326.55	16.48
33.41	1.125	149.44	10.66	336.56	16.73
36.89	1.464	158.07	11.06	345.49	16.96
40.89	1.883	167.33	11.48		

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., and 5% at 5°K. The heat capacity was extrapolated below 10°K. with a Debye function. Nuclear spin and isotope mixing contributions are not included in the entropy and free energy function. The estimated probable error in the entropy, heat content and free energy function is 0.1% above 100°K., but in order to make the table 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.

The molal heat capacity and thermodynamic functions (in calories per degree) may be extrapolated to higher temperatures by the following three formulas predicated on the method described by Shomate.[12]

$$C_p = 10.23 + 0.0212\ T - 7.02 \times 10^4\ T^{-2}$$

$$(H^\circ - H_0^\circ)/T = 10.23 + 0.0106\ T + 7.02 \times 10^4\ T^{-2} - 1447.9\ T^{-1}$$

$$S^\circ = 23.58 \log T + 0.0212\ T + 3.51 \times 10^4\ T^{-2} - 47.44$$

These formulas should be used with caution as they are an approximation justified only by the absence of experimental determinations. However, no thermal transformations or anomalies were detected by Morey and Merwin[1] by thermal analysis between 350°K. and the melting point.

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF SODIUM METABORATE

T, °K.	C_p, cal./deg.	S°, cal./deg.	$(H^\circ - H_0^\circ)$, cal.	$-(F^\circ - H_0^\circ)/T$, cal./deg.
5	0.002	0.0006	0.002	0.0001
10	.024	.008	.059	.002
15	.090	.028	.32	.007
20	.232	.071	1.09	.017
25	.479	.147	2.82	.034
30	.830	.264	6.05	.062
35	1.276	.425	11.28	.103
40	1.788	.628	18.92	.155
45	2.341	.870	29.23	.220
50	2.913	1.146	42.36	.299
60	4.054	1.779	77.22	.492
70	5.122	2.485	123.20	.725
80	6.102	3.234	179.38	.992
90	6.982	4.005	244.91	1.284
100	7.751	4.781	318.65	1.595
110	8.438	5.553	399.63	1.920
120	9.066	6.314	487.17	2.254
130	9.646	7.063	580.8	2.596
140	10.19	7.798	680.0	2.941
150	10.70	8.519	784.5	3.289
160	11.16	9.224	893.7	3.638
170	11.59	9.914	1007.5	3.988
180	12.00	10.588	1125.4	4.336
190	12.38	11.246	1247.3	4.681
200	12.74	11.891	1373.0	5.026
210	13.10	12.521	1502.2	5.368
220	13.44	13.139	1634.9	5.707
230	13.77	13.743	1771.0	6.043
240	14.10	14.337	1910.4	6.377
250	14.40	14.918	2052.9	6.707
260	14.70	15.489	2198.4	7.034
270	14.99	16.049	2346.9	7.357
280	15.27	16.600	2498.2	7.678
290	15.55	17.140	2652.3	7.994
300	15.81	17.672	2809.1	8.308
350	17.04	20.203	3631.0	9.829
273.16	15.08	16.224	2394.4	7.459
298.16	15.76	17.574	2780.0	8.250

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