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.

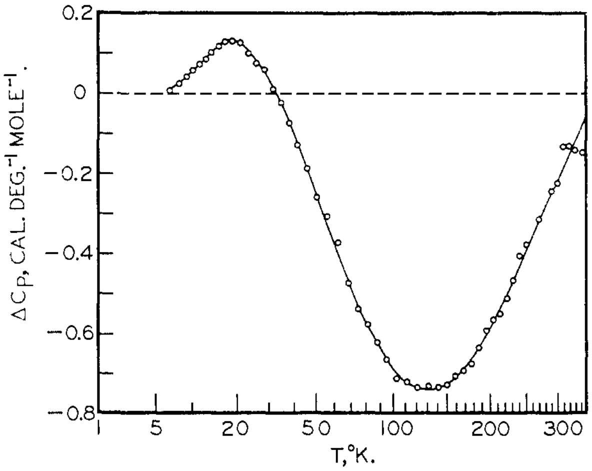

Fig. 1.—Deviation of the experimental measurements on vitreous $Na_2B_4O_7$ from those of crystalline $Na_2B_4O_7$ ($\Delta C_p = C_p$ (vit.) $- C_p$ (cryst)).

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, $\Delta H^\circ_{0^\circ\text{K.}} = -4.99$ kcal. mole^{-1}.

Acknowledgment.—The authors appreciate the coöperation of J. J. McBride and Seisho Tomoeda in the experimental measurements and that of Emilia R. Martin in the calculations. The work was supported in part through the Engineering Research Institute of the University of Michigan.

---

[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

---

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

nitrogen pressure. The sodium flow into the reactor was regulated by partially withdrawing a close-fitting steel twist drill from the capillary connecting the sodium cylinder to the reactor. The position of the drill was manipulated with a coaxial steel shaft which extended from the shank of the drill up through the sodium and out of the vacuum/nitrogen space through a vacuum-tight Teflon standard taper o-ring gland. The use of a drill made possible the penetration of a tip of solid sodium methoxide which occasionally formed on the reactor side of the capillary. The rate of addition of the sodium was limited by the capability of the exit tube reflux condenser to dissipate the heat of the reaction. The hydrogen left the exit tube *via* a mercury-seal-bubbler.

The excess methanol was removed by continuous evacuation over several days as the temperature was gradually increased to 100° to decompose any dialcoholate ($NaOCH_3 \cdot 2CH_3OH$) present. The product was subsequently exposed only to the anhydrous nitrogen atmosphere of the dry box for as short a time as possible.

Total alkali plus carbonate was determined by titration of weighed samples with standard acid to the methyl orange end-point yielding 99.87 ± 0.02% (as sodium methoxide). Total alkali was determined on additional weighed samples to the phenolphthalein end-point as 99.72 ± 0.01% (as sodium methoxide). The difference of the two titrations indicates the carbonate content to approximate 0.15%. No water or hydroxide was detected by high sensitivity Karl Fischer reagent. Perhaps the best indication of the absence of traces of water or of methanol is the freedom of the heat capacity curves of anomalous behavior near the fusion temperatures of these substances. Spectrochemical analysis confirmed the presence of less than 0.02% metallic contaminants.

Attempts to obtain macroscopic crystals were unsuccessful. The $NaOCH_3$ consisted of a fine, white powder. To increase the amount of material in the calorimeter and to improve the thermal conductivity, the material was pelleted into rods with rounded ends about 5 mm. in diameter and 10 mm. in length. The measurements were made on 39.8571 g. (*in vacuo*) of sodium methoxide, the molecular weight of which was taken to be 54.026.

Calorimetric Technique.—The heat capacity determinations were made with the Mark I adiabatic cryostat,[2] in calorimeter W-9.[3] The calorimeter was loaded in a dry box, evacuated under high vacuum and 2.8 cm. of helium gas was added at 27° to aid in the establishment of thermal equilibrium.

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

Heat Capacity and Thermodynamic Properties.—

The original experimental values of the molal heat capacity of sodium methoxide at the mean temperature of the runs are given in Table I. Since the determinations are presented in chronological sequence, the approximate temperature increments can be inferred readily. 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 full calorimeter. The results are

TABLE I

MOLAL HEAT CAPACITY OF SODIUM METHOXIDE (IN CAL./DEGREE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
5.84	0.41	39.69	5.266	177.95	13.76
6.74	0.53	44.20	5.659	187.57	14.03
8.14	0.71	49.22	6.105	197.05	14.27
9.65	0.96	54.53	6.590	206.37	14.49
7.92	0.76	60.23	7.114	215.62	14.72
8.92	0.81	66.45	7.682	218.71	14.79
10.16	1.05	72.62	8.203	228.60	15.03
11.50	1.260	79.33	8.773	238.62	15.25
12.94	1.517	86.88	9.390	248.52	15.48
14.27	1.777	94.52	9.937	258.24	15.71
15.85	2.079	101.56	10.38	268.09	15.89
17.41	2.387	108.92	10.86	278.11	16.13
19.02	2.707	117.64	11.36	288.23	16.38
20.83	3.063	127.63	11.88	298.40	16.55
22.99	3.464	138.03	12.35	308.44	16.86
25.86	3.994	148.20	12.77	318.46	17.10
28.93	4.570	158.20	13.14	328.73	17.23
32.15	5.062	168.15	13.41	339.41	17.48
35.66	5.173				

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF SODIUM METHOXIDE

T, °K.	C_p, cal./deg.	S°, cal./deg.	$(H° - H_0°)$, cal.	$-(F° - H_0°)/T$, cal./deg.
5	(0.318)	(0.106)	(0.40)	(0.026)
10	1.002	0.500	3.50	0.150
15	1.915	1.074	10.73	0.359
20	2.895	1.759	22.75	0.621
25	3.837	2.507	39.60	0.923
30	4.799	3.289	61.13	1.251
35	5.160	4.067	86.38	1.599
40	5.282	4.762	112.40	1.952
45	5.728	5.408	139.87	2.300
50	6.177	6.035	169.63	2.642
60	7.091	7.242	235.96	3.309
70	7.977	8.402	311.32	3.954
80	8.831	9.523	395.39	4.581
90	9.615	10.609	487.7	5.190
100	10.305	11.659	587.4	5.785
110	10.925	12.671	693.5	6.366
120	11.489	13.646	805.6	6.932
130	11.990	14.585	923.1	7.484
140	12.438	15.490	1045.2	8.024
150	12.840	16.362	1171.7	8.551
160	13.197	17.203	1301.9	9.066
170	13.520	18.013	1435.5	9.569
180	13.821	18.795	1572.2	10.060
190	14.098	19.549	1711.8	10.539
200	14.353	20.279	1854.1	11.009
210	14.593	20.985	1998.8	11.467
220	14.828	21.669	2145.9	11.915
230	15.058	22.333	2295.4	12.353
240	15.285	22.979	2447.1	12.783
250	15.511	23.608	2601.1	13.204
260	15.736	24.220	2757.3	13.615
270	15.960	24.818	2915.8	14.019
280	16.189	25.403	3076.5	14.415
290	16.417	25.975	3239.5	14.804
300	16.645	26.536	3404.9	15.186
350	17.722	29.185	4264.5	17.001
273.16	16.031	25.004	2966.3	14.145
298.16	16.604	26.433	3374.3	15.116

---

(2) E. F. Westrum, Jr., and A. F. Beale, Jr., to be published.

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

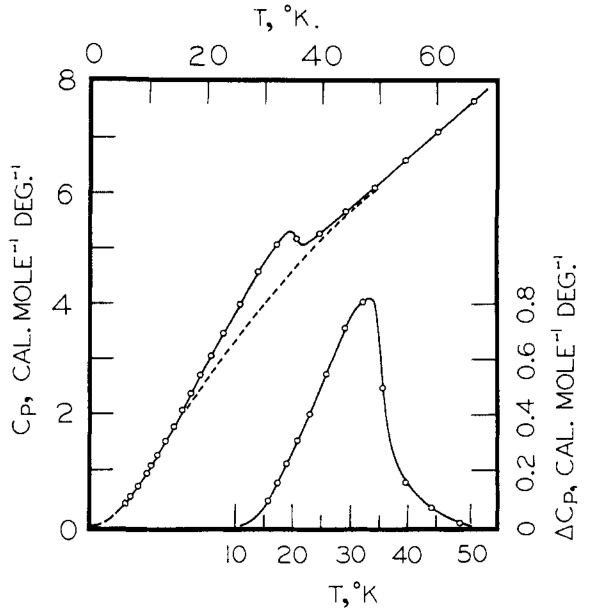

Fig. 1.—Molal heat capacity of sodium methoxide. Experimental heat capacities are plotted and resolved into the lattice contribution (dashed curve) and the anomalous portion (inset).

expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.16°K.

The molal heat capacity and the thermodynamic functions derived from the heat capacity are listed at rounded temperatures in Table II. These 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 10°K., and 4% at 5°K. The heat capacity was extrapolated below 6°K. with a T^3 function. The effect of nuclear spin is not included in the entropy and free energy function. The estimated probable error in the entropy, heat content and free energy function is 0.2% above 100°K., but in order to make the table internally consistent some of the values are given to one more figure than is justified by the estimated probable error.

The measured heat capacities from 5 to 70° are plotted in Fig. 1 together with an estimate of the "excess" heat capacity near 34° obtained by interpolating the temperature dependence of the Debye theta over the anomalous range. The molal enthalpy and entropy increments associated with this anomaly of unknown origin are 11.5 cal. mole^{-1} and 0.43 cal. mole^{1-} deg.$^{-1}$, respectively.

Acknowledgment.—The authors appreciate the assistance of Mrs. M. W. Klonowski with the adiabatic shield control and of Mrs. Margaret S. Anderson with the calculations.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Classical Partition Functions for Transition State Theory. Chlorine Atom Reactions

BY KENNETH S. PITZER

RECEIVED DECEMBER 22, 1956

The classical formulation of the partition function is a valid and useful approximation in calculations for activated complexes in most cases. Cases where one or both reactants consist only of very light atoms must be excepted. Examples are chosen from chlorine atom reactions. Serious discrepancies reported in the literature are eliminated.

Conventional transition state theory[1] requires a knowledge of all of the normal modes of vibration in the activated complex and their frequencies. While this method has been applied successfully to some relatively complex examples,[2] it is not easy to make good approximations for all of the vibration frequencies. The classical formulation of the partition function or phase integral has the advantage that less detailed information is required.

If we take 0.2 cal. per deg. mole as a maximum error, the classical formula for the entropy of a harmonic oscillator is valid for frequencies less than 330 cm.$^{-1}$ at room temperature, or in general for $\nu < 1.1\ T$. The frequencies associated with deviation of angular alignment of reacting groups (α in Fig. 1a) are probably near or below this value unless one of the groups consists only of hydrogen atoms or the activated complex has an unusually rigid structure. The frequency associated with deviations in distance between reacting groups (r in Fig. 1b) will also be in this range if the groups are reasonably heavy. Even if the frequencies are somewhat above the limit specified above, it may be desirable to use the classical method and then make corrections for quantum effects. This has proven to be the best method of treating the carbon skeleton motions of the *n*-paraffin hydrocarbons[3] even though some frequencies are above 1000 cm.$^{-1}$. In this case the equilibrium properties were being calculated, but the methods are equally applicable to kinetic problems.

The classical form of the partition function is

$$Q = \frac{q_e A}{\sigma} \int \cdots\cdots \int e^{-V/RT}\, dx_1 \cdots\cdots dz_n \qquad (1)$$

$$A = \left(\frac{2\pi kT}{h^2}\right)^{3n/2} \prod_{i=1}^{n} m_i{}^{3/2}$$

---

(1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(2) D. R. Herschbach, H. S. Johnston, K. S. Pitzer and R. E. Powell, *J. Chem. Phys.*, **25**, 736 (1956).

(3) K. S. Pitzer, *ibid.*, **8**, 711 (1940); **14**, 239 (1946); W. B. Person and G. C. Pimentel, THIS JOURNAL, **75**, 632 (1953).