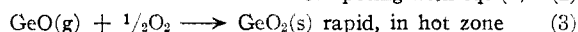
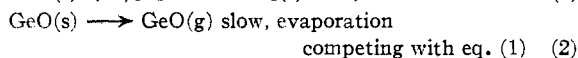
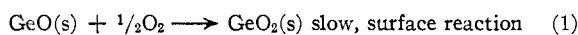


monoxide.⁶ Increasing the oxygen pressure decreases the rate of evaporation thus reducing the total amount of monoxide evaporated before the process is halted by the layer of dioxide.

The reactions to be considered are



Let $[\text{GeO}]_s$ and $[\text{GeO}_2]_s$ be the surface concentrations in moles per cm^2 of each species and Q the number of moles of oxygen consumed per cm^2 of sample. We assume that the rate of the surface reaction (1) is first order in $[\text{GeO}]_s$. Thus, $R_1 = d[\text{GeO}_2]_s/dt = k_1[\text{GeO}]_s$. The rate of evaporation is $R_2 = k_2f(p)[\text{GeO}]_s$, in which $f(p)$ is an approximately inverse pressure dependent factor. If it is

(6) Studies by Fonda (G. R. Fonda, see S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 78) on the evaporation of tungsten showed a pronounced dependence of the rate on the pressure of the argon or nitrogen added. The net rate of evaporation decreased with increasing external pressure in an approximately inverse manner.

assumed that the amount of oxygen needed to cover the sample with dioxide is negligible, the rate of consumption of oxygen is $dQ/dt = R_3 = k_2f(p) \cdot [\text{GeO}]_s = b[\text{GeO}]_s$. Since the surface is covered only by GeO and GeO_2 , then $d[\text{GeO}_2]_s = -d[\text{GeO}]_s$ and $[\text{GeO}]_s = [\text{GeO}]_s^0 e^{-k_1t}$. Thus $dQ/dt = b[\text{GeO}]_s^0 e^{-k_1t}$. When $t = 0$, $Q = 0$; so, $Q = b[\text{GeO}]_s^0 (1 - e^{-k_1t})/k_1$ or, $Q = Q_\infty (1 - e^{-kt})$.

Thus the mechanism proposed accounts for the experimentally observed facts. The exact form of the oxidation curve is derived. The weight loss of the specimens is accounted for on the basis of evaporation of the monoxide. The pressure dependence of Q_∞ originates in the pressure dependence of the evaporation rate. The temperature dependence of the parameter k arises because k is the rate constant for the conversion of the monoxide to the dioxide on the surface of the sample and would be expected to have a large temperature dependence.

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Low Temperature Thermodynamic Properties of Sodium Hydroxide¹

BY JOHN C. R. KELLY² AND PAUL E. SNYDER

The heat capacity of pure crystalline sodium hydroxide has been determined from 60 to 300°K. by use of a low-temperature adiabatic calorimeter. The sodium hydroxide used in this work was purified by mono-alcoholate formation. From the experimental data, smoothed values of the several thermodynamic functions were calculated at several temperatures. These calculations yield the value of 15.34 ± 0.1 entropy units for the entropy of this compound at 298.16°K.

Experimental

Purification of Sodium Hydroxide.—Although no satisfactory method has been reported for the preparation of pure, anhydrous sodium hydroxide, the most promising approach is the reported solubility of the compound in absolute ethyl alcohol,³ and the reported formation of a solid alcoholate which is easily decomposed at reduced pressures and slightly elevated temperatures.⁴

The starting material was Baker and Adamson special reagent grade sodium hydroxide containing approximately 1.1% H_2O and 1.2% Na_2CO_3 . One hundred gram quantities were dissolved in one liter portions of ethanol which had been dried and purified by the method of Kaufman and Dreger.⁵ This solution was transferred to a dry, CO_2 -free box wherein all further operations were performed. The solution was filtered under vacuum through a "fine" fritted glass disc in order to remove insoluble carbonates and halides. The resulting solution was pumped under mild heating conditions until a thick slurry of the mono-alcoholate was produced. This slurry was transferred to a "coarse" grade fritted glass disc and pumped free of the mother liquor. The alcoholate, appearing as white hexagonal crystals, was washed several times with purified alcohol to remove any last traces of water. The crystals were then transferred to

a filtering flask and pumped under mild heating for approximately 30 hours in order to decompose the alcoholate.

Analysis of the product by the usual methods showed that the maximum limits of Na_2CO_3 , SiO_2 and Cl^- were 0.02, 0.02 and 0.005%, respectively. The minimum assay of NaOH was 99.84%. The low silica content indicated negligible pick-up from the glass vessels used in this preparation. The final product, as placed in the calorimeter, appeared as a fine, white, crystalline powder.

Apparatus.—The calorimeter used in this work is of the adiabatic type and was constructed along the lines described by Southard and Brickwedde.⁶

The thermometer used with the calorimeter was constructed in the usual manner.⁷ A helix of 0.004 inch diameter platinum-10% rhodium wire was wound on a mica cross. The whole unit was then sealed in a platinum sheath. The thermometer was soldered in a well in the calorimeter with Woods metal. The thermometer also served as a heater during the heating periods. The potential drop across the thermometer as well as the current flowing was measured by means of a White double potentiometer with a range of 0-100,000 microvolts. To facilitate the work, the potentiometer was used as a null instrument by means of an effective fifth decade of the Lindeck-Rothe⁸ type. As a matter of fact, the sensitivity of the combined system was such that a potential could be rechecked to a few-tenths of a microvolt.

Standardization of the entire system was made in terms of a one and a ten ohm standard resistance each of which had been calibrated at the National Bureau of Standards. The standard cell used with the potentiometer likewise was calibrated at the National Bureau of Standards.

Temperature Scale.—Since the platinum-10% rhodium resistance thermometer served as the fundamental tempera-

(1) From a thesis submitted by John C. R. Kelly to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science in Chemistry. This work was performed under contract N6 ori-47, T.O. 8 between the Office of Naval Research and Carnegie Institute of Technology.

(2) Westinghouse Electric Corporation, Bloomfield, N. J.

(3) Gmelin, "Handbuch Anorg. Chem.," Vol. 21, J. Springer, Berlin, 1928, p. 121.

(4) Lescoeur, *Compt. rend.*, **121**, 889 (1895).

(5) Kaufman and Dreger, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 259.

(6) Southard and Brickwedde, *This Journal*, **55**, 4378 (1933).

(7) Meyers, *Natl. Bur. Standards J. Res.*, **9**, 807 (1932).

(8) Brooks and Spijks, *ibid.*, **9**, 781 (1932).

ture measuring instrument, it was calibrated over the range from -190 to 660° according to the recommendations for the International Temperature Scale (1948).⁹ To extend the range of the thermometer to 62°K ., the helium gas thermometer was used after the manner of Hoge and Brickwedde.¹⁰ The tie-in between the two methods of calibration was made at the normal oxygen point.

Experimental Results

Heat Capacity of NaOH.—During these measurements the calorimeter contained 29.3602 g. of NaOH which, assuming the molecular weight of NaOH to be 40.005, corresponds to 0.7339 mole. The experimental values of the molar heat capacity obtained are given in Table I in the form of values picked from the smooth curve drawn through the actual experimental values. These values are based on the "defined calorie" which is assumed to have a value of 4.1840 absolute joules.

Entropy, Heat Content and Free Energy of NaOH.—The method recommended by Kelley¹¹ was used in the extrapolation of the heat capacity data to 0°K . Graphical integration of the data in the proper form yielded the absolute entropy of NaOH as entered in Table I. The contribution to the entropy of the extrapolated part amounts to 1.16 e.u. at 60°K . Following the practice of Kelley,¹¹ an uncertainty of 5–10% is assigned to this value. For record purposes, the entropy of crystalline sodium hydroxide can be assigned the value

$$S_{298.16} = 15.3 \pm 0.1 \text{ e.u.}$$

This value compares with the value of 13.8 ± 1.5 e.u. as obtained by Shibata¹² from cell measurements.

By suitable graphical integration, the heat content function was obtained, based upon its value at

(9) Stimson, *Natl. Bur. Standards J. Res.*, **42**, 209 (1949).

(10) Hoge and Brickwedde, *ibid.*, **22**, 351 (1939).

(11) K. K. Kelley, United States Bureau of Mines Bulletin, No. 447 (1949).

(12) Shibata, *J. Chem. Soc. Japan*, **50**, 523 (1929).

0°K . By combining the entropy and heat content properly, the relative free energy function was then calculated. These two additional functions are given in Table I.

TABLE I

$T, ^\circ\text{K}$.	C_p , cal./degree/ mole	S_T , cal./degree/ mole	$(H_T^\circ - H_0^\circ)$, cal./mole	$-(F_T^\circ - F_0^\circ)$, cal./mole
60	2.075	1.16	51.6	18.2
75	4.417	1.97	106.3	41.6
100	6.877	3.61	251.1	109.4
125	8.553	5.33	447.4	221.6
150	9.870	7.01	680.8	370.5
175	10.92	8.61	940.9	566.1
200	11.76	10.13	1225	800.5
225	12.54	11.56	1529	1072
250	13.25	12.92	1821	1378
275	13.83	14.21	2190	1717
298.16	14.21	15.34	2534	2040
300	14.24	15.43	2541	2088

The several functions listed in Table I are given in four figures for possible future mathematical calculations only. The usual rounding off can then be done after calculation. By considering the deviations of the experimental heat capacities from the smoothed curve, a band of uncertainty can be drawn with the smoothed curve in the center. The area of this band is such that the maximum uncertainty at higher temperatures is approximately 1 in 500 for the entropy, 1 in 1000 for the heat content, and 1 in 200 for the free energy. At lower temperatures these would be doubled. Actually, however, it is felt that the real uncertainty will be considerably less than the above. However, because of the extrapolation below 60°K ., the uncertainty in the entropy at 298.16°K . is estimated to be about 0.1 e.u. as indicated above.

PITTSBURGH, PENNSYLVANIA RECEIVED DECEMBER 16, 1950

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Millicoulometry. II. The Purported Reduction of Nitrate at the Dropping Mercury Electrode

BY LOUIS MEITES

The waves secured on adding nitrate to weakly acidic solutions of lithium or cerium(III) chloride, which have in the past been attributed to reduction of the nitrate ion, are shown to be due to a catalytic reduction of water or hydrogen ion.

Introduction

The behavior of nitrate ion at the dropping electrode was first investigated by Tokuoka,¹ and by Tokuoka and Ruzicka,² who reported the 45° tangent potentials of the waves secured by adding nitrate to 0.1 *N* solutions of the chlorides of a number of uni-, di- and trivalent metals. These fell into three groups, depending on the charge of the cation: *i.e.*, -2.2 v. (*vs.* S.C.E.) in lithium or tetramethylammonium chloride, -1.8 v. in calcium, magnesium or strontium chloride, and -1.3 v. in lantha-

num or cerium(III) chloride. This effect was attributed to the formation of "ion pairs" in which the nitrate was in a more easily reducible condition than in the normal ion. A comparison of the diffusion currents of nitrate and cadmium ions indicated that the nitrate reduction consumed eight faradays per mole, giving ammonia as the product.

More recently it has been claimed³ that the reduction of nitrate from lanthanum or neodymium chloride solutions required seven faradays per mole, corresponding to reduction to an equimolar solution

(1) M. Tokuoka, *Collection Czechoslov. Chem. Commun.*, **4**, 444 (1932).

(2) M. Tokuoka and J. Ruzicka, *ibid.*, **6**, 339 (1934).

(3) S. I. Sinyakova and G. G. Karanovich, *Trudy Komissii Anal. Khim., Otdel. Khim. Nauk, Akad. Nauk S. S. S. R.*, [5] **2**, 65 (1949); *C. A.*, **44**, 9303 (1950).