acter of the medium is maintained by the addition of methanol and ethanol, the kinetic analog of A in equation (10) remains remarkably constant. On the other hand, when isopropanol, diethylene glycol, and particularly dioxane, are employed to produce media of very low dielectric constant, exact constancy of A is not obtained. This is to be expected since the addition of dioxane produces a greater change in specific solvent properties than does the addition of an alcohol most closely resembling water.

Differentiating equation (9) and evaluating coefficients from equation (2) yields

$$\Delta C_p = -b^2 Tc/D \qquad (11)$$

The value of ΔC_p calculated for protoacetic acid ($r = 0.70$ Å.) is -39.9, whereas the experimental value is -41.3 cal. deg.$^{-1}$ mole^{-1}.

Treating in the same manner the empirical Harned–Embree[8] equation

$$\log K_T = \log K_M - p(T - \Theta)^2 \qquad (12)$$
$$[\Delta C_p/2.3R]_{T = \Theta} = -6pT^2 + 4pT\Theta = -2p\Theta^2 \qquad (13)$$

Equating (11) and (13)

$$p = \frac{\epsilon^2}{(2.3R)rD^3} \left(\frac{\partial D}{\partial T}\right)^2 \frac{1}{2\Theta} \qquad (14)$$

Equation (14) can be shown to be correct by introducing numerical values for $T = \Theta$ and recovering the experimental value of $p \cong 4.5 \times 10^{-5}$.

Since D does not vary much for the values of $T = \Theta$ encountered for this group of acids and r proves to be almost a constant we have an explanation of why equation (12) represents the

(8) Harned and Embree, THIS JOURNAL, 56, 1050 (1934); Waldc. J. Phys. Chem., 39, 478 (1935).

facts so well with an almost universal value of p.[8]

Summary and Conclusions

1. The equation

$$\Delta H_T = \Delta H_x + c \, 1/D_T \left[1 + T \frac{\partial \ln D}{\partial T}\right]$$

represents with high precision ΔH, the heat of dissociation of deuteroacetic acid as a function of temperature, when $\Delta H_x = 2260$, and $c = 4.410 \times 10^{+5}$. The values for protoacetic acid are 2030 cal. and $4.714 \times 10^{+5}$, corresponding to (Born) r values of 0.75 and 0.70 Å., respectively.

2. ΔC_p for an acid–base exchange reaction involving deuterium and hydrogen in D_2O and in H_2O is practically zero since the radii of the ions and the dielectric properties of the two media are practically identical.

3. The difference in the heats of ionization of deutero and proto acids appears to be a function only of the characteristic temperature Θ at which the maximum value of the dissociation constants occurs.

4. The desirability of determining the temperature coefficients of dissociation constants of acids, not only in solvents of constant composition but also in solvents of constant dielectric constant, is pointed out.

5. The empirical constant $p \cong 4.5 \times 10^{-5}$ in the Harned–Embree equation is shown on theoretical grounds to be equal to

$$p = \frac{\epsilon^2}{(2.3R)rD^3} \cdot \left(\frac{\partial D}{\partial T}\right)^2 \cdot \frac{1}{2\Theta}$$

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Thermodynamics of Concentrated Aqueous Solutions of Sodium Hydroxide[1,2]

BY GÖSTA ÅKERLÖF AND GERSON KEGELES

Introduction

The thermodynamic properties of strong electrolytes in highly concentrated solutions over a large temperature range may conceivably be obtained by a number of different methods. In most cases, however, the methods applicable narrow down to a single one, the determination of the

(1) This communication contains part of the material of a dissertation to be presented by Gerson Kegeles to the Graduate School of Yale University in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1940.

(2) The tables of this paper are published with the financial assistance of the authors and of Yale University.

vapor pressure of the solution. The alkali hydroxides and hydrochloric acid belong to the few electrolytes forming exceptions to this general rule since it would appear to be possible to study their solutions using an electromotive force method. The properties of hydrochloric acid already have been studied for a considerable temperature range by Åkerlöf and Teare,[3] who used solutions up to 16 molal. Solutions of the alkali hydroxides have been the subject of a series of studies by Harned

(3) Åkerlöf and Teare, THIS JOURNAL, 59, 1855 (1937).

and co-workers,[4] but the upper limit of the concentration range covered was only 4 molal. Since there is no particular reason to suspect that either the flowing amalgam or hydrogen electrodes employed would fail at still higher concentrations it was considered worth while to attempt to extend these measurements in the case of solutions of sodium hydroxide to cover as large a concentration range as possible. As a result we have succeeded in getting accurate measurements for the concentration range 0.1–17 molal over the temperature range 0 to 70°.

Experimental Procedure.—In older set-ups for measurements of cells with flowing amalgam electrodes as a general rule so-called "droppers" were used. During the introduction of this dropper in the cell it was unavoidable to expose the surface of the solutions at least momentarily to the air. Since the initial speed with which oxygen is absorbed by an air-free solution is very high and the flowing amalgam would tend to give a rapid mixing of the surface layers of the solutions with the underlying ones, the observed electromotive force would tend to vary slightly erratically on account of the high sensitivity of the amalgam electrodes toward oxygen. Furthermore, in the case of measurements extending over a larger temperature range elaborate precautions are necessary to keep droppers at the correct temperature. Some of our electromotive force measurements showed a temperature coefficient of over one millivolt per degree, which sufficiently illustrates the necessity of precise temperature control of the amalgam.

Another possible source of error in older amalgam cell measurements should also be pointed out. For every new measurement it was as a rule also necessary or customary to make up a new reference solution. A small error in the absolute concentration of this solution would apparently be less serious than individual fluctuations of the same magnitude for the different solutions employed as reference, since what is measured is a ratio of activities. In our case we made up about 60 liters of the reference solution, stored it in a closed stainless steel tank and piped it directly from the tank into the cell, thus avoiding any possibility of variations in its concentration.

A diagrammatical sketch of the apparatus is shown in Fig. 1. The thermostat was mounted inside an angle iron frame which on top carried the tank for the reference solution and a two-liter flask for the amalgam. Under the thermostat the frame carried a shelf for receivers of used amalgam and solutions, which were blown out as needed with compressed air. Each half of the cell was provided with an individual receiver in order to eliminate any possibility of internal electrical leakage during the measurements. To prevent freezing of the stopcocks by the hydroxide solutions when unused for some time a number of them were provided with plugs of stainless steel, bored obliquely. All tubing used was made of Pyrex glass, but

(4) Harned, THIS JOURNAL, **47**, 676 (1925); Harned and Swindells, *ibid.*, **48**, 126. (1926); Harned and Hecker, *ibid.*, **55**, 4838 (1933); Harned and Cook, *ibid.*, **59**, 496 (1937); see also Knobel, *ibid.*, **45**, 70 (1923).
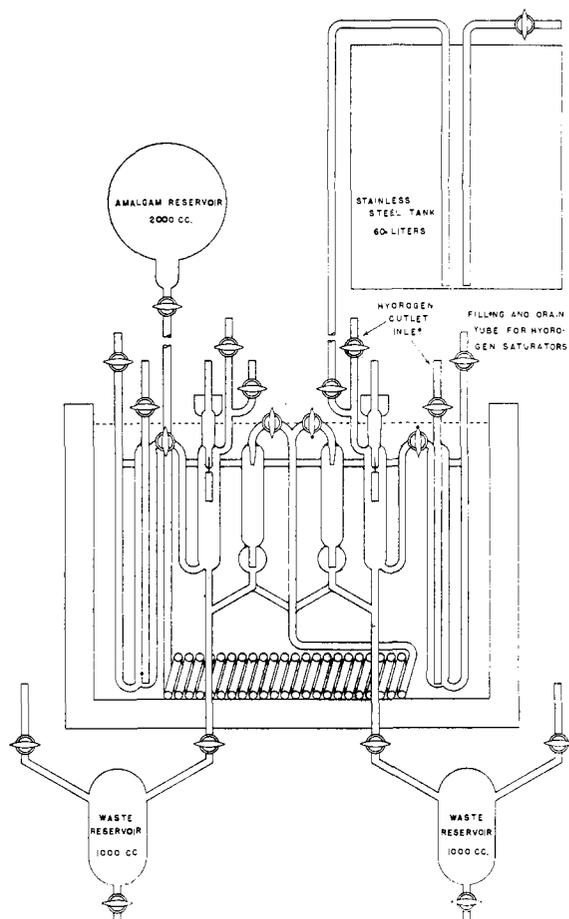
Fig. 1.—Diagrammatical sketch of apparatus used.

all parts of the cell had been left filled with concentrated sodium hydroxide solution for over a month and then carefully washed out with boiling hot solution and pure water before any of the final measurements were made. Errors due to subsequently dissolved silica should be negligible as already clearly shown by us in a previous paper.[5]

In setting up the cells all the usual precautions with regard to testing for leaks and pinholes were carefully observed and repeated several times during the course of the measurements due to the constant danger of cracks that might have developed, since it was impossible to relieve the cells entirely from small mechanical stresses. The design adopted proved, however, to be sufficiently strong and no cracks were found at any time. Due to the precautions taken and the absence of electrical leaks it was also found possible to extend our measurements up to 70°. A few measurements at 80° were, however, fairly erratic and the data for 70° have probably somewhat larger errors than those for lower temperatures.

The amalgam flowed from the reservoir through a heavy capillary down to the bottom of the thermostat, where it entered a long glass spiral to acquire the correct temperature. The exit tube from the glass spiral carried the amalgam upward and led it through two all-glass stopcocks

(5) Åkerlöf and Kegeles, *ibid.*, **61** 1027 (1939).

into the two halves of the cell. The entrance tubes had a bore of about 0.5 mm. and their tips were properly drawn out and adjusted before the tubes were sealed in. The hydrogen electrodes were made as usual of platinum foil covered with platinum black deposited from a strongly acidified solution of platinum chloride using a current of about 0.5 ampere for two minutes.

As already mentioned the reference solution was stored in a stainless steel tank. The tank was first, after proper cleaning, filled with distilled water and then a steady stream of oxygen-free hydrogen was bubbled through the water continuously over a period of about one week. With the gas still streaming, the calculated amount of the standard concentrated sodium hydroxide solution, prepared as previously described,[5] was added so as to give a 0.1 molal solution. Since the tank could not be moved the hydrogen bubbling was continued for four to five days after the hydroxide had been added to ensure uniform concentration of the solution throughout the tank. The reference solution was afterward always kept under a small excess gas pressure to prevent any possibility of air contamination. At various times during the course of the measurements, samples were taken and analyzed gravimetrically by neutralizing with hydrochloric acid and weighing the residue after light ignition. The different analyses all agreed to about one part in 5000 and gave as a general average 0.10166 as the molality of the reference solution. The hydroxide solution to be measured was prepared by diluting in a nitrogen atmosphere the standard concentrated solution, which was available in sufficient quantity (18 liters) to last for all our measurements without change. The diluting apparatus was the same as the one previously employed by Åkerlöf and Teare for the study of the thermodynamics of hydrochloric acid. The finished solutions were analyzed in triplicate in the same manner as already indicated for the analysis of the reference solution.

The electromotive force of the cells was measured with a Leeds and Northrup type K potentiometer. The working standard cells were thermostated and at frequent intervals checked against the laboratory primary standard set certified by the Bureau of Standards and permanently kept immersed in oil at 30.00°. The temperature of the cell thermostat was controlled by a mercury thermoregulator having a sensitivity of about 0.02°. The solid stem thermometer employed had previously been calibrated against a Bureau of Standards certified platinum resistance thermometer using a Mueller resistance bridge.

The cells were filled with the reference and the measuring solutions after they had been cleaned with hot hydroxide solution, thoroughly rinsed with warm distilled water and finally dried while evacuated. In all cases the cells were allowed to come to equilibrium over a period of at least twelve to fourteen hours. At increasingly higher concentrations of the measuring solution it was found, however, that longer and longer time was needed for the hydrogen electrodes to come to equilibrium. Above 14–15 molal extremely rigid exclusion of air contamination shortened the time needed to attain equilibrium and get reproducible results very appreciably but for solutions with a hydroxide concentration above 18 molal even after over a week's time definite end-points could not be obtained

although the solutions had been swept and saturated with hydrogen for several hours before they were introduced into the highly evacuated cells.

Preliminary Treatment of the Experimental Results.—Since it would have been very difficult and time consuming to adjust the thermoregulator for each new measurement to an exact temperature, the electromotive force values observed were first corrected linearly to round temperatures. The corrections needed were always very small and seldom exceeded 0.1 millivolt. Next in order to be considered are corrections due to changes in atmospheric pressure and the vapor pressure of the solutions. The cell measured has the following composition

$$\text{Pt,H}_2/\text{NaOH } (m_1)/\text{Na}_x\text{Hg}/\text{NaOH } (m_2)/\text{H}_2,\text{Pt}$$

where m_1 and m_2 represent the concentrations of the sodium hydroxide. The electromotive force E of the cell is given by the equation

$$E = \frac{RT}{F} \ln \frac{a_{\text{NaOH}(m_1)} a_{\text{H}_2\text{O}(m_2)} a_{\text{H}_2(m_1)}^{\frac{1}{2}}}{a_{\text{NaOH}(m_2)} a_{\text{H}_2\text{O}(m_1)} a_{\text{H}_2(m_2)}^{\frac{1}{2}}} \quad (1a)$$

where a denotes the thermodynamic activity of the species indicated. R, T and F have their usual significance. Differentiating with respect to pressure we obtain

$$\frac{\partial E}{\partial P} = \frac{1}{F} \left[(\bar{v}_{2(m_1)} - \bar{v}_{2(m_2)}) - (\bar{v}_{1(m_1)} - \bar{v}_{1(m_2)}) \right] + \frac{1}{2F} \left[(v_{\text{H}_2(m_1)} - v_{\text{H}_2(m_2)}) \right] \quad (2a)$$

where $\bar{v}_1$ and $\bar{v}_2$ represent the partial molal volumes of solvent and hydroxide, respectively. Since $v_{\text{H}_2} = RT/p_{\text{H}_2}$ and $p_{\text{H}_2} = P - p$, where P is the atmospheric and p the vapor pressure of the solution, equation (2a) takes the form

$$\frac{\partial E}{\partial P} = \frac{1}{F} \left[(\bar{v}_{2(m_1)} - \bar{v}_{2(m_2)}) - (\bar{v}_{1(m_1)} - \bar{v}_{1(m_2)}) \right] + \frac{RT}{2F} \left[\frac{1}{P - p_{(m_1)}} - \frac{1}{P - p_{(m_2)}} \right] \quad (2b)$$

Neglecting compressibilities and integrating between P and $P + \Delta P$, the atmospheric pressure correction would thus be given by the equation

$$\Delta E_p = \frac{1}{F} \left[(\bar{v}_{2(m_1)} - \bar{v}_{2(m_2)}) - (\bar{v}_{1(m_1)} - \bar{v}_{1(m_2)}) \right] \Delta P + \frac{RT}{2F} \ln \frac{(P - p_{(m_1)} + \Delta P)(P - p_{(m_2)})}{(P - p_{(m_2)} + \Delta P)(P - p_{(m_1)})} \quad (2c)$$

Using the values for $\bar{v}_1$ and $\bar{v}_2$ calculated from the density measurements of Åkerlöf and Kegeles,[5] it has been found that equation (2c) gives values for ΔE_p which even for unusually large variations of the atmospheric pressure are negligible. For a pressure change of 10 millimeters the order of magnitude of the first term is 10^{-7} and of the second 10^{-5} volt.

As already indicated the next correction to be considered is due to the vapor pressure of the solutions. To evaluate this correction we may write equation (2a) in the form

$$dE = \frac{1}{F} \left[(\bar{v}_{2(m_1)} - \bar{v}_{1(m_1)} + \tfrac{1}{2} v_{H_2(m_1)}) \, dP_{(m_1)} - \right.$$
$$\left. (\bar{v}_{2(m_2)} - \bar{v}_{1(m_2)} + \tfrac{1}{2} v_{H_2(m_2)}) \, dP_{(m_2)} \right] \quad (2a')$$

Neglecting the partial molal volume terms which in the worst case amount to 10^{-6} volt and using the ideal gas law for v_{H_2}, we may correct the electromotive forces measured to 760 mm. partial hydrogen pressure in each half cell by adding the following correction term

$$\Delta E_p =$$
$$\frac{RT}{2F} \left[\int_{P=P}^{760+p_{(m_1)}} \frac{dP}{P-p_{(m_1)}} - \int_{P=P}^{760+p_{(m_2)}} \frac{dP}{P-p_{(m_2)}} \right] =$$
$$\frac{RT}{2F} \ln \frac{P - p_{(m_2)}}{P - p_{(m_1)}} \approx \frac{RT}{2F} \ln \frac{760 - p_{(m_2)}}{760 - p_{(m_1)}} \quad (3)$$

To compute the value of this correction the measurements given in the literature[6] for the vapor pressure of sodium hydroxide solutions were plotted logarithmically and interpolated with respect to both temperature and concentration. Table I gives a summary of the values for log p thus obtained. As will be shown in the following, the data in Table I agree on the whole surprisingly well with the values calculated from our electromotive force measurements. The vapor pres-

TABLE I

VALUES FOR THE LOGARITHM OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AS INTERPOLATED FROM DATA IN THE LITERATURE

m	0°	10°	20°	30°	40°	50°	60°	70°
0	0.661	0.964	1.244	1.503	1.743	1.966	2.174	2.369
1	.651	.953	1.233	1.491	1.731	1.953	2.160	2.354
2	.637	.938	1.218	1.475	1.715	1.936	2.143	2.337
3	.616	.918	1.198	1.456	1.696	1.918	2.125	2.319
4	.590	.893	1.174	1.433	1.674	1.897	2.104	2.299
5	.560	.864	1.146	1.406	1.648	1.872	2.079	2.275
6	.525	.830	1.113	1.374	1.617	1.842	2.050	2.247
7	.484	.791	1.076	1.339	1.581	1.810	2.019	2.217
8	.437	.746	1.033	1.298	1.537	1.764	1.983	2.182
9	.384	.696	0.986	1.250	1.489	1.716	1.944	2.144
10	.322	.638	0.937	1.200	1.439	1.667	1.899	2.104
11	.258	.579	0.886	1.148	1.389	1.618	1.849	2.062
12	.188	.520	0.834	1.096	1.339	1.569	1.796	2.020
13	.118	.461	0.781	1.044	1.290	1.521	1.750	1.978
14	+ .051	.403	0.727	0.992	1.241	1.474	1.706	1.935
15	− .016	.345	0.673	0.940	1.192	1.428	1.662	1.892
16	− .083	.287	0.619	0.888	1.143	1.382	1.618	1.849
17	− .150	.229	0.565	0.836	1.094	1.336	1.573	1.807

(6) Dieterici, *Ann. Physik*, **42**, 513 (1891); *ibid.*, **50**, 47 (1893); *ibid.*, **62**, 616 (1897); *ibid.*, **67**, 859 (1899); Muralt, Diss. Zürich Techn. Hochsch.; Paranjpe, *J. Indian Inst. Sci.*, **2**, 59 (1918); Tammann, *St. Petersb., Ac. Sci. Mem.*, **35**, No. 9 (1887); Stock and Selig, *Ber.*, **52**, 678 (1919); Fricke, *Z. Elektrochem.*, **35**, 633 (1929); Baker and Waite, *Chem. Met. Eng.*, **25**, 1137 (1921); Hayward and Perman, *Trans. Faraday Soc.*, **27**, 59 and 66 (1931); Jänecke, *Z. anorg. Chem.*, **188**, 72 (1930); Shibata, *J. Sci. Hiroshima Univ.*, (A). **1**, 215 (1931); see also Monrad and Badger, *Ind. Eng. Chem.*, **21**, 42 (1929); Adams and Richards, *ibid.*, **20**, 470 (1928).

sure of the reference solution was computed using Raoult's law assuming that sodium hydroxide in 0.1 molal solution has an activity coefficient of 0.77 at all temperatures. The value of ΔE_p increases with temperature and concentration and reaches 4.0 millivolts at 70° and 17 molal. Table II gives a summary of the observed electromotive forces as corrected according to equation (3) and least squared at each concentration with respect to temperature using a second order equation.

The Calculation of the Water Transfer Potential.—Using mean ion activities for the electrolyte the expression for the observed electromotive force corrected to 760 mm. partial hydrogen pressure in each half cell takes according to equation (1a) the form

$$E = \frac{2RT}{F} \ln \frac{a_{NaOH(m_1)} a_{H_2O(m_2)}^{\frac{1}{2}}}{a_{NaOH(m_2)} a_{H_2O(m_1)}^{\frac{1}{2}}} \quad (1b)$$

The activity of the solvent is related to the activity of the solute according to the Gibbs–Duhem equation

$$d \ln a_{NaOH} = - 55.507/m \, d \ln a_{H_2O} \quad (4)$$

Differentiating (1b) at constant temperature and pressure regarding m_1 as a variable while keeping m_2 constant as reference concentration and introducing equation (4), gives

$$dE = - \frac{RT}{F} (55.507/m + 1) \, d \ln a_{H_2O} \quad (5)$$

Rearrangement and integration of equation (5) from $m = m_2$ to $m = m_1$ results then in the following expression for the water transfer potential E_{H_2O}

$$E_{H_2O} = - \frac{RT}{F} \ln \frac{a_{H_2O(m_1)}}{a_{H_2O(m_2)}} = \int_{m_2}^{m_1} \frac{m}{55.507 + m} \left(\frac{dE}{dm} \right) dm$$
$$(6a)$$

To obtain the coefficients dE/dm needed for the application of equation (6a), the data of Table II were plotted and least squared at each temperature with respect to m. It was found necessary, due to the shape of the E vs. m curves, to separate the least squaring into two ranges, one from 0.1 to 4 and the other from 4 to 17 molal. In the lower range it was found that E was adequately expressed by the formula

$$E = a \log m/0.10166 + b(m - 0.10166) +$$
$$c(m - 0.10166)^2 \quad (6b)$$

where 0.10166 is the reference concentration. In the upper range E was computed from a somewhat simpler equation

$$E = A + Bm + Cm^2 \quad (6c)$$

<div align="center">

TABLE II

CORRECTED ELECTROMOTIVE FORCE DATA, LEAST SQUARED WITH RESPECT TO TEMPERATURE

</div>

m	0°	10°	20°	30°	40°	50°	60°	70°
0.2505	0.03935	0.04065	0.04194	0.04324	0.04453	0.04583	0.04712	0.04842
.3523	.05310	.05543	.05754	.05945	.06113	.06258	.06382	.06485
.5058	.06928	.07194	.07449	.07693	.07926	.08148	.08359	.08560
.7562	.08757	.09120	.09465	.09792	.10102	.10394	.10669	.10926
1.0045	.10068	.10491	.10891	.11269	.11624	.11957	.12266	.12542
1.4191	.11689	.12230	.12729	.13186	.13600	.13973	.14304	.14592
1.8718	.13168	.13756	.14307	.14822	.15301	.15743	.16149	.16519
2.6601	.15239	.15925	.16559	.17139	.17666	.18140	.18562	.18930
3.3234	.16812	.17532	.18197	.18803	.19353	.19845	.20282	.20660
4.0484	.18396	.19166	.19882	.20545	.21154	.21708	.22210	.22657
5.0239	.20523	.21308	.22030	.22689	.23284	.23815	.24284	.24689
6.0351	.22729	.23484	.24183	.24825	.25411	.25941	.26415	.26833
7.0449	.24903	.25666	.26369	.27013	.27597	.28120	.28585	.28989
8.0963	.27075	.27846	.28544	.29169	.29722	.30202	.30610	.30945
9.3814	.30140	.30822	.31440	.31992	.32480	.32902	.33260	.33552
10.0434	.31362	.32131	.32800	.33367	.33832	.34197	.34460	.34623
11.0200	.33248	.34141	.34879	.35461	.35887	.36158	.36273	.36233
11.0524	.33335	.34195	.34911	.35484	.35913	.36197	.36339	.36336
12.1980	.35787	.36426	.36957	.37379	.37693	.37899	.37997	.37987
13.2982	.37659	.38445	.39089	.39590	.39949	.40166	.40241	.40174
13.9845	.38761	.39500	.40084	.40514	.40790	.40911	.40878	.40690
15.0087	.40695	.41344	.41831	.42156	.42319	.42320	.42159	.41836
16.4405	.43221	.43845	.44317	.44635	.44801	.44813	.44673	.44379
16.8395	.43885	.44583	.45117	.45488	.45695	.45737	.45617	.45332

<div align="center">

TABLE III

WATER TRANSFER POTENTIALS

</div>

m	0°	10°	20°	30°	40°	50°	60°	70°
0.2505	0.00011	0.00011	0.00011	0.00011	0.00011	0.00011	0.00011	0.00011
.3523	.00019	.00019	.00019	.00019	.00019	.00018	.00018	.00018
.5058	.00030	.00030	.00030	.00029	.00029	.00029	.00028	.00028
.7562	.00050	.00050	.00050	.00049	.00048	.00047	.00046	.00044
1.0045	.00069	.00069	.00068	.00067	.00066	.00065	.00064	.00062
1.4191	.00103	.00103	.00102	.00101	.00099	.00097	.00094	.00091
1.8718	.00141	.00140	.00139	.00137	.00134	.00131	.00128	.00125
2.6601	.00212	.00211	.00209	.00206	.00203	.00199	.00192	.00188
3.3234	.00279	.00277	.00275	.00272	.00268	.00263	.00256	.00247
4.0484	.00364	.00362	.00359	.00355	.00349	.00342	.00333	.00321
5.0239	.00507	.00504	.00500	.00494	.00486	.00476	.00466	.00448
6.0351	.00720	.00715	.00709	.00700	.00689	.00675	.00658	.00634
7.0449	.00958	.00956	.00947	.00937	.00921	.00900	.00875	.00845
8.0963	.01231	.01227	.01216	.01203	.01182	.01155	.01121	.01082
9.3814	.01594	.01590	.01575	.01558	.01530	.01494	.01450	.01398
10.0434	.01795	.01790	.01772	.01754	.01722	.01681	.01630	.01572
11.0200	.02107	.02102	.02087	.02060	.02021	.01970	.01909	.01838
11.0524	.02118	.02113	.02098	.02071	.02031	.01982	.01922	.01851
12.1980	.02468	.02461	.02436	.02408	.02362	.02302	.02231	.02147
13.2982	.02885	.02877	.02847	.02815	.02761	.02691	.02607	.02507
13.9845	.03140	.03131	.03099	.03063	.03004	.02928	.02835	.02724
15.0087	.03515	.03305	.03469	.03428	.03360	.03274	.03167	.03041
16.4405	.04058	.04047	.04005	.03956	.03875	.03773	.03647	.03499
16.8395	.04215	.04203	.04158	.04107	.04024	.03916	.03784	.03630

The constants obtained for equations (6b) and (6c) were then least squared as a function of temperature. Introduction of (6b) and (6c) into (6a) and integration leads to the following expressions:

A. For the lower concentration range 0.1 to 4 molal

$$E_{H_2O} = [a - 2.303 \cdot 55.507b - 4.605 \cdot 55.507(55.507 + 0.10166)c] \log \frac{55.507 + m}{55.507 + 0.10166} + [b - 2(0.10166 +$$

$2\cdot55.507)c](m - 0.10166) - c[(55.507 + m)^2 -$
$$(55.507 + 0.10166)^2]\quad(6d)$$

B. For the upper concentration range 4 to 17 molal

$E_{H_2O} = 2.303\cdot55.507(-B + 2\cdot55.507C)$ log
$$\frac{55.507 + m}{55.507 + 0.10166} + (B - 4\cdot55.507C)(m - 0.10166) +$$
$$C[(55.507 + m)^2 - (55.507 + 0.10166)^2]\quad(6e)$$

From equations (6d) and (6e) values of E_{H_2O} were calculated at the concentrations and temperatures given in Table II. These values were then cross-plotted with an accuracy of 0.01 millivolt. A summary of the interpolated values appears in Table III. Still better values could be obtained by a second approximation using smoothed values for the activity coefficient of the solute and the activity of the solvent. However, the experimental accuracy does not justify such a refinement. Subtraction of the data in Table III from the corresponding ones in Table II gives the sodium hydroxide transfer potential

$$E_{NaOH} = \frac{2RT}{F}\ln\frac{a_m}{a_{ref.}} = \frac{2RT}{F}\ln\frac{\gamma_m m}{\gamma_{ref.}m_{ref.}}\quad(7)$$

where γ represents the mean ion activity coefficient of sodium hydroxide.

Equations for the Activity Coefficient of Sodium Hydroxide.—The formal equation employed for this purpose was identical with the one used by Åkerlöf and Teare for hydrochloric acid solutions

$$\log\gamma = -\frac{u\sqrt{m}}{1 + \sqrt{2m}} + Bm + Cm^2 + Dm^3 + Em^4\quad(8)$$

where u is the universal constant of the limiting law, B, C, D and E are empirical constants. In the case of the acid these constants were found to vary linearly with the temperature. In the case of sodium hydroxide, however, the data indicated a more complicated behavior. Therefore the observed values for log $\gamma_m/\gamma_{ref.}$ in the concentration range 0.1 to 12.2 molal were least squared according to the equation

$$y = \log\frac{\gamma_m}{\gamma_{ref.}} + u\alpha = B(m - 0.10166) + C(m^2 - 0.10166^2) +$$
$$D(m^3 - 0.10166^3) + E(m^4 - 0.10166^4)\quad(9a)$$

where α is given by the formula

$$\alpha = \frac{\sqrt{m}}{1 + \sqrt{2m}} - \frac{\sqrt{0.10166}}{1 + \sqrt{2\cdot0.10166}}$$

We thus obtain for the normal equations the expressions

$\Sigma y(m - 0.10166) = B\Sigma(m - 0.10166)^2 + C\Sigma(m -$

$0.10166)(m^2 - 0.10166^2) + D\Sigma(m - 0.10166)(m^3 -$
$$0.10166^3) + E\Sigma(m - 0.10166)(m^4 - 0.10166^4)\quad(9b)$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\quad(9c)$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\quad(9d)$$
$\Sigma y(m^4 - 0.10166^4) = B\Sigma(m^4 - 0.10166^4)(m - 0.10166) +$
$C\Sigma(m^4 - 0.10166^4)(m^2 - 0.10166^2) + D\Sigma(m^4 - 0.10166^4)$
$$(m^3 - 0.10166^3) + E\Sigma(m^4 - 0.10166^4)^2\quad(9e)$$

The values for B, C, D and E calculated using equations (9b, c, d and e) were found to give curves very nearly having the form of symmetrical parabolas when plotted against the temperature. These constants were accordingly least squared assuming a second order equation in the following manner. The least squared values of B which were computed first were re-introduced in the normal equations and a new set of C values was obtained. The least squared new values for C changed the D values again a little and after they also had been treated the final values of E were calculated and least squared. A summary of the

TABLE IV

CONSTANTS USED FOR THE CALCULATION OF THE ACTIVITY COEFFICIENT OF THE SOLUTE IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

Part I. Constants for the concentration range 0 to 12 molal

$B = 0.006519 + 0.0015995\,t - 0.000018327\,t^2$
$C = 0.013713 - 0.00050071\,t + 0.0000056385\,t^2$
$D = 0.0005994 + 0.000050215\,t - 0.00000064754\,t^2$
$E = 0.00000596 - 0.0000018056\,t + 0.000000024073\,t^2$

Values of constants B, C, D and E at 10° intervals

Temp.	B	C	D	E
0°	0.006519	0.013713	−0.0005994	0.00000596
10	.021681	.009270	− .0001620	− .00000969
20	.031178	.005954	.0001459	− .00002052
30	.038010	.003767	.0003243	− .00002654
40	.041176	.002707	.0003731	− .00002774
50	.040676	.002773	.0002925	− .00002414
60	.036512	.003969	.0000824	− .00001572
70	.028682	.006292	− .0002573	− .00000247

Part II. Constants for the concentration range above 12 molal

$a = -0.32747 + 0.0030936\,t - 0.000032946\,t^2$
$b = 0.09880 - 0.000586\,t$
$c = -0.000002139 - 0.0000003927\,t + 0.000000005268\,t^2$

Values of constants a, b, c and u at 10° intervals

Temp.	a	b	c	u
0°	−0.32747	0.09880	−0.00000214	0.487
10	.29982	.09294	.00000554	.494
20	.27878	.08708	.00000789	.502
30	.26431	.08122	.00000918	.511
40	.25644	.07536	.00000942	.522
50	.25516	.06950	.00000861	.534
60	.26046	.06364	.00000674	.549
70	.27236	.05778	.00000382	.565
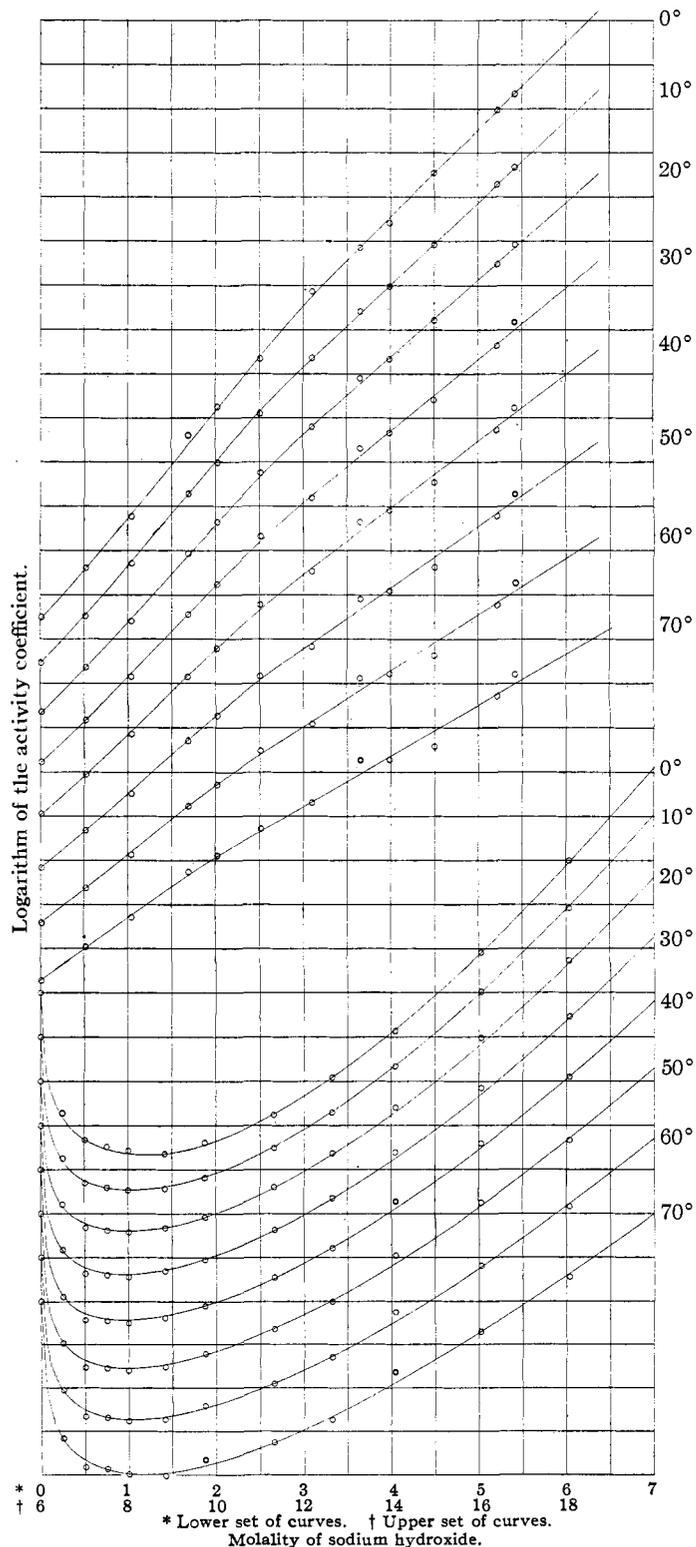
Fig. 2.—Isotherms for the logarithm of the activity coefficient of sodium hydroxide. The curves for the concentration range 6 to 17 molal are plotted on half the scale of those for the range 0 to 7 molal. Ordinates are shifted successively to avoid interference of the different curves.

constants obtained is given in Part I of Table IV. It is interesting to note that while the temperature variation of all the constants is given by parabolas, the corresponding values for B and C give when plotted against each other a practically straight line.

Equations for the activity coefficient of sodium hydroxide at concentrations above 12 molal were obtained by least squaring the observed values according to second order equations. Part II of Table IV summarizes the result. The purpose of dividing up our data in two groups, one for solutions with concentrations lower and the other one higher than 12 molal, was that this possibly would give us an indication whether the curves for the activity coefficient show a break at the concentrations where the corresponding curves for the apparent partial molal volume of the hydroxide appear to have one. As shown graphically in Fig. 2 the observed values for log γ do not have sufficient accuracy to give any definite indication of the presence of similar breaks. Due to thermodynamical reasons we know that breaks, if present, must be very faint and require an unusually high degree of accuracy in the experimental data for their detection.

Using the constants given in Table IV the value of the logarithm of the activity coefficient of sodium hydroxide has been calculated at a series of round concentrations. Table V contains the computed values. They agree quite well with those of Harned at 25° but differ particularly at higher concentrations appreciably from those of Harned and Hecker. On the other hand, our observed and calculated values agree very closely at concentrations up to 10 molal with an average difference of less than 0.2 millivolt in the corresponding electromotive force values.

Activity and Vapor Pressure of the Solvent.—The activity of the solvent may be computed most simply from the values of E_{H_2O} given in Table III but more accurate values for the concentration range 0.1 to 12 molal are ob-

TABLE V

CALCULATED VALUES FOR THE LOGARITHM OF THE ACTIVITY COEFFICIENT OF THE SOLUTE IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	−0.1056	−0.1056	−0.1065	−0.1079	−0.1100	−0.1126	−0.1163	−0.1205
.2	− .1316	− .1306	− .1311	− .1322	− .1347	− .1381	− .1429	− .1488
.4	− .1578	− .1547	− .1541	− .1548	− .1574	− .1616	− .1681	− .1762
.6	− .1713	− .1663	− .1648	− .1646	− .1672	− .1719	− .1797	− .1895
.8	− .1786	− .1720	− .1694	− .1688	− .1713	− .1765	− .1851	− .1963
1.0	− .1821	− .1738	− .1706	− .1696	− .1719	− .1774	− .1868	− .1993
1.5	− .1823	− .1684	− .1644	− .1626	− .1649	− .1713	− .1822	− .1970
2	− .1664	− .1539	− .1495	− .1475	− .1503	− .1573	− .1695	− .1858
3	− .1172	− .1048	− .1028	− .1020	− .1063	− .1152	− .1296	− .1482
4	− .0458	− .0360	− .0382	− .0406	− .0479	− .0594	− .0760	− .0969
5	+ .0426	+ .0484	+ .0405	+ .0337	+ .0225	+ .0073	− .0126	− .0365
6	+ .1438	+ .1451	+ .1309	+ .1189	+ .1028	+ .0828	+ .0582	+ .0298
7	.2545	.2514	.2305	.2131	.1909	.1649	.1344	.0996
8	.3718	.3646	.3372	.3134	.2847	.2517	.2133	.1708
9	.4929	.4816	.4475	.4171	.3812	.3399	.2930	.2407
10	.6153	.5994	.5578	.5204	.4765	.4266	.3699	.3075
11	.7367	.7148	.6646	.6191	.5667	.5076	.4413	.3688
12	.8547	.8242	.7633	.7085	.6469	.5786	.5036	.4226
13	.9565	.9075	.8519	.7900	.7216	.6469	.5657	.4781
14	1.0553	1.0003	.9388	.8710	.7967	.7161	.6292	.5358
15	1.1540	1.0930	1.0256	.9519	.8718	.7854	.6926	.5935
16	1.2528	1.1858	1.1125	1.0329	.9469	.8546	.7560	.6511
17	1.3515	1.2786	1.1993	1.1138	1.0220	.9238	.8195	.7088

tained by using the equation

$$\log a_1 = -\frac{2m}{2.303 \cdot 55.51} + \frac{u}{55.51\sqrt{2}}\left[(1 + \sqrt{2m}) - 2\ln(1 + \sqrt{2m}) - \frac{1}{1 + \sqrt{2m}}\right] - \frac{2}{55.51}(Bm^2/2 + 2Cm^3/3 + 3Dm^4/4 + 4Em^5/5) \quad (10)$$

At concentrations above 12 molal $\log a_1$ may be obtained in the following manner

$$\log a_1 = -\frac{2m}{2.303 \cdot 55.51} - \frac{2}{55.51}\int_0^m m\, d\log\gamma \quad (11)$$

Above 12 molal the value of $\log\gamma$ is given by a second order equation, which when introduced in (11) results in the expression

$$\log a_{1(m>12)} = \log a_{1.} - \frac{2(m-12)}{2.303\cdot 55.51} - \frac{2}{55.51}\int_{12}^m m(b + 2cm)dm \quad (12)$$

where b and c are empirical constants given in Part II of Table IV. The last term of equation (12) when integrated gives the formula

$$-\frac{2}{55.51}\int_{12}^m m(b + 2cm)\,dm = -\frac{(m^2 - 144)b}{55.51} - \frac{4(m^3 - 1728)c}{3\cdot 55.51}$$

The vapor pressure of the solutions may finally be calculated from the simple relation

$$\log p_m = \log a_1 p_0$$

where p_0 is the vapor pressure of the pure solvent.

The result of the calculation of solvent activity and vapor pressure is summarized in Tables VI and VII. A comparison between the data in Tables I and VII shows the good agreement obtained between experimentally observed values and those computed from our electromotive force measurements. However, even though this is the case, the accuracy of the vapor pressure data is far too low to allow their use for the reverse procedure, the calculation of the thermodynamic properties of the solute. In Fig. 3 the variation of $\log a_1$ with the hydroxide concentration is shown graphically. The different isotherms are quite similar to the corresponding ones for hydrochloric acid but their curvature and dispersion is considerably larger. The direct measurements of Shibata and Murata[6a] of $\log a_1$ give values which agree very closely with ours at 20 and 30° over the entire concentration range.

Relative Partial Molal Free Energy of Solute and Solvent.—These quantities which we will need for the calculation of the entropy changes may be computed from the equations

$$\overline{F}_2 - \overline{F}_2{}^\circ = 2RT\,2.303\log\gamma m \quad (13)$$
$$\overline{F}_1 - \overline{F}_1{}^\circ = RT\,2.303\log a_1 \quad (14)$$

The calculated values are collected in Tables VIII and IX.

(6a) Shibata and Murata. J. Chem. Soc. Japan, 52, 393 (1931).

TABLE VI

CALCULATED VALUES FOR THE LOGARITHM OF THE ACTIVITY OF THE SOLVENT IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE. *All Values Negative*

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015
.2	.0029	.0029	.0028	.0028	.0028	.0028	.0028	.0028
.4	.0057	.0058	.0058	.0058	.0058	.0058	.0058	.0058
.6	.0086	.0086	.0087	.0087	.0088	.0088	.0086	.0086
.8	.0116	.0116	.0118	.0118	.0117	.0117	.0116	.0115
1.0	.0145	.0147	.0148	.0149	.0148	.0148	.0147	.0146
1.5	.0226	.0230	.0230	.0230	.0231	.0229	.0228	.0226
2	.0312	.0316	.0317	.0317	.0319	.0316	.0314	.0311
3	.0514	.0516	.0517	.0516	.0515	.0511	.0507	.0502
4	.0762	.0761	.0756	.0751	.0746	.0739	.0731	.0723
5	.1061	.1055	.1040	.1027	.1015	.1002	.0990	.0978
6	.1419	.1403	.1375	.1355	.1332	.1310	.1289	.1265
7	.1834	.1809	.1766	.1730	.1695	.1659	.1622	.1585
8	.2309	.2272	.2210	.2158	.2106	.2050	.1993	.1935
9	.2834	.2786	.2705	.2633	.2556	.2478	.2392	.2306
10	.3411	.3347	.3238	.3143	.3039	.2929	.2814	.2691
11	.4026	.3939	.3799	.3672	.3537	.3392	.3240	.3078
12	.4672	.4548	.4365	.4199	.4026	.3844	.3655	.3458
13	.5273	.5122	.4912	.4720	.4520	.4312	.4097	.3874
14	.5910	.5731	.5492	.5271	.5043	.4806	.4562	.4311
15	.6582	.6371	.6102	.5849	.5591	.5324	.5050	.4768
16	.7290	.7046	.6744	.6459	.6168	.5867	.5561	.5248
17	.8033	.7754	.7416	.7096	.6770	.6435	.6094	.5746

TABLE VII

CALCULATED VALUES FOR THE LOGARITHM OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	0.6593	0.9627	1.2424	1.5013	1.7414	1.9647	2.1728	2.3672
.2	.6579	.9613	1.2411	1.5000	1.7401	1.9634	2.1715	2.3659
.4	.6551	.9584	1.2381	1.4970	1.7371	1.9604	2.1685	2.3629
.6	.6522	.9555	1.2352	1.4941	1.7341	1.9574	2.1657	2.3601
.8	.6492	.9524	1.2321	1.4911	1.7312	1.9545	2.1627	2.3572
1.0	.6463	.9494	1.2291	1.4879	1.7281	1.9514	2.1596	2.3541
1.5	.6382	.9412	1.2209	1.4798	1.7198	1.9433	2.1515	2.3461
2	.6296	.9326	1.2122	1.4711	1.7110	1.9346	2.1429	2.3376
3	.6094	.9126	1.1922	1.4512	1.6914	1.9151	2.1236	2.3185
4	.5846	.8881	1.1683	1.4277	1.6683	1.8923	2.1012	2.2964
5	.5547	.8587	1.1399	1.4001	1.6414	1.8660	2.0753	2.2709
6	.5189	.8239	1.1064	1.3673	1.6097	1.8352	2.0454	2.2422
7	.4774	.7833	1.0673	1.3298	1.5734	1.8003	2.0121	2.2102
8	.4299	.7370	1.0229	1.2870	1.5323	1.7612	1.9750	2.1752
9	.3774	.6856	0.9734	1.2395	1.4873	1.7184	1.9351	2.1381
10	.3197	.6295	.9201	1.1885	1.4390	1.6733	1.8929	2.0996
11	.2582	.5703	.8640	1.1356	1.3892	1.6270	1.8503	2.0609
12	.1936	.5094	.8074	1.0829	1.3403	1.5818	1.8088	2.0229
13	.1335	.4520	.7527	1.0308	1.2909	1.5350	1.7646	1.9813
14	.0698	.3911	.6947	0.9757	1.2386	1.4856	1.7181	1.9376
15	.0026	.3271	.6337	.9179	1.1838	1.4338	1.6693	1.8919
16	− .0682	.2596	.5695	.8569	1.1261	1.3795	1.6182	1.8439
17	− .1425	.1888	.5023	.7932	1.0659	1.3227	1.5649	1.7941

Relative Partial Molal Heat Content of Solute and Solvent.—The former quantity is given in the case of sodium hydroxide concentrations below 12 molal by the formula

$$\bar{L}_2 = -6.9078RT \frac{u\sqrt{m}}{1+\sqrt{2m}} (1 - \beta T) -$$

$$4.6052RT^2\left[m \frac{dB}{dT} + m^2 \frac{dC}{dT} + m^3 \frac{dD}{dT} + m^4 \frac{dE}{dT}\right] \quad (15)$$

where β is the constant of Åkerlöf[7] for expressing the change of the dielectric constant of the solvent with temperature. For concentrations above 12

(7) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).
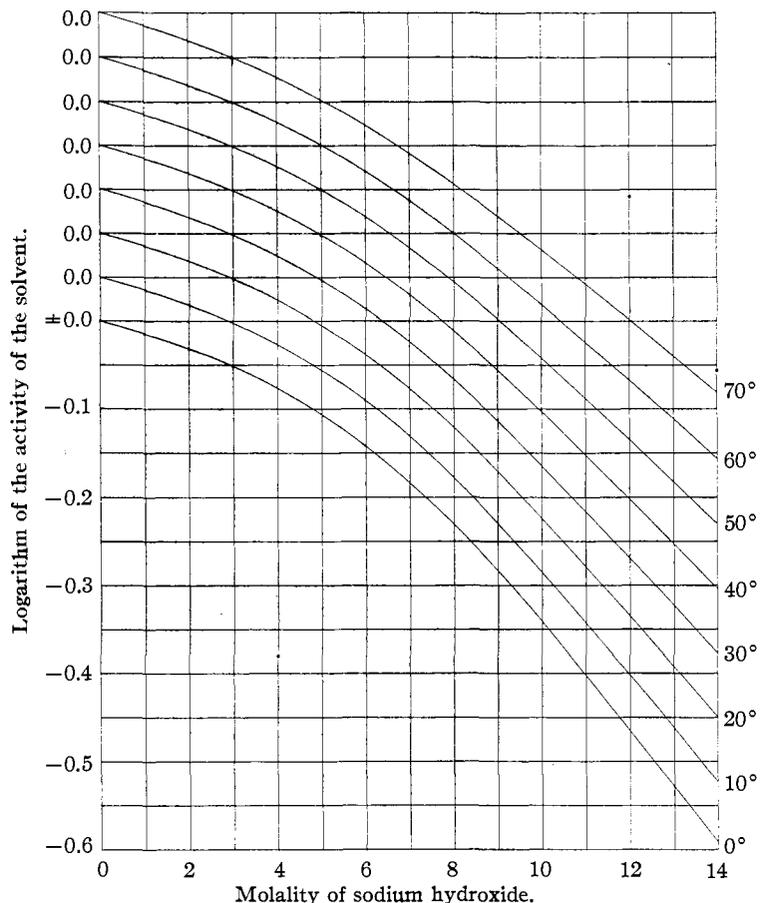
Fig. 3.—Isotherms for the logarithm of the activity of the solvent in aqueous solutions of sodium hydroxide. Ordinates are shifted successively for the different curves.

molal the following equation should be used

$$\overline{L}_2 = -2RT^2 2.303 \ \mathrm{d} \log \gamma/\mathrm{d}T = -4.6052RT^2[\mathrm{d}a/\mathrm{d}t - m \ \mathrm{d}b/\mathrm{d}t - m^2 \ \mathrm{d}c/\mathrm{d}t] \quad (16)$$

where a, b and c are the empirical constants given in Table IV for the equation

$$\log \gamma = a + bm + cm^2$$

The heat content of the solvent in solutions belonging to the lower concentration range may be computed from the formula

$$\overline{L}_1 = \frac{6.9078RTu(1 - \beta T)}{2 \cdot 55.51 \cdot \sqrt{2}} \left[(1 + \sqrt{2m}) - 4.6052 \log (1 + \sqrt{2m}) - \frac{1}{1 + \sqrt{2m}} \right] + \frac{4.6052RT^2}{55.51} \left[\frac{m^2}{2} \frac{\mathrm{d}B}{\mathrm{d}T} + \frac{2m^3}{3} \frac{\mathrm{d}C}{\mathrm{d}T} + \frac{3m^4}{4} \frac{\mathrm{d}D}{\mathrm{d}T} + \frac{4m^5}{5} \frac{\mathrm{d}E}{\mathrm{d}T} \right] \quad (17)$$

where the constant β has the same meaning as in equation (15). For the higher concentration range we obtain the expression

$$\overline{L}_{1(m>12)} = -2.303RT^2 \ \mathrm{d} \log a_1/\mathrm{d}T = \overline{L}_{1(12)} + \frac{2.303RT^2}{55.51} [(m^2 - 144)\mathrm{d}b/\mathrm{d}t + 4/3(m^3 - 1728)\mathrm{d}c/\mathrm{d}t] \quad (18)$$

Tables X and XI contain a summary of the values computed for $\overline{L}_1$ and $\overline{L}_2$. The values of the latter quantity calculated by Harned and Hecker from their data agree in dilute solutions quite well with ours but separate appreciably at higher concentrations. A graphical representation of our results is shown in Figs. 4 and 5. The former figure illustrates in particular the large deviations of the heat content of the hydroxide from the limiting law already in fairly dilute solutions.

Relative Partial Molal Entropy of Solute and Solvent.—As $F = H - TS$ the relative partial molal entropies may most simply be calculated from the free energies and heat contents

$$-(\overline{S}_2 - \overline{S}_2^\circ) = [(\overline{F}_2 - \overline{F}_2^\circ) - (\overline{H}_2 - \overline{H}_2^\circ)]/T \text{ and} \quad (19)$$

$$-(\overline{S}_1 - \overline{S}_1^\circ) = [(\overline{F}_1 - \overline{F}_1^\circ) - (\overline{H}_1 - \overline{H}_1^\circ)]/T \quad (20)$$

TABLE VIII

RELATIVE PARTIAL MOLAL FREE ENERGY OF THE SOLUTE IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	−2766	−2867	−2971	−3076	−3184	−3293	−3406	−3522
.2	−2078	−2151	−2229	−2308	−2391	−2477	−2569	−2664
.4	−1390	−1433	−1482	−1535	−1593	−1656	−1727	−1804
.6	− 983	−1006	−1038	−1073	−1116	−1165	−1225	−1293
.8	− 689	− 697	− 715	− 738	− 769	− 809	− 860	− 921
1.0	− 456	− 451	− 458	− 471	− 493	− 525	− 570	− 626
1.5	− 16	+ 20	+ 31	+ 37	+ 32	+ 14	− 19	− 66
2	+ 337	+ 381	+ 407	+ 426	+ 432	+ 425	+ 401	+ 362
3	900	965	1005	1041	1064	1071	1060	1034
4	1392	1468	1514	1559	1590	1606	1605	1588
5	1855	1938	1986	2034	2069	2090	2094	2082
6	2307	2394	2441	2491	2527	2548	2552	2539
7	2751	2843	2888	2938	2971	2989	2988	2969
8	3190	3287	3330	3377	3407	3418	3406	3375
9	3620	3723	3764	3807	3830	3830	3805	3755
10	4041	4148	4183	4221	4235	4222	4180	4109
11	4448	4554	4581	4610	4612	4584	4524	4432
12	4838	4936	4947	4963	4951	4906	4829	4720
13	5180	5242	5278	5286	5265	5211	5124	5003
14	5507	5566	5598	5600	5572	5511	5416	5286
15	5829	5884	5912	5908	5874	5805	5701	5561
16	6147	6197	6220	6211	6169	6093	5980	5831
17	6459	6506	6524	6508	6460	6376	6254	6095

TABLE IX

RELATIVE PARTIAL MOLAL FREE ENERGY OF THE SOLVENT IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE. *All Values Negative*

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	1.9	1.9	2.0	2.1	2.2	2.2	2.3	2.4
.2	3.6	3.8	3.8	3.9	4.0	4.1	4.3	4.4
.4	7.1	7.5	7.8	8.1	8.3	8.6	8.8	9.1
.6	10.8	11.2	11.7	12.1	12.6	13.0	13.1	13.5
.8	14.5	15.0	15.8	16.2	16.8	17.3	17.7	18.1
1.0	18.1	19.1	19.9	20.7	21.2	21.9	22.4	22.9
1.5	28.3	29.8	30.9	31.9	33.1	33.9	34.8	35.5
2	39.0	41.0	42.6	44.0	45.7	46.8	47.9	48.9
3	64.3	66.9	69.4	71.6	73.9	75.6	77.3	78.9
4	95.3	98.7	101.5	104.3	107.0	109.4	111.5	113.6
5	132.7	136.8	139.6	142.6	145.6	148.3	151.0	153.7
6	177.5	181.9	184.6	188.1	191.0	193.9	196.6	198.8
7	229.4	234.5	237.1	240.2	243.1	245.5	247.4	249.1
8	288.8	294.6	296.7	299.6	302.0	303.4	304.0	304.1
9	354.5	361.2	363.1	365.5	366.6	366.7	364.9	362.4
10	426.7	434.0	434.7	436.3	435.8	433.4	429.3	422.9
11	503.6	510.7	510.0	509.7	507.2	501.9	494.3	483.7
12	584.4	589.7	586.0	582.9	577.4	568.8	557.6	543.4
13	659.6	664.1	659.4	655.2	648.2	638.1	625.0	608.8
14	739.3	743.1	737.3	731.7	723.2	711.2	695.9	677.4
15	823.3	826.1	819.2	812.0	801.8	787.8	770.4	749.2
16	911.9	913.6	905.4	896.6	884.6	868.2	848.3	824.7
17	1004.8	1005.4	995.6	985.1	970.9	952.3	929.6	902.9

TABLE X

RELATIVE PARTIAL MOLAL HEAT CONTENT OF THE SOLUTE IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	+ 9	+ 53	+103	+159	+223	+293	+373	+462
.2	− 60	+ 7	+ 85	172	272	384	509	648
.4	−208	−102	+ 20	159	317	496	697	921
.6	−345	−207	− 48	134	341	575	840	1132
.8	−463	−300	−110	107	358	638	956	1308
1.0	−565	−377	−162	86	371	692	1054	1456
1.5	−742	−511	−250	57	405	801	1245	1741
2	−823	−564	−275	67	454	893	1388	1939
3	−761	−477	−170	195	611	1079	1607	2193
4	−502	−207	+88	449	858	1319	1835	2409
5	−145	+162	445	800	1203	1652	2154	2711
6	+237	575	857	1228	1644	2104	2618	3184
7	602	996	1300	1712	2174	2684	3249	3868
8	938	1411	1763	2248	2789	3385	4043	4764
9	1260	1834	2251	2832	3479	4188	4973	5829
10	1616	2297	2783	3467	4227	5060	5978	6982
11	2080	2862	3398	4166	5019	5954	6979	8099
12	2756	3603	4144	4950	5839	6805	7865	9018
13	3136	3842	4621	5482	6426	7455	8575	9789
14	3544	4277	5086	5977	6952	8012	9164	10411
15	3952	4713	5552	6471	7477	8568	9752	11032
16	4361	5150	6018	6966	8002	9125	10341	11653
17	4769	5587	6483	7461	8527	9681	10928	12272

The results of the calculations appear in Tables XII and XIII. A graphical representation is given in Figs. 6 and 7. The curves for the solute show an increasingly sharper minimum and large changes of form with increasing temperature. As a comparison the corresponding entropy curves for hydrochloric acid are all practically symmetrical parabolas.

Relative Partial Molal Heat Capacity of the Solute.—According to definition $\bar{c}_{p_2} - \bar{c}_{p_2}° = d\bar{L}_2/dT$ and we thus obtain for the lower concentration range the following expression for the calculation of the heat capacity of the solute

$$\bar{c}_{p_2} - \bar{c}_{p_2}° = 3.4539R(1 - 2\beta T + 3\beta^2 T^2)\frac{u\sqrt{m}}{1 + \sqrt{2m}} -$$
$$9.2104RT\left[m\frac{dB}{dT} + m^2\frac{dC}{dT} + m^3\frac{dD}{dT} + m^4\frac{dE}{dT} \right] -$$

TABLE XI
RELATIVE PARTIAL MOLAL HEAT CONTENT OF THE SOLVENT IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	0.0	0.0	0.0	− .0.1	− 0.1	− 0.1	− 0.2	− 0.2
.2	+ 0.3	+ .2	+ .1	− .1	− .3	− 0.4	− 0.6	− 0.8
.4	1.0	.7	.3	.0	− .4	− 1.0	− 1.6	− 2.2
.6	2.2	1.6	.9	+ .2	− .6	− 1.5	− 2.8	− 4.2
.8	3.7	2.8	1.8	.6	− .9	− 2.5	− 4.3	− 6.3
1.0	5.4	4.2	2.4	1.0	− 1.0	− 3.4	− 6.0	− 8.8
1.5	9.2	7.1	4.4	1.6	− 2.0	− 5.8	− 10.3	− 15.1
2	11.7	8.6	5.3	1.3	− 3.5	− 8.6	− 14.6	− 21.2
3	8.6	4.3	0.3	− 4.7	− 10.6	− 17.1	− 24.4	− 32.6
4	− 8.0	− 12.8	− 16.1	− 20.1	− 26.4	− 32.3	− 38.9	− 46.1
5	− 37.0	− 43.0	− 45.2	− 49.7	− 54.3	− 59.5	− 65.0	− 70.9
6	− 74.8	− 83.8	− 86.1	− 92.1	− 98.2	− 104.6	− 111.0	− 118.0
7	− 117.7	− 133.0	− 138.1	− 149.0	− 160.7	− 172.5	− 185.3	− 198.5
8	− 162.9	− 189.2	− 200.6	− 221.4	− 243.8	− 267.6	− 292.8	− 319.7
9	− 212.6	− 253.8	− 275.3	− 310.6	− 349.4	− 390.6	− 435.3	− 483.1
10	− 273.3	− 333.4	− 366.4	− 419.4	− 477.7	− 539.9	− 607.5	− 680.4
11	− 361.3	− 440.0	− 482.8	− 552.0	− 627.6	− 708.8	− 796.7	− 891.6
12	− 502.1	− 594.2	− 637.9	− 714.2	− 797.3	− 885.2	− 980.0	−1081.5
13	− 593.8	− 692.3	− 742.6	− 825.7	− 915.7	−1010.7	−1112.7	−1221.7
14	− 692.9	− 798.3	− 855.7	− 946.0	−1043.5	−1146.1	−1256.0	−1373.0
15	− 799.5	− 912.3	− 977.2	−1075.3	−1180.8	−1291.6	−1409.7	−1535.2
16	− 913.6	−1034.2	−1107.3	−1213.5	−1327.5	−1446.9	−1573.9	−1708.4
17	−1035.4	−1164.2	−1245.8	−1360.7	−1483.7	−1612.1	−1748.6	−1892.6

TABLE XII
RELATIVE PARTIAL MOLAL ENTROPY OF THE SOLUTE IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE. VALUES OF $-(\bar{S}_2 - \bar{S}_2°)$

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	−10.016	−10.314	−10.488	−10.673	−10.882	−11.099	−11.345	−11.612
.2	− 7.389	− 7.623	− 7.895	− 8.182	− 8.505	− 8.855	− 9.240	− 9.653
.4	− 4.328	− 4.702	− 5.124	− 5.589	− 6.100	− 6.660	− 7.277	− 7.942
.6	− 2.336	− 2.822	− 3.378	− 3.982	− 4.653	− 5.385	− 6.199	− 7.068
.8	− 0.827	− 1.402	− 2.064	− 2.788	− 3.600	− 4.478	− 5.452	− 6.497
1.0	+ 0.399	− 0.262	− 1.010	− 1.838	− 2.760	− 3.768	− 4.875	− 6.068
1.5	2.658	+ 1.876	+ 0.959	− 0.066	− 1.231	− 2.436	− 3.795	− 5.267
2	4.248	+ 3.338	+ 2.327	+ 1.184	− 0.070	− 1.448	− 2.963	− 4.596
3	6.082	5.094	4.009	+ 2.791	+ 1.447	− 0.015	− 1.642	− 3.378
4	6.935	5.917	4.865	3.662	+ 2.340	+ 0.888	− 0.690	− 2.393
5	7.323	6.273	5.258	4.071	2.766	+ 1.356	− .180	− 1.833
6	7.580	6.425	5.404	4.167	2.820	1.374	− .198	− 1.880
7	7.867	6.524	5.418	4.045	2.547	0.944	− .784	− 2.620
8	8.246	6.627	5.346	3.725	1.974	0.102	− 1.912	− 4.048
9	8.641	6.673	5.162	3.217	1.121	− 1.108	− 3.506	− 6.045
10	8.880	6.538	4.776	2.448	0.003	− 2.594	− 5.398	− 8.374
11	8.671	5.977	4.036	1.465	− 1.300	− 4.240	− 7.370	−10.688
12	7.624	4.709	2.740	0.043	− 2.836	− 5.877	− 9.114	−12.527
13	7.484	4.945	2.242	− 0.647	− 3.708	− 6.945	−10.360	−13.949
14	7.188	4.553	1.747	− 1.244	− 4.408	− 7.741	−11.252	−14.935
15	6.873	4.136	1.228	− 1.857	− 5.120	− 8.552	−12.162	−15.946
16	6.540	3.698	0.689	− 2.491	− 5.854	− 9.384	−13.092	−16.969
17	6.188	3.246	0.140	− 3.144	− 6.602	−10.229	−14.032	−18.003

$$4.6052RT^2\left[m\,\frac{d^2B}{dT^2} + m^2\,\frac{d^2C}{dT^2} + m^3\,\frac{d^2D}{dT^2} + m^4\,\frac{d^2E}{dT^2}\right] \quad (21)$$

For the upper concentration range differentiation of equation (16) would give the desired quantity, but the accuracy of the measurements is too low to warrant a second differentiation. The values calculated from equation (21) are presented in Table XIV. In the first part of Table XV our values at 25° are compared with values obtained

TABLE XIII

RELATIVE PARTIAL MOLAL ENTROPY OF THE SOLVENT IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE. VALUES OF $-(\bar{S}_1 - \bar{S}_1°)$

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	−0.0070	−0.0069	−0.0068	−0.0067	−0.0066	−0.0065	−0.0065	−0.0065
.2	− .0143	− .0140	− .0133	− .0125	− .0118	− .0114	− .0111	− .0108
.4	− .0297	− .0289	− .0279	− .0267	− .0252	− .0235	− .0216	− .0201
.6	− .0476	− .0452	− .0430	− .0406	− .0383	− .0356	− .0309	− .0271
.8	− .0666	− .0629	− .0600	− .0554	− .0508	− .0458	− .0402	− .0344
1.0	− .0860	− .0823	− .0761	− .0714	− .0645	− .0572	− .0492	− .0411
1.5	− .137	− .130	− .120	− .110	− .0993	− .0869	− .0735	− .0594
2	− .186	− .175	− .163	− .149	− .135	− .118	− .100	− .0807
3	− .267	− .251	− .238	− .221	− .202	− .181	− .159	− .135
4	− .320	− .303	− .291	− .277	− .257	− .238	− .218	− .196
5	− .350	− .331	− .322	− .307	− .292	− .274	− .258	− .241
6	− .376	− .346	−.336	− .317	− .296	− .276	− .257	− .235
7	− .409	− .358	− .338	− .301	− .263	− .226	− .186	− .147
8	− .461	− .372	− .328	− .258	− .186	− .111	− .034	+ .045
9	− .520	− .379	− .300	− .181	− .055	+ .074	+ .211	.351
10	− .561	− .355	− .233	− .056	+ .134	.329	.534	.750
11	− .521	− .250	− .093	+ .140	.384	.640	.908	1.189
12	− .301	+ .016	+ .177	.433	.702	.979	1.268	1.568
13	− .241	.100	.284	.563	.854	1.153	1.464	1.786
14	− .170	.195	.404	.707	1.023	1.346	1.681	2.027
15	− .087	.304	.539	.869	1.211	1.559	1.919	2.290
16	+ .006	.426	.689	1.046	1.415	1.791	2.178	2.575
17	+ .112	.561	.854	1.239	1.638	2.042	2.459	2.884

TABLE XIV

RELATIVE PARTIAL MOLAL HEAT CAPACITY OF THE SOLUTE IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	4.9	5.2	5.7	6.3	6.8	7.4	8.1	8.8
.2	7.6	8.4	9.1	9.8	10.7	11.6	12.6	13.5
.4	12.4	13.9	14.6	15.8	17.2	18.5	20.0	21.5
.6	16.2	17.7	19.3	20.8	22.4	24.2	26.1	28.0
.8	19.6	21.2	23.0	24.9	27.0	29.0	31.3	33.6
1.0	22.3	24.3	26.4	28.5	30.7	33.1	35.6	38.4
1.5	27.5	29.8	32.4	34.9	37.7	40.6	43.7	46.8
2	30.4	33.1	35.8	38.7	41.7	44.4	48.2	51.8
3	32.0	34.8	37.7	40.6	44.0	48.2	50.7	54.5
4	30.5	33.1	35.9	38.7	41.7	45.0	48.5	52.0
5	28.5	31.0	33.5	36.0	39.1	42.0	45.2	48.6
6	27.6	30.0	32.4	35.0	37.8	40.6	43.7	46.9
7	28.9	31.4	34.0	36.6	39.5	42.5	45.7	49.1
8	32.6	35.3	38.1	41.1	44.3	47.7	51.2	54.9
9	37.7	41.0	44.2	47.7	51.3	55.3	59.3	63.6
10	43.4	47.1	50.7	54.7	58.9	63.3	67.9	72.6
11	47.3	51.4	55.3	59.7	64.1	68.8	73.8	79.0
12	46.4	50.3	54.2	58.3	62.8	67.4	72.2	77.2

from direct calorimetric measurements made by Rossini[8] and by Gucker and Schminke[9] through 2 molal solutions. The agreement is remarkably good, our values above 0.6 molal all falling between the two sets of calorimetric data. The values calculated by Harned and Hecker are also in good agreement with ours. A graphical repre-

(8) Rossini, Bur. Standards J. Res., 6, 791 (1931).

(9) Gucker and Schminke, THIS JOURNAL, 55, 1013 (1933).

TABLE XV

COMPARISON OF THE HEAT CAPACITY DATA IN TABLES XIV AND XVI INTERPOLATED TO 25° WITH DATA IN THE LITERATURE, ALSO AT 25°

I. Relative partial molal heat capacity of the solute

m	$\sqrt{m}$	Rossini	Åkerlöf and Kegeles	Gucker and Schminke
0.1	0.3162	9.01	6.0	8.29
.2	.4472	12.75	9.5	11.73
.4	.6325	18.0	15.2	16.6
.6	.7746	22.1	20.1	20.3
.8	.8944	25.5	24.0	23.5
1.0	1.0000	28.5	27.5	26.2
1.5	1.2247	34.9	33.7	32.1
2.0	1.4142	40.3	37.3	37.1

II. Relative partial molal heat capacity of the solvent

m	$m^{3/2}$			
0.1	0.0316	−0.0054	−0.002	−0.0050
.2	.0894	.0152	.008	.0141
.4	.2530	.0433	.035	.0400
.6	.4648	.0794	.081	.0734
.8	.7155	.122	.139	.113
1.0	1.0000	.171	.205	.158
1.5	1.8372	.314	.386	.290
2.0	2.8284	.484	.572	.447

sentation of the changes of the heat capacity of the hydroxide is given in Fig. 8. All the curves show a maximum around 3, a minimum around 6, and a second maximum near 12 molal seems to be indicated. In contrast the corresponding curves for hydrochloric acid are practically straight lines.
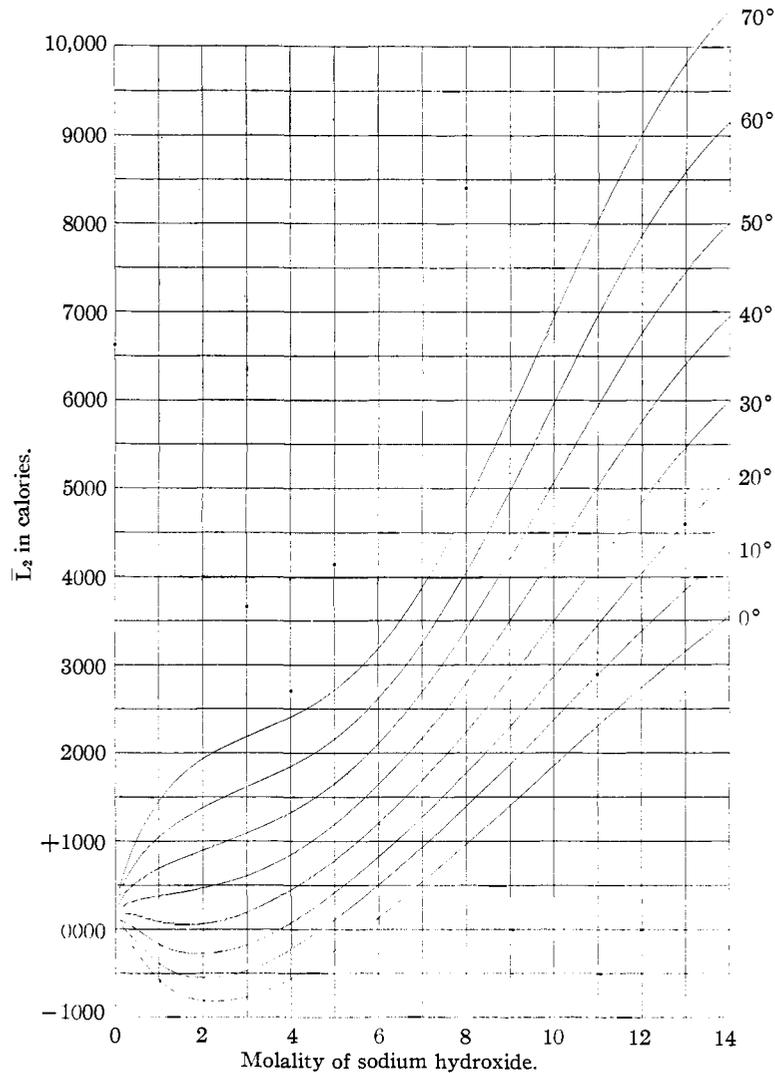
Fig. 4.—Isotherms for the relative partial molal heat content of the solute in aqueous solutions of sodium hydroxide.

Relative Partial Molal Heat Capacity of the Solvent.—For the lower concentration range differentiation of equation (17) gives directly

$$\bar{c}_{p_1} - \bar{c}_{p_1}{}^\circ = \frac{3.4539Ru}{2 \cdot 55.51\sqrt{2}}(1 - 2\beta T + 3\beta^2 T^2)\left[1 + \right.$$
$$\left. \sqrt{2m} - 4.6052 \log (1 + \sqrt{2m}) - \frac{1}{1 + \sqrt{2m}}\right] +$$
$$\frac{9.2104RT}{55.51}\left[\frac{m^2}{2}\frac{dB}{dT} + \frac{2m^3}{3}\frac{dC}{dT} + \frac{3m^4}{4}\frac{dD}{dT} + \frac{4m^5}{5}\frac{dE}{dT}\right] +$$
$$\frac{4.6052RT^2}{55.51}\left[\frac{m^2}{2}\frac{d^2B}{dT^2} + \frac{2m^3}{3}\frac{d^2C}{dT^2} + \frac{3m^4}{4}\frac{d^2D}{dT^2} + \frac{4m^5}{5}\frac{d^2E}{dT^2}\right]$$
$$(22)$$

As in the case of the solute, values of the heat capacity of the solvent above 12 molal have not been calculated, although rough values could be obtained by differentiation of equation (18).

Table XVI contains a summary of the values calculated from equation (22). In the second part of Table XV is again made a direct comparison with the result of the calorimetric measurements of Rossini and of Gucker and Schminke. As in the case of the solute the absolute agreement is quite good and only in one case, near the upper limit of the extrapolation function used by these authors, is the discrepancy between their values and ours greater than 0.1 calorie. Figure 9 gives a graphical representation of the changes of the heat capacity of the solvent. The curves have a very uniform appearance over the entire temperature range employed, but they are complicated in form. As a comparison the corresponding curves for hydrochloric acid solutions are practically
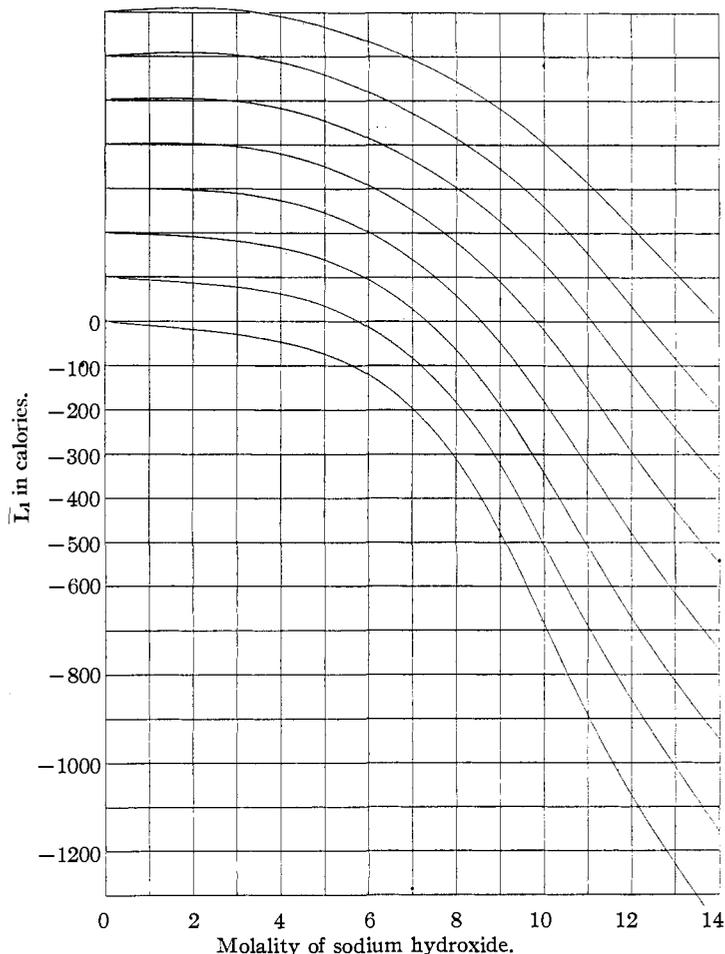
Fig. 5.—Isotherms for the relative partial molal heat content of the solvent in aqueous solutions of sodium hydroxide. Ordinates are shifted successively for the different curves.

TABLE XVI

RELATIVE PARTIAL MOLAL HEAT CAPACITY OF THE SOLVENT IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE. *All Values Negative*

m	0°	10°	20°	30°	40°	50°	60°	70°
0.1	0.001	0.002	0.002	0.002	0.003	0.001	0.002	0.002
.2	.008	.008	.007	.008	.008	.009	.010	.010
.4	.029	.031	.034	.036	.040	.042	.044	.047
.6	.066	.072	.078	.083	.090	.095	.100	.107
.8	.115	.124	.134	.143	.152	.163	.174	.178
1.0	.168	.182	.198	.211	.213	.241	.255	.272
1.5	.319	.346	.372	.399	.426	.455	.484	.515
2	.475	.513	.552	.591	.634	.676	.719	.763
3	.733	.790	.847	.909	.972	1.035	1.099	1.167
4	.925	.994	1.066	1.145	1.214	1.292	1.371	1.451
5	1.137	1.221	1.305	1.392	1.482	1.574	1.667	1.765
6	1.526	1.637	1.748	1.866	1.982	2.105	2.229	2.356
7	2.240	2.405	2.568	2.741	2.918	3.100	3.286	3.477
8	3.381	3.637	3.889	4.154	4.427	4.707	4.995	5.293
9	4.939	5.316	5.690	6.084	6.491	6.910	7.340	7.784
10	6.737	7.255	7.772	8.314	8.877	9.455	10.049	10.663
11	8.387	9.033	9.675	10.351	11.054	11.774	12.517	13.281
12	9.220	9.928	10.623	11.359	12.122	12.905	13.712	14.543

linear when plotted against the square of the molality.

The Total Heat Capacity and the Specific Heat of the Solution.—These quantities are obtained from the relations: $C_p = 55.51\bar{c}_{p_1} + m\bar{c}_{p_2}$ per $1000 + Mm$ grams of solution and $s = C_p/(1000 + Mm)$ per gram of solution (M molecular weight of sodium hydroxide) respectively, in cases where it is possible to obtain values of $\bar{c}_{p_1}^o$ and $\bar{c}_{p_2}^o$. For sodium hydroxide solutions values of the latter quantity are given by Rossini at 18 and 21.5° and by Gucker and Schminke at 25°. Rossini also gives as a mean value for $d\bar{c}_{p_2}^o/dT = {}^2/_7$ cal. per degree. Using the value -26.6 of Gucker and Schminke, whose data are in better agreement with ours than those of Rossini, and the latter's value for $d\bar{c}_{p_2}^o/dT$ we get at 20° $\bar{c}_{p_2}^o = -28.0$ calories. This value combined with the values of $\bar{c}_{p_2}^o - \bar{c}_{p_2}^o$ in Table XIV for 20° would give values for $\bar{c}_{p_2}$ up to 12 molal.

The value of $\bar{c}_{p_1}^o$ is obtained by multiplying the specific heat of water by its molecular weight. The value used for the specific heat is 0.9988 cal. per degree, giving $\bar{c}_{p_1}^o = 18.014$. This value combined with the data in Table XVI for $\bar{c}_{p_1}^o - \bar{c}_{p_1}^o$ at 20° would give values for $\bar{c}_{p_1}$ up to 12 molal. With both $\bar{c}_{p_2}^o$ and $\bar{c}_{p_1}^o$ known, the total heat capacity and specific heat of the solutions may be calculated using the relations given above. A summary of the results is shown in Table XVII. An error analysis based on the data in Table XV indicates that the specific heats should have an accuracy of one unit in the third decimal place up to concentrations well above 2 molal. At higher concentrations the errors would be increasingly larger as found by a comparison with the calorimetric data of Bartetti and McCabe.[9a]

The Total Relative Heat Content of the Solutions.—This quantity which is equal to the heat evolved upon dilution to zero concentration is de-

(9a) Bartetti and McCabe, *Ind. Eng. Chem.*, **28**, 375 (1936).
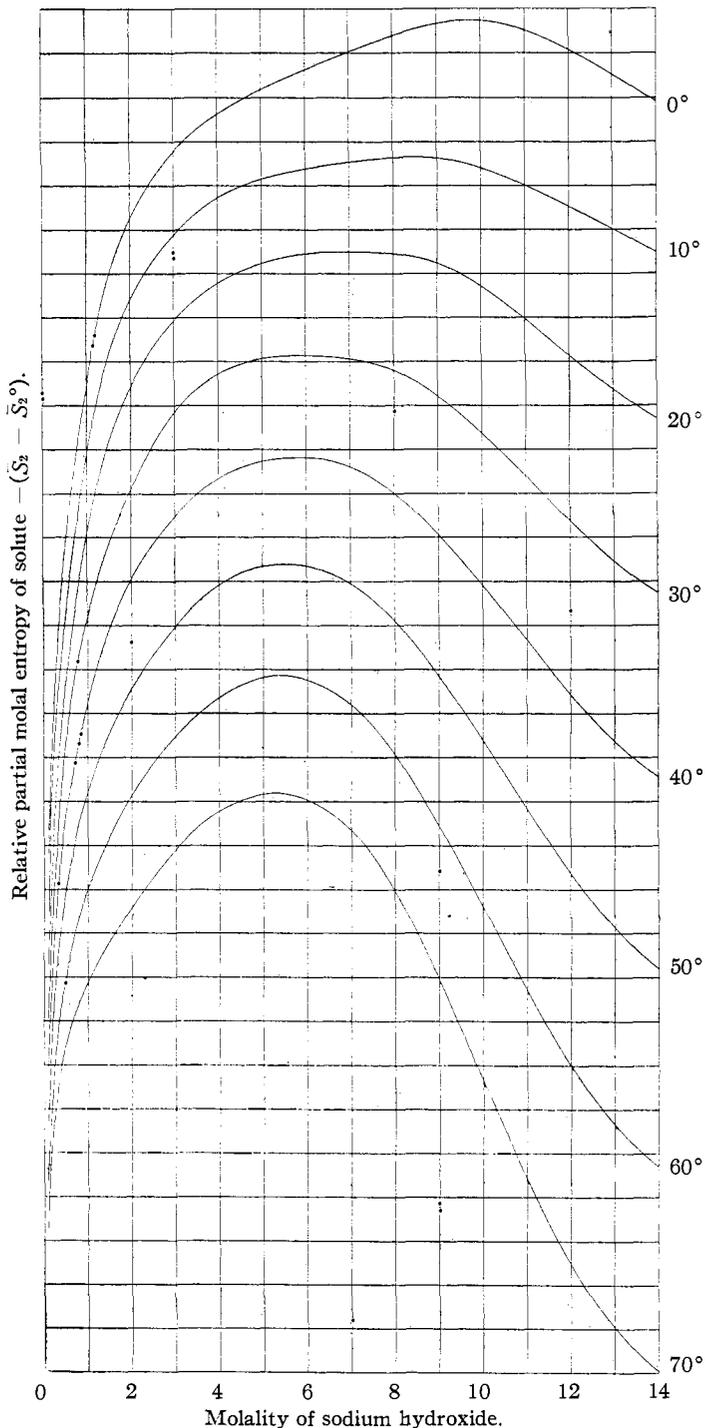
Fig. 6.—Isotherms for the relative partial molal entropy of the solute in aqueous solutions of sodium hydroxide. Ordinates are shifted successively for the different curves.

fined by the relation: $L_{(m)} = 55.51\,\bar{L}_1 + m\bar{L}_2$ per $1000 + Mm$ grams of solution. The molal value L/m, usually called the integral heat of dilution, also has considerable interest. Values

70°

60°

50°

40°

$-(\bar{S}_1 - S_1^\circ)$.

30°

20°

10°

0°

0   2   4   6   8   10   12   14

Molality of sodium hydroxide.

Fig. 7.—Isotherms for the relative partial molal entropy of the solvent in aqueous solutions of sodium hydroxide. Ordinates are shifted successively for the different curves.

The Heat of Dilution between Two Finite Concentrations.

—If n moles of water are used to dilute a solution of mass M and molality m to a molality m'

$$m' = \frac{55.51 \cdot M \cdot m}{55.51 M + (1000 + 40m)n} \quad (23)$$

the isothermal heat absorbed by the system is given by the equation

$$\Delta H = \frac{M}{1000 + 40m} [L_{(m')} - L_{(m)}] + \frac{Mnm\bar{L}_{2(m')}}{55.51 M + (1000 + 40m)n} + n\bar{L}_{1(m')} \quad (24)$$

The use of equation (24) permits the calculation of the heat of dilution of sodium hydroxide solutions at any temperature in the range 0 to 70° for any arbitrary amount of solution between any two molalities from 0.1 to 17 molal. Values of $\Delta H/m$ calculated from (24) agree remarkably well with the data of Richards and co-workers and Fricke.[9b]

The Differential Heat of Vaporization.

—This quantity ΔH_v is defined as the amount of heat necessary to vaporize one mole of the solvent at constant temperature and pressure from a sufficiently large body of the solution so that no concentration change takes place. To calculate this quantity we will make use of the relationship

$$\bar{L}_1 = -RT^2 \partial \ln p_1/\partial T + RT^2 \partial \ln p_1^\circ/\partial T \quad (25)$$

The second term of equation (25) is recognized immediately as the approximate Clausius–Clapey-

of L and L/m are simply obtained by the use of the data in Tables X and XI for $\bar{L}_2$ and $\bar{L}_1$, respectively. Those calculated for 20° are collected in

TABLE XVII
TOTAL HEAT CAPACITY AND SPECIFIC HEAT OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AT 20°

m	C_p	s
0.1	997.58	0.9936
.2	995.75	.9878
.4	992.67	.9770
.6	990.37	.9672
.8	988.48	.9578
1.0	987.3	.9493
1.5	985.9	.9300
2.0	984.9	.9119
3.0	982.0	.8767

Table XVIII. They are needed for the computation of the following quantity which has a practical value.

TABLE XVIII
TOTAL RELATIVE HEAT CONTENT OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AT 20°
(Heat of Infinite Dilution)

m	L	L/m	m	L	L/m
0.1	10	100	4	−542	−136
.2	23	115	5	−284	− 57
.4	25	63	6	363	61
.6	21	35	7	1434	205
.8	12	15	8	2969	371
1.0	− 29	− 29	9	4978	593
1.5	−131	− 87	10	7442	744
2.0	−256	−128	11	10579	962
3.0	−493	−164	12	23319	1943

(9b) Richards and Rowe. THIS JOURNAL. 43, 770 (1921); Richards and Gucker. ibid., 51, 712 (1929); Richards and Hall. ibid., 51, 731 (1929); Fricke. Z. Elektrochem., 35, 631 (1929).

TABLE XIX

DIFFERENTIAL HEATS OF VAPORIZATION OF THE SOLVENT FROM AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE

m	0°	10°	20°	30°	40°	50°	60°	70°
0.0	1091.4	1080.9	1070.5	1060.3	1049.9	1039.5	1029.1	1018.4
.1	1091.4	1080.9	1070.5	1060.4	1050.0	1039.6	1029.3	1018.2
.2	1091.1	1080.7	1070.4	1060.4	1050.2	1039.9	1029.7	1019.2
.4	1090.4	1080.2	1070.2	1060.3	1050.3	1040.5	1030.7	1020.6
.6	1089.2	1079.3	1069.6	1060.1	1050.5	1041.0	1031.9	1022.6
.8	1087.7	1078.1	1068.7	1059.7	1050.8	1042.0	1033.4	1024.7
1.0	1086.0	1076.7	1068.1	1059.3	1050.9	1042.9	1035.1	1027.2
1.5	1082.2	1073.8	1066.1	1058.7	1051.9	1045.3	1039.4	1033.5
2	1079.7	1072.3	1065.2	1059.0	1053.4	1048.1	1043.7	1039.6
3	1082.8	1076.6	1070.2	1065.0	1060.5	1056.6	1053.5	1051.0
4	1099.4	1093.7	1086.6	1080.4	1076.3	1071.8	1068.0	1064.5
5	1128.4	1123.9	1115.7	1110.0	1104.2	1099.0	1094.1	1089.3
6	1166.2	1164.7	1156.6	1152.4	1148.1	1144.1	1140.1	1136.4
7	1209.1	1213.9	1208.6	1209.3	1210.6	1212.0	1214.4	1216.9
8	1254.3	1270.1	1271.1	1281.7	1293.7	1307.1	1321.9	1338.1
9	1304.0	1334.7	1345.8	1370.9	1399.3	1430.1	1464.4	1501.5
10	1364.7	1414.3	1436.9	1479.7	1527.6	1579.4	1636.6	1698.8
11	1452.7	1520.9	1553.3	1612.3	1677.5	1748.3	1825.8	1910.0
12	1593.5	1675.1	1708.4	1774.5	1847.2	1924.7	2009.1	2099.9
13	1685.2	1773.2	1813.1	1886.0	1965.6	2050.2	2141.8	2240.1
14	1784.3	1879.2	1926.2	2006.3	2093.4	2185.6	2285.1	2391.4
15	1890.9	1993.2	2047.7	2135.6	2230.7	2331.1	2438.8	2553.6
16	2005.0	2115.1	2177.8	2273.8	2377.4	2486.4	2603.0	2726.8
17	2126.8	2245.1	2316.3	2421.0	2533.6	2651.6	2777.7	2911.0

ron expression for the heat of vaporization $\Delta H_v°$ of one mole of the pure solvent. By rigorous thermodynamic methods the first term is found to represent the analogous quantity for solvent in the solution, provided no concentration change takes place during the loss of one mole of solvent. This quantity is therefore the differential heat of vaporization as defined above.

Using the measurements of $\Delta H_v°$ for water by Keyes, Smith and Gerry[10] after conversion from cc. atm./g. to cal./mole and the values of $\bar{L}_1$ in Table XI, the values calculated for ΔH_v have been collected in Table XIX. These data are limiting values for the next quantity to be considered.

The Integral Heat of Vaporization.—This quantity is defined as the amount of heat necessary to vaporize one mole of solvent from a given finite amount of solution, the accompanying concentration change being determined by the original concentration and mass of the solution. If one mole of water is vaporized from a sodium hydroxide solution of original mass M and molality m, the isothermal heat absorbed by the system is thus given by the integral heat of vaporization

$$Q = \Delta H_v° + \frac{M}{1000 + 40m} [L_{(m')} - L_{(m)}] -$$

(10) Keyes, Smith and Gerry, Proc. Amer. Acad. Arts and Sci., 70, 318 (1936).
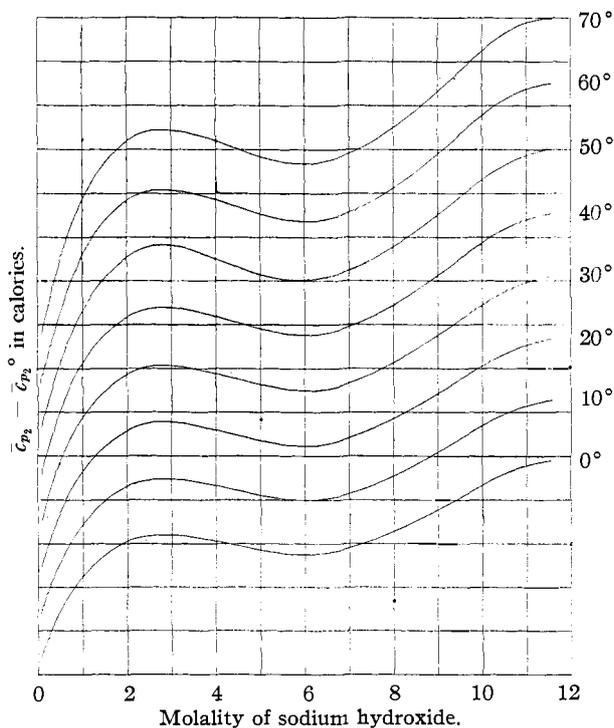
Fig. 8.—Isotherms for the relative partial molal heat capacity of the solute in aqueous solutions of sodium hydroxide. Ordinates are shifted successively for the different curves.

$$\frac{Mm\bar{L}_{2(m')}}{55.51M - 1000 - 40m} - \bar{L}_{1(m')} \quad (26)$$
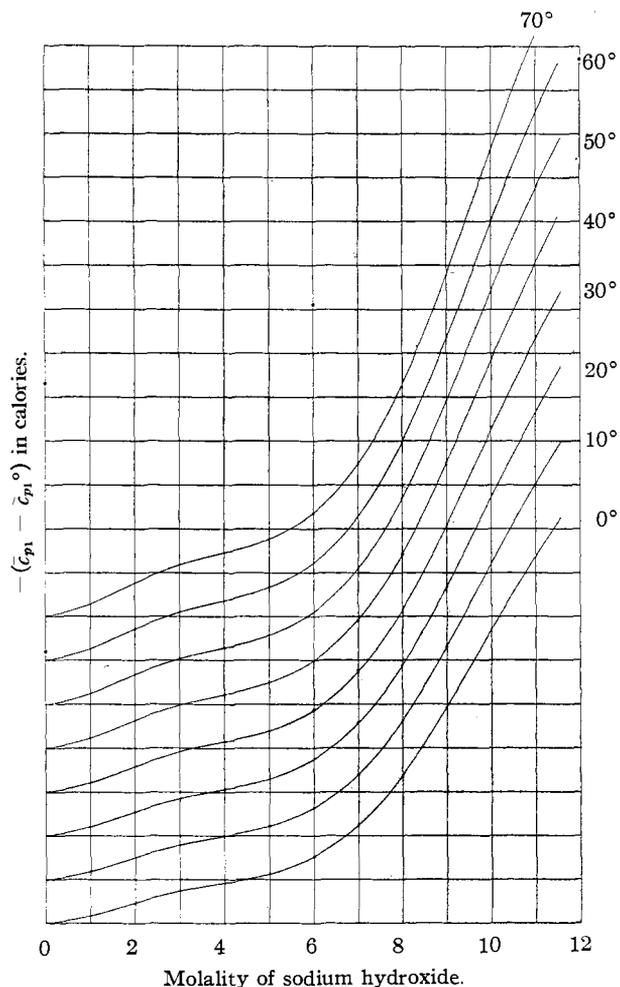
Fig. 9.—Isotherms for the relative partial molal heat capacity of the solvent in aqueous solutions of sodium hydroxide. Ordinates are shifted successively for the different curves.

where the resulting concentration m' should be computed from the following formula, analogous to equation (23)

$$m' = \frac{55.51 Mm}{55.51 M - 1000 - 40m}$$

For the vaporization of n moles of water from the same solution a similar equation is obtained

$$Q' = n\Delta H_v{}^\circ + \frac{M}{1000 + 40m}[L_{(m')} - L_{(m)}] -$$
$$\frac{Mnm\bar{L}_{2(m')}}{55.51 M - (1000 + 40m)n} - n\bar{L}_{1(m')} \quad (27)$$
$$\text{where } m' = \frac{55.51 Mm}{55.51 M - (1000 + 40m)n}$$

By use of the data in Tables X and XI and the values of $\Delta H_v{}^\circ$ in Table XIX, equation (27) allows the calculation of the heat absorbed when an arbitrary amount of solvent is vaporized from a

sodium hydroxide solution in the temperature range 0 to 70° at any concentrations between 0.1 to 17 molal. From Table XIX, $\Delta H_v{}^\circ = 1070.5$ cal., while ΔH_v for a ten molal solution is 1436.9 cal. This is to be compared with 1501.6 cal., the integral heat in going from 10 to 11 molal, computed from equation (26) with $M = 277.45$ g.

Pressure Variations of the Thermodynamic Properties of Solute and Solvent.—The rate of change of the chemical potentials of solute and solvent with pressure is given by the expressions

$$\left[\frac{\partial(\bar{F}_2 - \bar{F}_2^\circ)}{\partial P}\right]_T = 2RT\left[\frac{\partial \ln \gamma}{\partial P}\right]_T = \bar{v}_2 - \bar{v}_2^\circ \quad (28)$$

$$\left[\frac{\partial(\bar{F}_1 - \bar{F}_1^\circ)}{\partial P}\right]_T = RT\left[\frac{\partial \ln a_1}{\partial P}\right]_T = \bar{v}_1 - \bar{v}_1^\circ \quad (29)$$

The measurements of Smith and Keyes[11] show that the specific volume of pure liquid water changes by only 1 part in 1000 for a pressure change from 1 to 25 atmospheres. Since there is no reason to expect the compressibility of aqueous solutions to be much different from that of pure water, we may assume that in the pressure range mentioned the values of the partial molal volumes in equations (28) and (29) are constant within the experimental errors. This would give the following simple integrated equations

$$\log \gamma_P = \log \gamma + \frac{\bar{v}_2 - \bar{v}_2^\circ}{2 \cdot 2.303 RT}(P - 1) \quad (30)$$

$$\log a_{1P} = \log a_1 + \frac{\bar{v}_1 - \bar{v}_1^\circ}{2.303 RT}(P - 1) \quad (31)$$

where the pressure P is measured in atmospheres. The data for $\bar{v}_1$ and $\bar{v}_2$ needed for calculations using equations (30) and (31) are given in our previous study of the density of solutions of sodium hydroxide, which covers the temperature range 0 to 70° up to 27 molal.

Using the same fundamental thermodynamic relationships with $\log \gamma_P$ and $\log a_{1P}$ as those employed with $\log \gamma$ and $\log a_1$ in relation to other properties treated above, it is possible to calculate the values of the latter at higher pressures. It should be noted that in general the pressure correction term is so small that even if it has a large percentage error, this will not contribute any appreciable error to the final quantity obtained. Hence it would probably be quite feasible to apply equations (30) and (31) and all equations derived from them up to pressures of 100 atmospheres without introducing any serious errors. To obtain the derived equations it is necessary to know the temperature dependence of $\bar{v}_2$ and $\bar{v}_1$.

(11) Smith and Keyes, Proc. Am. Acad. Arts Sci., **69** 285 (1934).

This may be calculated from the known variation of k with temperature according to the expressions

$$\bar{v}_2 - \bar{v}_2^\circ = k_1 \sqrt{m} \quad \text{and} \quad \bar{v}_1 - \bar{v}_1^\circ = -\frac{18.016}{2000} k_1 m^{3/2}$$

where the concentration ranges from $m = 0$ to the density "break." The explicit temperature dependence of k_1 is obtained from third order equations given in our density paper.

The Chemical Significance of the Data.—Ions composed of single atoms like those of the alkali halides may probably without any large errors be considered to be non-deformable. The activity coefficients of strong electrolytes dissociating into ions of this type seem to follow with surprising accuracy, as has been tested for a large number of cases, the approximate rule of Åkerlöf and Thomas[12]

$$\log \gamma_1/\gamma_2 = km \qquad (32)$$

where the indices designate two electrolytes of the same valence type. The value of k is practically independent of the concentration except in very dilute solutions. The hydroxyl ion of the alkali hydroxides is composed of two atoms and should, in contrast to the behavior of single atom ions, be polarizable since it is unsymmetrical with respect to the electrical field of its associated positive ions. At infinite dilution the electrical strain and distortion must be at its minimum. With increasing concentration of the hydroxide the electrical distortion or induced polarization may be assumed as a first approximation to grow proportionally but the size of the effect would be unknown as there is no method available for the calculation of the "normal" thermodynamic properties of the alkali hydroxides. However, a saturation effect also should be present since the force needed to change the dimensions of an already stressed structure by a given amount would tend to increase with the hydroxide concentration or expressed in other words, the polarization per mole decreases with increasing concentration.

The presence of polarization of the hydroxyl ion is indicated already by the reversal of the behavior of the alkali hydroxides when compared to that of the corresponding alkali halides as previously

(12) Åkerlöf and Thomas, THIS JOURNAL, **56**, 593 (1934); Åkerlöf, J. Phys. Chem., **41** 1053 (1937).

pointed out by Harned and Åkerlöf.[13] A further support should according to the above be obtained by applying the rule of Åkerlöf and Thomas, which would indicate the presence of a saturation effect. The result is shown graphically in Fig. 10 where the value of k in equation (32) is plotted against the concentration. The data of Åkerlof and Teare for the activity coefficient of hydro-
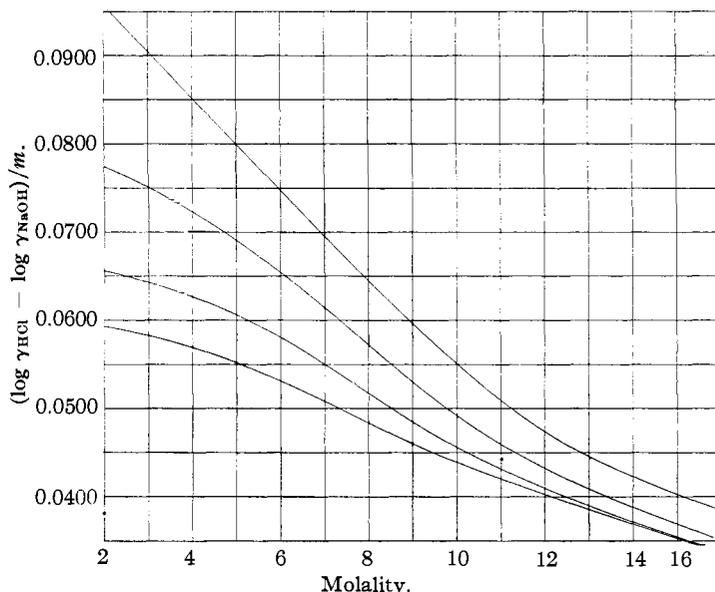
Fig. 10.—Isotherms at 0 (top curve), 20, 40 and 60° of the value for $(\log \gamma_{HCl} - \log \gamma_{NaOH})/m$.

chloric acid were used for the calculations since they were the only ones available in the literature covering the temperature and concentration ranges needed.

The curves in Fig. 10 illustrate clearly the expected behavior of sodium hydroxide. Instead of a series of practically horizontal straight lines, they show a rapidly decreasing value of k with increasing concentration. The tendency of the curves to converge at higher concentrations and temperatures had also to be expected since when the ions of the hydroxide are brought closer and closer to each other the hydroxyl ion approaches its maximum polarization and the influence of the nature of the surrounding medium must decrease.

Summary

The electromotive force of the cell: $Pt,H_2/$ $NaOH$ $(m_1)/Na_xHg/NaOH$ $(m_2)/H_2,Pt$ has been measured at a large number of hydroxide concentrations from 0.1 to 17 molal over the tempera-

(13) Harned and Åkerlöf, Physik. Z., **27**, 411 (1926).

ture range 0 to 70° using a considerably improved experimental procedure. The water transfer potential of the cell was calculated by a direct method eliminating tedious successive approximations.

The activity coefficient of the hydroxide for the concentration range 0.1 to 12 molal was found to be expressed adequately by the equation

$$\log \gamma = -\frac{u\sqrt{m}}{1 + \sqrt{2m}} + Bm + Cm^2 + Dm^3 + Em^4$$

where u is the universal constant of the limiting law, m the molality of the hydroxide, B, C, D and E empirical constants varying according to second order equations with the temperature.

At higher concentrations a second order equation was used for the calculation of $\log \gamma$. The curves for $\log \gamma$ do not within the experimental accuracy show any breaks at higher concentra-

tions like those of the apparent partial molal volumes.

Using the formulas for $\log \gamma$ equations have been given for the calculation of the activity and vapor pressure of the solvent, the relative partial molal free energy, heat content, entropy, and heat capacity of both solute and solvent. Other properties that have been discussed are the total heat capacity, specific heat and relative heat content of the solutions, the heat of dilution between two finite concentrations, differential and integral heats of vaporization of the solvent and finally the effect of pressure upon the thermodynamic properties of sodium hydroxide. The computed values of most of the properties treated are given in a series of tables.

The Fluorination of Thionyl Chloride[1]

BY HAROLD SIMMONS BOOTH AND FRANCIS CARL MERICOLA

In 1896, M. Meslans[2] found that when thionyl chloride was treated with certain metallic fluorides such as zinc fluoride, a gaseous product, thionyl fluoride was formed. He reported this gas as being colorless and boiling in the neighborhood of −30° and added that the gas attacked the respiratory organs vigorously. Later Moissan and Lebeau[3] prepared this gas using free fluorine and also arsenic trifluoride as the fluorinating agents.

In 1905, Ruff and Thiel[4] prepared thionyl fluoride by heating N_4S_4 and hydrogen fluoride in the presence of water and cupric oxide in a sealed glass tube for two hours at 100°.

Since none of the previous investigators found any intermediate fluorination products, it seemed advisable to study the fluorination of thionyl chloride by means of antimony fluoride in the presence of a catalyst. This reaction has been successfully applied to the stepwise fluorination of various non-polar halides in this Laboratory.[5,6]

Experimental

The generator was similar to that described by Booth and Bozarth.[6] The sublimed antimony trifluoride was slowly fed into the refluxing reaction mixture of 80% thionyl chloride and 20% antimony pentachloride (maintained at 50°, and at 200 mm. pressure) at such a rate that the automatic bleed-off valve would be continually in the open position but such that it would not allow the pressure to rise more than a few millimeters above this point. In this way as soon as any thionyl chlorofluoride was formed it was immediately removed from the reaction zone, thus ensuring the maximum yield. Reaction took place immediately.

The distillation analysis revealed the product to consist of 50% thionyl fluoride, 20% thionyl chlorofluoride, 5% sulfur dioxide and about 25% unreacted thionyl chloride. The yields were dependent upon the conditions of the reaction. Higher temperatures and pressures increased the percentage of thionyl fluoride and thus decreased the yield of the chlorofluoride. If the pressure were kept too low, thionyl chloride would distil out of the reaction zone.

The design and operation of the purification system was as already described[7] save that a glass spiral replaced the copper spiral in the fractionating column since copper was attacked. After the first rough separation two distillations in the column were sufficient to obtain pure gases for the determination of properties.

Analysis.—The samples were taken in small bulbs as liquids and absorbed in aqueous sodium hydroxide as usual.[8] Chlorine was determined gravimetrically as silver

(1) From a portion of a thesis submitted by Francis Carl Mericola in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry, to the Graduate School of Western Reserve University, May, 1938.

(2) M. Meslans, *Bull. soc. chim.*, [3] **15**, 391 (1896).

(3) H. Moissan and P. Lebeau, *Compt. rend.*, **130**, 1436 (1900).

(4) O. Ruff and K. Thiel, *Ber.*, **38**, 549 (1905).

(5) H. S. Booth and C. F. Swinehart, THIS JOURNAL, **54**, 4751 (1932).

(6) H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927 (1939).

(7) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(8) Booth and Dutton, THIS JOURNAL, **61**, 2937 (1939).