[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Sodium Hydroxide Solutions from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND JOHN C. HECKER

Harned and Nims[2] by measurements of the electromotive forces of the cells Ag | AgCl | NaCl (m) | Na_xHg | NaCl (0.1) | AgCl | Ag through the temperature range of 0 to 40° have computed the activity coefficient, the partial molal heat content relative to 0.1 M sodium chloride, and the relative partial molal specific heat of sodium chloride in aqueous solution. These results are the first of their kind in which cells containing sodium amalgam electrodes were employed. More recently, Harned and Ehlers by employing the cells H_2 | HCl (m) | AgCl | Ag have made a very comprehensive study of the above thermodynamic properties of hydrochloric acid in aqueous solution from 0 to 60°.[3] In order to complete a work in which we have in the first place measured the sodium amalgam electrode and in the second place the hydrogen electrode against the silver–silver chloride electrode, we have completed measurements of the cells H_2 | NaOH (m_2) | Na_xHg | NaOH (m_1) | H_2, in which the hydrogen electrode is measured against the amalgam electrode. The only earlier measurements of these cells were made by Harned, whose results were obtained at only one temperature, 25°. The present measurements are much more comprehensive and include results at 5° intervals from 0 to 35° inclusive.[4]

There is little doubt that measurements of this kind are very valuable for the determination of partial free energies and activity coefficients. Since the relative partial molal heat contents and specific heats are obtained from the first and second derivatives of the original electromotive forces great accuracy in the evaluation of these quantities is difficult to obtain. In the case of hydrochloric acid solutions, excellent agreement with the best calorimetric determinations of these quantities was attained. Amalgam cells are difficult and, consequently, it is not to be expected that so great precision is possible as with the simpler cells. We shall show, however, that good values of the heat data are obtainable.

In the case of sodium chloride solutions, Harned and Nims did not extrapolate their values of the partial molal heat content to zero concentration of salt but gave their results relative to zero at 0.1 M. An important feature of the present study is the introduction of a method of extrapolation of this quantity which we have employed not only with our results but with those of Harned and Nims.

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(1) This communication contains material from a dissertation presented by John C. Hecker, to the Graduate School in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1933.

(2) Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

(3) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(4) Harned, *ibid.*, **47**, 677 (1925).

Materials, Experimental Technique and Electromotive Forces of the Cells: $H_2 | NaOH (m) | Na_xHg | NaOH (0.05) | H_2$.—The highest grade of sodium hydroxide purified by alcohol was used. A saturated solution was prepared and the sodium carbonate which is insoluble in this solution settled to the bottom of the flask. The clear solution was drawn off into freshly distilled carbon dioxide-free water which formed a stock solution of approximately 4 *M*. This solution was boiled under reduced pressure and kept in an atmosphere of carbon dioxide-free air. From this solution 15 liters of 0.05 *M* solution was prepared and kept under nitrogen. A glass tube led directly from the vessel containing this solution to the cells which were fixed in the thermostat. The solutions at the different concentrations in the other half of the cell were made by diluting the stock solution, were boiled under reduced pressure and kept in an atmosphere of nitrogen until introduced into the cell.

Titration with weight burets against gravimetrically analyzed hydrochloric acid solutions was employed for purposes of standardization. The concentrations were known to ±0.05%.

A type of cell similar to that employed by Harned[4] which contained flowing sodium amalgam electrodes was used. A vacuum technique was employed. One modification of the cell design should be mentioned. An additional stopcock was placed between the hydrogen and amalgam electrode compartments in each half cell. This made it possible to use the same hydrogen electrode half cells at each of the eight temperatures at which measurements were made. The cells were filled with the oxygen free solutions at 0° with the stopcock open, hydrogen electrodes were introduced and four hours allowed for them to attain equilibrium. The amalgam was allowed to flow and a measurement taken. At the end of the measurement after all the amalgam had flowed from the dropper, the stopcocks between the hydrogen and amalgam electrodes were closed. The amalgam droppers were removed and replaced by rubber stoppers. The amalgam half cells were then drained, evacuated and refilled with solution, and the amalgam introduced into the dropper. In the meantime, the thermostat temperature was raised 5°. Two hours were allowed for the cell to reach equilibrium before the 5° measurement of electromotive force was made. The same procedure was repeated for each succeeding measurement until a temperature of 35° was reached.

The hydrogen electrodes were of the usual platinized platinum foil type. The sodium amalgam was prepared as described by Harned and was approximately 0.01% by weight of sodium. The temperature control was ±0.02°.

The original electromotive forces made at fourteen concentrations and eight temperatures were of necessity at odd concentrations and were first smoothed to round concentrations. In the first place, a small correction was made to remedy the fact that the reference solution was not quite 0.05 *M*. The smoothing to round concentrations was then carried out in the following manner. The electromotive forces of the cells are given by

$$E - \frac{2RT}{NF}\ln\frac{m}{0.05} = \frac{2RT}{NF}\ln\frac{\gamma}{\gamma_{0.05}} + \frac{RT}{NF}\ln\frac{p_{0.05}}{p_m} \qquad (1)$$

where γ is the activity coefficient of sodium hydroxide in a solution of concentration m, and $\gamma_{0.05}$ is its activity coefficient in the 0.05 *M* reference solution. The second term on the right represents the contribution to the electromotive force produced by the transfer of water which takes place in the cell according to the equation NaOH (m) + H_2O (0.05) = NaOH (0.05) + H_2O (m). p_m and $p_{0.05}$ are the vapor pressures of water over the solutions of concentrations m and 0.05, respectively. A sensitive large graph was made by plotting the left side of equation (1) against $m^{1/2}$ at each temperature. From the values of this function at round concentrations, smoothed values of E were obtained at each temperature. At constant composition, E may be expressed as a function of the temperature by the equation

$$E = E_0 + at + bt^2 \qquad (2)$$

where E_0 is the electromotive force at 0°, a and b are constants and t is centigrade temperature. The constants were determined by the method of least squares. Table I contains the values of the electromotive forces computed by equation (2) as well as the values of the constants of this equation. Comparison with measured values is shown by parenthesized

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: H_2 | NaOH (m) | Na_xHg | NaOH (0.05) | H_2, CALCULATED BY EQUATION (2), AND DEVIATIONS, $E_{\text{calcd.}} - E_{\text{obs.}}$

m	*t*...0°	5°	10°	15°
0.25	0.06929	0.07070(12)	0.07207(4)	0.07341(−3)
.5	.10018	.10027(15)	.10431(3)	.10628(−8)
1	.13156	.13444(4)	.13725(−4)	.13997(0)
1.5	.15113	.15445(4)	.15767(−2)	.16082(−2)
2	.16600	.16963(3)	.17317(−2)	.17662(−2)
2.5	.17853	.18261(−17)	.18652(−9)	.19030(2)
3	.19033	.19471(−19)	.19893(−8)	.20296(−1)
3.5	.20176	.20618(−9)	.21046(−16)	.21459(−1)
4	.21261	.21711(−4)	.22148(−9)	.22572(0)

m	*t*...20°	25°	30°	35°
0.25	0.07471(3)	0.07596(−5)	0.07719(−9)	0.07839(9)
.5	.10826(0)	.11017(−1)	.11203(−6)	.11385(6)
1	.14261(−2)	.14519(1)	.14767(3)	.15007(−3)
1.5	.16386(−3)	.16682(1)	.16969(7)	.17247(−4)
2	.17997(−1)	.18322(0)	.18637(6)	.18944(−4)
2.5	.19392(5)	.19740(8)	.20072(3)	.20391(−8)
3	.20683(8)	.21050(6)	.21402(9)	.21734(−11)
3.5	.21859(17)	.22245(−1)	.22617(5)	.22973(−7)
4	.22981(0)	.23375(7)	.23758(6)	.24126(−7)

TABLE I (*Concluded*)

Constants of equation (2)

m	0.25	0.5	1	1.5	2	2.5	3	3.5	4
$a \times 10^6$	285	422	585	672	736	829	895	898	915
$-b \times 10^6$	0.73	0.90	1.59	1.79	1.91	2.97	2.52	2.82	2.76
$-b' \times 10^6$	.6	1.0	1.55	1.90	2.15	2.45	2.62	2.78	2.94

figures, which give the deviations in hundredths of millivolts. The values of b were plotted against the temperature and the smoothed values b', to be used later on to compute the relative partial molal heat capacity, are also given in the table.

Activity Coefficients.—In order to compute γ, or $(\gamma_{\mathrm{Na}}\gamma_{\mathrm{OH}})^{1/2}$, it is first necessary to compute the vapor pressures of the solutions. By rearranging equation (1) and substituting k for 2.3026 RT/F, we obtain

$$\log \frac{\gamma}{\gamma_{0.05}} = \frac{E}{2k} - \log \frac{m}{0.05} - \frac{1}{2} \log \frac{p_{0.05}}{p_m} \qquad (3)$$

The vapor pressure of the solvent is related to the activity coefficient of the solute by the equation

$$-\partial \ln p = \frac{\nu}{55.51} \int \partial m + \frac{\nu}{55.51} \int m \, \partial \ln \gamma \qquad (4)$$

Upon substituting the limits corresponding to m and 0.05, integrating and rearranging this equation, we obtain

$$\frac{1}{2} \log \frac{p_{0.05}}{p_m} = \frac{1}{55.51} m \log \frac{\gamma}{\gamma_{0.05}} + \frac{(m - 0.05)}{55.51 \times 2.303} \qquad (5)$$

The desired term on the left was evaluated by arithmetical approximation. As a first approximation the last term on the right was employed to compute this quantity. This approximate value along with E and m were substituted on the right of equation (3) and the first approximation to the logarithm of the activity coefficient ratios was obtained. With these values the first term on the right of equation (5) was evaluated graphically. This plus the last term of equation (5) served to give a closer approximation to one-half the logarithm of the vapor pressure ratio which latter when substituted in equation (3) gave a closer estimate of the logarithm of the activity coefficient ratios. This process was repeated until the values of equation (5) remained constant. Table II contains the results of this calculation at the designated molalities and at 0 and 35°. It is important to note that the temperature coefficient of the quantity in question is small and varies only in the fourth decimal place. One in this decimal place corresponds to only a difference of 0.01 mv. Consequently, the correction may be regarded as constant or independent of the temperature since this assumption is within the experimental error. As a consequence the effect of the vapor pressure ratios upon the temperature coefficient of E is negligible, a fact which is of considerable value when we come to the computations of the heat data.

TABLE II

THE VAPOR PRESSURE TERM

m	0.25	0.5	1	1.5	2	2.5	3	3.5	4
$^1/_2 \log p_{0.05}/p_m$:									
0°	0.0015	0.0033	0.0071	0.0110	0.0152	0.0197	0.0248	0.0313	0.0369
35°	.0015	.0033	.0072	.0111	.0152	.0199	.0251	.0311	.0367

The final values of log $\gamma_{0.05}$ are given in Table III. In order to obtain $\gamma_{0.05}$ from these data, we employed the equation of Hückel or equation (11) in the communication of Harned and Ehlers.[3] The values used for the constant of the Debye and Hückel theory were those computed by Harned and Ehlers and given in the second column of their Table VII. The A and B constants of this equation were evaluated and are given in Table III.

TABLE III

ACTIVITY COEFFICIENT DATA AND CONSTANTS OF HÜCKEL'S EQUATION

log ($\gamma/\gamma_{0.05}$)

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.25	− .0611	− .0598	− .0590	− .0584	− .0592	− .0584	− .0572	− .0593
.5	− .0789	− .0765	− .0748	− .0737	− .0726	− .0721	− .0719	− .0702
1	− .0941	− .0898	− .0864	− .0838	− .0821	− .0809	− .0803	− .0807
1.5	− .0935	− .0886	− .0846	− .0813	− .0793	− .0780	− .0772	− .0774
2	− .0855	− .0802	− .0758	− .0723	− .0700	− .0685	− .0677	− .0678
2.5	− .0713	− .0640	− .0584	− .0541	− .0514	− .0501	− .0498	− .0509
3	− .0467	− .0386	− .0322	− .0276	− .0247	− .0236	− .0235	− .0245
3.5	− .0146	− .0103	+ .0024	+ .0013	+ .0034	+ .0044	+ .0047	+ .0032
4	+ .0219	+ .0275	+ .0315	+ .0343	+ .0358	+ .0360	+ .0355	+ .0337

Constants of Hückel's equation

	0°	5°	10°	15°	20°	25°	30°	35°
A	0.688	0.721	0.738	0.752	0.718	0.754	0.825	0.814
a(Å.)	3.00	3.14	3.20	3.25	3.10	3.24	3.54	3.45
B	0.0410	0.0410	0.0422	0.0432	0.0472	0.0460	0.0420	0.0434
$-\log \gamma_{0.05}$	.0861	.0859	.0861	.0863	.0868	.0875	.0871	0.0881
$\gamma_{0.05}$	.820	.821	.820	.820	.819	.818	.818	.816

Normal concentrations, c

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	0.05002	0.05002	0.05000	0.04997	0.04992	0.04986	0.04978	0.04971
.25	.2506	.2505	.2503	.2501	.2497	.2494	.2491	.2488
.50	.5023	.5020	.5015	.5010	.5003	.4998	.4988	.4980
1.0	1.0058	1.005	1.004	1.003	1.002	.9990	.9981	.9957
1.5	1.510	1.508	1.506	1.504	1.501	1.499	1.489	1.483
2.0	2.013	2.010	2.007	2.005	2.001	1.997	1.994	1.989
2.5	2.514	2.510	2.506	2.505	2.500	2.496	2.490	2.484
3.0	3.015	3.009	3.003	2.998	2.994	2.985	2.976	2.972
3.5	3.508	3.504	3.498	3.492	3.485	3.477	3.469	3.463
4.0	4.000	3.993	3.985	3.976	3.969	3.962	3.950	3.941

The values of the apparent ionic diameter, "a," computed from A by means of equation (12) and the values of K' in Table VII of Harned and Ehlers' paper are also given. By employing these constants, $-\log \gamma_{0.05}$ was obtained, from which the values of $\gamma_{0.05}$ given in Table III were evaluated. The concentrations c, in moles per liter of solution, which are necessary for these calculations are recorded in the lower part of this table.

It is important to note that the Hückel equation may be used to compute the experimental values of γ from 0.05 to 1 M and is not valid in the more concentrated solutions. This is similar to the behavior of hydrochloric acid in aqueous solution as found by Harned and Ehlers. We have not resorted to the additional refinements imposed by Harned and Ehlers since owing to the greater difficulties inherent in our measurements, the accuracy although good is not equal to that obtainable with the simpler cell employed by them. However, the use of the Hückel equation may be expected to yield a good extrapolation for γ and a value of $\gamma_{0.05}$ which is probably correct to within ±0.002. Incidentally, the present results at 25° agree well up to 1.5 M with those of Harned.[4] The values of the mean distance of approach "a" are reasonable. The fact that they show a tendency to increase with the temperature should not be taken seriously, since in the cases where "a" appears to increase, B tends to decrease. Therefore, we conclude from these results that as a first approximation "a" is not a function of the temperature and has a value of approximately 3.3 Å.

The Relative Partial Molal Heat Content of Sodium Hydroxide.— By the Gibbs–Helmholtz equation

$$\overline{H}_m - \overline{H}_{0.05} = NEF - NFT\,(\mathrm{d}E/\mathrm{d}T) \tag{6}$$

the partial molal heat content relative to the 0.05 M solution may be computed from the electromotive forces. We desire the partial molal heat content of the hydroxide and not that of both hydroxide and water which as previously pointed out would be derived from the processes taking place within the cell. Fortunately, since the vapor pressure term in equation (3) can be taken to be independent of the temperature without interfering with the accuracy, it is only necessary to apply the vapor pressure correction to the electromotive forces and not to their temperature coefficients. Therefore, we may express the electromotive forces, E', resulting from the transfer of sodium hydroxide only by

$$E' = E_0' + at + bt^2 \tag{7}$$

whence it is obvious that the original a and b values can be employed for computing the temperature coefficients without further change.

Since we desire $\overline{L}_2$ or $\overline{H}_m$–$\overline{H}_0$, it is necessary for us to devise methods for the evaluation of $\overline{H}_{0.05}$–$\overline{H}_0$. If, as shown by Harned and Ehlers, the Debye and Hückel equations with supplementary constants permit an accurate calculation of the activity coefficients, this can be done by substitution of log γ in the Gibbs–Helmholtz equation and subsequent differentiation. In the following treatment of this subject, we have developed this method in a general manner and in a way which renders the computations relatively easy. From the equations thus derived an empirical extrapolation formula has been obtained which has proved useful in the present instance and also permits the extrapolation of the results obtained by Harned and Nims with sodium chloride solutions.

$\overline{L}_2$ may be computed from the well known equation

$$\overline{L}_2 = -\nu RT^2 \frac{\partial \ln f}{\partial T} \tag{8}$$

by substitution of the value of $\ln f$, the logarithm of the "rational" activity coefficient, or the activity divided by the mole fraction, as expressed by an equation which is the equivalent of Hückel's equation. Thus

$$\overline{L}_2 = \nu RT^2 \frac{\partial}{\partial T} \left\{ \frac{z_1 z_2 e^2}{2kDT} \frac{\kappa}{1 + \kappa a} - bc \right\} \tag{9}$$

Taking D, c, a, T and b as variables, this differentiation gives

$$\overline{L}_2 = \nu z_1 z_2 \, L \frac{\sqrt{\Gamma}}{1 + \mathrm{A}\sqrt{\Gamma}} - \nu z_1 z_2 \, w \frac{\Gamma}{(1 + \mathrm{A}\sqrt{\Gamma})^2} \left[\frac{\mathrm{d}a}{\mathrm{d}T} + \frac{a}{z} \frac{\mathrm{d}\, ln\, \Gamma}{\mathrm{d}T} - y \right] - \nu RT^2 \left(b \frac{\mathrm{d}c}{\mathrm{d}t} + c \frac{\mathrm{d}b}{\mathrm{d}T} \right) \tag{10}$$

At constant temperature, L, w, and y are constants. The first term is the limiting slope resulting from the Debye–Hückel theory and is expressed by

$$L = -\frac{3}{4} \frac{Re^2\, 3.557 \times 10^9}{kD\,(DT)^{1/2}} \left(1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T} + \frac{T}{3V}\frac{\mathrm{d}V}{\mathrm{d}T} \right) \tag{11}$$

$$w = \frac{2.0635 \times 10^{16}}{D^2};\ y = \frac{1}{2T}\left[1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T} \right]$$

By using the values of $\mathrm{d}D/\mathrm{d}T$ computed from the equation according to Wyman[5] and the values of d "d"/dT obtained from the densities of water,[6] the values of L, w and y given in Table IV were evaluated. It is obvious that $-\mathrm{d} \log v/\mathrm{d} \log T = \mathrm{d} \log$ "d"$/\mathrm{d} \log T$. "a" in centimeters may be

TABLE IV

VALUES OF QUANTITIES IN EQUATIONS (10) AND (16)

t, °C.	L	Q	$-y \times 10^4$	$x \times 10^8$	$w \times 10^{-12}$
0	153	3.40	8.360	4.358	2.665
5	169	3.67	9.238	4.349	2.787
10	190	3.96	10.092	4.338	2.916
15	210	4.22	10.909	4.327	3.053
20	231	4.48	11.692	4.315	3.195
25	254	4.72	12.452	4.302	3.345
30	278	4.96	13.177	4.288	3.503
35	303	5.19	13.869	4.274	3.668
40	329	5.44	14.539	4.258	3.844
45	357	5.67	15.326	4.243	4.026
50	385	5.89	15.776	4.226	4.218
55	414	6.08	16.318	4.209	4.418
60	446	6.30	16.863	4.192	4.633

Values of constants: $e = 4.774 \times 10^{-10}$; $N = 6.061 \times 10^{23}$; $k = 1.372 \times 10^{-16}$; $R = 1.9885$; 1 cal. = 4.185 joules; $F = 96{,}500$.

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(5) Wyman, *Phys. Rev.*, **35**, 623 (1930); Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III.

calculated from the parameter, A, of Hückel's equation by $a = \mathrm{A}x$, and b is related to the parameter B in Hückel's equation by $bc = 2.3026\ \mathrm{B}\Gamma$. Values of x are also given in Table IV.

At constant temperature it can be seen that the second term of equation (10) is a function of $c/(1 + \mathrm{A}\sqrt{\Gamma})^2$, and the third term is a function of c. Therefore, at a given temperature

$$\overline{L}_2 = \nu z_1 z_2 L \frac{\sqrt{\Gamma}}{(1 + \mathrm{A}\sqrt{\Gamma})} + \frac{Kc}{(1 + \mathrm{A}\sqrt{\Gamma})^2} + K'c \qquad (12)$$

in which K and K' are constants.

The cell measures $\overline{H}_m - \overline{H}_{0.05}$ and not $\overline{L}_2$. Therefore, it is necessary to construct two equations at two concentrations at which $\overline{H}_m - \overline{H}_{0.05}$ has been measured and solve simultaneously for K and K'. In the present instance, the values of $\overline{H}_m - \overline{H}_{0.05}$ at 0.25 M and 1 M were substituted, and the constants obtained are given in Table V. With the use of these constants in equation (12), the values of $\overline{H}_{0.05} - \overline{H}_0$ were computed. From these and the values of $\overline{H}_m - \overline{H}_{0.05}$ calculated by equation (6) and smoothed by plotting against $m^{1/2}$, the values of $\overline{L}_2$ in the table were compiled.

TABLE V

RELATIVE PARTIAL HEAT CONTENT OF SODIUM HYDROXIDE: $\overline{L}_2 = \overline{H} - \overline{H}_0$ (CAL.)

m	0°	5°	10°	15°	20°	25°	30°	35°
0.05	− 7	22	50	80	108	137	167	200
.25	− 200	− 130	− 50	30	100	180	250	330
.5	− 390	− 305	−190	− 95	− 10	80	115	315
1	− 670	− 540	−410	−280	−160	− 20	130	270
1.5	− 810	− 670	−520	−360	−205	− 50	100	260
2	− 940	− 770	−615	−420	−240	− 80	100	300
2.5	−1060	− 870	−700	−460	−260	− 70	145	360
3	−1125	− 925	−730	−475	−260	− 35	200	430
3.5	−1175	− 980	−750	−485	−250	5	250	520
4	−1190	−1000	−795	−490	−240	50	310	600
$-K \times 10^{-3}$	3.26	3.02	2.22	1.54	1.24	0.934	0.485	0.014
$-K' \times 10^{-3}$	0.1	0.102	0.236	0.316	0.390	.277	.286	.330

As a check upon this computation of $\overline{H}_{0.05} - \overline{H}_0$, we have employed equation (9), and obtained 18, 100 and 180 cals. at 5, 20 and 35°, respectively. These results agree as well as expected with 22, 108 and 200 cal. obtained by the use of equation (12).

The final results are shown in Fig. 1 in which $\overline{L}_2$ is plotted against $m^{1/2}$ at 0, 20, 25 and 30°. The dotted line represents the values obtained by Rossini[7] from calorimetric data at 18° whence it is seen that good agreement has been obtained. The curves are of the same form as those obtained in the case of sodium chloride by Harned and Nims. This could be predicted by equation (10) and a knowledge of the temperature coefficients of a and B. The first term of this equation is positive. da/dT will be

[7] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

zero or nearly so. This will make the second term negative since y is negative and larger than the contribution due to the term containing the temperature coefficient of log Γ. Now, if dB/dT is positive and greater than dc/dT, which in all cases is negative above 5°, the third term of equation (10) will be negative. This state of affairs is true in the cases of sodium chloride and hydroxide solutions. If dB/dT is negative, as with hydrochloric acid solutions, then the third term of equation (10) will be positive, a fact previously discussed by Harned and Ehlers.

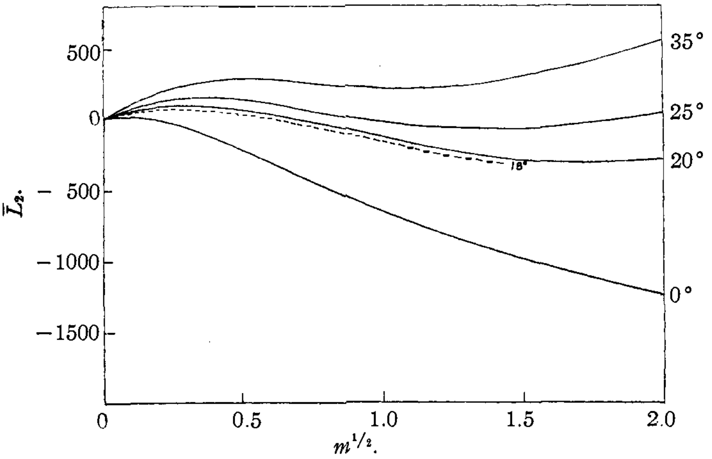

Fig. 1.—The relative partial molal heat content of sodium hydroxide in aqueous solution.

The peculiar tendency of the curves in Fig. 1 to bend upward in the concentrated solutions indicates that empirical equation (12) is not valid at concentrations above 1 M. An additional term such as Dc^n in the original Debye and Hückel equation for ln f should remedy this defect. Harned and Ehlers employed a term Dc^2 with success in their treatment of hydrochloric acid solutions. Since our data are not of as high accuracy as theirs, we have not resorted to this refinement. This discrepancy does not detract from the usefulness of equation (12) to determine $\bar{L}_2$ at some low reference concentration such as 0.05 M.

The Relative Partial Molal Heat Capacity of Sodium Hydroxide in Aqueous Solution.—$\bar{C}_p - \bar{C}_{p_0}$ was obtained in a manner similar to that described by Harned and Ehlers. For the cells in question, the relation between E and relative partial molal heat capacity is given by

$$\bar{C}_{p_{0.05}} - \bar{C}_p = NFT\frac{\partial^2 E}{\partial T^2} \qquad (13)$$

From equation (2)

$$\partial^2 E/\partial T^2 = 2b \qquad (14)$$

Hence

$$\bar{C}_p - \bar{C}_{p_{0.05}} = -NFT2b \qquad (15)$$

The values of this quantity may be computed from the smoothed values of b, given by b' in Table I. If these are added to 6 cal., which is found to be the value of $\bar{C}_{p_{0.05}} - \bar{C}_{p_0}$ from the slope of the plot of $\bar{H}_{0.05} - \bar{H}_0$ against T, $\bar{C}_p - \bar{C}_{p_0}$ may readily be obtained. The limiting equation of the Debye and Hückel theory can conveniently be expressed by

$$\bar{C}_p - \bar{C}_{p_0} = \nu z_1 z_2 Q \sqrt{\Gamma} \tag{16}$$

Values of Q from 0 to 60° were computed and are included in Table IV.

In Fig. 2, $\bar{C}_p - \bar{C}_{p_0}$ at 25° is plotted against $m^{1/2}$. The dotted line represents the results recently obtained by Gucker and Schminke[8] from calorimetric measurements from 0.04 to 2.5 M. The agreement is good when we consider that the maximum deviation is 2 cal., which occurs at 1 M. Our results also check those computed by Rossini to within a few calories.[9]

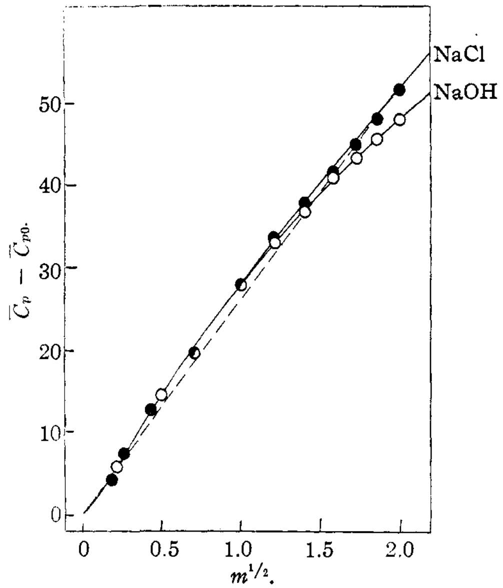

Fig. 2.—The relative partial molal specific heat of sodium hydroxide in aqueous solution at 25°.

$\bar{H} - \bar{H}_0$ and $\bar{C}_p - \bar{C}_{p_0}$ of Sodium Chloride from Electromotive Force Data.—We have previously mentioned that Harned and Nims in their investigation of sodium chloride solutions determined $\bar{H} - \bar{H}_{0.1}$ of this electrolyte but did not extrapolate their results to zero concentration. Further, they used a graphical method involving plots of first order differences of the electromotive forces against the temperature in order to obtain the constants of equation (2) and subsequently, $\bar{H} - \bar{H}_{0.1}$. Since our earlier computations did not agree with the calorimetric data so well as in the cases of sodium hydroxide and hydrochloric acid solutions, we have subjected the results to a recalculation by using the method of least squares for evaluation of a and b constants of equation (2). We found that the new values of $\bar{H} - \bar{H}_{0.1}$ derived therefrom did not differ sufficiently from those obtained by Harned and Nims to warrant a published revision. Our next step was to employ equation (12) in order to determine $\bar{L}_2$ at 0.1 M. The values of A employed were those given by Harned and Nims. Suffice to say that $\bar{H}_{0.1} - \bar{H}_0$ was found to be -88, -50, -10, 29, 68,

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

(9) Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

106, 146, 186 and 225 at 0, 5, 10, 15, 20, 25, 30, 35 and 40°, respectively. If these be added to the values given in Table III of Harned and Nims, $\bar{L}_2$ as measured from their electromotive forces may be computed. From the slope of the plot of $\bar{L}_2$ at 0.1 M against T, $\bar{C}_p - \bar{C}_{p_0}$ at this concentration is found to be 8 cals.

The agreement with calorimetric data is only fair. At 18° the results agree with values recently computed by Rossini to within ±30 cal., which is considered very good.[7,9] At 25°, our results do not check those recently computed by Robinson[10] nearly so well. They agree up to 0.5 M quite closely. Above this concentration, the difference increases until it reaches a maximum of 100 cal. at 1.5 M and then decreases to 50 cal. at 4 M. This maximum deviation corresponds to an error of approximately 0.01 mv. per degree in the temperature coefficient of electromotive force. In general, our values of $\bar{L}_2$ show a wider spread with temperature than those computed from the calorimetric data. This leads to higher values for $\bar{C}_p - \bar{C}_{p_0}$ than were found by Randall and Rossini.[11]

For the sake of comparison, we have reëvaluated $\bar{C}_p - \bar{C}_{p_0}$ by the method employed in the present communication. Thus, according to equation (15), we have

$$(\bar{C}_p - \bar{C}_{p_0}) = (\bar{C}_p - \bar{C}_{p_{0.1}}) + (\bar{C}_{p_{0.1}} - \bar{C}_{p_0}) = -NFT2b + 7.9 \qquad (17)$$

In Table VI are given the values of b and $\bar{C}_p - \bar{C}_{p_0}$ at 25° which latter are shown in Fig. 2 by inked-in circles. It is to be noted that these results are nearly the same as those for sodium hydroxide. As previously pointed out by Harned and Nims, the agreement with the values of Randall and Rossini is only fair.

TABLE VI

$(\bar{C}_p - \bar{C}_{p_0})_{25}$ OF SODIUM CHLORIDE

m	0.05	0.1	0.2	0.5	1	1.5	2	2.5	3	3.5	4
$(-b) \times 10^6$	−0.25	..	0.32	0.90	1.47	1.93	2.22	2.50	2.75	2.98	3.20
$(\bar{C}_p - \bar{C}_{p_0})$	4.5	7.9	12.3	20.3	28.1	34.4	38.4	42.3	45.7	48.9	51.9

Further Considerations.—The present investigation completes a series of results in which the hydrogen, silver–silver chloride and sodium amalgam electrodes have been combined with each other to form three separate cells from the measurements of which the thermodynamic properties of aqueous hydrochloric acid, sodium hydroxide and sodium chloride have been computed. The most important feature of results of this kind is the determination of the partial free energies and activity coefficients, since such determinations yield directly information regarding the fundamental parameters which are employed to express these quantities. When we attempt the determination of partial molal heat contents and heat capacities, we are subjecting the original data to a very severe test, since the

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(10) Robinson, THIS JOURNAL, **54**, 1311 (1932).

(11) Randall and Rossini, *ibid.*, **51**, 323 (1929).

determination of these quantities involves the first and second differential coefficients of the original results with the temperature. If our results agree with those determined by well conducted calorimetric measurements, we have reason to believe in the accuracy of the original electromotive forces as well as the calorimetric data. In matters of this sort, it is very important to obtain agreement by the use of entirely different experimental mechanisms.

Considering all the difficulties, both experimental and arithmetical, we regard the agreement so far obtained to be very encouraging, particularly in those cases when the amalgam electrode has been employed. This among other facts surely indicates that these measurements approach closely the cell mechanism which has been premised.

Summary

1. Measurements of the cells $H_2 | NaOH\ (m) | Na_xHg | NaOH\ (0.05) | H_2$ have been made from 0 to 35° at 5° intervals.

2. From these, activity coefficients, relative partial molal heat contents and heat capacities of sodium hydroxide from 0 to 35° have been computed. Good agreement has been obtained with calorimetric data.

3. A useful equation for the extrapolation of the partial molal heat content has been developed.

STERLING CHEMISTRY LABORATORY
NEW HAVEN, CONNECTICUT

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A Study of the Cell, Pt/Quinhydrone, HCl (0.01 *M*)/AgCl/Ag, and the Normal Electrode Potential of the Quinhydrone Electrode from 0 to 40°[1]

BY HERBERT S. HARNED AND DONALD D. WRIGHT

Since its introduction in 1921, the quinhydrone electrode has found wide use as a convenient substitute for the hydrogen electrode in determining the *P*H of acid solutions, particularly in cases where the substances under examination are reduced by hydrogen in the presence of platinum black. However, in relatively few instances has it been employed in cells without liquid junctions, for the precise evaluation of thermodynamic data. Therefore, preliminary to using such cells in a determination of the dissociation constants of chloroacetic and other substituted acids, we found it necessary to study carefully the cell

$$Pt/Quinhydrone,\ HCl\ (m)/AgCl/Ag \qquad (I)$$

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[1] The material contained in this paper forms part of the dissertation presented to the Faculty of the Graduate School of Yale University by Donald D. Wright in June, 1933, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.