Hughes.[20] The energy of activation for this reaction in solvents of constant dielectric constant appears to be "normal." However, the values reported in this paper are not sufficiently precise for use in testing modern theories.

Summary

Experimental velocity measurements have been made for the reactions of ethyl iodide with the solvent, sodium hydroxide, triethylamine, sodium acetate, and lithium nitrate in aqueous alcohol mixtures at 25 and 50°.

Velocity constants have been calculated by

(20) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, London, 1935, p. 1122.

graphical methods which correct for the solvent reaction and have been correlated with modern acid-base theories.

An explanation of the "dilution effect" has been suggested and evidence has been presented which indicates that the nitrate ion is a direct reactant with ethyl iodide so that the influence of lithium nitrate is not primarily "inert salt catalysis."

Approximate values of the energies of activation for the reaction of ethyl iodide with the various bases have been calculated.

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The Thermodynamics of Aqueous Sodium Chloride Solutions from 0 to 40° from Electromotive Force Measurements

BY HERBERT S. HARNED AND MELVIN A. COOK

This communication contains a brief summary of the thermodynamic properties of aqueous sodium chloride solutions from 0 to 40° derived principally from the measurements of cells without liquid junction containing a dilute sodium amalgam. Our recent studies of solutions of sodium[1] and potassium hydroxides[2] and potassium chloride[3] have shown that reasonable agreement between the results derived from electromotive forces with those derived from calorimetric or vapor pressure data is obtained if certain precautions regarding extrapolation and the numerical treatment of the data be observed. In the present communication, we have subjected the earlier data of Harned and Nims[4] to a more recently developed technique of calculation with the result that better agreement with results of other measurements is obtained.

Activity Coefficients.—The electromotive force data of Harned and Nims were extrapolated by the use of the equation

$$\log \gamma = -\frac{u/\sqrt{c}}{1 + A\sqrt{2c}} + Bc - \log(1 + 0.036m) \quad (1)$$

Only the results in the region of concentration of 0.1 to 1 M were employed. As shown by us,[3] this method leads to an accurate extrapolation

(1) Harned and Hecker, THIS JOURNAL, **55**, 4838 (1933).
(2) Harned and Cook, ibid., **59**, 496 (1937).
(3) Harned and Cook, ibid., **59**, 1290 (1937).
(4) Harned and Nims, ibid., **54**, 423 (1932).

whereas if the equation is applied over a wider concentration range, for example 0.1 to 3 M, low values of A and γ are obtained. Using the precise evaluation of γ in dilute solution by Brown and MacInnes[5] from cells with liquid junction and the accurate determination of the relative partial molal heat content, $\bar{L}_2$, from 10 to 25° by Gulbransen and Robinson,[6] we are able to obtain an entirely independent check of our extrapolation. The values of $\bar{L}_2$ at 0.1 M determined by the latter are given as a function of temperature by

$$\bar{L}_{2(0.1)} = -1277 + 4.62T \quad (2)$$

Upon substitution in the equation for the variation of the activity coefficient with temperature, integration, and evaluation of the integration constant by employing Brown and MacInnes' value of 0.7784 for γ at 0.1 M and 25°

$$-\log \gamma_{0.1} = \frac{139.56}{T} + 1.1625 \log T - 3.2358 \quad (3)$$

is obtained from which $\gamma_{0.1}$ may be computed as a function of temperature. A comparison of the two methods of extrapolation is illustrated in Table I.

The value of the apparent ionic diameter, a, was found equal to 4.0 ± 0.1 Å. at all temperatures. In the computations by equation (1),

(5) Brown and MacInnes, ibid., **57**, 1356 (1935).
(6) Gulbransen and Robinson, ibid., **56**, 2637 (1934).

TABLE I

$\gamma_{0.1}$ BY TWO INDEPENDENT METHODS OF EXTRAPOLATION

t	0	5	10	15	20	25	30	35	40
$\gamma_{0.1}$ (Eq. 3)	0.7809	0.7809	0.7807	0.7802	0.7793	0.7784	0.7773	0.7757	0.7743
$\gamma_{0.1}$ (Eq. 1)	.781	.782	.782	.782	.781	.779	.776	.774	.773
d_0	˙.9999	1.0000	.9997	.9991	.9982	.9970	.9957	.9940	.9922
$-A'$	.0160	0.0166	.0171	.0176	.0180	.0183	.0186	.0188	.0189

4 Å. was used for "a" and values of B employed were computed by

$$B = 0.0340 + 143 \times 10^{-5} t - 2.6 \times 10^{-5} t^2 + 0.013 \times 10^{-5} t^3 \quad (4)$$

valid at 0.1 M. The values of c employed in equation (1) were obtained from the equation

$$c/m = d_0 + A'm \quad (5)$$

the isothermal constants of which are given in Table I.

The agreement between values of $\gamma_{0.1}$ obtained by equations (3) and (1) shown in the second and third rows of the table is good at all temperatures. Only at two temperatures is a difference as great as 0.002 obtained.

A confirmation of the accuracy of the results at 25° is obtained by comparing the values of γ of potassium[3] and sodium chloride obtained from amalgam cell measurements with those derived from isopiestic vapor pressure measurements by Robinson and Sinclair.[7] The ratios of the activity coefficient of sodium chloride to that of potassium chloride obtained by us are 1.013, 1.020, 1.046, 1.084, 1.122, 1.165, 1.261 and 1.368 at 0.1, 0.2, 0.5, 1, 1.5, 2, 3 and 4 M while 1.013,

TABLE II

ACTIVITY COEFFICIENTS OF AQUEOUS SODIUM CHLORIDE SOLUTION FROM AMALGAM CELL MEASUREMENTS

m	γ_0	γ_{15}	γ_{25}	γ_{40}
0.05	(0.825)	(0.823)	(0.821)	(0.817)
.1	(.781)	(.782)	(.779)	(.773)
.2	.731(2)	.735(0)	.733(0)	.727(2)
.5	.671(2)	.680(2)	.681(1)	.675(2)
1	.638(2)	.654(2)	.658(0)	.655(0)
1.5	.626	.650	.657	.656
2	.631	.661	.671	.673
2.5	.641	.679	.692	.695
3	.660	.704	.720	.725
3.5	.687	.736	.753	.760
4	.717	.773	.793	.799
A	.918	.924	.930	.935
B	.0340	.0485	.0533	.0575

The numbers in parentheses following the values of γ are the differences in the third decimal places between the observed values of γ and those computed by equation (1). They are positive when the calculated value is greater than that observed.

(7) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934).

1.022, 1.047, 1.087, 1.126, 1.170, 1.256 and 1.363 are obtained from the vapor pressure measurements at these concentrations. This agreement is excellent since the maximum difference in the two sets of values is 0.5%.

Values of γ at some temperatures are given in Table II. Those in parentheses at 0.05 and 0.1 M were calculated by equation (1) using values of B obtained by equation (4). At 0.05 M, the results of Harned and Nims are in error to a small extent and have been omitted from consideration. The results at 25° are in very close agreement with those obtained from electromotive force measurements by Harned.[8]

At 0°, our results are in accord with those derived by Scatchard and Prentiss[9] from freezing point data, provided that their results be changed to conform with our value of 0.781 at 0.1 M.[10]

The Relative Partial Molal Heat Content and Heat Capacity.—The relative partial molal heat content at lower concentrations was obtained by the differentiation of equation (1) by the method previously used by us.[2,3] At the higher concentrations, it was obtained by the Gibbs–Helmholtz equation. The final results may be expressed within the error of estimation by the equation

$$\bar{L}_2 = \bar{L}_{2(0)} + \alpha t + \beta t^2 \quad (6)$$

Values of $\bar{L}_{2(0)}$, α and β are given in Table III. The results from 0 to 1 M are plotted in Fig. 1. The diameter of the circles is 60 cal. and represents an error of ± 30 cal., which is the order of magnitude to be expected from the electromotive force measurements. The dots, diameter 20 cal., represent Gulbransen and Robinson's results. Up to $m^{1/2}$ equal to 0.5, there is no appreciable difference in the two series of results. At $m^{1/2}$ equal to 0.65, the results are the same at 10, 15 and 20° but the result of Gulbransen and

(8) Harned, *ibid.*, **51**, 416 (1929).

(9) Scatchard and Prentiss, *ibid.*, **55**, 4355 (1933).

(10) We note that this value differs considerably from 0.787 which was obtained by graphical extrapolation by Scatchard and Prentiss. In a private communication, Professor Scatchard has informed us that by employing the least square method and series formulas of varying number of terms, values of $\gamma_{0.1}$ from 0.782 to 0.785 were obtained. Guggenheim[11] by a special method obtained 0.783.

(11) Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

TABLE III
THE RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT
CAPACITY CONSTANTS OF EQUATION (6)

m	$\bar{L}_{2(0)}$	α	β	$(\bar{C}_p - \bar{C}_{p0})_{25}$	$\frac{(C_p - C_{p0})_{25}{}^{6}}{}$	$\frac{(C_p - C_{p0})_{25}{}^{12}}{}$
0.05	20	2.6	0.015	3.3	3.5	4.8
.1	− 10	4.4	.020	5.4	5	6.8
.2	− 105	7.8	.025	9.0	7.1	9.6
.5	− 330	14.4	.038	16.2	11.2	15.3
1	− 640	20.5	.046	22.7	15.6	21.6
1.5	− 917	25.2	.053	26.5	....	26.4
2	−1160	30.9	.059	33.8	....	31.0
2.5	−1435	37.0	.064	40.2	....	34.2
3	−1625	41.2	.071	44.7	....	37.2

Fig. 1.—$\bar{L}_2$ versus $m^{1/2}$: ○, 60 cal.; ●, 20 cal.

Robinson at 25° is somewhat lower than ours. At $m^{1/2}$ equal to 0.9, their value at 20° agrees with ours but their result at 25° is lower. We have also indicated by the dotted line the results of Rossini's[13] computations at 18°. The agreement with our results is within the estimated error of the two series.

Values of the relative partial specific heat derived from the electromotive force data are compiled in the fifth column of Table III. The values obtained by Gulbransen and Robinson at the lower concentrations and those obtained by Rossini at the higher concentrations are given in the last two columns. Excellent agreement with Rossini's results is obtained from 0.2 to 2 M and with Gulbransen and Robinson's from 0.05 to 0.2 M. At 0.5 and 1 M Gulbransen and Robin-

(12) Rossini, *Bur. Standards J. Research*, **7,** 47 (1931).
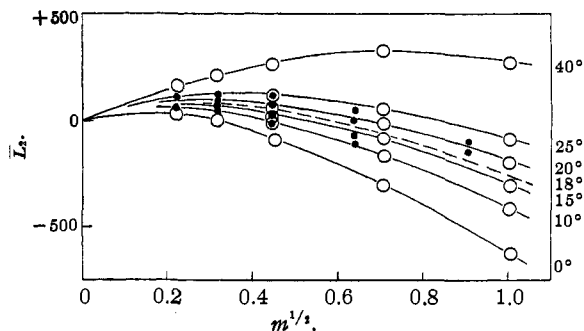(13) Rossini, *ibid.*, **6**, 791 (1931).

son's values are lower than either of the other series of data. At the higher concentrations, 2 to 3 M, our results are higher than Rossini's. This indicates that our values of $\bar{L}_2$ spread too rapidly from 2 M to the higher concentrations since the calorimetric determination of $\bar{C}_p - \bar{C}_{p_0}$ should be accurate in the concentrated solutions.

Summary

1. The thermodynamics of aqueous sodium chloride solutions derived from electromotive force measurements has been reconsidered.

2. The results have been considered in their relation to other electromotive force measurements, vapor pressure, freezing point, heat of dilution and specific heat measurements. Good coördination between the results derived from all these sources is obtained.

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The Boiling Point Elevation.   I.   Apparatus for the Study of Aqueous Solutions with Non-Volatile Solutes

BY RODNEY P. SMITH

In recent years considerable progress has been made in the development of the physical chemistry of ionized solutes, through a comprehensive program of experimental research on the thermodynamic properties of solutions, carried out by a large number of investigators. Many different types of measurement have been used, each method giving the same fundamental thermodynamic quantities, within certain limits of the more important variables involved, namely, the concentration, the temperature, the dielectric constant, and the pressure.[1]   It is of considerable im-

(1) For a general review of the subject see Harned, *J. Franklin Inst.*, **225**, 623 (1938).

portance to extend the measurements over as wide a range of the variables as is practical. Extensive data are already available for a number of solutions of widely varying concentration and dielectric constant in the temperature range 0 to 50°, while very little work is available in the temperature range 60 to 100°. As a part of this general program we have undertaken a systematic study of the properties of solutions in the latter temperature range, by measuring the boiling point rise. These results combined with the material already available from measurements of the freezing point lowering, electromotive force, and vapor pressure lowering will yield a knowledge of the