

A 13-junction thermel of similar construction, except that the entire case was glass, was calibrated with one set of junctions in melting ice at 0° and the other set at each of ten different temperatures between 40 and 130°. The temperature of the hot junctions was determined within 0.01° with a platinum resistance thermometer that had been calibrated by the Bureau of Standards; the resistance was measured with a Leeds and Northrup Mueller-type bridge. The calibration was performed in duplicate, first with one set of junctions in ice and then with the hot and cold junctions reversed. The agreement between the two sets of results was within the experimental error and indicated a satisfactory homogeneity of the thermel. The 26-junction thermel was calibrated against the 13-junction thermel by a direct differential method.⁴ The single-junction thermel used in the measurement of the reference temperature of the boiling point elevations was calibrated by a method similar to that described for the 13-junction thermel.

Example of Reproducibility

As a typical example of the observed deviations, the measurements obtained with a 0.3 *M* sodium chloride solution are given in Table I. Each value of the boiling point elevation θ is the average of three sets of observations, each set consisting of 10 consecutive readings taken at quarter minute intervals. A small correction has been applied to the observed values of θ to make them correspond to a concentration of exactly 0.3 *M* and to the even reference temperature *t*; $\Delta\theta$ is the difference in θ for two independent determinations; columns A, B, and C give the deviation, to one hundred thousandth of a degree, of the average

(4) See Burtlew and Smith, *THIS JOURNAL*, 61, in press (1939), for a description of the technique of calibration of a thermel by a direct differential method.

<i>t</i>	θ	$\Delta\theta \times 10^5$	A	B	C	D	E
60	0.21570		+ 2	+1	-3	+25	-22
60	.21634	64	+ 7	-7	0	+47	-32
70	.23115		+ 1	-5	-4	+27	-20
70	.23109	6	-13	+8	+6	+33	-41
80	.24703		- 4	+8	-4	+16	-27
80	.24695	8	- 6	+1	+4	+33	-22
90	.26359		+ 4	+4	-8	+38	-32
90	.26362	3	+ 4	+2	-6	+16	-20
100	.37443		+ 3	-1	-2	+20	-31
100	.37478	35	+ 3	+5	-8	+32	-32

of each of the three sets of 10 readings from the mean of the thirty readings; columns D and E give the maximum positive and negative deviation, to one hundred thousandth of a degree, of the individual observations from the mean of the thirty. The value of $\Delta\theta$ represents the combined errors of the temperature and the concentration determinations. A consideration of these results together with those obtained at other concentrations shows no systematic relation between the magnitude of the deviations and the reference temperature.

Summary

1. An apparatus for measuring the boiling point elevation of aqueous solutions at pressures of 150 to 760 mm. is described.

2. The reproducibility of the boiling point elevations was found to be $\pm 0.0002^\circ$. A typical example of the observed deviations is given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Boiling Point Elevation. II. Sodium Chloride 0.05 to 1.0 *M* and 60 to 100°

BY RODNEY P. SMITH

The thermodynamic properties of aqueous sodium chloride solutions have been determined accurately in the temperature range 0 to 40°.¹⁻³ To extend the knowledge of these properties to higher temperatures we have determined the boiling point elevation of these solutions in the temperature range 60 to 100°. The evaluation of the activity coefficient of one salt in this temperature range may also be used as a basis for the determination of the activity coefficient of other salts in the same temperature range, by the iso-

piestic vapor pressure method of Robinson and Sinclair.⁴

Results and Calculations

If the boiling point of the solvent under a certain pressure *p* is T_0 and that of the solution under the pressure *p* is $T_0 + \theta$, and if the molal heat of vaporization of the solvent under the same pressure is expressed as a function of θ by the equation⁵

$$\Delta H = \Delta H_0 - b\theta - c\theta^2 - d\theta^3 \quad (1)$$

(4) Robinson and Sinclair, *ibid.*, 56, 1830 (1934).

(5) The constants of equation (1) were evaluated from the data given by Keyes and Keenan, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936, and Osborne, Stimson and Fiock, *Bur. Standards J. Research*, 5, 411 (1930).

(1) Harned and Cook, *THIS JOURNAL*, 61, 495 (1939).

(2) Brown and MacInnes, *ibid.*, 57, 1356 (1935).

(3) Scatchard, *ibid.*, 55, 4355 (1933).

TABLE I
CONSTANTS FOR EQUATIONS (2), (3), (5) AND (6)

t	$\frac{\Delta H_0}{\text{int. j./mole}}$	b'	c'	$d' \times 10^3$	μ'	A'	$B/2 \times 10^2$
60	42488.9	295.6377	1.36659	5.5272	1.2499	1.3392	5.468
70	42043.1	285.2212	1.25139	4.7772	1.2793	1.3461	5.484
80	41590.5	275.3535	1.14276	4.0915	1.3108	1.3542	5.476
90	41127.6	265.7926	1.01500	3.2606	1.3439	1.3625	5.391
100	40655.8	256.9587	0.95652	2.9994	1.3790	1.3710	5.274

the activity of the solvent at the temperature $T_0 + \Theta$ and the pressure p is given by⁶

$$\ln a'_1 = - \int_{T_0}^{T_0 + \Theta} \frac{\Delta H}{RT^2} dT = - 1/RT_0^2 (\Delta H_0 \Theta - b'\Theta^2/2 + c'\Theta^3/3 - d'\Theta^4/4 + \dots) \quad (2)$$

The osmotic coefficient, φ' , at the temperature $T_0 + \Theta$ and at the pressure p may be defined by the equation⁷

$$\varphi' = -55.5074 \ln a'_1 / \nu m = 55.5074 \frac{\Delta H_0 \Theta}{\nu RT_0^2} m (1 - b'\Theta/2 \Delta H_0 + c'\Theta^2/3 \Delta H_0 - d'\Theta^3/4 \Delta H_0 + \dots) \quad (3)$$

where ν is the number of ions formed from one molecule of solute. The constants of equation (3) are given in Table I. The last term of this equation is negligible in this calculation. The mean activity coefficient at the corresponding temperature and pressure is given by the equation

$$\ln \gamma' = \varphi' - 1 + \int_0^m (\varphi' - 1) d \ln m \quad (4)$$

which is readily derived from the fundamental equation $d(m[1 - \varphi']) = -m d \ln \gamma$, obtained by Bjerrum.⁸

The values of φ' calculated from equation (3) may be smoothed by plotting $\delta\varphi$, defined by the equation

$$\varphi' = 1 - \frac{\mu'}{(A')^3 m} [1 + A' \sqrt{m} - 2 \ln(1 + A' \sqrt{m}) - 1/(1 + A' \sqrt{m})] + B m/2 + \delta\varphi \quad (5)$$

against m or \sqrt{m} . In equation (5) μ' and A' are the constants of Hückel's⁹ equation multiplied by the square root of the density of the solvent and B is the constant of the linear term. The numerical values of μ' and A' as determined from the data given in the "International Critical Tables" together with Wyman's¹⁰ values of the dielectric constants, and the assumption that the mean collision diameter of the ions at all tempera-

(6) Equation (2) is analogous to equation (2) of Saxton and Smith, *THIS JOURNAL*, **54**, 2626 (1932).

(7) The present method of evaluating γ' employing the φ' function has been suggested by Professor George Scatchard, Massachusetts Institute of Technology, and is similar to that used by Scatchard and Prentiss, *ibid.*, **50**, 2314 (1934).

(8) Bjerrum, *Fysisk. Tids.*, **15**, 66 (1916); *Z. Elektrochem.*, **24**, 325 (1918).

(9) Hückel, *Physik. Z.*, **26**, 93 (1925).

(10) Wyman, *Phys. Rev.*, **35**, 623 (1930).

tures is equal to 4.0 Å. as found by Harned and Cook¹ from data in the temperature range 0 to 40° are given in Table I. The B constants were chosen to fit the experimental results in the most concentrated solutions. Equations (4) and (5) then give

$$\ln \gamma' = - \mu' \sqrt{m} / (1 + A' \sqrt{m}) + Bm + \int_0^m \delta\varphi d \ln m + \delta\varphi \quad (6)$$

The activity coefficient, γ' , may also be evaluated by a method analogous to that given by Lewis and Randall¹¹ for the calculation of γ' from measurements of the freezing point depression.^{12,6} If their j function is defined by the equation $j = 1 - \Theta/\nu\lambda m$ where λ is the molal elevation of the boiling point, equation (2) becomes

$$\ln \gamma' = -j - \int_0^m j d m/m - b'' \int_0^m \Theta d \Theta/m + c'' \int_0^m \Theta^2 d \Theta/m + \dots \quad (7)$$

where b'' and c'' differ from b' and c' by the factor $55.5074/\nu RT_0^2$. The experimental values of Θ for the dilute solutions may be smoothed with the equation

$$\Theta = - \nu\lambda\mu'/(A')^3 [1 + A' \sqrt{m} - 2 \ln(1 + A' \sqrt{m}) - 1/(1 + A' \sqrt{m})] + \nu\lambda B' m^2/2 + \frac{\lambda}{0.018} \ln(1 + 0.018 \nu m) \quad (8)$$

If the results in the dilute range of concentration are not of sufficient accuracy to allow the direct evaluation of the first integral of equation (7), this equation may be used to calculate the ratio of γ' to $\gamma'_{0.1}$. Hückel's⁹ equation is then used to calculate $\gamma'_{0.1}$ by an extrapolation which has been shown to be valid in the case of electromotive force measurements at lower temperatures.¹

The activity coefficients have been calculated by both methods. Since the first is largely analytical while the second is principally graphical, this procedure serves as a check on the accuracy of the numerical computations.

(11) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y.

(12) Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

The average experimental values of the boiling point elevation, Θ , are given in Table II.

TABLE II

BOILING POINT ELEVATIONS					
m	Θ_{60}	Θ_{70}	Θ_{80}	Θ_{90}	Θ_{100}
0.05	0.0368	0.0394	0.0421	0.0450	0.0479
.079	.0577	.0618	.0660	.0704	.0751
.10	.0727	.0778	.0832	.0888	.0946
.14	.1014	.1084	.1159	.1237	.1318
.20	.1441	.1543	.1650	.1760	.1874
.30	.2160	.2311	.2470	.2636	.2808
.40	.2882	.3083	.3298	.3518	.3746
.50	.3615	.3867	.4135	.4413	.4699
.60	.4356	.4658	.4979	.5311	.5656
.70	.5105	.5459	.5837	.6221	.6629
.80	.5864	.6273	.6700	.7146	.7613
1.00	.7406	.7926	.8467	.9028	.9614

Table III gives the smoothed values of the osmotic coefficient, ϕ' , determined from equations (3) and (5) and the curves of Fig. 1. In this

TABLE III
OSMOTIC COEFFICIENTS

m	ϕ'_{60}	ϕ'_{70}	ϕ'_{80}	ϕ'_{90}	ϕ'_{100}
0.05	0.9404	0.9390	0.9380	0.9362	0.9351
.079	.9328	.9311	.9300	.9281	.9266
.10	.9291	.9273	.9263	.9242	.9226
.14	.9245	.9226	.9216	.9193	.9175
.20	.9210	.9190	.9178	.9156	.9135
.30	.9194	.9174	.9161	.9139	.9114
.40	.9207	.9186	.9170	.9149	.9123
.50	.9234	.9212	.9195	.9174	.9145
.60	.9267	.9246	.9228	.9207	.9178
.70	.9307	.9280	.9267	.9243	.9214
.80	.9350	.9239	.9310	.9285	.9256
1.00	.9442	.9424	.9402	.9374	.9345

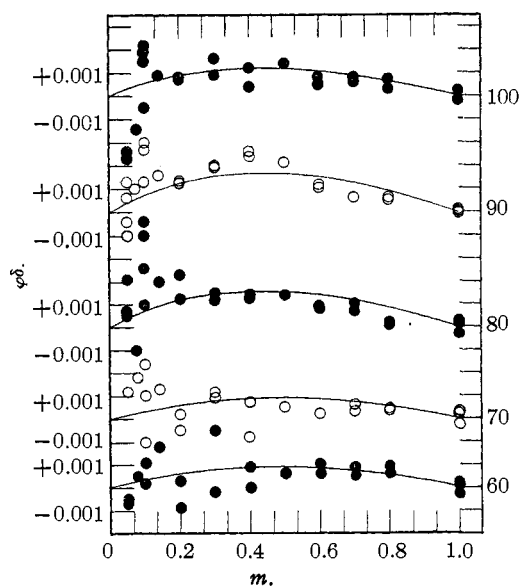


Fig. 1.—Deviations of osmotic coefficients.

figure the solid lines give the smoothed values of $\delta\phi$ and the circles represent the deviations of the individual measurements. In terms of Θ the largest deviation corresponds to 0.0004° while the greater number of the results show deviations of 0.0002° or less.¹³

The activity coefficients, γ' , determined from equation (6) are given in Table IV. The numbers in parentheses are the differences in the third places between γ' calculated by equation (6) and by the second method involving equation (7). They are positive when the former is greater than the latter. The greatest difference in γ' as calculated by the two methods is 0.002. While the values of γ' calculated by equation (6) tend to be a little higher at the lower temperatures, the difference is not of sufficient magnitude to be of significance.

Within the pressure range employed the values of γ' may be considered as equal to those at normal pressure.¹⁴ The values of γ' and γ the activity coefficient at the temperature T_0 are the same except for the 1 molal solution at 80, 90 and 100° , for which the latter is 0.001 greater.

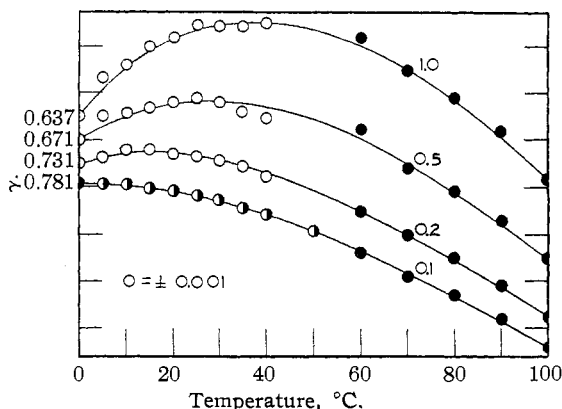


Fig. 2.—The activity coefficient of sodium chloride in solutions of 0.1, 0.2, 0.5, and 1.0 M concentration as a function of the temperature: \circ , calculated^{1,15}; \bullet , e. m. f.; \bullet , boiling point.

The values of $\gamma'_{0.1}$ given in Table IV compare favorably with the values of $\gamma_{0.1}$ at 100, 90, 80, 70, and 60° , calculated by Harned¹⁵ from $\gamma_{0.1}$ at 25° determined by Brown and MacInnes,² and the heat data of Gulbransen and A. L. Robinson.¹⁶ He obtained 0.745, 0.751, 0.756, 0.761, and 0.766 at these temperatures, respectively. In Fig. 2

(13) For a typical example of the deviations of the individual measurements see Smith, *THIS JOURNAL*, **61**, 497 (1939).

(14) Adams, *Chem. Rev.*, **19**, 1 (1936).

(15) Harned, *J. Franklin Inst.*, **225**, 497 (1938).

(16) Gulbransen and Robinson, *THIS JOURNAL*, **56**, 2637 (1934).

TABLE IV
 ACTIVITY COEFFICIENTS

m	γ'_{80}	γ'_{70}	γ'_{80}	γ'_{90}	γ'_{100}
0.05	0.811	0.807	0.808	0.799	0.794
.079	.782	.777	.773	.768	.763
.10	.766(0)	.762(+1)	.757(0)	.752(0)	.746(0)
.14	.744(0)	.739(+1)	.734(0)	.729(+1)	.722(0)
.20	.721(0)	.717(+1)	.711(0)	.705(0)	.698(0)
.30	.697(0)	.691(0)	.686(0)	.679(-1)	.672(-1)
.40	.682(0)	.676(+1)	.671(+1)	.663(-1)	.655(-1)
.50	.672(0)	.667(+2)	.660(0)	.653(-1)	.644(-2)
.60	.665(0)	.659(+2)	.653(+1)	.645(0)	.636(-1)
.70	.661(+1)	.654(+1)	.648(+1)	.640(0)	.631(-1)
.80	.657(0)	.651(+1)	.644(+1)	.636(0)	.627(-1)
1.00	.655(+1)	.648(+1)	.641(+1)	.632(-1)	.622(-2)

the activity coefficients of sodium chloride determined from the boiling point elevation and from electromotive force measurements,¹ are plotted against the temperature. To save space each curve has a different reference point, the ordinate figures give the values of γ at 0° for the corresponding curve. The diameter of each circle represents a variation in γ of ± 0.001 . An inspection of Fig. 2 shows an excellent agreement between the results obtained by the two methods. While the values of γ at 60° appear to be too high by 0.001 to 0.002 at concentrations above 0.2 M , these deviations are not greater than the expected experimental error. However, the fact that they are all in the same direction would indicate that the observed values

of θ at 60° were slightly too high. This is quite reasonable in view of the greater uncertainty of the measurements at the lower pressures.¹³

Summary

1. The boiling point elevations of aqueous sodium chloride solutions have been measured at reference temperatures of 60, 70, 80, 90, and 100°, and at a number of concentrations between 0.05 and 1.0 M .

2. The activity coefficients of the solute have been calculated.

3. A comparison of the results obtained from the boiling point rise with those obtained from e. m. f. measurements is given.

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The Hydrogenation of Ethane on Cobalt Catalysts

BY ELLISON HALL TAYLOR AND HUGH S. TAYLOR

The immediate precursor of the present study was the work of Morikawa, *et al.*,^{1,2,3} on the activation of the C-H and C-C bonds in hydrocarbons at the surface of a nickel catalyst. By studying two reactions of the same two reactants on the same surface, these authors were able to give to the term "specificity" a concrete meaning. It became immediately a problem of interest to extend the study to other catalysts, in order to see how the factors affecting such reactions would vary from catalyst to catalyst. The hydrogenation-decomposition of ethane gave results of more

interest than the exchange, first because of the abnormally high hydrogen dependence and apparent activation energy, and second because it involved breaking a carbon-carbon bond, a step of more general importance in the transformations of other hydrocarbons than breaking a carbon-hydrogen bond. It was therefore decided to study that reaction on a different catalyst.

Cobalt presented itself as an interesting catalyst for such a study. One reason for the selection of cobalt was its rising industrial importance as a catalyst in the Fischer process.⁴ It was therefore decided to use first a catalyst typical of those actually used in that process, one of

(1) Morikawa, Benedict and Taylor, *THIS JOURNAL*, **58**, 1445 (1936).

(2) *Ibid.*, **58**, 1795 (1936).

(3) Morikawa, Trenner and Taylor, *ibid.*, **59**, 1103 (1937).

(4) Franz Fischer, *Brennstoff Chemie*, **16**, 1 (1935).