Solid below 61.55°K.

$$\log P(\text{cm.}) = -\frac{418.2}{T} + 4.127 \log T + 1.47365 - 0.02623\,T$$

The free energy function for carbon monoxide was calculated from spectroscopic data and tabulated to 5000°K. These data were combined with similar data on oxygen and with the available calorimetric data on graphite to give ΔF for the reaction $C_{\text{graphite}} + \frac{1}{2}O_2 = CO$ to 3000°K.

The free energy of formation of carbon monoxide from β graphite and oxygen at 298.1°K. was found to be $\Delta F^\circ_{298.1} = -33,000$.

BERKELEY, CALIFORNIA

THE ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION FROM BOILING POINT DATA[1]

BY BLAIR SAXTON AND RODNEY P. SMITH

Although the thermodynamic properties of aqueous salt solutions at ordinary temperatures have been extensively investigated, few data are available for the study of these properties at higher temperatures. Measurements of the boiling point elevation of solutions could be used for such a study if sufficient accuracy in the measurement could be attained. Considerable data[2] have been published on the boiling point elevation of salt solutions. However, due to superheating, variation of pressure, errors of analysis or temperature measurement, the results are not of sufficient accuracy for a calculation of the activity coefficient. It has seemed worth while, therefore, to attempt to design an apparatus for a more accurate determination of the boiling point elevation.

Apparatus

Of the different methods used for the elimination of superheating, the one suggested by Cottrell[3] and used by Washburn and Read,[4] Pearce and Hicks,[5] and Bancroft and Davis[6] seems to be the most satisfactory.

The first apparatus, Fig. 1, consisted of a Pyrex tube, A, 43 cm. long and 7.6 cm. inside diameter, over which was sealed a larger tube, B, 28 cm. long, 11.5 cm. inside diameter. A condenser, C, and a small drain tube, D, were sealed into the outer tube, B. A tube, E, for the "cold" junction of the thermocouple was also sealed into the

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[1] Part of this paper is from a dissertation submitted by Rodney P. Smith to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] For summary of results see "International Critical Tables," Vol. III, p. 324.

[3] Cottrell, THIS JOURNAL, 41, 721 (1919).

[4] Washburn and Read, ibid., 41, 729 (1919).

[5] Pearce and Hicks, J. Phys. Chem., 30, 1678 (1926).

[6] Bancroft and Davis, ibid., 33, 591 (1929).

outer tube, B. (For all but the dilute solutions, however, it was found that the cold junction was affected by the temperature of the solution tube, thus necessitating the use of an outside hypsometer.) The solution tube, G, fitted into the ground opening, F. A ground-glass stopper carried a tube, J, for the hot junction of the thermocouple, and two small tubes, I, for the lead-wires to the platinum heating coil. The heating coil was of No. 22 wire and had a resistance of about 0.04 ohm. The seal through the lead-wire tubes was made with heavy tungsten wire, the platinum wire being soldered to the tungsten with hard silver solder. Con-

tact between the lead wires and the tungsten was made with mercury. The lead-wires were of sufficient size to carry 20 to 25 amperes without heating. A Cottrell pump, L, was fixed in the center of the solution tube. Samples for analysis were withdrawn through a large capillary tube, N. The pure solvent in the outer tube was heated with a gas flame. The entire apparatus was protected from air currents by a transite box.

Fig. 1.

The apparatus has the advantages of electric heating and the Cottrell pump as a means of eliminating super-heating. Since the solution is heated nearly to its boiling point by the vapor of the pure solvent, only a small amount of heat is required from the electric heating coil. Thus, it is possible to boil the solution with a drop of potential across the heating coil below the decomposition potential of the solution. A small transformer was used as a source of current for the heating coil.

A 20-junction No. 36 copper–No. 30 constantan thermocouple, constructed according to the specification of White,[7] was used to measure the elevations. The thermocouple was calibrated from the following fixed points: freezing point of mercury, transition point of sodium sulfate, transition point of manganous chloride, boiling point of water and boiling point of naphthalene. The e. m. f. of the thermocouple was measured with a shielded Leeds and Northrup type K potentiometer.

The pressure was maintained constant to less than 0.1 mm. by an apparatus similar to that described by Carroll, Rollefson and Mathews.[8]

The degree of superheating was found to be zero by using pure water, both in the inside and in the outer tubes. The accuracy of this apparatus was found to be 0.0025°.

With the Cottrell pump it is not possible to raise the solution very high above the surface of the liquid; therefore, unless the end of the thermocouple tube is near the surface of the liquid, its immersion depth is not very great. Due to the large heat con-
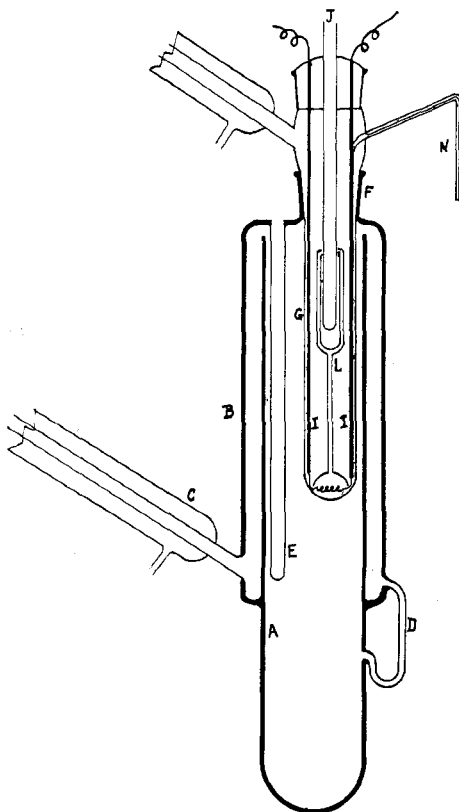
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[7] White, THIS JOURNAL, **36**, 2292, 2313 (1914).

[8] Carroll, Rollefson and Mathews, *ibid.*, **47**, 1791 (1925).

ductivity of multi-junction thermocouples, there is the danger that the observed eleva-tions are too low. With the view of eliminating this possible error, a second apparatus, shown in Fig. 2, was designed. The solution tube consisted of a two-liter Pyrex round-bottomed flask, connected through a ground-glass stopper to an upper chamber, B, by three tubes, C, D and E. The tube,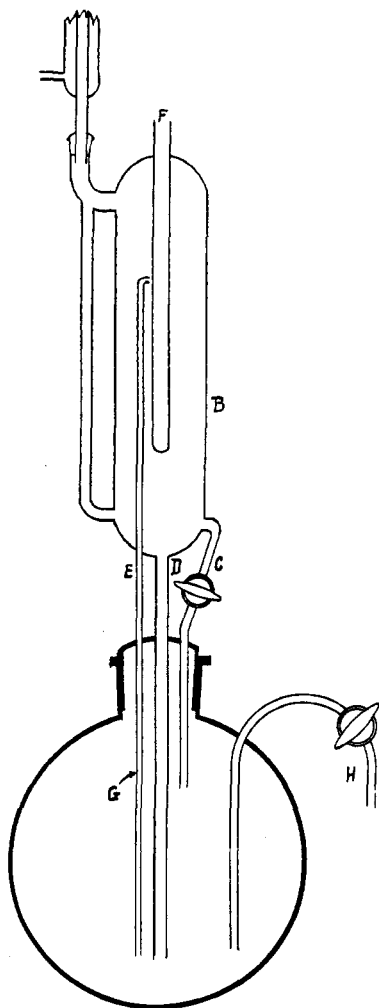 F, for the thermocouple was sealed in the center of the upper chamber, B. By partially closing the stopcock in tube C, a slight pressure was developed in the solution flask, causing the solution to rise slightly in the tube E; vapor was allowed to pass into the tube E through a pin-hole, G. The vapor, in rising through the tube E, carried small amounts of solution with it, thus causing an intimate mixture of liquid and vapor to squirt continuously over the thermo-couple tube, F. With this arrangement, the immersion depth of the thermocouple was more than doubled. The tube D served to return the solution to the solution flask. Samples for analysis were withdrawn through the tube H. Since the volume of the solution used with this apparatus was relatively large, it was possible to draw off samples for analysis of 100 to 150 cc., thus decreasing the error due to evapora-tion while the sample was being taken.

The "cold" junction of the thermocouple was in another apparatus of exactly similar design. The entire apparatus was enclosed in an insulating box. Gas flames were used as a source of heat.

A 26-junction copper–constantan thermo-couple, calibrated against a standard platinum resistance thermometer with a Bureau of Stand-ards certificate, was used with this apparatus.

Readings constant to $0.0005°$ could be obtained over time periods of about an hour; however, due to some error which we were not able to eliminate, readings over longer periods of time may vary as much as $0.0015°$.

Fig. 2.

Theory.—The theory of the calcula-tion of the activity coefficient of a non-volatile strong electrolyte from the boil-ing point of the solution is identical with that developed by Lewis and Randall[9] for the case of freezing point lowering, the proper changes having been made. Taking the pure liquid solvent as the standard state and expressing T as $T_0 + \theta$, where T_0 is the boiling point of the pure solvent and θ is the eleva-tion of the boiling point; and expressing ΔH as $\Delta H_{(T_0)} + \Delta C_p \theta$, where

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Sub-stances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 282 ff.

$\Delta H_{(T_0)}$ is the molal heat of vaporization of the pure solvent at its boiling point and ΔC_p is the molal increase in heat capacity of the pure solvent on vaporization, we obtain

$$\text{d} \ln a_1' = - \frac{\text{d}\theta}{RT_0^2} \left[\Delta H_{(T_0)} - \left(\frac{2 \Delta H_{(T_0)}}{T_0} - \Delta C_p \right) \theta + \left(\frac{3 \Delta H_{(T_0)}}{T_0^2} - \frac{2 \Delta C_p}{T_0} \right) \theta^2 + \ldots . \right]$$

(1)

Using the values given in Volume 5 of the "International Critical Tables," we obtain

$$\Delta H_{(T_0)} = 40.679 \text{ j. mole}^{-1} \text{ }^{10a}$$
$$C_{p(l)} = 75.72 \text{ j. mole}^{-1} \text{ }^{10b}$$
$$C_{p(v)} = 36.34 \text{ j. mole}^{-1} \text{ }^{10c}$$
$$\Delta C_p = -39.38 \text{ j. mole}^{-1}$$

Hence, taking T_0 as $373.1°$ and R as 8.315 j. mole^{-1} degree^{-1}

$$\text{d} \ln a_1' = (-0.03514 + 0.0002224 \; \theta + \ldots .) \; \text{d}\theta$$

(2)

where a_1' is the activity of the solvent at the boiling point of the solution. The geometrical mean activity of a solute completely dissociated into ν ions is then given by

$$\text{d} \ln a_{\pm}' = \frac{\text{d}\theta}{\nu \lambda m} - 0.01235 \frac{\theta \text{d}\theta}{\nu m}$$

(3)

where m is the molality of the solute and $\lambda = \text{d}\theta/\text{d}m$ at infinite dilution. Hence, $\lambda = 1/55.508 \times 0.03514 = 0.5126.$[11] The mean activity coefficient of the solute at the boiling point of the solution is given by

$$\text{d} \ln \gamma' = - \text{d}j - \frac{j}{m} \text{d}m - \frac{0.01235}{\nu} \frac{\theta}{m} \text{d}\theta$$

(4)

where j, which is equal to one minus Φ, the osmotic coefficient of Bjerrum,[12] is defined as in Lewis and Randall[13] by the equation

$$j = 1 - \frac{\theta/m}{\nu \lambda}$$

Integration of equation (4) gives the equation

$$\log \gamma' = -0.4343 \, j - 0.4343 \int_0^m \frac{j}{m} \text{d}m - \frac{0.00536}{\nu} \int_0^m \frac{\theta}{m} \text{d}\theta$$

(5)

These equations differ from that used by Cann and Gilmore[14] in that our value of λ is slightly lower and in accord with that given by Randall[15] (0.5125), but particularly in the numerical coefficient of the last term of the equation. We differ in sign and magnitude. Apparently they have used a value identical with that given by Lewis and Randall for freezing point

[10] "International Critical Tables," Vol. V, p. (a) 138, (b) 113, (c) 82.

[11] This value varies slightly with the barometric pressure. See Washburn and Read, THIS JOURNAL, 41, 729 (1919).

[12] Bjerrum, Z. Elektrochem., 24, 321 (1918).

[13] Lewis and Randall, Ref. 9, p. 347.

[14] Cann and Gilmore, J. Phys. Chem., 32, 72 (1928).

[15] Randall, Trans. Faraday Soc., 23, 502 (1927).

lowering. It is quite obvious that their value is wrong in both sign and magnitude since, for the boiling point, $dT = d\theta$, and the coefficient contains both $\Delta H_{(T_0)}$ and ΔC_p.

Since the last integral in equation (5) is relatively small, it offers no difficulty and is evaluated graphically as usual. The first integral, however, requires that accurate values of j be obtained in very dilute solutions in order that it be similarly treated. This is more difficult to accomplish than it is with the freezing point method, due mainly to the facts that λ is smaller and that it is more difficult to obtain true equilibrium between solution and saturated vapor than it is between solution and ice. We have, therefore, used the Debye–Hückel theory in dealing with the dilute solutions.

In sufficiently dilute solutions the activity coefficient may be calculated by means of the equation of Debye and Hückel; hence, we may write

$$\ln \gamma = \frac{-k \sqrt{c}}{1 + A \sqrt{c}}$$

where c is the concentration in moles of solute per liter of solution and in dilute solutions may be set equal to m, the molality of the solution, times d, the density of the pure solvent. At $100°$ the error in $\sqrt{c}$ at 0.1 m thus introduced is only 0.1%. Making this substitution, we obtain

$$\ln \gamma = \frac{-k \sqrt{d} \sqrt{m}}{1 + A \sqrt{d} \sqrt{m}}$$

At $25°$ this equation expresses the activity coefficient of potassium chloride up to 0.1 m within the accuracy of our measurements. The value of A is, however, different from the value obtained if the equation of Hückel[16] be used. Taking the density of water at $100°$ as 0.9584,[17] we may write

$$\ln \gamma = \frac{-0.9790 \, k \sqrt{m}}{1 + 0.9790 \, A \sqrt{m}} = \frac{-k' \sqrt{m}}{1 + A' \sqrt{m}} \tag{6}$$

Differentiating, and equating the differential to the first two terms in equation (4), we obtain

$$d \, (mj) = \frac{k' \sqrt{m} \, dm}{2 \, (1 + A' \sqrt{m})^2}$$

Then

$$j = \frac{k'}{(A')^3 m} \left[1 + A' \sqrt{m} - 2 \ln (1 + A' \sqrt{m}) - \frac{1}{1 + A' \sqrt{m}} \right] \tag{7}$$

or

$$j = k' \left[\frac{1}{3} m^{1/2} - \frac{2}{4} A' m^{2/2} + \frac{3}{5} (A')^2 m^{3/2} \ldots \ldots \right] \tag{8}$$

$$= -k' \sum_{n=1}^{n=\infty} (-1)^n \frac{n}{n+2} (A')^{n-1} m^{n/2}$$

[16] Hückel, *Physik. Z.*, **26**, 93 (1925).

[17] "International Critical Tables," Vol. III, p. 26.

For a uni-univalent strong electrolyte, equation (7) is practically identical with equation (53) of Debye and Hückel[17a] which they obtained in a different manner. The limiting law of Debye and Hückel has been used in the calculation of j for dilute aqueous solutions near the freezing point by Debye and Hückel[17a] and by Scatchard.[18] Gronwall, La Mer and Sandved,[18a] in their equation (113), give, for strong electrolytes of the symmetrical valence type, the additions to the equation for j which result from considering the higher terms of the Debye–Hückel theory, while the corresponding expression for unsymmetrical electrolytes is given by La Mer, Gronwall and Greiff[18b] in their equation (9). The application to freezing point depression is discussed in each paper. We do not believe the accuracy of our data warrants our use of the "Extended Theory."

From equation (8) the limiting value of $j/\sqrt{m}$ at $100°$ becomes $k'/3$. Randall[19] has made similar calculations of this limit for lower temperatures.

From equation (7) or (8), the dielectric constant of water at $100°$, and an accurate value of j in dilute solution, the value of A' can be calculated and all the values of j and of the first integral of equation (5) can be computed up to $m = 0.1$, or the values of γ for the dilute solutions can be computed, using equation (6). The integration can be performed either graphically or analytically. We have used the latter method, which gives

$$\int_0^m \frac{j}{m}\, dm = \frac{k'}{A'}\left[\frac{2\ln(1 + A'\sqrt{m})}{(A')^2 m} - \frac{2}{A'\sqrt{m}} + 1\right] \tag{9}$$

or

$$\int_0^m \frac{j}{m}\, dm = k'\left[\frac{2}{3}m^{1/2} - \frac{2}{4}A'm^{2/2} + \frac{2}{5}(A')^2 m^{3/2}\ldots\ldots\right] \tag{10}$$

$$= -k'\sum_{n=1}^{n=\infty}(-1)^n \frac{2}{n+2}(A')^{n-1} m^{n/2}$$

In Table I this is referred to as Method I.

An alternate method which places less weight on a single value of j can be developed by integrating equation (4) between limits, the lower of which is an arbitrarily fixed value of the molality, m_0. This gives

$$\log \gamma' = \log \gamma'_{m_0} + 0.4343\, j_{m_0} - 0.4343\, j - 0.4343 \int_{m_0}^m \frac{j}{m}\, dm - 0.00268 \int_{m_0}^m \frac{\theta}{m}\, d\theta \tag{11}$$

Since the correction of γ' to $100°$ is small even in fairly concentrated solutions, we may evaluate $\log \gamma'$ by means of the equation of Hückel[16]

$$\log \gamma = \frac{-0.4343\, k\sqrt{c}}{1 + A\sqrt{c}} + Bc - \log(1 + 0.036\, m)$$

[17a] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[18] Scatchard, THIS JOURNAL, **47**, 648 (1925).

[18a] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[18b] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

[19] Randall, THIS JOURNAL, **48**, 2512 (1926).

Combining the first two terms on the right side of equation (11) into a constant, C, we then have

$$-\frac{0.4343\,k\,\sqrt{c}}{1 + A\,\sqrt{c}} + Bc - \log(1 + 0.036\,m) = C - 0.4343\,j - 0.4343 \int_{m_0}^{m} \frac{j}{m}\,dm$$

$$(12)$$

$$- 0.00268 \int_{m_0}^{m} \frac{\theta}{m}\,d\theta$$

The integrals can be evaluated graphically, k can be calculated from the dielectric constant for water at $100°$; hence the constants A, B and C can be determined by solving three such equations simultaneously. The activity coefficients at 0.1 molal or at m_0 and the lower concentrations can then be calculated by using Hückel's equation. In Table I this is called Method II.

The dielectric constant of water has been measured near $100°$ by Kockel[20] and Wyman.[21] The average of their results for $100°$ is 55.3. Using this value, $0.4343\,k$ becomes 0.612, k' becomes 1.380 and the limiting value of $j/\sqrt{m}$ becomes 0.460.

Experimental Results

The observed values of θ were first plotted against m on a large scale, giving greater weight to the results obtained with the second apparatus. The values of θ read from the plot are given in Table II. Values of j were then calculated and plotted against m on a large scale, giving the values in Table II. The original data are plotted in Fig. 3 in a manner which has been used by Randall[22] for freezing point and vapor pressure data. The values of j used in Table II are identical with those read from this curve. Values of $\gamma_{0.1}$ were then calculated by the two methods described above. The results are given in Table I.

TABLE I

Method I

m	j	k'	A'	$\gamma_{0.1}$
0.1	0.082	1.380	1.44	0.741

Method II

m_0	m_1	m_2	m_3	A	B	$\gamma_{0.1}$
0.1	0.2	1.0	2.0	1.22	0.042	0.733
.2	.5	1.0	2.0	1.13	.046	.729

The average value of $\gamma_{0.1} = 0.731$ obtained by the second method agrees with that calculated from the value of $\gamma_{0.1}$ at $25°$ (see Table IV); hence, we have taken it as our reference value. If it be substituted in equation (6), A' becomes 1.24 and this equation was then used to compute the

[20] Kockel, *Ann. Physik*, [4] **77**, 417 (1925).

[21] Wyman, *Phys. Rev.*, **35**, 623 (1930).

[22] (a) Randall, THIS JOURNAL, **48**, 2512 (1926); (b) Randall and White, *ibid.*, **48**, 2514 (1926).

activity coefficients of the more dilute solutions. The values so found are identical with those obtained by using the equation of Hückel with $A = 1.18$ and $B = 0.044$, the averages of the values given in Table I. The activity coefficients of these dilute solutions are included in Table II. The value of the integral from $m = 0$ to $m = 0.1$ was then calculated from $\gamma_{0.1}$ and $j_{0.1}$, while the integrals from 0.1 to higher concentrations were determined graphically. The results are given in Table II.

TABLE II

m	θ	$0.4343\,j$	$0.4343\int_0^{0.1}\frac{j}{m}\,dm$	$0.4343\int_{0.1}^{m}\frac{j}{m}\,dm$	$0.00268\int_0^{m}\frac{\theta}{m}\,d\theta$	γ
0.001						0.959
.005						.914
.01	0.010					.884
.05	.048					.785
.1	.094	0.0356	0.1005		0.0002	.731
.2	.186	.0413		0.0269	.0005	.677
.5	.459	.0458		.0673	.0012	.610
1	.917	.0454		.0991	.0023	.566
1.5	1.398	.0404		.1167	.0035	.548
2	1.894	.0331		.1274	.0047	.542
2.5	2.410	.0256		.1340	.0061	.542
3	2.949	.0174		.1379	.0074	.545
3.5	3.506	.0100		.1400	.0089	.550
4	4.063	.0035		.1409	.0104	.555
4.5	4.635	− .0026		.1410	.0120	.561
5	5.215	− .0078		.1405	.0136	.566
5.5	5.805	− .0130		.1395	.0153	.572
6	6.408	− .0180		.1382	.0170	.578
6.5	7.011	− .0228		.1365	.0188	.585
7	7.624	− .0274		.1347	.0205	.591
7.5	8.260	− .0319		.1326	.0223	.598
7.8	8.622	− .0343		.1313	.0234	.601

Up to 4 molal solution, there are available sufficient data to correct the values of γ' to $100°$. Rossini[23] gives values of $\overline{L}_1$ at $18°$ up to $m = 2.0$. Using the heat capacity data of Randall and Rossini[24] we have calculated these values to $25°$. The values of $\overline{L}_1$ given by Wüst and Lange[25] have been used from two to four molal. Randall and Rossini[24,26] give values of $\overline{C}_{p_1}$ up to $m = 2.5$. Up to this molality, they have shown that $\overline{C}_{p_1}$ and Φ, the apparent molal heat capacity of the solute, are both substantially

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

[24] Randall and Rossini, THIS JOURNAL, **51,** 323 (1929).

[25] Wüst and Lange, *Z. physik. Chem.,* **116,** 161 (1925).

[26] Up to $m = 2.0$ the heat capacity data for aqueous solutions of potassium chloride have been summarized by Rossini [Rossini, *Bur. Standards J. Research,* **7,** 47 (1931)]. He gives an equation for $(\overline{C}_{p_1} - \overline{C}_{p_1}^\circ)$ which results in slightly different values for this difference than those we have used. No change in γ would result from their use.

linear functions of $\sqrt{m}$. We have therefore extrapolated their results to 4 molal. Since the resultant values of $\overline{C}_{p_2}$ so obtained are in fairly good agreement with those calculated from the specific heat data in the "International Critical Tables,"[27] they are sufficiently accurate for our present
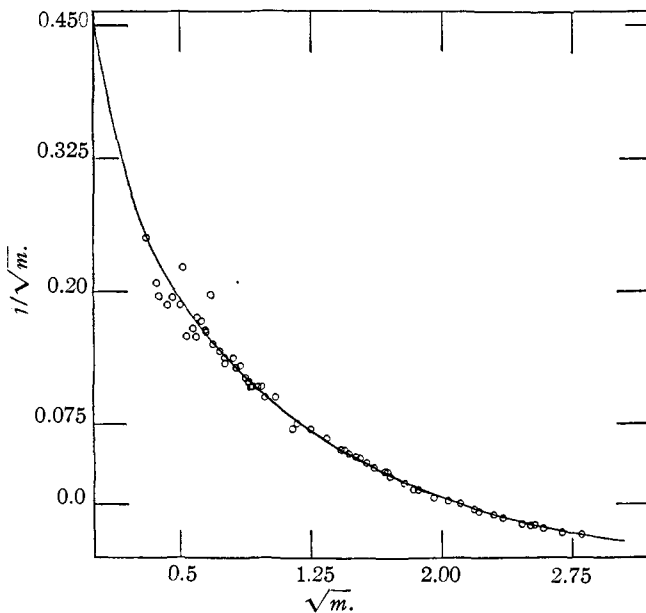

Fig. 3,

purpose. $\overline{C}_{p_1}$ was then calculated from $\overline{C}_{p_2}$, Φ, and $\overline{C}_{p_1}^{\circ}$. The data used and the results obtained are given in Table III.

TABLE III

m	$\overline{L}_1{}_{(298.1)}$	$(\overline{C}_{p_1} - \overline{C}_{p_1}^{\circ})_{(298.1)}$	$\gamma_{373.1}$
0.2	0.02	−0.009	0.677
.5	.76	− .033	.610
1	2.88	− .099	.566
1.5	5.85	− .187	.549
2	9.81	− .310	.544
2.5	14.6	− .410	.544
3	19.0	− .532	.548
3.5	23.2	− .664	.553
4	27.1	− .805	.559

Up to 2 molal, we have the necessary data for calculating the activity coefficients at 100° from those at 25° as given by Harned.[28] The values of $\overline{L}_2$ were calculated to 25° from those at 18° as compiled by Rossini.[23] The heat capacity data are from Randall and Rossini.[24,26] Table IV gives

[27] "International Critical Tables," Vol. V, p. 115.
[28] Harned, THIS JOURNAL, **51**, 416 (1929).

the data used and the results, together with our observed values for comparison. The agreement is satisfactory.

TABLE IV

m	$\bar{L}_{2(298.1)}$	$(\bar{C}_{p2} - \bar{C}^0_{p2})_{(298.1)}$	$\gamma_{298.1}$	$\gamma_{373.1}$ (calcd.)	$\gamma_{373.1}$ (obs.)
0.001	24	0.47	0.965	0.959	0.959
.005	54	1.06	.926	.912	.914
.01	60	1.50	.899	.882	.884
.05	87	3.35	.815	.787	.785
.1	95	4.75	.764	.731	.731
.2	70	6.80	.712	.676	.677
.5	− 58	10.95	.644	.610	.610
1	−195	15.85	.597	.562	.566
1.5	−327	19.75	.576	.542	.549
2	−448	23.15	.569	.536	.544

Finally, we have evaluated the constants A and B in the equation of Hückel, using 55.3 as the dielectric constant. The densities used are those given in the "International Critical Tables."[29] Up to 4 molal the activity coefficients at 100° can be represented satisfactorily by the equation

$$\log \gamma = \frac{-0.612 \sqrt{c}}{1 + 1.19 \sqrt{c}} + 0.046\, c - \log(1 + 0.036\, m)$$

The comparison of the observed results with those calculated from the equation are given in Table V.

Although density data are given only up to about 5 molal, we have extrapolated up to our highest concentration and give the calculated values of γ in comparison with the measured values of γ' which will not differ greatly from γ, even at these high concentrations. It is apparent that the equation is satisfactory through the entire concentration range. Since correction to 100° raises the values of γ', it is probable that the agreement in the concentrated solutions would be improved if such a correction could be made.

TABLE V

m	0.001	0.005	0.01	0.05	0.1	0.2	0.5	
γ (calcd.)	.959	.914	.884	.786	.732	.676	.606	
γ (obs.)	.959	.914	.884	.785	.731	.677	.610	
m	1.0	1.5	2.0	2.5	3.0	3.5	4.0	
γ (calcd.)	0.566	0.551	0.545	0.545	0.547	0.551	0.556	
γ (obs.)	.566	.549	.544	.544	.548	.553	.559	
m	4.5	5.0	5.5	6.0	6.5	7.0	7.5	7.8
γ (calcd.)	0.562	0.569	0.576	0.583	0.590	0.598	0.606	0.610
γ' (obs.)	.561	.566	.572	.578	.585	.591	.598	.601

From the value of A and the dielectric constant, the parameter, a, representing the distance of closest approach of the ions, becomes 3.40 Å., as

[29] "International Critical Tables," Vol. III, p. 87.

compared with 3.28 Å. calculated from Harned's constant at 25°. This increase would seem to confirm the results of Harned and Nims,[30] whose data on sodium chloride show that a increases from 3.60 Å. at 25° to 3.78 Å. at 40°. On the other hand, if our value of A is lowered to 1.15, the values of a would be the same at the two temperatures. Such a value of A with an increase in B to 0.049 gives an equation which reproduces our measured values up to 4 molal nearly as well as the one used, but gives larger deviations at the higher concentrations, unless the correction of the activity coefficient to 100° is larger than we think it to be. Thus, our results up to 4 molal may also be said to agree with the findings of Cowperthwaite and La Mer,[31] who found a to remain constant from 0 to 37.5° for dilute solutions of zinc sulfate. Our results, therefore, offer no conclusive evidence on the effect of temperature on a. The constant B has increased with temperature. From the work of Butler[32] it follows that if we assume the lowering of the dielectric constant of the solvent and the ionic radii of the solute to be independent of temperature, the constant B should be inversely proportional to the temperature and the square of the dielectric constant. Using Harned's value of $B = 0.034$ and our own result, the ratio $B_{100°}/B_{25°}$ is 1.35, while the ratio calculated from Butler's relation and Wyman's values of the dielectric constants is 1.61.

Summary

Two new apparatus for measuring the elevation of the boiling point at constant pressure have been described.

The elevations for potassium chloride in water have been measured up to 7.8 molal solution. From the results, the activity coefficients of the solute have been calculated. Up to 4 molal, these coefficients have been corrected to 100°, and up to 2 molal they have been compared with those calculated from 25°. The constants of the equation of Hückel have been evaluated. The equation is satisfactory through the entire concentration range.

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[30] Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

[31] Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[32] Butler, *J. Phys. Chem.*, **33**, 1015 (1929).