precipitated with magnesium turnings. The filtrate is made acid with concd. hydrochloric acid, evaporated nearly to dryness, diluted and the *ruthenium* precipitated with alcoholic sodium hydroxide on boiling. The residue is dissolved in hydrochloric acid and the metallic ruthenium precipitated with zinc dust. The filtrate is then made distinctly acid with hydrochloric acid, after evaporating to remove alcohol, and the metals iridium and osmium are precipitated in the finely divided state with metallic zinc. The two metals are then treated with a fresh solution of sodium hypochlorite; this dissolves the osmium and leaves the *iridium* unattacked. The latter is filtered off. The osmium filtrate is made acid with hydrochloric acid and the metallic *osmium* is precipitated with zinc dust. Each of the metallic precipitates is subsequently dried, ignited in air (osmium to 190° only), heated in hydrogen, cooled and the metal weighed.

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THE FREEZING-POINT LOWERING AT INFINITE DILUTION

BY MERLE RANDALL

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In calculating the activity coefficients of strong electrolytes in dilute solution it is convenient to use a method that will give a criterion of the accuracy of the experimental points in the most dilute solutions. Moreover, it is most important that the method used should be, so far as is possible, empirical.

If we plot the j-function of Lewis and Randall[1] divided by the square root of the molality against the square root of the molality, then we obtain a series of points such as is shown in Fig. 1 of the following article. Because of the experimental errors and the sensitiveness of such a plot to small errors in the dilute end, the points are scattered, but with more exact data the scattering is diminished. From a study of the freezing-point data of all strong salts we may conclude that the best average curve that can be drawn in each case is the one that will extrapolate to the limit at $m = 0$ which is given below.

In the following paper it will be shown that the activity coefficient of a salt is given by the equation

$$\log \gamma = -\frac{j}{2.303} - \frac{2}{2.303}\int_0^m \frac{j}{m^{1/2}}\,dm^{1/2} \qquad (1)$$

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[1] Lewis and Randall, (a) THIS JOURNAL, **43,** 1112 (1921); (b) "Thermodynamics," McGraw-Hill Book Co., New York, **1923,** pp. 285–290, 341–352. $j = 1 - (\theta/1.858\,\nu m)$, where θ is the freezing-point lowering, ν the number of ions formed per molecule, and m the molality. A quantity Φ identical in value with $1 - j$ was called the osmotic coefficient by Bjerrum [*Z. Elektrochem.*, **24,** 321 (1918)]. While the molality of the solute is involved in the definition of j, it is an empirical quantity directly related to the properties of the solvent alone.

where the value of the integral is the area under the curve. If the slope of the curve does not become infinite, but retains a finite value, then from the geometry of the curve when $m^{1/2}$ is nearly zero, $\log \gamma = -3j/2.303$. The same result was obtained by Lewis and Randall when α = exactly one-half in the empirical equation $j = \beta m^{\alpha}$, in which α and β are constants.

From the theory of inter-ionic attraction of Debye and Hückel[2] we have in very dilute solutions

$$\log \gamma = -A\, w'\, m^{1/2} \tag{2}$$

in which the value of A is calculated from the dielectric constant of the water and other fundamental constants. The value of w' depends only on the valence type of the salt.

Equating the two expressions we find the following values of $j/m^{1/2}$ in the limit, $m = 0$, for several valence types. The second row of the table gives the values[3] at 0° when the dielectric constant is assumed to be 87.9, and the third, the values[4] at 25° when the value of the dielectric constant is assumed to be 77.8.

Table I

Values of the function $j/m^{1/2}$ in the limit, $m = 0$

Valence type:	uni-uni	uni-bi	uni-tri	bi-bi	bi-tri
0°	0.375	1.300	2.760	3.00	8.73
25°	.394	1.365	2.895	3.15	9.14

Bjerrum[5] has shown that the treatment of Debye and Hückel is inadequate when the ionic diameter is small. He introduces an association factor. However, in the limiting case, the value of $j/m^{1/2}$ will be the same as the one given here. The plot here suggested will prove of great value in interpreting such cases.

The value of the dielectric constant here assumed is somewhat in doubt, but the uncertainty will produce an error in $\log \gamma$ of less than 0.1% at 0.01 M for uni-univalent salts, above which concentration the empirical data alone are adequate. Moreover, as has been pointed out, the empirical extrapolation alone gives results within the uncertainty of the assumed dielectric constant. Notwithstanding possible flaws in the theoretical derivation of Debye and Hückel, the form of Equation 2 in the limiting case probably is correct.

Summary

In the empirical extrapolation of freezing-point measurements the plot of $j/m^{1/2}$ against $m^{1/2}$ is found to be useful. The plots for strong elec-

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[2] Debye and Hückel, *Physik. Z.*, **24,** 185 (1923). The value of j is given directly by Equation 40, but the derivation of this equation involves assumptions unnecessary to the derivation of the simple form here used.

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

[4] A vapor-pressure function, of similar form, will approach these limits at 25°. (See following article.)

[5] Bjerrum, *Det. Kgl. Danske Videnskab Selskab Math.-fys. Medd.*, **7,** No. 9 (**1926**).

trolytes agree in dilute solutions with the results of the inter-ionic attraction theory.

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THE ACTIVITY COEFFICIENT OF ELECTROLYTES FROM THE VAPOR PRESSURE OF THE SOLVENT

BY MERLE RANDALL AND A. MCLAREN WHITE

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This article extends to solutions of electrolytes the special graphical method given by Lewis and Randall[1] for the activity coefficient of nonelectrolytes in aqueous solution.

If in the dilute solution one molecule of the solute dissociates into ν molecules (which may be either ions or uncharged molecules), then the rate of decrease of the activity of the solvent (a_1) as the mole fraction of the solute (N_2) is increased, is ν times the rate if there were no dissociation.[2] We will accordingly alter the divergence function h of Lewis and Randall, so that

$$h = 55.51\, ln\, a_1/\nu m + 1 \tag{1}$$

where m is the molality.[3]

Differentiating, we have

$$dh = (55.51/\nu m) d\, ln\, a_1 - (55.51/\nu m^2)\, ln\, a_1\, dm \tag{2}$$

whence, substituting in the equation

$$d\, ln\, a_2 = -(N_1/N_2) d\, ln\, a_1 \tag{3}$$

and rearranging, we find,

$$(d\, ln\, a_2)/\nu = d\, ln\, a_{\pm} = -dh - (h - 1)\, d\, ln\, m. \tag{4}$$

Subtracting $d\, ln\, m_{\pm}$ from both sides of the equation,[4] integrating and dividing by 2.303, we have

$$\log \frac{a_{\pm}}{m_{\pm}} = \log \gamma = -h/2.303 - \int_0^m h\, d \log m \tag{5}$$

As in the case of the j function of Lewis and Randall, this equation is in a convenient form if the activity coefficient is known for one fairly dilute solution, as the value of the last term may then be found by plotting h against log m and taking the area under the curve between the two values of log m. The integral in this form, however, is not suitable for evaluation

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 273–275. See also pp. 286, 342–346.

[2] Ref. 1, pp. 303–306.

[3] $ln\, a_1 = -\frac{p_1^0 - p_1}{p_1^0} - \frac{1}{2}\left(\frac{p_1^0 - p_1}{p_1^0}\right)^2 - \ldots$, where p_1^0 and p_1 are the vapor pressures of the pure solvent and solute, respectively.

[4] $ln\, m_{\pm} = ln\, m + ln\, \text{const.}$; $d\, ln\, m_{\pm} = d\, ln\, m$.