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

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

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

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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 non-electrolytes 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

$$h = 55.51\, ln\, a_1/\nu m + 1 \qquad (1)$$

where m is the molality.[3]

Differentiating, we have

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

whence, substituting in the equation

$$d\, ln\, a_2 = -(N_1/N_2) d\, ln\, a_1 \qquad (3)$$

and rearranging, we find,

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

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

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

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

if the lower limit is infinite dilution. However, we may transform the integral, making h a function of the square root of m, and write

$$\log \gamma = -h/2.303 - \frac{2}{2.303}\int_0^m \frac{h}{m^{1/2}}\, dm^{1/2}. \qquad (6)$$

If we now plot $h/m^{1/2}$ against $m^{1/2}$, the integral is the area under the curve.

The form of Equation 6, in which $m^{1/2}$ is used as the integration variable, enables us to obtain an activity coefficient based almost entirely upon an empirical extrapolation, for $h/m^{1/2}$ will tend to a finite limit at $m^{1/2} = 0$.

An inspection of the h and j functions shows that, at 0°, the two functions will become identical in the limit. Equation 6 is an exact equation, while the corresponding equation in which j is substituted for h neglects two terms that become negligible at infinite dilution, namely, the term in θ due to the change of the heat of fusion of ice with the temperature, and the term involving the increase in partial molal heat content and heat capacity.[5] In extrapolating to infinite dilution we may thus make the curve of $h/m^{1/2}$ at 0° become identical with the $j/m^{1/2}$ curve, and approach the theoretical and empirical limit as was done in the previous paper.

In the case of measurements at other temperatures, the theoretical limit will differ slightly owing to a slight change of the product of the dielectric constant by absolute temperature with the temperature. In any case, since the measurements of vapor-pressure lowering are very difficult at low concentrations, the $j/m^{1/2}$ curve will greatly aid us in determining the best curve to infinite dilution.

As an example, we have plotted in Fig. 1 the values of $h/m^{1/2}$ calculated from the data of Lovelace, Frazer and Sease[6] for potassium chloride. The figure also includes the values of $j/m^{1/2}$ taken from the freezing-point measurements of Adams, Barnes, Flügel, Hovorka and Rodebush, Jahn, Kistiakowsky, Loomis, Ponsot, Rivett, Rodebush, and Roloff.[7] The results of Hebb[8] show a general agreement with the curve. Two values of $j/m^{1/2}$ below 0.01 M of Hovorka and Rodebush and two of Flügel are between 0.4 and 0.7. We have also plotted all the data of the other investigators,[9] the results of whom are in fair agreement with those shown,

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[5] See Ref. 1, p. 284; Equation 14, p. 347; pp. 348–350.

[6] Lovelace, Frazer and Sease, THIS JOURNAL, **43**, 102 (1921).

[7] (a) Adams, *ibid.*, **37**, 494 (1915). (b) Barnes, *Trans. Nova Scotian Inst. Sci.*, **10**, 139 (1900). (c) Flügel, *Z. physik. Chem.*, **79**, 585 (1912). (d) Hovorka and Rodebush, THIS JOURNAL, **47**, 1614 (1925). (e) Jahn, *Z. physik. Chem.*, **50**, 138 (1904); (f) **59**, 35 (1907). (g) Kistiakowsky, *ibid.*, **6**, 97 (1890). (h) Loomis, *Ann. physik. Chem.*, [3] **57**, 495 (1896); (i) **60**, 522 (1897). (j) Ponsot, *Ann. chim. phys.*, [7] **10**, 79 (1897). (k) Rivett, *Z. physik. Chem.*, **80**, 537 (1912). (l) Rodebush, THIS JOURNAL, **40**, 1208 (1918). (m) Roloff, *Z. physik. Chem.*, **18**, 572 (1895).

[8] Hebb, *Trans. Nova Scotian Inst. Sci.*, **10**, 422 (1902).

[9] (a) Abegg, *Z. physik. Chem.*, **20**, 207 (1896). (b) Barmwater, *ibid.*, **28**, 115 (1899). (c) Bedford, *Proc. Roy. Soc.*, **83**, 459 (1910). (d) Biltz, *Z. physik. Chem.*, **40**, 185 (1902). (e) Dernby, *Medd. Vetenskapsakad. Nobelinst.*, **3**, No. 18 (1916). (f)

but we have omitted their points in Fig. 1. In every case the concentrations were reduced to moles per 1000 g. of water.

The dotted curve shows the one chosen from the freezing-point data, and the solid curve is the corresponding curve from the vapor-pressure data. In the concentrated solutions the solid curve lies below the dotted. This would be predicted qualitatively from the values of the partial molal heat contents and heat capacities in potassium chloride solutions. The solid curve must, however, pass to the theoretical limit, $h/m^{1/2} = 0.390$, corresponding to a value of the dielectric constant[10] equal to 79.75 at 20°. As we have drawn the curve, we have assumed that the six lowest points of Lovelace, Frazer and Sease are too high.

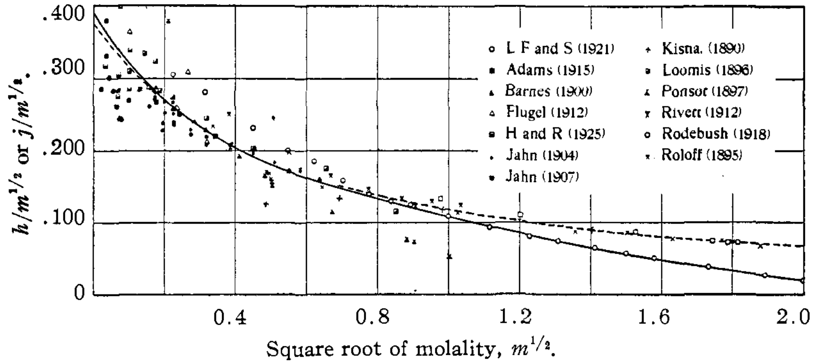

Fig. 1.—Vapor-pressure and freezing-point functions for potassium chloride.

The points from the freezing-point data are scattered, but if we give most weight to the work of Barnes, Adams, Jahn, Hovorka and Rodebush, Flügel, Hebb and Loomis in the dilute solutions, the curve extrapolated to 0.375 represents the data fairly.

If we are to accept different limits of $h/m^{1/2}$ at different temperatures, as is demanded by the present form of the inter-ionic attraction theory, then the curves must cross. There is, however, no experimental evidence of a change in the sign of the partial molal heat content at moderate dilutions. We have drawn the curve so that the crossing must occur in a fairly dilute solution. This involves the assumption that there is a systematic

Fernau, *Z. anorg. Chem.*, **17**, 327 (1898). (g) Jones, Barnes and Hyde, *Am. Chem. J.*, **27**, 22 (1902). (h) Jones and Carroll, *ibid.*, **28**, 284 (1902). (i) Jones and Getman, *Z. physik. Chem.*, **46**, 244 (1903); *Phys. Rev.*, [1] **18**, 146 (1904). (j) Klein and Svanberg, *Medd. Vetenskapsakad. Nobelinst.*, **4**, No. 1 (1918). (k) LeBlanc and Noyes, *Z. physik. Chem.*, **6**, 385 (1890). (l) Lewis, *J. Chem. Soc.*, **67**, 1 (1895); *Z. physik. Chem.*, **15**, 365 (1894). Wildermann, *ibid.*, **15**, 337 (1894). (m) Oholm, *ibid.*, **50**, 343 (1905). (n) Prytz, *Ann. Physik*, [4] **7**, 882 (1902). (o) Raoult, *Z. physik. Chem.*, **27**, 617 (1898). (p) Richards, *ibid.*, **44**, 563 (1903). (q) Young and Sloan, THIS JOURNAL, **26**, 913 (1904).

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

error in the vapor-pressure measurements, all the values of $h/m^{1/2}$ being slightly high, but from the nature of the function the relative amount will be larger the more dilute the solution. The uncertainty in log γ due to the difference of limits corresponds to about 0.2% in the activity coefficient.

We give in Table I the activity coefficient calculated from the curve of Fig. 1. The first row gives the molality, moles per 1000 g. of water, and the second the values of the activity coefficient at 20° from vapor-pressure data. Below 0.1 *M*, the values of the activity coefficient at 0° calculated from this same curve are in agreement with those calculated by Scatchard[11] by another method.

Table I

The Activity Coefficient of Potassium Chloride at 20°

m	0.1	0.2	0.5	1.0	2.0
γ	.772	.715	.651	0.601	0.570

Summary

We have extended the application of the divergence function *h* of Lewis and Randall to the calculation of the activity coefficient of electrolytes, and have shown the application of this method in the case of potassium chloride.

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THE ACTIVITY COEFFICIENT OF SOAP SOLUTIONS

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The work of McBain and others has shown that we may consider dilute aqueous soap solutions as typical electrolytes and that in the more concentrated solutions such properties as the conductance, viscosity, etc., are explainable if we assume the existence of micelles.[1]

McBain and Salmon[2] have determined the vapor-pressure lowering of the sodium and potassium soaps from the acetate to the behenate by measuring the change in dew point at 90°. McBain, Laing and Titley[3]

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[11] Scatchard, This Journal, **47**, 648 (1925).

[1] For references see McBain, "The Study of Soap Solutions and Its Bearing upon Colloid Chemistry." Union Internationale de la Chimie Pure et Appliquée, Cambridge, June, **1923**; *J. Soc. Chem. Ind.*, **42**, 615 (1923); *Chimie et Industrie*, **11**, 3 (1924); *Am. Dyestuff Rep.*, **12**, 822 (1923). Bogue, "Colloidal Behavior," McGraw-Hill Book Co., New York, **1924**, vol. I, p. 427.

[2] McBain and Salmon, This Journal, **42**, 426 (1920); *Proc. Roy. Soc.*, **97A**, 49 (1920).

[3] McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1289 (1919).