Acetates, tartrates and ammonium salts do not interfere but decrease the sensitivity of the test.

The test can be used most efficiently as a substitute for the classical magnesium ammonium phosphate test commonly employed in qualitative analysis procedures. Used in this way, 3×10^{-6} g. of magnesium can be detected.

WASHINGTON, D. C.

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

THE INTERPRETATION OF THE COLLIGATIVE PROPERTIES OF WEAK ELECTROLYTES

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Introduction

Although the importance, in the study of solutions, of the activities or activity coefficients[1,2] of the components has been most emphasized in the field of strong electrolytes, these quantities are, of course, of no less importance to the study of weak electrolytes and of non-electrolytes. Moreover, although the methods of determining the activity coefficients[1,2] have been most widely studied in the case of strong electrolytes, these methods are, of course, equally applicable to weak electrolytes and non-electrolytes. The application of these methods is illustrated by the work of Randall and Failey[3] in determining the activity coefficients of gases, of non-electrolytes, and of the undissociated part of weak electrolytes in solutions of electrolytes.

In the study of electrolytes it has been customary to regard as strong those completely or practically completely dissociated in dilute aqueous solution, and as weak those incompletely dissociated at finite concentrations. The question as to the actual extent of dissociation of a strong electrolyte in a given solution is of importance from a kinetic standpoint and has received considerable attention. To account for apparent evidences of incomplete dissociation of strong electrolytes consisting of small ions or those having "un-centrally located charges," Bjerrum[4] suggested a modification of the inter-ionic attraction theory of Debye and Hückel[5] whereby such ions, of opposite charge, when closer together than a certain minimum distance (dependent upon the dielectric constant of the medium and the absolute temperature) would be regarded as associated—behaving

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, Chapters XXII to XXVIII.

[2] Randall, *Trans. Faraday Soc.*, **23**, 498, 502 (1927).

[3] (a) Randall and Failey, *Chem. Reviews*, **4**, 271, 285, 391 (1927); see also (b) Livingston, THIS JOURNAL, **48**, 45 (1926).

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

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

osmotically as though undissociated. Mueller,[6] Gronwall,[7] and, more recently, Gronwall, LaMer and Sandved,[8] have shown, however, that Bjerrum's practical results can be explained by a more thorough consideration of the postulates of Debye and Hückel.

Whether or not we consider an electrolyte as completely dissociated, especially for thermodynamic treatment, is largely a matter of convenience. For example, it has been convenient for a long time to consider such substances as ammonium hydroxide, acetic acid and mercuric chloride as mostly undissociated in solution and to consider a definite equilibrium between the ions and undissociated portions. On the other hand, with substances as strong as dichloro-acetic acid it is perhaps more convenient to consider them strong electrolytes but having activity coefficients less than those of the typically strong electrolytes.

It is not the purpose of this paper to discuss the colligative properties of weak electrolytes on the basis of any particular mechanistic theory, but rather to indicate methods whereby the activity of weak electrolytes may be calculated from measurements of the activity of the solvent, and to clarify our conceptions of the thermodynamic treatment of "so-called" incompletely dissociated substances.

Theoretical

For clearness we shall confine our discussion entirely to an aqueous solution of a univalent electrolyte. We shall use the symbols employed by Lewis and Randall[1] and by Randall and Failey.[3]

The stoichiometrical molality of the electrolyte will be denoted by m, the molality of the undissociated portion by m_u, that of the negative ion by m_- and that of the positive by m_+; a_u, a_- and a_+ will represent the corresponding activities, and a_1 that of the solvent. Also we will for simplicity call $m_+ = m_- = m_\pm$, so that $m = m_u + m_\pm$ and call $m_\pm/m = \alpha$, the degree of dissociation in the usual sense.

Now, if we use the basis of treatment which we have used for strong electrolytes,[1,2] the activity of the solute, a_2, is equal to the product a_+a_-, or $a_\pm = a_2^{1/2}$. For slightly weak electrolytes, or weak electrolytes at very low concentrations (if the effect of the ions of the solvent upon the dissociation is neglected), the activity of the solute is more nearly equal to the square of the mean molality of the ions than to the molality of the undissociated substance.

We therefore define the following activity coefficients:

$$\gamma_0 = a_2/m, \quad \gamma = a_2^{1/2}/m, \quad \gamma_u = a_u/m_u, \quad \gamma_\pm = a_\pm/m_\pm$$

where γ_0 is the stoichiometrical activity coefficient of a solute considered as undissociated; γ is the stoichiometrical activity coefficient of a univalent

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[6] Mueller, (a) *Physik. Z.*, **28,** 324 (1927); (b) **29,** 78 (1928).

[7] Gronwall, *Proc. Nat. Acad. Sci.*, **13,** 198 (1927).

[8] Gronwall, LaMer and Sandved, *Physik. Z.*, **29,** 358 (1928).

electrolyte, regardless of whether or not the electrolyte is completely dissociated, and, moreover, by our conventions, is the stoichiometrical mean activity coefficient of the ions; γ_u is the activity coefficient of the undissociated portion of the solute, and $\gamma_\pm$ the mean activity coefficient of the ions. By these definitions

$$\gamma \equiv \alpha\gamma_\pm; \ \log \gamma = \log \alpha + \log \gamma_\pm \qquad (1)$$

By virtue of the rapid interconvertibility of the solute constituents, we have also the relation[1]

$$\mathrm{HA} = \mathrm{H}^+ + \mathrm{A}^-; \ K = a_\pm{}^2/a_u \qquad (2)$$

where K is the dissociation constant.

For an aqueous solution of a binary electrolyte, the general partial molal equation[1] in the form

$$m \ \mathrm{d} \ln a_2 = -55.51 \ \mathrm{d} \ln a_1 \qquad (3)$$

is equivalent to

$$\mathrm{d} \ln \gamma_0 = -(55.51/m) \ \mathrm{d} \ln a_1 - \mathrm{d} \ m/m \qquad (4)$$
$$\mathrm{d} \ln \gamma = -(55.51/2m)\mathrm{d} \ \ln a_1 - \mathrm{d} \ m/m \qquad (5)$$

At the freezing point of the solution, these equations become[1]

$$\mathrm{d} \ln \gamma_0 = \mathrm{d} \ \theta/\lambda m + \theta \ \mathrm{d} \ \theta/\lambda'' m + \cdots - \mathrm{d} \ m/m \qquad (6)$$
$$\mathrm{d} \ln \gamma = \mathrm{d} \ \theta/2\lambda m + \theta \ \mathrm{d} \ \theta/2\lambda'' m + \cdots - \mathrm{d} \ m/m \qquad (7)$$

where $\lambda = 1.858$ and $\lambda'' = (0.00057)^{-1}$ are constants, and θ is the freezing point lowering.

Introducing the Lewis and Randall divergence functions[1]

$$1 - \theta/\lambda m = j_1, \ (\nu = 1) \ \text{and} \ 1 - \theta/2\lambda m = j_2, \ (\nu = 2)$$

and integrating, we have

$$\ln (\gamma_0/\gamma_0') = -(j_1 - j_1') - \int_{m'}^{m} (j_1/m)\mathrm{d} \ m - \int_{m'}^{m} (\theta/\lambda'' m)\mathrm{d} \ \theta \ldots \qquad (8)$$

and, following Randall and White[9]

$$\ln (\gamma/\gamma') = -(j_2 - j_2') - 2 \int_{m'}^{m} (j_2/m^{1/2}) \ \mathrm{d} \ m^{1/2} - \int_{m'}^{m} (\theta/2\lambda'' m) \ \mathrm{d} \ \theta \qquad (9)$$

For a binary electrolyte at infinite dilution

$$\underset{m \longrightarrow 0}{\text{Limit}} \ (a_2/m^2) = 1; \ \underset{m \longrightarrow 0}{\text{Limit}} \ (\gamma_0/m) = 1; \ \underset{m \longrightarrow 0}{\text{Limit}} \ (\gamma) = 1 \qquad (10)$$

By definition, if we wish to use the quantity γ_0 in a region in which the divergence function using $\nu = 1$ is most convenient, we may refer γ_0 to a proper standard state by the relation

$$\log \gamma_0 = \log (\gamma)^2 + \log m \qquad (11)$$

and where we wish to use the quantity γ, in the region in which $\nu = 2$ is most convenient, we have

$$\log \gamma = -0.4343 \ [j_2 + 2 \int_0^m (j_2/m^{1/2}) \ \mathrm{d} \ m^{1/2} + \int_0^m (\theta/2\lambda'' m) \ \mathrm{d} \ \theta + \cdots] \qquad (12)$$

Equation 12 may be easily evaluated by means of Equation 1 if we also know the α, $\gamma_\pm$ and m relations (in dilute solutions).

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[9] Randall and White, THIS JOURNAL, **48**, 2514 (1926).

Application of Foregoing Considerations.—Our correlation of γ_u, $\gamma_\pm$ and α with the empirical freezing point lowering equations of Lewis and Randall is to facilitate the treatment, in certain cases, of weak electrolytes in very dilute solution. Similar relations, of course, hold for the generalized divergence function of Randall and White.[2,9] Moreover, it is fully as important as in the case of strong electrolytes to adopt a consistent and logical standard state for the activity of weak electrolytes. (Values of quantities proportional to the activity coefficients have recently been obtained for several weak acids[10] by measurements of the freezing point lowering in concentrated solution. These quantities were given on the basis of an activity coefficient equal to unity in one molal solution. Such a standard state is not to be recommended and must ultimately cause confusion.) It is our immediate purpose to show that, on the basis of complete dissociation of the electrolyte at infinite dilution, we may evaluate the activity coefficients of weak electrolytes in dilute solution and that where K is known this is facilitated.

To this end we shall examine the consequences of two postulates: (1) that the mean activity coefficient of the ions of a partially dissociated univalent electrolyte at small molalities is the same as that of hydrochloric acid[11] at the same ionic strength and that the activity coefficient of the acid would not be considerably affected by the presence of small amounts of undissociated substance. (If the effect on the dielectric constant of dilute hydrochloric acid due to small additions of non-electrolyte were thought considerable, it could, of course, be corrected for on the basis of the interionic attraction theory.)

(2) That in sufficiently dilute solution the freezing point lowering or other similar colligative property due to the ions, $2\theta_i$, is the same as it would be if the undissociated part were not present; that the freezing point lowering of the undissociated part, θ_u, is the same as that if the dissociated part were not present, and that the total freezing point lowering is the sum of these two quantities.

The validity of Assumption 1 has to a large extent been demonstrated,[3] by methods which give directly the activity of the solute. If, as Randall and Failey found, the quotient, logarithm of activity coefficient of undissociated part of weak electrolyte by ionic strength, is approximately constant for weak electrolytes in salt solutions (the constant varies with the weak electrolyte or salt being considered), then in sufficiently dilute solution

$$(\ln \gamma_u)/\mu = k', \quad \gamma_u = e^{\mu k'} = 1 + \mu k' + (\mu k')^2/2 + \cdots \doteq 1 \qquad (13)$$

Furthermore, we offer here the possibility of verification of Assumption 2 by a correlation of the activity of the undissociated portion of an electrolyte with the activity of the solvent.

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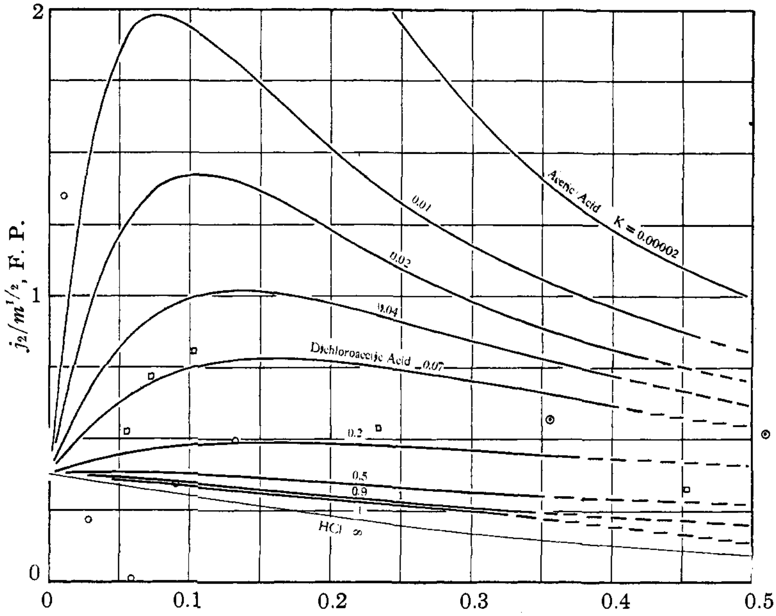
[10] Jones and Bury, *Phil. Mag.*, [7] **4**, 841 (1927).

[11] For bases we would take sodium hydroxide as a type strong base.

Inasmuch as the apparent dissociation constant from conductivity measurements, extrapolated to infinite dilution, K_{Λ}°, must be equal[1] to K (the correct interpretation[12,13] of α will give us K) we are frequently in a position to utilize this quantity, by the relations developed in the present section, to evaluate activity coefficients of weak electrolytes from measurements which give directly the activity of the solvent.[14]



○, Hausrath; ▫ Wildermann, ⊙, Petersen.

Fig. 1.—Freezing point function for weak univalent electrolytes of various dissociation constants and for dichloro-acetic acid.

The curves of Fig. 1 were prepared from Randall and Young's[15] plots of the activity coefficient of hydrochloric acid at 0°. Knowing the true dissociation constant, $K = a_{\pm}^2/a_u$, of any univalent electrolyte, we may calculate the molality of the electrolyte corresponding to given values of ionic strength and ionic activity coefficients in the region where $\gamma_u \doteq 1$, *i. e.*

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[12] Sherrill and Noyes, This Journal, **48,** 1861 (1926).

[13] MacInnes, *ibid.*, **48,** 2068 (1926).

[14] The following experimental methods all give the activity of the solvent: freezing point lowering, vapor pressure lowering, boiling point raising, osmotic pressure, "dew-point" lowering, distribution ratio of the solvent and, in the case of a few solvents, measurements of the electromotive force in which the solvent is the substance involved in the electrode reactions. See Ref. 2.

[15] Randall and Young, This Journal, **50,** 989 (1928).

$$K = (\gamma_{\pm}m_{\pm})^2/\gamma_u m_u \doteq (\gamma_{\pm}m_{\pm})^2/m_u;\ m_u \doteq (\gamma_{\pm}m_{\pm})^2/K;$$
$$m \doteq m_{\pm} + (\gamma_{\pm}m_{\pm})^2/K \quad (14)$$

Although we use the assumption that the freezing point lowering caused by the undissociated part is the same as that of a perfect solution

$$\theta = 2\theta_i + \theta_u \doteq 2\theta_i + \lambda m_u \quad (15)$$

j_1, j_2, etc., are independent of this assumption.

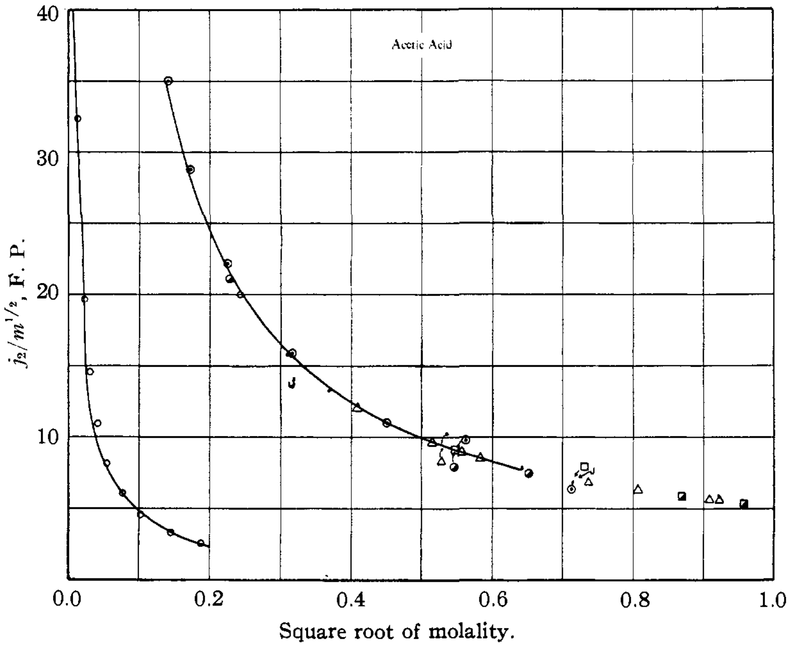

Fig. 2.—Freezing point function for acetic acid. ○ Hausrath, ◐ Jahn, △ Jones and Bury, J Jones and Getman, ☐ Kendall, ◪ Kendall and King, ◉ Ostwald, • Roth.

In Figs. 1 and 2 are given the plots of $j_2/m^{1/2}$ thus calculated for univalent electrolytes of various dissociation constants.

In Fig. 1 we have also placed the points, $j_2/m^{1/2}$, calculated from the data of three investigators,[16] of the freezing point lowering of dichloroacetic acid. These points are evidently in very poor agreement among themselves. According to the dissociation constant at 18°, $K_{291} = 0.0583$,[17] and the heat of dissociation given by Steinwehr,[18] K_{273}, should be approximately 0.07. In cases of this sort, where the freezing point data

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[16] (a) Hausrath, *Ann. Physik,* [4] **9,** 522 (1902); (b) Petersen, *Z. physik. Chem.,* **11,** 174 (1893); (c) Wildermann, *ibid.,* **15,** 337 (1894); (d) *ibid.,* **19,** 233 (1894).

[17] Schreiner, *Z. anorg. allgem. Chem.,* **122,** 201 (1922).

[18] Steinwehr, *Z. physik. Chem.,* **38,** 185 (1901).

are very discordant, curves of this type serve to indicate the probable accuracy of the data.

In Fig. 2 are given the points, $j_2/m^{1/2}$, calculated from all the available data[19] of the freezing point lowering of acetic acid. These points show excellent agreement among themselves and, in turn, lie very closely along the curve for $K = 2 \times 10^{-5}$, which according to the extrapolation by Lewis and Randall of the data of Noyes and Cooper,[20] very likely represents the true K of acetic acid within 4 or 5%.

The curves of j_1/m for weak electrolytes are not given, as these, of course, rapidly approach extreme negative values in dilute solution, as is always the case when the value of ν assigned the substance is less than the true value (see Randall and Cann).[21]

Regarding the sharp peaks shown in the $j_2/m^{1/2}$ curves for weak electrolytes of low dissociation constant,[22] we see from our previous discussion that in just the region where they manifest themselves and graphical integration becomes laborious (very dilute solution) we may place most confidence in our postulates.

According to our discussion, we should have the relations

$$\log (\alpha\gamma_\pm/\alpha'\gamma_\pm') = -0.4343\left[(j_2 - j_2') + 2\int_{m'}^{m} (j_2/m^{1/2})\mathrm{d}\, m^{1/2}\right] \qquad (16)$$

and

$$\log \alpha\gamma_\pm = -0.4343\left[j_2 + 2\int_{0}^{m} (j_2/m^{1/2})\mathrm{d}\, m^{1/2}\right] \qquad (17)$$

true in very dilute solution where the integral of the θ term is negligible and our postulates should almost certainly be valid. As we have drawn our curves of Figs. 1 and 2 from our values of $m_\pm$, $\gamma_\pm$ and θ_i, and m's calculated from the K's, satisfaction of Equations 16 and 17 in these cases is, of course, to be expected.

Higher accuracy in determining the activity coefficients of weak electrolytes from freezing point lowering data is to be gained by higher accuracy in the values of the dissociation constant at 0°, as well as in the freezing point measurements.

The values of γ_0 and γ for acetic acid at round values of $m^{1/2}$ at the freezing point are given in Table I.

It will be noted that the values of γ_0 are very near the value of K, namely, 2×10^{-5}. The quotient γ_0/K given in the third column of the table shows

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[19] (a) Hausrath, Ref. 16a; (b) Jahn, *Ann. Physik. Chem.*, [3] **60,** 119 (1897); (c) Jones and Bury, Ref. 10; (d) Jones and Getman, *Am. Chem. J.*, **30,** 198 (1903); (e) Kendall, THIS JOURNAL, **39,** 2318 (1917); (f) Kendall and King, *J. Chem. Soc.*, **127,** 1380 (1925); (g) Ostwald, *Z. physik. Chem.*, **75,** 278 (1898).

[20] Noyes and Cooper, *Pub. Carnegie Inst.*, No. 63 (1907).

[21] Randall and Cann, THIS JOURNAL, **50,** 347 (1928).

[22] It is a characteristic of the curves of Fig. 1 that the maximum appears in more and more dilute solution the smaller the value of K.

TABLE I

THE ACTIVITY COEFFICIENT OF AQUEOUS ACETIC ACID AT THE FREEZING POINT

$m^{1/2}$	$\gamma_0 \times 10^5$	γ_0/K	γ
0.1	1.910	0.955	0.0440
.15	1.940	.970	.0295
.2	1.956	.978	.0220
.25	1.964	.982	.0175
.3	1.970	.985	.0143
.35	1.974	.987	.0121
.4	1.976	.988	.0108

that in solutions as strong as 0.1 M the effect of ionization of the acid may be disregarded. The quotient is easily interpolated and convenient for this purpose. When using this value of γ_0, however, we in effect make the same convention as in the case of a strong electrolyte, namely, that the standard state of aqueous acetic acid is one which is defined by the infinitely dilute solution; moreover, it is so defined that the standard free energy of the aqueous acid is the same as the sum of the free energies of the ions. The value of γ is as is to be expected very nearly the value of the degree of dissociation as ordinarily used, being the product of this quantity and $\gamma_\pm$, the activity coefficient. Since the effective ionic strength is very small, $\gamma_\pm$ is nearly unity.

It will be seen that the effect of our definitions is to make a distinction between the quantities γ and $\gamma_\pm$ as formerly employed by Lewis and Randall, who made these quantities as well as m and $m_\pm$ identical for a univalent electrolyte. We have retained that part of their convention which makes the activity of the solute the geometrical product of the activities of the ions.

Regarding the possibility of testing the validity of the assumption $\gamma_u = 1$ from measurements of the activity of the solvent, we should be able to subtract the calculated quantity $2\theta_i$ from observed freezing point depressions, form the function $j_u/m_u = [1 - (\theta_u/\lambda m_u)]/m_u$ and examine its approach to constancy in dilute solution. (A plot of $2\theta_i$ and $m_\pm$ against m for the electrolyte studied, $K = 2.0 \times 10^{-5}$ in this example, is useful for the purpose.)

Table II shows j_u/m_u for acetic acid, calculated from the data of Hausrath[16a,23] and Jones and Bury,[19c] probably as accurate data as any in existence in their respective ranges of molality. The values are of the expected order of magnitude[3a] (see Equation 13) except in the most dilute solutions. Such a test is exacting and enormously magnifies the experimental errors.[24]

It might be pointed out that our postulates have intrinsically rather a wide field of applicability. That is, the assumption that the ions of weak

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[23] Hausrath, *Ann. Physik*, [4] **9**, 548 (1902).

[24] For the purposes of this paper we may neglect the common ion from the solvent.

TABLE II

VALUES OF j_u/m_u FOR AQUEOUS ACETIC ACID

m	θ	m_u	j_u/m_u	Author
0.001749	0.003522	0.001569	−14.357	Hausrath[16a,23]
.003007	.006062	.002767	−1.352	Hausrath[16a,23]
.005902	.01172	.005562	−1.899	Hausrath[16a,23]
.01048	.02061	.01002	−1.501	Hausrath[16a,23]
.02082	.04035	.02017	−0.589	Hausrath[16a,23]
.03535	.06839	.03449	− .502	Hausrath[16a,23]
.05876	.11124	.05765	− .00509	Hausrath[16a,23]
.1669	.314	.1650	− .00899	Jones and Bury[19c]
.2653	.497	.2629	+ .00201	Jones and Bury[19c]
.2811	.526	.2786	.00520	Jones and Bury[19c]
.3097	.578	.3071	.01202	Jones and Bury[19c]
.3401	.636	.3374	.00373	Jones and Bury[19c]
.5432	1.002	.5397	.02480	Jones and Bury[19c]
.6514	1.197	.6476	.02575	Jones and Bury[19c]

electrolytes act like those of hydrochloric acid (at the same ion molality) makes little difference in electrolytes of $K < 0.01$, because the important thing is how far the undissociated portion departs from the ideal. On the other hand, with electrolytes of $K > 0.5$, the assumption of $\gamma_u = 1$ makes little difference. Of course, such assumptions should not be employed and are not needed except in quite dilute solution. Our postulates appear to be very nearly valid in the case of acetic acid up to about 0.4 M, far beyond the range in which they are needed.

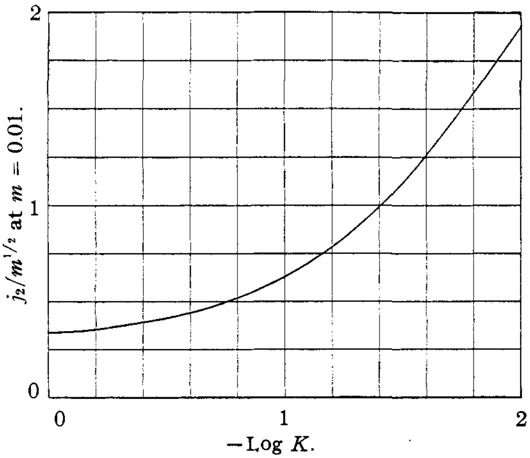

Fig. 3.—Freezing point function at 0.01 M for univalent acids of various dissociation constants.

Curves of the type shown in Fig. 1, in addition to serving as a criterion for the accuracy of data, may also be employed for the detection of and estimation of the degree of dissociation. Inasmuch as freezing point measurements are frequently not dependable in solutions more dilute than 0.01 M, we may employ a simple modification of the curves of Fig. 1 as an aid in evaluating divergence functions in more dilute solutions. For example, values of $j_2/m^{1/2}$ at $m = 0.01$ (Fig. 1 and Table III) are plotted against log K as illustrated in Fig. 3, giving us a plot whereby we may determine probable values of K from a single value of the freezing point lowering at 0.01 M. Thus if we have a single measurement of the freezing point at 0.01 M, we may calculate the value of $j_2/m^{1/2}$ and by interpolation along the curve of Fig. 3 we find the value of log K, or, having K, may complete the divergence function in the very dilute range. This method is most valuable in the range of $K > 10^{-3}$.

TABLE III

STOICHIOMETRIC ACTIVITY COEFFICIENTS OF WEAK ACIDS AT $m = 0.01$

K	$m_{\pm}$ at $m = 0.01$	$\gamma_{\pm}$	$m_{\pm}/m$	γ	$j_2/m^{1/2}$
0.9	0.0099	0.907	0.99	0.898	0.343
.2	.0094	.909	.94	.854	.479
.07	.0090	.910	.90	.819	.747
.04	.0084	.913	.84	.767	.993
.02	.0075	.917	.75	.687	1.425
.01	.0065	.921	.65	.599	1.935
2×10^{-5}	.0005	.975	.05	.044	4.85

Summary

The methods of Lewis and Randall for determining activity coefficients from freezing point measurements or from other measurements of the activity of the solvent are formally reviewed for weak univalent electrolytes.

The logarithm of the activity coefficient of a weak electrolyte (basis of strong electrolytes) is equal to the sum of the logarithm of the degree of dissociation and the logarithm of the activity coefficient of the ions as such.

Use of the dissociation constant, $K = a_{\pm}^2/a_u$, in evaluating the divergence functions of weak electrolytes in very dilute solution is introduced.

The procedure to be followed in determining the activity coefficient of acetic acid in dilute solution from measurements of the activity of the solvent is shown as an example of the treatment of a typical weak electrolyte.

In dealing with weak electrolytes it is expedient to have an easily interpolated activity coefficient for employment where dissociation is inappreciable and one for use where dissociation is considerable. These should be thermodynamically related and should permit of evaluation in very dilute solution. In addition, these coefficients should reduce in the limiting cases, on the one hand to the activity coefficient of a non-electrolyte, and on the other to that of a completely dissociated electrolyte. They should also be defined so that the reference solution is the same for solvent and solute. These requirements are entirely satisfied by the methods described in this paper.

A method of determining the dissociation constant of moderately weak electrolytes from a single measurement of the freezing point at 0.01 M is given.

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