THE CALCULATION OF THE THERMODYNAMIC PROPERTIES AND THE ASSOCIATION OF ELECTROLYTE SOLUTIONS[1, 2, 3]

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A convenient system of representing thermodynamic data for salt solutions is described, in which: (1) the Debye κ is taken proportional to the ionic strength per unit volume of solvent; (2) the Debye limiting law is expressed as an analytical function of the temperature; (3) the mean collision diameter a is taken inversely proportion to μ at constant composition; (4) the function

$$Z = 1 + \kappa a - \frac{1}{1 + \kappa a} - 2 \ln (1 + \kappa a)/(\kappa a)^3$$

is presented in a table of Z vs. $g = \kappa a/(1 + \kappa a)$; (5) the deviations from the Debye–Hückel approximation are treated as an apparent association, with the constant determined to agree with analytical methods for the term proportional to the ionic strength; (6) the calculation of association, either electrostatic or chemical, is made on the assumption that short-range forces are independent of the association; (7) deviations from these relations are expressed graphically, as deviations from a power series in the concentrations.

The methods are illustrated for aqueous solutions of sodium chloride and of sulfuric acid.

The Debye–Hückel limiting law for the electrostatic interaction of ions depends upon the interaction of ions which are very far apart, and so may be related to the charge on the ions and the macroscopic properties of the solvent without any necessity for a detailed model of ion or of solvent. The rest of the Debye–Hückel expression arises from the interactions of molecules which are close together and does depend largely upon the details of the models of the ions and the solvent. The models usually used do not correspond very closely to most of the solutions to which they are applied. The differences between the models and real solutions lead to deviations from the theoretical equations for simple models which begin with the first power of the concentration. We therefore propose that smoothing of the measured properties and calculation of other properties from them be carried out by the use of convenient functions which represent the limiting law exactly and change with the concentration approximately as the functions for simple models, but which do not pretend to

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represent these properties exactly beyond the limiting law. Any errors due to these approximations will be grouped with the deviations which arise from the inadequacies of the simple models. This procedure is equivalent to choosing a model which differs from the simple one in a way which leads to only slight differences in behavior, although it differs in a way which cannot be pictured by a simple change in the model.

This proposal must not be interpreted as a recommendation to abandon attempts to determine the properties of more complicated models. It is our belief that further progress in the theory can come only through such attempts. One of the easiest ways to check such theories will be to compare the results of the theories with the experimental results smoothed by our methods.

We express the function κ in terms of moles per unit quantity of solvent rather than moles per unit volume of solution:

$$\kappa = (4\pi\epsilon^2\mathrm{N}^2\rho_0\Sigma_i N_i z_i^2/D_0RTw_0N_0)^{1/2} = (8\pi\epsilon^2\mathrm{N}^2\rho_0\mu/1000D_0RT)^{1/2} \tag{1}$$

in which ϵ is the charge on the proton, N is Avogadro's number, R is the gas constant per mole, T is the absolute temperature, N_i is the number of moles of the i^{th} species and z_i its valence, N_0 is the number of moles of solvent of molecular weight w_0, density ρ_0, and dielectric constant D_0, and μ is the ionic strength in moles per kilogram of solvent, $1000\Sigma_i N_i z_i^2/2w_0N_0$. This procedure has been followed in our laboratory for several years. It has been justified theoretically (25) in that it corresponds to the dielectric constant of the solution being proportional to the concentration of the solvent. To make κ proportional to the concentration in moles per liter of solution, which is the assumption usually made, it is necessary to assume that the dielectric constant is independent of the electrolyte concentration. For most electrolytes the assumption which leads to weight molal concentrations is much more probable than the other one. A still more cogent argument is the pragmatic one that the thermodynamic functions may thus be expressed directly in terms of temperature, pressure, and quantities of the components.

We express the limiting-law ratios of the logarithm of the activity coefficient to the square root of the ionic strength *directly* as a power series of the temperature. Since the smoothing of the density and the dielectric constant are empirical, there is no theoretical argument for or against the expression of $(\rho_0/T^3D_0^3)^{1/2}$ as a simple power series in t. There is a very great practical advantage in a simple analytical expression for the quantity which is the basis of our calculations. Using $T = 273.16$°C., $\mathrm{N} = 6.021 \times 10^{23}$, $\epsilon = 4.805 \times 10^{-10}$ E.S.U., $RT = 2.2711 \times 10^{10}$ ergs (2), the density of water from the *International Critical Tables*, and the dielectric constants of Wyman and Ingalls (31), we obtain for water at 1 atm. pressure

$$\frac{\ln \gamma_k}{z_k^2\sqrt{\mu}} = 1.1254[1 + 0.15471(t/100) + 0.03569(t/100)^2 + 0.02389(t/100)^3] \tag{2}$$

in which γ_k is the activity coefficient of the k^{th} species and t is the Centigrade temperature. We are also interested in

$$\frac{\ln \gamma_k}{z_k^2 \kappa} = 3.472 \times 10^{-8}[1 + 0.10194(t/100) + 0.04269(t/100)^2 + 0.00976(t/100)^3] \qquad (3)$$

and

$$\kappa/\sqrt{\mu} = 0.3241 \times 10^8[1 + 0.05217(t/100) = 0.00916(t/100)^2 + 0.00888(t/100)^3] \qquad (4)$$

The maximum deviation of equations 2 and 3 from the value calculated from the density and Wyman's value of the dielectric constant at each temperature is 0.02 per cent, and the average of the absolute values of the deviations is 0.01 per cent. For equation 4 the maximum deviation is less than 0.005 per cent. The equations are consistent to a maximum error of 0.014 per cent, but there is no need for using all three together. If more than equation 2 is used, the more convenient of equations 3 and 4 should be chosen.

The relation of dielectric constant to pressure has not been measured accurately enough to warrant an equation for this relation. Probably the best approximation we can make at present is that, at constant temperature, the dielectric constant is proportional to the density. If this relation is exact, $\kappa/\sqrt{\mu}$ is independent of the pressure, and equations 2 or 3 may be made to apply at various pressures by multiplying the right-hand member of each by ρ_{0p}/ρ_{01}, in which ρ_{0p} is the density of water at the pressure p and ρ_{01} is the density at 1 atm. pressure. Redlich's method of obtaining the coefficients of equations 2 and 3 is discussed later.

We assume that the collision diameter a varies with the temperature as D_0T/ρ_0, so that the product κa is independent of the temperature and the pressure. If the dielectric constant of the solvent is proportional to its density at constant temperature, this proposal assumes that a is independent of the pressure; this is strictly consistent with the assumptions made in the derivation of the Debye equations. However, there is a variation of a with the temperature which is not consistent with these assumptions. The assumed decrease in size is only 5 per cent for water from 0° to 100°C. and real ions are neither spherical nor rigid, so that the effective collision diameters of real ions should decrease with the temperature. However, our justification is the pragmatic one that this proposal, together with the first, makes the electrostatic contribution to the free energy a function of the temperature and pressure multiplied by a function of the quantities of the components. The practical advantage is very great. The contribution to any "total" thermodynamic function has the same form as the contribution to the total free energy; the contribution to any "partial" quantity of an electrolyte solute has the same form as the contribution to the partial free energy, or chemical potential, of that solute; and the contribution to any partial quantity of the solvent has the same form as the contribution to the chemical potential of the solvent. If G' be taken as the symbol for the electrostatic contribution to any thermodynamic property, these assumptions make

$$\bar{G}'_k = (g/a)z_k^2 x/(1 + x) = (g/a)z_k^2 y \tag{5}$$

in which $x = \kappa a = a'\sqrt{\mu}$, and $y = x/(1 + x)$, and g is defined by this equation. The appropriate value of g for each property may be determined from equation 5 with equation 2 and the corresponding relation to the pressure, since all the thermodynamic functions may be determined from F expressed as a function of T, p, and the N_i's. Then

$$G' = (g/a)\Sigma_i N_i z_i^2 (y - Z) \tag{6}$$

and

$$\bar{G}'_0 = -(g/a)\Sigma_i N_i z_i^2 Z/N_0 \tag{7}$$

$$\begin{aligned} Z &= [1 + x - 1/(1 + x) - 2 \ln (1 + x)]/x^2 \\ &= x/3 - 2x^2/4 + 3x^3/5 - 4x^4/6 + \cdots \end{aligned} \tag{8}$$

$$\begin{aligned} &= [1 - y - (1 - y)^3 + 2(1 - y) \ln (1 - y)]/y^2 \\ &= y/3 - y^2/6 - y^3/15 - y^4/30 - \cdots \end{aligned} \tag{9}$$

We determine Z of equations 6 and 7 from a table of Z vs. y. For small values of x the logarithm cannot be determined accurately enough for the direct determination of Z, but Z may be determined from the power series of equation 8 or that of equation 9. That of equation 9 has the advantage in dilute solutions that the convergence is much more rapid. The use of y as the independent variable has the much more important advantage that y approaches unity as x approaches infinity. A table of Z vs. y with a hundred entries is sufficient to give Z to 0.001 by linear interpolation up to $y = 0.95$. The curve of Z vs. y is shown in figure 1. In table 1 the value of y is the sum of the number at the head of the column and that at the left of the row, the upper entry in each square is the value of Z, and the lower (italicized) entry is the increment of Z for a change of 0.01 in y.

In our early studies of electrolyte solutions we gave a the value zero for all electrolytes and so obtained from the theory only terms in the square root of the ionic strength multiplied by a constant or by integral powers of the concentration of any non-electrolyte solute (23, 24). This method is quite satisfactory for uni-univalent electrolytes at ionic strengths less than unity, and we were able to reproduce our measurements accurately with a five-term series of the form

$$\begin{aligned} (F - F^*)/RT = \Sigma_i N_i [\ln (N_i/w_0 N_0) - 1 + A z_i^2 \sqrt{\mu}] \\ + \Sigma_{ij}(B_{ij} + C_{ij}\sqrt{\mu})N_i N_j/w_0 N_0 \\ + \Sigma_{ijk}(D_{ijk} + E_{ijk}\sqrt{\mu})N_i N_j N_k/(w_0 N_0)^2 \end{aligned} \tag{10}$$

More recently (26) we have taken a' equal to unity for all electrolytes. Guggenheim (8) has suggested that with this value of a', one additional term proportional to m is sufficient to represent the measurements up to an ionic strength of 0.1 M. We find very little advantage in using a' as unity rather than zero up to 1 M, and for higher concentrations there is a great advantage in choosing a' to fit the data.

Guggenheim and Wiseman (8, 9) have also claimed that the term in log γ proportional to m "hardly varies with the temperature," which would require that the corresponding term in the heat of dilution be nearly zero. This is true for hydrochloric acid, as they point out, but it is not true in general. They criticize the freezing-point measurements of Scatchard and Prentiss (22) on aqueous potassium chloride solutions because the value they yield for the coefficient of this term, which Guggenheim calls λ, differs from that obtained from electromotive-force measurements at higher temperatures more than the value yielded by earlier freezing-point measurements. From the heat of dilution measurements of Lange and Leighton (18), we obtain for $d\lambda/dt$ 0.00156 at 12.5°C. and 0.00110 at 25°C. The use of this quantity requires the use of the limiting law, which varies with the temperature like equation 2 rather than the approximate values of Guggenheim. This gives $\lambda = 0.077$ at 20°C. from the measurements of Güntelberg (11) and $\lambda = 0.099$ at 25°C. from the measurements of Shedlovsky and MacInnes (28). At 0°C. the freezing-point measurements of Scatchard and Prentiss yielded 0.056, and earlier freezing-point measurements gave 0.083. The assumption that the value of $d\lambda/dt$ at 12.5°C. is the average from 0° to 20°C. and from 0° to 25°C. gives λ at 0°C. from the electromotive-force measurements as 0.046 and 0.060. The agreement with the freezing-point measurements of Scatchard and Prentiss is excellent.

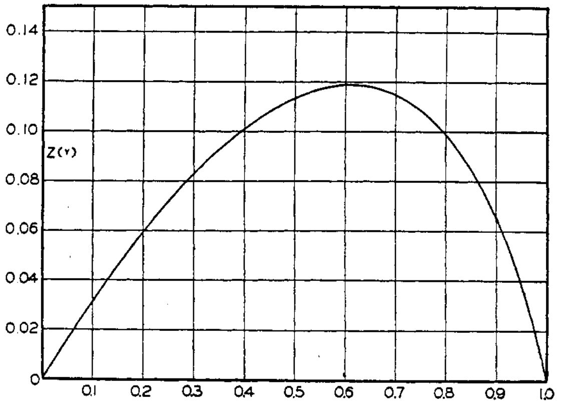

FIG. 1. Debye function Z vs. y

To determine the proper size from measurements of the osmotic coefficient, we plot

$$\Delta\phi = \phi + (A/a')Z_{a'} + b'm \tag{11}$$

against m, choosing b' so that $\Delta\phi$ is approximately zero for the most concentrated solution. For a single electrolyte $\Sigma_i m_i c_i^2/\Sigma_i m_i = -z_+z_-$, if z_- be taken as negative. The procedure is illustrated for the measurements of the freezing points of aqueous sodium chloride solutions (22) in figure 2, where $\Delta\phi$ is plotted for a' equal to 1.0, 1.3, and 1.55, with b' equal to 0.0378, 0.0160, and 0.0029. The three curves correspond to the same values of ϕ. The experimental points are shown only above 0.05 M, as those at lower concentrations cluster so closely that they confuse the picture. For a' equal to unity, the curve shows a high

TABLE 1*

Values of the Debye function, Z

y	0	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	y
0.0	0.00000 *332*	0.03160 *296*	0.05941 *255*	0.08287 *209*	0.10129 *152*	0.11371 *86*	0.11885 *5*	0.11487 *−100*	0.09882 *−244*	0.06537 *−467*	0.0
0.01	0.00332 *328*	0.03456 *292*	0.06196 *251*	0.08496 *203*	0.10281 *147*	0.11457 *80*	0.11890 *−4*	0.11387 *−112*	0.09638 *−261*	0.06070 *−498*	0.01
0.02	0.00660 *325*	0.03748 *288*	0.06447 *246*	0.08699 *197*	0.10428 *141*	0.11537 *72*	0.11886 *−14*	0.11275 *−125*	0.09377 *−280*	0.05572 *−531*	0.02
0.03	0.00985 *321*	0.04036 *284*	0.06693 *242*	0.08896 *193*	0.10569 *134*	0.11609 *64*	0.11872 *−23*	0.11150 *−138*	0.09097 *−299*	0.05041 *−567*	0.03
0.04	0.01306 *318*	0.04320 *281*	0.06935 *237*	0.09089 *187*	0.10703 *128*	0.11673 *56*	0.11849 *−34*	0.11012 *−152*	0.08798 *−320*	0.04474 *−607*	0.04
0.05	0.01624 *314*	0.04601 *276*	0.07172 *233*	0.09276 *182*	0.10831 *122*	0.11729 *48*	0.11815 *−44*	0.10860 *−165*	0.08478 *−341*	0.03867 *−651*	0.05
0.06	0.01938 *311*	0.04877 *272*	0.07405 *228*	0.09458 *176*	0.10953 *115*	0.11777 *40*	0.11771 *−54*	0.10695 *−180*	0.08137 *−363*	0.03216 *−701*	0.06
0.07	0.02249 *307*	0.05149 *268*	0.07633 *223*	0.09634 *171*	0.11068 *108*	0.11817 *31*	0.11717 *−66*	0.10515 *−195*	0.07774 *−387*	0.02515 *−759*	0.07
0.08	0.02556 *304*	0.05417 *264*	0.07856 *218*	0.09805 *165*	0.11176 *101*	0.11848 *23*	0.11651 *−77*	0.10320 *−211*	0.07387 *−412*	0.01756 *−830*	0.08
0.09	0.02860 *300*	0.05681 *260*	0.08074 *213*	0.09970 *159*	0.11277 *94*	0.11871 *14*	0.11575 *−88*	0.10109 *−227*	0.06975 *−438*	0.00926 *−926*	0.09
0.10	0.03160	0.05941	0.08287	0.10129	0.11371	0.11885	0.11487	0.09882	0.06537	0.00000	0.10
y	0.00000	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	y

* y is the sum of the number at the top or bottom of the column and that at the side of the row. Z is the main entry.

The change in Z for a change of 0.01 in y is the lower (italicized) entry.

maximum. As a' decreases, the maximum becomes lower and shifts to smaller concentrations, and an inflection, which is outside the range of these measurements for $a' = 1$, also shifts to lower concentrations. We try to choose the smallest value of a' which will give neither maximum nor inflection in dilute solutions. Our choice from these measurements is the lower curve with $a' = 1.55$. It is often possible to choose a' so that $\Delta\phi$ may be represented by a quadratic in m, but we have had little success with attempts to reduce it to a linear term as in the Hückel equation. In the present case the smallest deviations from the Hückel equation would occur with a' about 1.3, which corresponds to the middle curve. Since any change in a' will increase the deviations in either dilute or concentrated solutions, both of which are already considerably greater than the scatter of the measurements, no choice of a' will represent these measurements within their apparent accuracy.

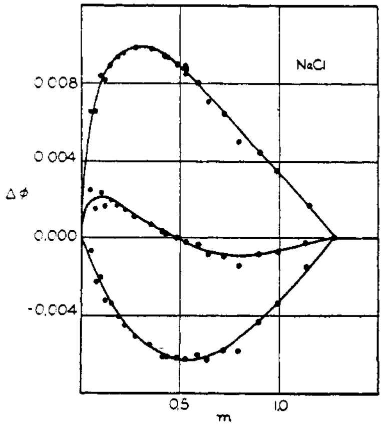

FIG. 2

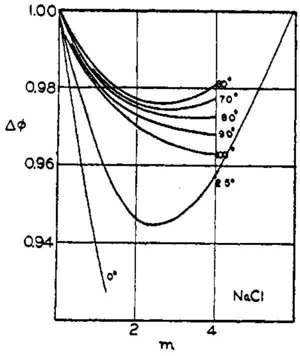

FIG. 3

FIG. 2. Deviation function for osmotic coefficient of sodium chloride for various sizes

FIG. 3. Deviation function for osmotic coefficient of sodium chloride

We illustrate our method of handling the measurements with various properties of aqueous solutions of sodium chloride. In figure 3, the osmotic coefficient is represented by equation 11 with $a' = 1.55$ and $b' = 0.06$. This value of b' is chosen to make $\Delta\phi$ approximately zero for saturated sodium chloride solutions at 25°C. The experimental values are the freezing-point measurements of Scatchard and Prentiss (22), the smoothed curve of Scatchard, Hamer, and Wood (26) at 25°C., and the boiling-point measurements of Smith (29) and of Smith and Hirtle (30) at higher temperatures. It is obvious that $\Delta\phi$ must pass through a maximum between 25° and 60°C.

Figure 4 shows the activity coefficients of sodium chloride from the electromotive-force measurements of Harned and Nims (13), expressed as

$$\Delta \log \gamma = \log \gamma + 0.4343\,[(A/1.55)y_{1.55} - 0.12m] \qquad (12)$$

This is the type of equation which we would use to determine the size of a' from measurements which yielded the activity of the electrolyte, but in this case we have used the value of a' already determined, and the $0.12m$ is obtained from the $0.06m$ for the osmotic coefficient.

Figure 5 shows the heat of dilution of sodium chloride from the measurements of Gulbransen and Robinson (10) and of Lipsett, Johnson, and Maas (19), expressed as

$$\Delta(H/m) = (H - H^*)/m - (2RT/1.55)(\mathrm{d}A/\mathrm{d}T)(y_{1.55} - Z_{1.55}) + 140m \qquad (13)$$

If the value of a' were not chosen the same as for the measurements of the freezing points, we would use an equation of the type of equation 13 to determine an appropriate value. The term proportional to m is again chosen to give a very small deviation for the most concentrated solution at 25°C. The decrease in $\Delta(H/m)$ with increasing temperature corresponds to the behavior of $\Delta\phi$ and of $\Delta \log \gamma$, for $\Delta(H/m)$ must be zero when the other two pass through maxima.

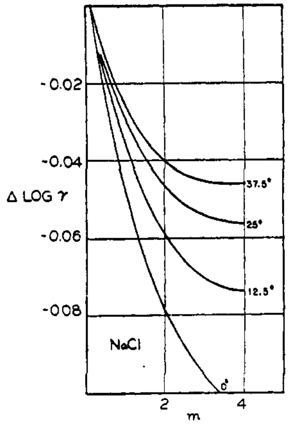

FIG. 4

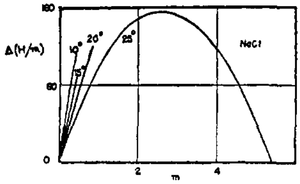

FIG. 5

FIG. 4. Deviation function for logarithm of activity coefficient of sodium chloride
FIG. 5. Deviation function for molal heat of dilution of sodium chloride

Figure 6 shows the apparent molal volumes of aqueous sodium chloride solutions at 25°C. from the measurements of Baxter and Wallace (1), of Geffcken (5), and of Geffcken, Beckmann, and Kruis (6), expressed as

$$\begin{aligned}\Delta\Phi_{v_2} &= \Phi_{v_2} - (2RT\beta A/1.55)(y_{1.55} - Z_{1.55}) - 0.6m \\ &= \Phi_{v_2} - 1.665(y_{1.55} - Z_{1.55}) - 0.6m \qquad (14)\end{aligned}$$

in which β is the compressibility. The term $0.6m$ is again chosen to make the deviation approximately zero for the most concentrated solution. The coefficient of the first term corresponds to the assumption that the dielectric constant is proportional to the concentration of water at constant temperature. This leads to a limiting law 7.5 per cent smaller than that determined by Redlich (23) from the apparent volumes of sodium and potassium chlorides and bromides. Dr. Redlich and the authors agree that the available volume measurements are not quite sufficient to furnish an unquestionable decision between the two, and we are not proposing a revision of his value. For our present purpose, however, we consider a value given by an approximate assumption preferable to one obtained from the volume measurements themselves.

In the case of the apparent molal volumes, the form we have chosen for the electrostatic term is not helpful, for the deviation from the limiting law is smaller than that from our expression, and it may be represented more closely by a term linear in m.

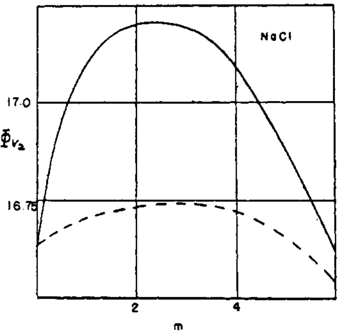

FIG. 6. Deviation function for apparent molal volume of sodium chloride

$$\Delta\Phi_{v_2}' = \Phi_{v_2} - \frac{4}{3}RT\beta A\sqrt{m} - 0.1m = \Phi_{v_2} - 1.72\sqrt{m} - 0.1m \qquad (15)$$

The corresponding function for Redlich's treatment is

$$\Delta\Phi_{v_2}'' = \Phi_{v_2} - 1.86\sqrt{m} \qquad (16)$$

Up to $m = 0.4$, it is a horizontal line at 16.61, which is 0.02 cc. per mole smaller than the intercept of our curves.

If there is association of a considerable fraction of the ions, the deviations corresponding to figures 2 to 6 will be large and the curves will be complex. It is possible to obtain a much more accurate interpolation by taking the association into account. Before discussing the treatment of association, we note that it is not possible to distinguish experimentally between chemical association and that part of the electrostatic interaction which is neglected in the Debye–Hückel approximation, and which is called "electrostatic association" by Bjerrum and the "higher term correction" by La Mer and Gronwall, except in the case that the effect is so large that it leads to an unreasonably small distance a when calculated as an electrostatic effect. We believe that the calculation by the law of mass action affords the most satisfactory treatment of the higher term effect. Why is the analytical method of La Mer and Gronwall

(7,17) not entirely satisfactory? Their result is given as the first terms in an infinite power series in $(-z_i z_i \epsilon^2/DkT)$, and partially as the first terms in infinite power series in κa. The computation of any further terms would require considerable labor. Moreover, the result would be uncertain because the conditions of integrability are violated and the value calculated for the work of charging the ions reversibly depends upon the method of adding the charge (15, 20). The conditions of integrability are satisfied for terms in the electrical potential containing the first power of $(-z_i z_i \epsilon^2/DkT)$, which is the Debye–Hückel approximation. They are also satisfied for terms containing the first power of $(\kappa^2 a^2)$, and it is this fact which we utilize. The uncertainty introduced by the violation of these conditions apparently becomes more serious as the exponents of $(-z_i z_i \epsilon^2/DkT)$ and of $(\kappa^2 a^2)$ increase.

The method of Bjerrum (3), on the other hand, suffers from the arbitrary choice of the distance $(-z_i z_i \epsilon^2/2DkT)$ in the calculation of the association constant. Bjerrum's expression of the equilibrium constant of the reaction.

$$\mathrm{A} + \mathrm{B} = \mathrm{AB}$$

which need not be limited to the case in which the valence of the product AB is zero, is

$$K_{\mathrm{AB}} = -\frac{4\pi \mathrm{N}}{1000}\left(\frac{z_A z_B \epsilon^2}{DkT}\right)^3 Q_{\mathrm{AB}} \tag{17}$$

$$Q_{\mathrm{AB}} = \int_2^{b_{\mathrm{AB}}} \frac{e^t}{t^4}\,\mathrm{d}t \tag{18}$$

$$b_{\mathrm{AB}} = -z_{\mathrm{A}} z_{\mathrm{B}} \epsilon^2/DkTa_{\mathrm{AB}} \tag{19}$$

This equation is used only if b_{AB} is more positive than 2. If b_{AB} is more negative than 2, K_{AB} is assumed to be zero.

We choose the value of K_{AB} so as to fit precisely the analytical expression for the term proportional to the ionic strength. This is the logical extension of the method we use for the Debye–Hückel approximation, and it avoids the difficulties of the violation of the conditions of integrability and of the arbitrary distance. To evaluate the constant we use the expression of Kirkwood[5] for the term in the logarithm of the activity coefficient proportional to the ionic strength.

$$K_{\mathrm{AB}} = -\frac{4\pi \mathrm{N}}{1000}\left(\frac{z_{\mathrm{A}} z_{\mathrm{B}} \epsilon^2}{DkT}\right)^3 [B_{\mathrm{AB}} - (B_{\mathrm{AA}} + B_{\mathrm{BB}})/2] \tag{20}$$

$$\begin{aligned} B_{jk} &= \int_0^{b_{jk}} \frac{1}{t^4}(e^t - 1 - t - t^2/2 - t^3/6)\,\mathrm{d}t \\ &= \{b_{jk}^3 E_i(b_{jk}) - \ln b_{jk} - C_0 - e^{b_{jk}}[2 + b_{jk} + b_{jk}^2] \\ &\qquad + [2 + 3b_{jk} + 3b_{jk}^2 + 11b_{jk}^3/6]\}/6b_{jk} \end{aligned} \tag{21}$$

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[5] Private communication from J. G. Kirkwood. We are very grateful to Professor Kirkwood for calculating these terms from the general expression given by him (16) and for computing the B's in table 2. It should be noted, however, that our use of them to calculate the association constant is not the same as his method of calculating that constant.

$C_0 = 0.5772$ (Euler's constant). Some values of B_{jk} and of Q_{jk} are given in table 2.

The constant of equation 20 is finite and positive for all values of b_{AB}. For small values it is proportional to b_{AB}. For larger values it is slightly smaller than the Bjerrum constant. For symmetrical electrolytes, the ratio of our constant to that of Bjerrum is the sum of the third and fifth columns of table 2 divided by the second column. For unsymmetrical electrolytes, which are discussed later, our constant is increased, but only by an amount which is small relative to the difference from Bjerrum's constant. Our constant should be slightly smaller than his to yield the same values of log γ, for our method gives a more negative value for the Debye–Hückel term, since we use the size a and Bjerrum uses $ab/2$. The relative difference between the two constants is very small except in the range of small values of b_{AB} where the Bjerrum treatment is unsatisfactory.

TABLE 2

Some values of Q_{jk} and of B_{jk}

b_{jk}	Q_{jk}	B_{jk}	$-b_{jk}$	$-B_{jk}$
1		0.046	1	0.037
2	0.000	0.105	2	0.069
3	0.325	0.181	3	0.097
4	0.550	0.285	4	0.120
5	0.755	0.414	5	0.141
6	1.041	0.645	6	0.159
7	1.417	0.979	7	0.176
8	1.996	1.525	8	0.192
9	2.950	2.450	9	0.206
10	4.547	4.023	10	0.219
12	13.51	12.84	12	0.242
15	101.8	101.2	15	0.272

If a is independent of the temperature, b_{AB} changes with the temperature as $1/D_0T$; but if a' is independent of the temperature, b_{AB} changes as $(1/D_0T)^{1/2}$. A change in a_{AB} leads to the same relative change in K for small values of b_{AB} and to a more rapid relative change for larger values of b_{AB}. In addition, K is proportional to $(1/D_0T)^3$ from the part outside the integral, so that most of the variation with temperature is independent of the behavior of b_{AB}. We therefore keep a' independent of the temperature, as in the Debye–Hückel approximation.

The treatment of electrolytes of unsymmetrical valence type is complicated by the fact that the Debye–Hückel term is not the only one which depends upon the action at large distances, but there is a second term which results from the fact that the ionic strength effective for a cation depends more upon the anions than upon the cations, and *vice versa*. Formally it arises from the third term in the expansion of the Boltzmann exponential, and it is zero if all the ions have valences z or $-z$. By the Güntelberg–Müller charging process it leads to the following term in $\ln \gamma$:

$$\ln \gamma'' = \frac{1}{6}\left(\frac{\epsilon^2}{DkT}\right)^3 \frac{z_k^3 \kappa^2}{\Sigma_i n_i z_i^2} \Sigma_i n_i z_i^3 \frac{e^{3\kappa a}}{(1 + \kappa a)^3} \int_{t+3\kappa a}^{\infty} \frac{e^{-t}}{t^4}\, \mathrm{d}t \qquad (22)$$

The Debye charging process leads to a somewhat smaller result, which differs from equation 22 by a power series in κ beginning with κ^2 and $\ln \kappa$ times another power series in κ beginning with κ^3. The contribution to the osmotic coefficient which corresponds to equation 22 contains two similar power series. If we expand and retain only terms in $\kappa^2 \ln \kappa$ and in κ^2 beyond the Debye–Hückel approximation, we obtain by the Kirkwood method and the Debye charging process

$$\begin{aligned}\ln \gamma_k &= -\frac{\epsilon^2 z_k^2}{2DkT}\frac{\kappa}{1 + \kappa a} - \frac{\epsilon^4 z_k^3}{6(DkT)^2}\frac{\kappa^2}{\Sigma_i n_i z_i^2}\Sigma_i n_i z_i^3\left[\ln 3\kappa a - C_0 - \frac{1}{12} + 6B_{ik}\right] \\ &= -\frac{\epsilon^2 z_k^2}{2DkT}\frac{\kappa}{1 + \kappa a} \\ &\qquad - \frac{\epsilon^4 z_k^3}{6(DkT)^2}\frac{\kappa^2}{\Sigma_i n_i z_i^2}\Sigma_i n_i z_i^3\left[\ln 3\kappa a - C_0 - \frac{1}{12} + 3(B_{ii} + B_{kk})\right] \\ &\qquad - \frac{\epsilon^4 z_k^3}{(DkT)^2}\frac{\kappa^2}{\Sigma_i n_i z_i^2}\Sigma_i n_i z_i^3[B_{ik} - (B_{ii} + B_{kk})/2] \end{aligned} \qquad (23)^6$$

The Güntelberg–Müller charging process gives a result which differs only by the omission of the term 1/12 in the first square bracket. Although it arises from the $\kappa^2 \ln \kappa$ term in the electrical potential, the difference is proportional to κ^2. We prefer the Debye charging process, but the difference from the Güntelberg–Müller process is extremely small. This difference is probably an approximate measure of how much the activity coefficient is affected by the violation of the conditions of integrability in this term. The last term of the second form of equation 23 corresponds to the association constant of equation 20, and we treat more concentrated solutions by assuming association and determining the activity coefficients of the ions from the first two terms of this equation with the n_i's and κ determined from the concentrations of the unassociated ions. For symmetrical valence types $n_A z_A^3 = -n_B z_B^3$, so the second term vanishes in the summation.

For unsymmetrical valence types we also take into account higher types of association, although they lead to no effect proportional to the concentration. As an example, for the series of reactions

$$\begin{aligned} A^+ + B^{---} &= AB^{--} \\ A^+ + AB^{--} &= A_2B^- \\ A^+ + A_2B^- &= A_3B \end{aligned}$$

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[6] If B_{jk} of equation 21 is expanded in an infinite power series in b_{jk} and the result is substituted in equation 23, the equation becomes equivalent to that obtained by Gronwall, La Mer, and Sandved (7). Kirkwood's expression in a closed form gives a great advantage over the power series, which converges very slowly.

we calculate a constant for each, using the value of a determined to fit the first. We ignore the very small values of the constant for the association of two anions or two cations, such as

$$\mathrm{B}^{---} + \mathrm{AB}^{--} = \mathrm{AB}_2^{-----}$$

and compensate by replacing $(B_{ii} + B_{kk})$ in the second term by $2B_{ik}$ when i and k are both positive or both negative. If $i = k$, the third term vanishes automatically.

In salt mixtures we determine K for each electrolyte from an appropriate value of a as though that electrolyte were present alone, but use an average value, the same for all the ions, in the first two terms of equation 23. If a_{AA} be taken equal to a_{AB} in the calculation of K_{AB}, the association constant of A and B, but if it be taken equal to $a_{\mathrm{AB'}}$ in the calculation of $K_{\mathrm{AB'}}$, this may lead to different sizes of the ion A. In the second term the value of B_{AA} corresponding to a_{AB} should be used in the coefficient of n_{B}, and the value of B_{AA} corresponding to $a_{\mathrm{AB'}}$, should be used in the coefficient of $n_{\mathrm{B'}}$. In the coefficient of $n_{\mathrm{A'}}$, $(B_{\mathrm{AA}} + B_{\mathrm{A'A'}})/2$ should be replaced by $B_{\mathrm{AA'}}$, which should be calculated from average values of $(a_{\mathrm{AA}} + a_{\mathrm{A'A'}})/2$ weighted according to the contribution of the terms containing these sizes to the chemical potentials.

We calculate the effect of association, either electrostatic or chemical, by assuming that the non-electrostatic interactions do not affect the association, or conversely, that the association does not affect the short-range interactions. One of us (27) has noted that the success of treating reaction kinetics by simple electrostatic theory depends upon the validity of this assumption in many cases. It is probable that many of the failures of the simple theory may be attributed to the failure of this assumption. We have practically no method of measuring the magnitude of these effects, and the assumption that they are zero does lead to great simplification. We thus divide the deviations into two parts: the electrostatic part which is calculated from the concentrations of the species assumed present, and the non-electrostatic part which is calculated from the stoichiometric concentrations of the component ions regardless of any reaction which may have occurred.

We define the apparent constant K'_{AB} by the relations

$$K'_{\mathrm{AB}} = \frac{(\mathrm{AB})}{(\mathrm{A})(\mathrm{B})} = K_{\mathrm{AB}} \frac{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}}{\gamma_{\mathrm{C}}} \tag{24}$$

If the logarithm of the activity of each ion is divided into an electrostatic part $\ln \gamma_{ke}$, given by the first line of the second form of equation 23 in terms of the species, and a non-electrostatic part given by a series of integral powers of the concentrations as

$$\ln \gamma_k = \ln \gamma_{ke} + 2\Sigma_i \beta_{ki} m_i + 3\Sigma_{ij} \delta_{kij} m_i m_j + \cdots \tag{25}$$

we may state our last assumption as

$$\beta_{k\mathrm{AB}} = \beta_{k\mathrm{A}} + \beta_{k\mathrm{B}}, \qquad \delta_{ki\mathrm{AB}} = \delta_{ki\mathrm{A}} + \delta_{ki\mathrm{B}}, \text{ etc.} \tag{26}$$

which leads to

$$\begin{aligned}\ln K'_{\mathrm{AB}} &= \ln K_{\mathrm{AB}} + \ln \gamma_{\mathrm{A}_e} + \ln \gamma_{\mathrm{B}_e} - \ln K_{\mathrm{AB}_e} \\ &= \frac{2Az_{\mathrm{A}}z_{\mathrm{B}}\sqrt{\mu}}{1 + a'\sqrt{\mu}} + A^2 z_{\mathrm{A}}z_{\mathrm{B}}(z_{\mathrm{A}} + z_{\mathrm{B}})\Sigma_i m_i z_i^3 \\ &\qquad \times \Bigg[\ln 3a'\sqrt{\mu} - C_0 - \frac{1}{12} + 3B_{ii} \\ &\qquad + \frac{(z_{\mathrm{A}} + z_{\mathrm{B}})^3 B_{\mathrm{AB,AB}} - z_{\mathrm{A}}^3 B_{\mathrm{AA}} - z_{\mathrm{B}}^3 B_{\mathrm{BB}}}{3z_{\mathrm{A}}z_{\mathrm{B}}(z_{\mathrm{A}} + z_{\mathrm{B}})}\Bigg] \end{aligned} \tag{27}$$

The second term of equation 27 vanishes if $\Sigma_i m_i z_i^3 = 0$ or if $z_{\mathrm{A}} + z_{\mathrm{B}} = 0$, except for very small terms involving the differences in B's for pairs of ions of the same kind. These terms may well be ignored. Then the second term vanishes if the solution is electrically symmetrical or if the product AB has zero valence.

Computation by these equations is greatly simplified by the simple device of choosing as independent variable the ionic strength rather than the stoichiometric concentration. If we denote by asterisks the stoichiometric concentrations and activity coefficients, and attribute the unstarred coefficients to the species

$$\ln \gamma_k^* = \ln \gamma_k + \ln (m_k/m_k^*) \tag{28}$$

and the mean activity coefficient of the electrolyte is determined as

$$(\Sigma_j \nu_j \ln \gamma_j^*)/(\Sigma_j \nu_j) \tag{29}$$

in which the summation is carried only over the simple ions. The osmotic coefficient is

$$\begin{aligned}\phi^* = \Sigma_i m_i \Bigg\{&(1 - A/a')z_i^2 Z_{a'} \\ &- \frac{A^2 z_i^3}{12}\Sigma_j m_j z_j^3 \times [\ln 3a'\sqrt{\mu} + 1 - C_0 - \tfrac{1}{12} + 3(B_{jj} + B_{ii})]\Bigg\} \\ \div (\Sigma_j m_j^*) &+ (\Sigma_{jk} m_j^* m_k^* \beta_{jk})/(\Sigma_j m_j^*) + 2(\Sigma_{jkl} m_j^* m_k^* m_l^* \delta_{jkl})/(\Sigma_{jk} m_j^* m_k^*)\end{aligned} \tag{30}$$

in which m_j^* is zero except for the component ions or neutral molecules. The simplest case is that of symmetrical electrolytes with but a single type of association. Fixing the value of the ionic strength fixes the value of K'_{AB} by equation 27 if K_{AB} is known, and it also fixes the concentration of each species of ions, so the concentration of the associated molecules is easily determined from equation 24. Any value of the stoichiometric concentration can be approximated as closely as desired in a very short time.

For unsymmetrical electrolytes it is necessary to choose trial values of as many concentrations as there are associations to be calculated and to find by trial and error the concentrations of the other species. For a single association this is not very difficult, and even for more complicated systems it will usually be possible to select species with concentrations so small that a large relative change will have very little effect on the concentrations of the other species. The complications are increased because the value of K'_{AB}, etc. depends upon the lack of symmetry of the solution as well as upon the ionic strength. This difficulty is not so serious as it appears. Although the number of equations to be satisfied is doubled, the work necessary to satisfy them is not increased so much.

The calculations including association may be illustrated with sulfuric acid. The constant determined by Hamer (12) from measurements in sodium bisulfate–sodium sulfate mixtures is 82 and corresponds to an a of less than 0.7 by equation 20. We may therefore assume that the association is not entirely electrostatic, choose 1.5 as a reasonable value of a', and ignore the association to H_2SO_4. We choose as variable the ionic strength, μ, and the sulfate-ion concentration, which we will call x. The hydrogen-ion concentration is $\mu - x$, the hydrosulfate ion concentration is $\mu - 3x$, the stoichiometric acid concentration is $\mu - 2x$, and

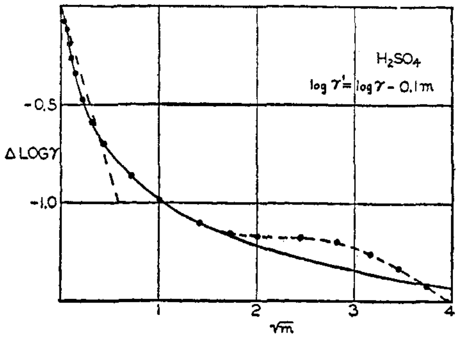

FIG. 7

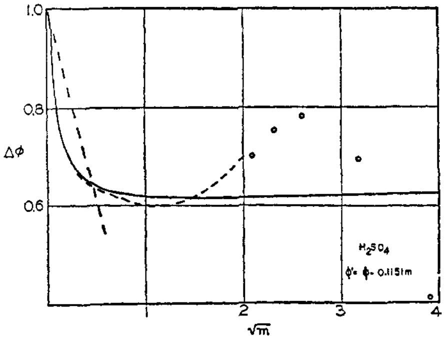

FIG. 8

FIG. 7. Logarithm of activity coefficient of sulfuric acid minus term proportional to concentration

FIG. 8. Osmotic coefficient of sulfuric acid minus term proportional to concentration

$$K'_{HSO_4^-} = (\mu - 3x)/x(\mu - x) \tag{31}$$

The second equation to be satisfied is

$$\log K'_{HSO_4^-} + 1.9124 - 2.036\sqrt{\mu}/(1 + 1.5\sqrt{\mu}) - 16.48\,(\log 4.5\sqrt{\mu} - 0.7887)x \tag{32}$$

For each value of μ, x is varied until equations 31 and 32 yield the same value of $K'_{HSO_4^-}$. Then the activity coefficient and osmotic coefficient are obtained as

$$\log\gamma^* = [2\log(\mu - x) + \log x - \log 4]/3 - \log(\mu - 2x) - 1.018\sqrt{\mu}/(1 + 1.5\sqrt{\mu}) - 5.493\,[\log 4.5\sqrt{\mu} - 0.7887]\,x \tag{33}$$

$$\phi^* = 2/3 + \frac{x - 2.303\,[1.018\,Z_{1.5} + 8.240(\log 4.5\sqrt{\mu} - 0.3544)]\,x^2}{3(\mu - 2x)} \tag{34}$$

The full curve in figure 7 represents equation 33. The broken line, with filled circles to show its course where the two curves overlap, represents the measurements of Harned and Hamer (14) minus $0.1m$. Up to 2 M the agreement is well within the thickness of the lines. The scale of this figure is, of course, much smaller than those in the preceding figures. The full line in figure 8 is the osmotic coefficient calculated from equation 23. The broken line is the smoothed ϕ of Scatchard, Hamer, and Wood (26) minus $0.11513m$, and the circles represent ϕ minus $0.11513m$ from the vapor-pressure measurements of Collins (4) for solutions more concentrated than 4 M. The differences between the calculated and measured values are apparent at lower concentrations than in the preceding figure, but they are small in dilute solutions. In spite of the complications due to the unsymmetrical solution effect represented in equation 22 and to the apparent association, the method works very well up to high concentrations. This application to sulfuric acid includes all the proposals that we have made in this paper.

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