CONCENTRATED SOLUTIONS OF STRONG ELECTROLYTES[1]

GEORGE SCATCHARD

Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

Received October 19, 1936

The limiting law of the Debye theory of strong electrolytes (7) is now firmly established. As experimental technique improves, the measurements agree better and better with the theory. The extension to concentrated solutions is more difficult, because many specific properties of the ions must be taken into account. Much progress can be made, however, both in the rational expression of the properties of solutions of simple ions and in the application of a few general principles to give treatments of the properties of solutions of mixtures in terms of the properties of solutions of their components which are very useful in the study of chemical equilibria.

The limiting law depends only on the valences of the ions, the temperature, and the dielectric constant of the solvent. In more concentrated solutions the sizes of the ions and their effects on the dielectric constant must be taken into consideration. The latter is not the effect on that dielectric constant measurable by macroscopic instruments, which is an increase due to the electrostatic interaction between the ions (10, 38, 39), but is the effect on the microscopic dielectric constant, which is a much smaller decrease due largely to the displacement of the solvent (29). Recently Wyman (40) has shown that the dielectric constants of polar and non-polar mixtures are proportional to the concentrations of the polar liquids, and Onsager (21) appears to have explained this finding theoretically. If this is also true for the microscopic dielectric constant of electrolyte solutions, then the square of the reciprocal thickness of the ion atmosphere, κ^2 of the Debye theory, is proportional, not to the number of ions in unit volume of the solution, but rather to the number in unit volume of the solvent, or, at constant temperature and pressure, to the number in unit weight of the solvent. This relation simplifies greatly the correlation of the theory with thermodynamic treatments. We should not expect the relation to be exact, but it is certainly very much better than the one usually

---

[1] Contribution No. 377 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

made that the ions do not affect the dielectric constant. Those who have felt themselves forced to use ionic strengths in moles per liter of solution because the theory demands it, may be relieved to know that a much better theory demands that the ionic strength be in moles per unit quantity of solvent.

Not only does the electrostatic interaction between the charges depend upon the sizes of the ions and their effects on the dielectric constant of the solution in concentrated solutions, but there are also other interactions between ions which correspond to the salting out of non-electrolytes and to the deviations of purely non-electrolyte solutions from the ideal solution laws. The exact treatment would require the insertion of three kinds of energy in the statistical expressions and would give equations much too complicated for solution. To obtain an approximate solution we assume that the distribution of the ions is determined solely by the electrostatic interaction of their charges and, except in the calculation of the "higher terms" of Bjerrum (6) and Gronwall and LaMer (12), we assume the Debye–Hückel first approximation for this distribution. Then the total ion concentration is independent of the distance from the central ion, but the fraction of this concentration made up of ions with charges of the same sign as that of the central ion is very small in the neighborhood of the central ion. We assume that it is zero for all distances at which the short range interactions come into play. This is exactly the basic assumption of Brønsted's theory (4, 5) of "specific ion interaction."[2]

Using the methods of Debye and his colleagues for the charge–charge interaction (7) and the "salting out" (8, 19), and my own expression for the non-electrolyte term (28), we obtain the following expression for the non-ideal free energy per mole of ion of a solution of two kinds of ions.

$$\frac{F - F_I}{\nu_s N_s} = \frac{\epsilon^2 N}{2D_0}\left[z_1 z_2 X + z_1 z_2 X V_s m + \frac{2\,\nu_1 \nu_2}{\nu_s}\left(\frac{V_2 z_1^2}{b_1} + \frac{V_1 z_2^2}{b_2}\right) m\right] + \frac{Am}{1 + V_s m}$$

in which $F - F_I$ is the non-ideal free energy of the system; N_s is the number of moles of electrolyte; ν_1 and ν_2 are the numbers of ions of the two kinds per molecule of electrolyte, z_1 and z_2 their valences, one of which must be negative, and V_1 and V_2 their molal volumes; ϵ is the electronic charge; N is Avogadro's number; N_0 is the number of moles of solvent,

---

[2] An expression for the thermodynamic properties of electrolyte solutions including the non-electrolyte effects was published by the author some years ago (29). It differed from the present expression in that the relation between the volume and the effect on the dielectric constant was left arbitrary and that the distribution of the ions was considered uniform for the calculation of the "salting out" and the non-electrolyte terms. The expression given here is believed to be a considerable improvement.

V_0 is its molal volume, and D_0 its dielectric constant; b_1 and b_2 are the radii of the two ions effective for salting out. The other symbols are defined in the following equations, in which a is the sum of the two radii effective in collisions between ions, and a_{12}, a_{10}, and a_{20} are the mutual cohesive energy densities.

$$m = N_s/V_0N_0$$

$$\nu_s = \nu_1 + \nu_2$$

$$V_s = \nu_1V_1 + \nu_2V_2$$

$$D = D_0V_0N_0/V$$

$$\kappa^2 = -\frac{8\pi N^2\epsilon^2 z_1z_2\nu_sN_s}{1000\,RTDV} = -\frac{8\pi N^2\epsilon^2 z_1z_2\nu_s m}{1000\,RTD_0}$$

$$X = \frac{\kappa}{1 + \kappa a} - Y$$

$$Y = \left[1 + \kappa a - \frac{1}{1 + \kappa a} - 2\ln(1 + \kappa a)\right] \Big/ \kappa^2\alpha^3$$

$$A = 2\nu_1\nu_2V_1V_2\,(2a_{12} - a_{10} - a_{20})/\nu_s$$

The first term in the brackets is nearly the same as the Debye–Hückel expression for the charge–charge interaction for constant dielectric constant. It is negative and initially proportional to the square root of the concentration, but the slope decreases so rapidly with increasing concentration that the effect of the difference between κ and κ_0 of Debye and Hückel is very small. The second term represents the effect of the changing dielectric constant on the charge–charge interaction. It is also negative and is proportional to the first term times the concentration. The last term in the brackets represents the charge–molecule part of the "salting out." It is usually positive, and is proportional to the concentration at all concentrations. The term outside the brackets represents the non-electrolyte molecule–molecule interaction, which is usually negative. It is initially proportional to the concentration, but the slope decreases as the concentration increases. Wyman's theory of the dielectric constant is used whenever D_0, κ, X, or Y appear in an equation. Brønsted's specific ion interaction is used to determine a from the sum of the two effective ion radii alone for the charge–charge term, to substitute 2 $(V_2z_1^2/b_1 + V_1z_2^2/b_2)$ for

$V_s(z_1^2/b_1 + z_2^2/b_2)$ in the charge-molecule term, and to substitute $2\nu_1 V_1 \nu_2 V_2$ for V_s^2 in the molecule-molecule term.

It may surprise you to see the charge-molecule effect given by the expression which corresponds to the Debye-MacAulay (8) salting-out equation rather than to the modified expression of Debye (9), particularly since we have recently shown that the experimental salting-out results agree with the latter (36). This choice is correct, however, and follows from our assumption that the distribution is determined solely by the charge-charge interactions.

With this expression for the non-ideal free energy we have no further need of approximations. The other quantities may be calculated from it exactly by thermodynamics alone. The equations for the logarithm of the activity coefficient, ln γ, and for the osmotic coefficient, ϕ, follow.

$$\ln \gamma = -\ln(1 + \nu_s N_s/N_0) + \frac{\epsilon^2 N}{2RTD_0}\left[\frac{z_1 z_2 \kappa}{1 + \kappa a} + \left(\frac{\kappa}{1 + \kappa a} + X\right) z_1 z_2 V_s m + \frac{4\nu_1\nu_2}{\nu_s}\left(\frac{V_2 z_1^2}{b_1} + \frac{V_1 z_2^2}{b_2}\right) m\right] + \frac{Am(2 + V_s m)}{RT(1 + V_s m)^2}$$

$$\phi = \frac{\ln(1 + \nu_s N_s/N_0)}{\nu_s N_s/N_0} + \frac{\epsilon^2 N}{2RTD_0}\left[z_1 z_2 Y + \frac{z_1 z_2 \kappa V_s m}{1 + \kappa a} + \frac{2\nu_1\nu_2}{\nu_s}\left(\frac{V_2 z_1^2}{b_1} + \frac{V_1 z_2^2}{b_2}\right)\right] + \frac{Am}{RT(1 + V_s m)^2}$$

In each the first term gives the value for ideal solutions, which is approximately $-0.018\ \nu_s m$ for ln γ and approximately $1-0.009\ \nu_s m$ for ϕ. The other terms correspond to the free energy equation in order, and have the same sign in each equation. If the slope is strictly proportional to some power of m in the free energy equation it is in the others also; if the slope decreases with increasing concentration it decreases more rapidly in the equation for ln γ and still more rapidly in the equation for ϕ.

The equations for ln γ and ϕ are not very much more complicated than the approximate equations of Hückel (19), which are given by taking the first term and the first and third terms in the bracket, using the volume of the solution rather than that of the solvent in the terms in the bracket, and giving another definition to the constant coefficient in the third term. The added complication of the second term in brackets and the last term is partially compensated by the more convenient concentration units. These equations also have the advantage that they are thermodynamically consistent.

The Bjerrum-Gronwall-LaMer "higher term correction" is omitted from the above equations. The Gronwall–LaMer expressions (12) for $\ln \gamma_h$ and ϕ_h for the case that $z = z_1 = -z_2$ are:

$$\ln \gamma_h = -\sum_{n=1}^{\infty} \left[\frac{N\epsilon^2 z^2}{RTD_0 a}\right]^{2n+1} (1 + V_s m)^{2n+1} \left[\left(\frac{X_n}{2} - 2nY_n\right) + V_s m\left(Y_n - \frac{V_s m X_n}{2}\right)\right]$$

$$\phi_h = -\sum_{m=1}^{\infty} \left[\frac{N\epsilon^2 z^2}{RTD_0 a}\right]^{2n+1} (1 + V_s m)^{2n} \left[\frac{X_n}{2} - (2n + 1)Y_n + \frac{V_s m X_n}{2}\right]$$

in which X_n and Y_n have the same meanings as in the original paper.

This treatment might be extended to the heat and volume changes on dilution and to their temperature and pressure derivatives, but the temperature and pressure derivatives of so many parameters are involved that it seems advisable to omit this extension for the present. For the equations given above we need know only the temperature, the molal volume and dielectric constant of the solvent, the valence, molal volume in solution, and radius effective in salting out for each ion, the effective collision diameter a of the pair of ions, and their molecule–molecule interaction coefficient, A. The alkali and halide ions may be assumed spherical, and we shall use the values of their radii determined by Pauling (22) from the crystal lattices.[3] For spheres $b = r$ and $a = r_1 + r_2$. The volume in solution may be expected to be somewhat less than four times the actual volume of the molecules, $4\pi r^3/3$, and the constant A may be assumed to be the same for all the alkali halides and may be expected to be about the same as that for the aliphatic hydrocarbons in water.

We shall make the comparison with the experimentally determined osmotic coefficients, which have the advantages over the activity coefficients of the solutes that they may be determined for a much larger number of solutions and that they involve no extrapolation to zero concentration. Freezing-point measurements give the most accurate values of the osmotic coefficients, but they have the disadvantage that they are not isothermal. For concentrated solutions measurements of vapor pressure or by the isopiestic or isotonic method are much superior. Of these the latter are considerably more accurate. We shall use the measurements of Sinclair and Robinson by this method, but we shall use as standard our curve for sodium chloride, which appears to me much better established than that of potassium chloride. Our measurements of the relation of the osmotic coefficient of potassium chloride to that of sodium chloride check theirs very closely. They have made measurements with all the alkali chlorides,

---

[3] These values in Ångström units are: Li, 0.574; Na, 0.873; K, 1.173; Rb, 1.294; Cs, 1.434; F, 1.225; Cl, 1.589; Br, 1.702; I, 1.867.

bromides, and halides up to saturated solutions or to solutions isotonic with saturated potassium chloride.

We cannot be satisfied with approximate values of the ratio of the volume in solution to the actual volume of the ions or of the non-electrolyte reaction coefficient, *A*, but each of these quantities must be determined more precisely than the osmotic coefficient itself. They were therefore determined from the osmotic coefficients of 1 molal lithium bromide and cesium bromide. The volume so determined is $0.008r^3$ if the volume is in liters per mole and *r* in Ångström units, which is 3.15, or somewhat less than four, times the actual volume of the molecules. This value for the volume leads to $A/RT = 0.0089\ r_1^3r_2^3$, which is one-third the value for an aliphatic hydrocarbon in water. Of the two parameters whose exact values must be determined from the experimental data, one corresponds very closely to the expected value, the other only approximately so. The agreement is perhaps as good as should be expected, for the calculated values depend upon an unjustified extension of the theory of non-polar mixtures, and our treatment is such that an error in any of our other approximations is carried over to this parameter. For example, a small error in the volume ratio given above would be doubled in the calculation of *A*.

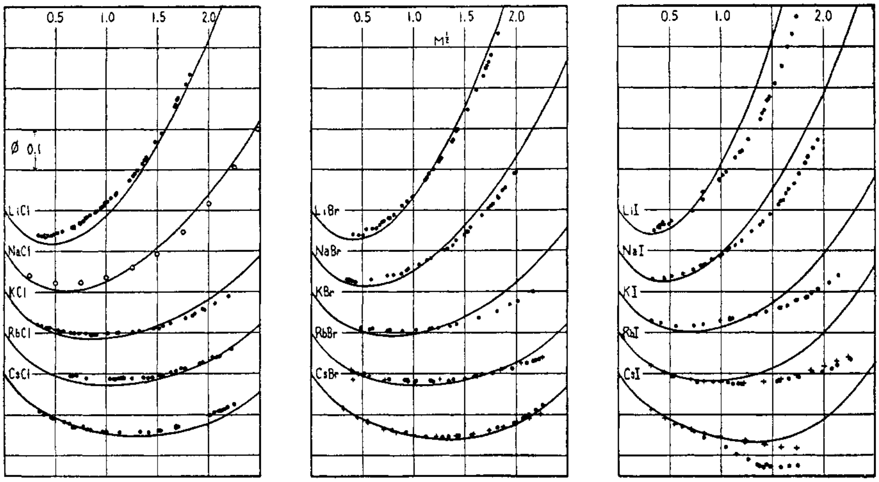

FIG. 1. Osmotic coefficients of alkali halides at 25°C.

In figure 1 the curves represent the calculated values of the osmotic coefficients and the dots represent the published experimental results of Robinson and Sinclair (23, 24). For sodium chloride the circles represent our choice (37) of the most probable curve through the results from electromotive force and vapor pressure determinations. Our curve was also influenced by measurements on potassium chloride, sulfuric acid, sucrose, and α-methylglucoside. For rubidium bromide and iodide the crosses represent experimental measurements reported privately by Dr. Robinson (26), and for the cesium salts the crosses are his smoothed values from new measurements. The differences between the crosses and circles are small except for cesium iodide, but wherever there is any difference the crosses should be accepted.

The curves for lithium bromide and cesium bromide, which are made to fit the experimental points at 1 molal, show very satisfactory agreement throughout, if we consider that there are only two arbitrary parameters for the two curves. The agreement is about as good for the other chlorides and bromides, although they were not used at all in the determination of the parameters. The calculated values for dilute solutions with small ions are distinctly low. There is also a tendency, increasing from chlorides through bromides to iodides, for the calculated values to be too high in concentrated solutions. On the whole, however, the agreement is very satisfactory.

It would be entirely legitimate to tinker with the calculated results to give better agreement with the measurements. Pauling's ionic radii are only approximate, and there is no reason to suppose that the radii in solution are exactly the same as those in the crystal lattices. A slight increase in the sizes of the smaller ions would greatly improve the fit in dilute solutions. It is impossible to predict whether such a change would also remedy the difficulties in concentrated solutions. It might be necessary to alter the molecule–molecule term also so that it remains more nearly proportional to the concentration to correspond to the behavior of less polar solutes in water rather than to the too simple theory. It seems advisable for the present, however, to determine from the properties of the solutions only those parameters which are absolutely necessary, and to be satisfied with this approximate agreement.

These results do show that the alkali and halide ions are characterized by their valences and sizes alone. The decrease of the osmotic coefficient with increasing size of the cation for the chlorides, bromides, and iodides and the decrease with increasing size of the anions for the cesium salts are explained by the facts that the term for the charge–charge interaction is of secondary importance in concentrated solutions and that the deviation of the osmotic coefficient from unity is not far from the difference between the salting-out term and the non-electrolyte term. The first of these is largest when one ion is small and the other large; the second becomes more important when both ions are large. The theory does make the osmotic coefficients of the rubidium salts increase with increasing size of the anion like those of the lithium, sodium, and potassium salts, while the experimental osmotic coefficients decrease like those of the cesium salts. The calculated increase and the measured decrease are both so small, however, that the difference in sign is unimportant. The theory also agrees with the freezing-point measurements (11) in making the osmotic coefficients of the fluorides increase with increasing size of the cation in the opposite order to those of the other halides. Quantitative agreement would require a larger radius for the fluoride ion than that given by Pauling, for the calculated potassium, rubidium, and cesium curves are all about the same as that of cesium chloride, and Lannung's direct vapor-pressure measurements (20) indicate that they should be about the same as that of sodium bromide.

The application of this method to polyatomic ions is considerably more complicated, for such ions cannot be assumed to be spherical and several parameters for each ion must be determined from the properties of the solutions. There are at least two types of variations from the behavior of the halides (31). The hydroxides behave very much as the fluorides, and the formates and acetates behave as though a, b, and A were about the same as for the fluorides, but V were very much larger. The nitrates, chlorates, and perchlorates, on the other hand, behave as though a, b, and V were about the same as for the bromides, but A were very much larger. The application to mixtures is even more complicated, largely because the presence of two kinds of cations, or two kinds of anions, with different sizes makes the expressions for the interaction of the ionic charges very much more complicated (29).

We may make considerable progress, particularly in the study of mixtures, without such a detailed treatment. We start with the very general result of statistical mechanics that that part of the non-ideal free energy per unit quantity of solution which is contributed by short range forces may be expressed as a multiple integral power series in the molalities of the various components. We use also the result of the Debye–Hückel theory that the effect of the long range forces between the ionic charges requires a multiple power series containing the square root of the ionic strength as well as the concentration of each component, and we combine the two to give the following series, in which the numerical values of the A's are given by the Debye–Hückel theory (33, 34):

$$\frac{F - F^*}{RT} = \Sigma_i N_i \left(\ln \frac{N_i}{w_0 N_0} - 1 + A_i \sqrt{I}\right) + \Sigma_{ij} \frac{N_i N_j}{w_0 N_0} (B_{ij} + C_{ij} \sqrt{I})$$

$$+ \Sigma_{ijk} \frac{N_i N_j N_k}{w_0^2 N_0^2} (D_{ijk} + E_{ijk} \sqrt{I}) + \cdots\cdots$$

N_i is the number of moles of ions of the i^{th} component in the system, N_0 is the number of moles of the solvent, and w_0N_0 is unit mass of solvent; I is twice the ionic strength in moles per unit mass of solvent. The B's, C's, D's, and E's are determined by the properties of the solution. The following expressions for the activity coefficients and the osmotic coefficient are obtained from the free energy expression by thermodynamics alone.

$$\ln \gamma_p = \tfrac{3}{2} A_p \sqrt{I} + 2\, \Sigma_i B_{ip} m_i + \left(2\ \Sigma_i C_{ip} m_i + \frac{z_p^2}{2I}\ \Sigma_{ij} C_{ij} m_i m_j\right)\sqrt{I}$$

$$+ 3\ \Sigma_{ij} D_{ijp} m_i m_j + \left(3\ \Sigma_{ij} E_{ijp} m_i m_j + \frac{z_p^2}{2I}\ \Sigma_{ijk} E_{ijk} m_i m_j m_k\right)\sqrt{I} + \cdots\cdots$$

$$\phi = 1 + \tfrac{1}{2}\sqrt{I}\, \Sigma_i A_i x_i + M\, \Sigma_{ij}\, (B_{ij} + \tfrac{3}{2}\, C_{ij} \sqrt{I})\, x_i x_j$$

$$+ M^2\, \Sigma_{ijk}\, (2D_{ijk} + \tfrac{5}{2}\, E_{ijk} \sqrt{I})\, x_i x_j x_k + \cdots\cdots$$

in which $m_i = N_i/w_0N_0$, $M = \Sigma_i m_i$, $x_i = m_i/M$.

There is no theory which tells us that these series must converge conveniently. In fact they will be divergent if there is a fairly large amount of chemical combination or any other interaction which is limited to a pair of molecules or ions, such as that described by the "higher term correction." This difficulty could probably be remedied by adding to each term in the concentrations another coefficient times the logarithm of the ionic strength, but there are as yet no experimental data to warrant this extension. If an interaction is not limited to two molecules its effect may be large and still lead to convenient convergence. We have found that the freezing-point depressions of most uni-univalent electrolytes may be represented up to concentrations of 1 molal by the five terms given above, and I shall show later that no type of series can be simpler than this one with four terms.

For a single solute these equations have little advantage over graphic methods, provided that the latter also make use of the Debye limiting law. For mixed solutes, on the other hand, the gain is enormous. We made about thirty determinations for each single salt (35). To cover the field as completely would require four hundred fifty determinations for a binary mixture, forty-five hundred for a ternary mixture, and almost thirty-four thousand for a reciprocal salt pair, and the graphical treatment of the results would be a stupendous task. The use of these equations reduced the measurements needed to one one-hundredth, and probably reduced the labor of handling the data more than that.

A still further gain for mixtures is obtained from the assumption that the short range forces between two ions with charges of the same sign may be neglected unless there is a third ion of the opposite sign in their immediate neighborhood. Then the *B* and *C* coefficients for any mixture can be determined from the single salt solutions, and the *D* and *E* coefficients can be determined from the single salt solutions and one solution of each mixture with a common ion.

The most comprehensive test of the application of this method to mixtures is our own study of the freezing-point depressions of mixtures of potassium nitrate, potassium chloride, lithium nitrate, and lithium chloride

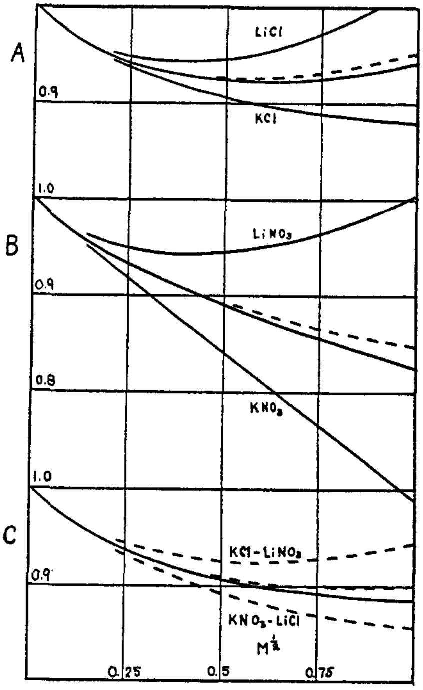

FIG. 2. Osmotic coefficients of mixtures at 0°C. A, KCl–LiCl; B, KNO_3–$LiNO_3$; C, KCl–$LiNO_3$ or KNO_3–LiCl.

(35). The series, simplified as described in the last paragraph, describe the measurements exactly. Since this method requires very precise and comprehensive measurements which are not yet available in any other case, we shall be more interested in the conclusion that all the parameters may be determined approximately from measurements on single salts alone. If they were exactly determined the osmotic coefficients of mixtures with a common ion would be additive. Figure 2A shows the osmotic coefficients of potassium chloride, lithium chloride, and their 1–1 mixture, plotted against the square root of the molality. The broken curve is the mean of the curves for the two salts. It agrees closely with the experimental curve for the mixture in dilute solutions as our theory demands, and the difference is not very great even at 1 molal. Figure 2B shows about the same agreement for potassium nitrate, lithium nitrate, and their 1–1 mixture in spite of the greater spread between the two salts. I shall omit the curves for the mixtures potassium nitrate–potassium chloride and lithium nitrate–lithium chloride, for they show no difference between the calculated results and the measurements up to 1 molal, which is the limit of our measurements. Figure 2C shows the 1–1 mixture of potassium nitrate and lithium chloride, which is also the 1–1 mixture of potassium chloride and lithium nitrate. The lowest broken curve is the mean of the curves of the first pair, and the highest is the mean of those of the second pair. Neither agrees well with the experimental curve. Our theory demands, however, that in this case without a common ion the curve be given by the mean of those for all four salts of the reciprocal salt pair. This is given by the middle broken curve, which agrees with the experimental measurements about as well as those in which only the anion is changing.

It is not at all necessary to represent the Debye–Hückel limiting law by a term proportional to the square root of the ionic strength, but any function of the ionic strength which reduces to this in very dilute solutions may be substituted. Ever since Hückel's first paper on concentrated solutions (19), attempts have been made to find some function of the ionic strength depending only on the valence type, the individual deviations from which should be proportional to the concentration. If there were any such function the osmotic coefficients of mixtures with a common ion would be strictly additive at all concentrations; so figure 2 shows that such a function cannot exist. We will also see from measurements on single salts that such a function is impossible. Nevertheless, it is very convenient to subtract from the logarithm of the activity coefficient the Debye–Hückel limiting law divided by 1 plus the square root of the ionic strength

$$Az_1z_2\sqrt{\mu}/(1+\sqrt{\mu})$$

The corresponding expression for the osmotic coefficient is

$$1+Az_1z_2\,[1+\sqrt{\mu}-1/(1+\sqrt{\mu})-2\ln(1+\sqrt{\mu})]/\mu$$

The next figures show as $\Delta\phi$ the deviations of the osmotic coefficients from this function plus a term linear in the ionic strength. Figure 3 gives $\Delta\phi$ up to 1 molal determined from freezing points for potassium nitrate (30), potassium chloride (31), and potassium acetate (32). It shows that this function is a convenient one from which to plot deviations, but that these deviations are much larger than the experimental errors. It also shows conclusively that no other function common to all three salts will reduce the deviations of all of them. Figure 4 shows $\Delta\phi$ for the same salts up to 3.5 M, determined from the isotonic measurements of Robinson and Sinclair (23,25) at 25°C. and our curve for the osmotic coefficient of sodium chloride. It confirms the conclusions from the previous figure, and shows that these do not depend on the temperature variation in the freezing-point method.

Figure 5 illustrates the complications that may be expected with salts of higher valence type, or with solvents of lower dielectric constant than water. It shows $\Delta\phi$ determined by the isotonic method at 25°C. for magnesium, manganese, nickel, zinc, copper, and cadmium sulfates by Robinson and Jones (26). The linear term is 0.1 M in all cases. It may appear that the differences between these curves and any one of them taken as standard would be more nearly proportional to the concentration than the deviations shown here, but the actual gain is very small. All of the curves are positive in dilute solutions and must come to zero very steeply. Moreover, if the theory of "higher terms" is even qualitatively correct, they should all be negative in very dilute solutions, and they must therefore descend very rapidly with decreasing concentration and then rise still more steeply. Hausrath (18) has measured the freezing-point depressions in very dilute solutions of all but manganese sulfate, and his measurements yield negative values of $\Delta\phi$, more negative for those salts whose values are lower in this figure. The insert shows the first two points of Robinson and Jones for magnesium sulfate and also $\Delta\phi$ from the freezing-point measurements of Hall and Harkins (14). The scale of ordinates of

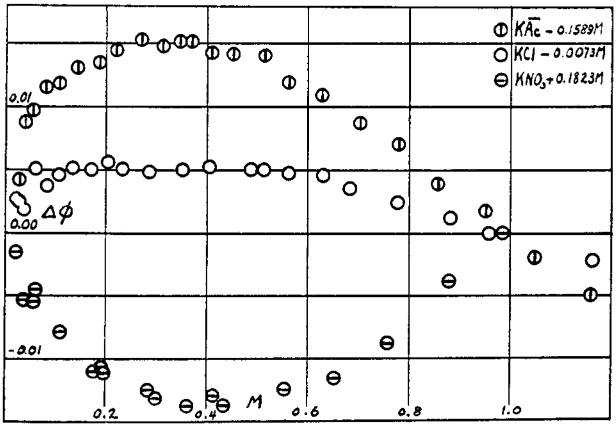

FIG. 3. Deviations of osmotic coefficients at 0°C.

this inset are the same as in the main figure, but the scale of abscissas is magnified ten times. The agreement of the two series in the more concentrated solutions is as good as could be expected at such different temperatures. In more dilute solutions the freezing points yield negative values of $\Delta\phi$, in agreement with Hausrath's measurements and the theory.

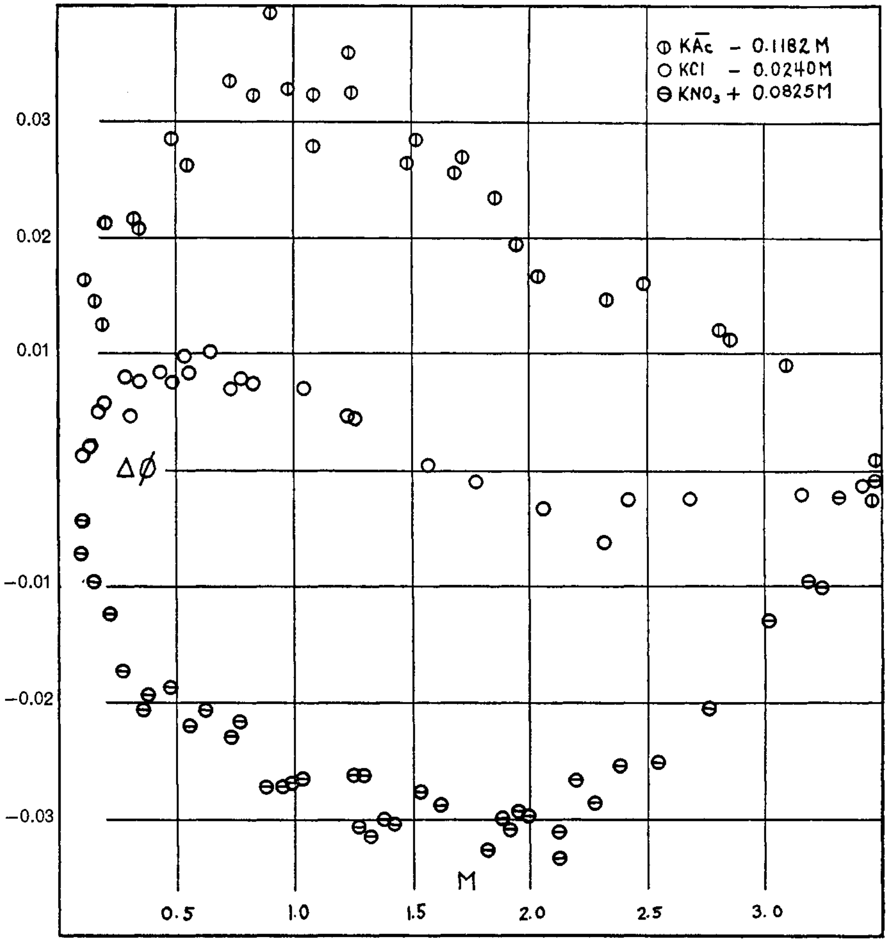

FIG. 4. Deviations of osmotic coefficients at 25°C.

Similar expressions for the logarithm of the activity coefficient have frequently been used, and always with the assumption that the term corresponding to our $\Delta\phi$ is zero. The expression used by Hückel (19) and by Harned and Åkerlöf (15, 16) for hydrochloric acid and the alkali chlorides differs only in the inclusion of the ideal solution expression as in our first equation, in the expression of the ionic strength per unit volume of solution rather than of solvent, and in the use of a constant k greater than unity in the expression $1 + k\sqrt{\mu}$. Guggenheim (13) has extended the use of their expression, changed only by making k unity, to all strong electrolytes. Instead of subtracting the ideal solution term for the osmotic coefficient, Guggenheim invents a new osmotic coefficient for which this subtraction is unnecessary. This is somewhat less convenient than our form, but not seriously so. However, in the calculation of activity coefficients of the solute from the osmotic coefficients, he uses thermodynamic relations which are exact for our coefficients but only approximate for his. This sacrifice of exact thermodynamics seems quite inexcusable. Guggenheim limits the use of his expression to ionic strengths less than 0.1 molal, and appears to consider the expression exact within these limits. An examination of figure 3 shows that a straight line through the point at 0.1 molal will not miss seriously any of the points in more dilute solutions,

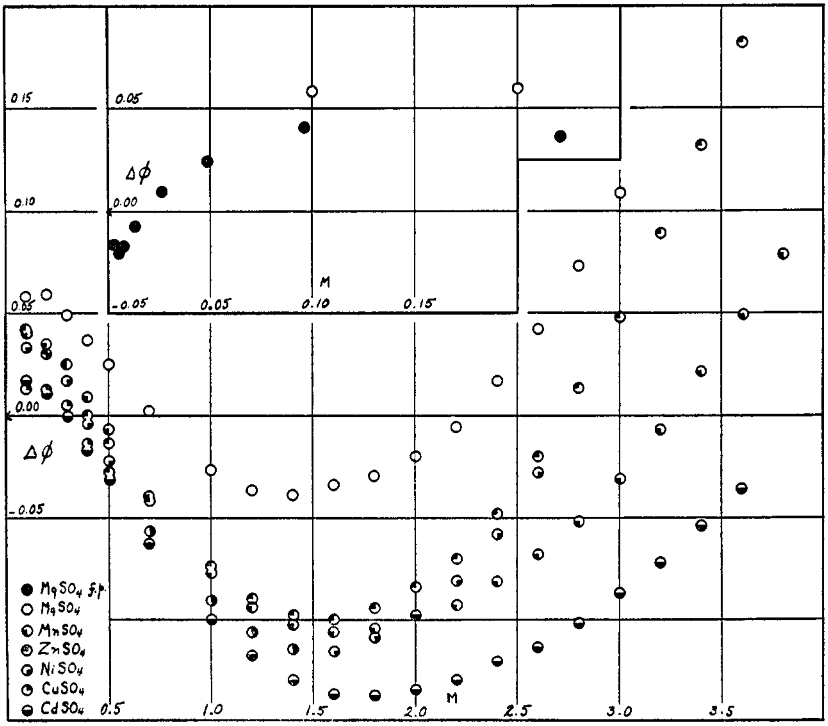

FIG. 5. Deviations of osmotic coefficients of sulfates of bivalent metals

but that the best smooth curve through all the points shows considerable curvature below 0.1 molal and differs from the straight line by an amount which is not unimportant in the calculation of the activity coefficient of the solute by integration. With salts of higher valence type the discrepancy is still more serious. Guggenheim claims that the measurements of Hall and Harkins are fitted by his expression up to 0.025 M, and the error which he ascribes to the measurements is not many times those made by these observers with other solutes. An examination of figure 7 shows, however, that a straight line through the point at 0.025 M intersects the best smooth curve through all the measurements almost at right angles.

Åkerlöf (1, 2, 3) uses as norm the experimental curve for hydrochloric acid, and assumes that the deviations for other electrolytes are proportional to the ionic strength in moles per unit quantity of solvent. For uni-univalent electrolytes this corresponds closely to the use of our expression, with k considerably larger than unity. For other valence types his treatment is contrary to the Debye–Hückel theory and to experiment.

Although the relation is inexact as we have just seen, it is often convenient to assume as an approximation that $\Delta\phi$ and the corresponding expression for the logarithm of the activity coefficient are zero. It is still more convenient, and at the same time more accurate, to make two other approximations which would be exact if there were any such function and if Brønsted's theory (4, 5) of "specific interaction" were exact. If all the ions have the same absolute value for the ionic charge, these two assumptions are sufficient. If they have not, there is an ambiguity which may be removed by treating the ions as independent components. It is therefore convenient to express our approximations in terms of the individual ion activities, although we shall use them only in such combinations that the addition or removal of the corresponding ions leaves the solution electrically neutral. We shall assume that

$$\ln \gamma_k = \frac{-Az_k^2\sqrt{\mu}}{1+\sqrt{\mu}} + \Sigma_j f_{kj}(\mu)m_j$$

in which μ is the ionic strength, A is given by the Debye–Hückel limiting law, z_k is the valence of the k^{th} type of ion, m_j is the molality of the j^{th} ion species. If the expression corresponding to $\Delta\phi$ were zero, $f_{kj}(\mu)$ would be independent of the ionic strength, so we know that it varies only slowly with the ionic strength. The use of a function of the ionic strength rather than of the concentrations of all the solutes makes $\ln\gamma$ a linear function of the composition at constant ionic strength. This relation has been shown, particularly by Harned and his coworkers (17), to hold almost within the experimental error up to the highest concentrations studied. If $f_{kj}(\mu)$ is strictly constant, it is zero by Brønsted's theory of "specific ion interaction," if the j and k ions have charges of the same sign; $f_{kj}(\mu)/z_k = f_{jk}(\mu)/z_j$ by the condition of integrability, assuming the ions to be independent components, if z_k and z_j have opposite signs; and $f_{kj}(\mu) = f_{jk}(\mu)$ by the same condition if either z_k or z_j is zero. We may extend these relations as approximations even to concentrated solutions.

If both ions have the same absolute value of the charge, it follows that the activity coefficients of the two ions are equal to each other and to the mean activity coefficient in a solution of a single salt. In a solution of another salt of the same valence type, the mean activity coefficient is the geometric mean of those of the solute salt and of the solvent salt if they have an ion in common, and it is the geometric mean of those of the reciprocal salt pair if there is no common ion. In the case of ions with different absolute values of the valence the relations are more complicated, because the first part of the expression is proportional to the square of the valence, and the second part is proportional to the absolute value of the valence, but the relations are given just as definitely by the assumptions we have made. The important result of these assumptions is that the activity coefficients of any salt in any salt mixture may be determined from measurements on single salts alone.

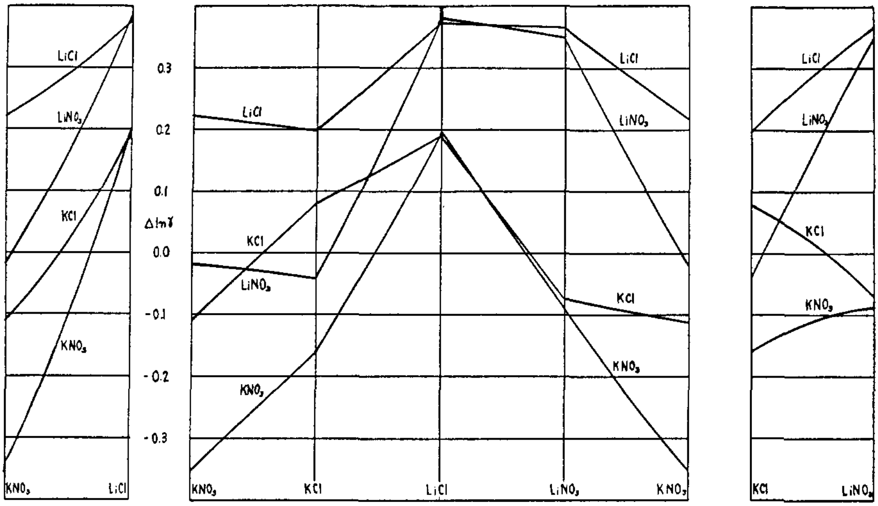

FIG. 6. Deviations of logarithms of activity coefficients at constant ionic strength of unity.

In case the solubility is too limited to permit the determination of the activity coefficients from measurements on solutions of the salt itself, they may be determined by measurements with a single mixture and the use of the above approximations. If there are not enough measurements to use the above principles, the functions of the ionic strength may be taken as contents with sufficient accuracy for many purposes. This corresponds closely to Åkerlöf's treatment of uni-univalent electrolytes (1). If there are no measurements at all with the salts in question, the magnitude of the functions may be estimated from the behavior of other similar salts.

If either z_k or z_j is zero, the function $f_{jk}(\mu)$ can be determined only from measurements on mixtures, or from theoretical considerations. The terms for the individual ions cannot be separated, but as long as the function is strictly constant, it must be additive for the ions. For the distribution of either electrolyte or non-electrolyte between the solution and another phase, our treatment tells us only that the logarithm of the activity coefficient is nearly proportional to the concentration of the other species. For homogeneous chemical equilibria it is helpful to make another approximation. If there is a reaction A + B = C, we assume that $f_{cj}(\mu) = f_{aj}(\mu) + f_{bj}(\mu)$. If either z_a or z_b is different from zero, this assumption is contradictory to those we have made concerning the relation of these functions to the valence, but there are compensating errors which should make it fairly satisfactory in spite of that fact.

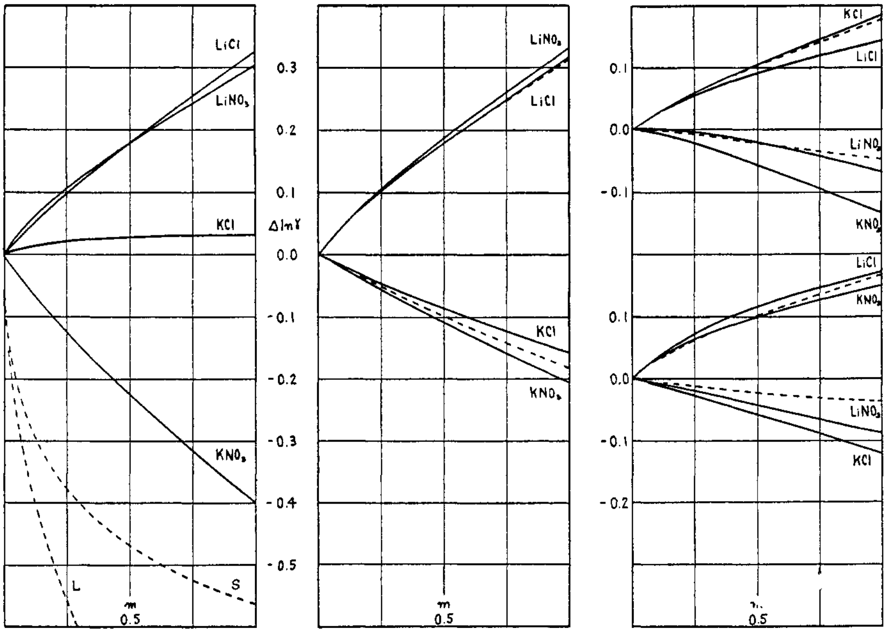

FIG. 7. Deviations of logarithms of activity coefficients at constant composition of solute.

Many of these assumptions may be tested only in isolated cases which would require too much space for presentation. The application to mixtures of uni-univalent electrolytes in aqueous solution may be tested from the activity coefficients determined by the freezing-point measurements on mixtures of potassium nitrate, potassium chloride, lithium nitrate, and lithium chloride discussed above (35). The results are all expressed as deviations from the first term in the logarithm of the activity coefficient given above, $\Delta \ln \gamma$. Figure 6 shows the second term for each of the four salts in all the possible binary mixtures at a constant ionic strength of 1 molal. The mixtures with a common ion are in the center and those without are at the sides. It shows that the logarithm of the activity coefficient is very nearly a linear function of the composition even in these concentrated solutions. None of these curves is a straight line, but the deviations are so small as to be scarcely visible in most, and the assumption of linearity would produce no great error in any of them.

Figure 7 shows $\Delta \ln \gamma$ versus the molality at constant composition. The left-hand side gives as full curves the results for the four salts, each in its own solution. The broken curves are the Debye limiting law (*D*) and the first term, or standard from which the deviations are calculated (*S*). In the rest of the figure a full line represents $\Delta \ln \gamma$ for the salt indicated on the curve in a solution of the salt indicated on the companion curve, and the broken line is the calculated value for either. This figure shows that the calculation from the properties of single salt solutions is not only more useful than the assumption of proportionality, but that it is also more accurate. Yet interpolation from concentrated to dilute solutions with the assumption of proportionality would not lead to serious errors even in the worst cases. The deviation of the measured values from those calculated from the properties of single salt solution varies widely from salt to salt, but in no case is the difference more than a few per cent, even in molal solutions.

This paper includes two quite different subjects: the calculation of the equilibrium properties of solutions of simple ions from the physical properties of the ions, and the calculation of the properties of mixed solutions from those of solutions of the single salts. There is one objective common to both treatments,—to show that much may be, and already has been, accomplished in the treatment of concentrated solutions. The extension of the first treatment to more complicated ions may be left to the specialists, but the application of the second method may be made with profit in any study of the physical or chemical equilibria involving electrolyte solutions. It is not necessary that the method used be the same in all its details as that outlined here, but it is important that we realize that a fairly simple and fairly accurate approximate treatment is possible. The uncertainties do increase with increasing concentration, but not very rapidly. A little further systematic work should reduce the uncertainties, but even now our methods of handling the results are as good as all but the best experimental work.

REFERENCES

(1) Åkerlöf, G., and Thomas, H. C.: J. Am. Chem. Soc. **56**, 593 (1934).
(2) Åkerlöf, G.: J. Am. Chem. Soc. **56**, 1439 (1934).
(3) Åkerlöf, G., and Turck, H. E.: J. Am. Chem. Soc. **56**, 1875 (1934).
(4) Brønsted, J. N.: J. Am. Chem. Soc. **44**, 877 (1922).
(5) Brønsted, J. N.: J. Am. Chem. Soc. **45**, 2898 (1923).
(6) Bjerrum, N.: Kgl. Danske Videnskab. Selskab Math-fys. Medd. **1**, No. 9 (1926).
(7) Debye, P., and Hückel, E.: Physik. Z. **24**, 185 (1923).
(8) Debye, P., and McAulay, J.: Physik. Z. **26**, 22 (1925).
(9) Debye, P.: Z. physik. Chem. **130**, 56 (1927).
(10) Debye, P., and Falkenhagen, H.: Physik. Z. **29**, 121, 401 (1928).
(11) Fajans, K., and Karagunis, G.: Z. angew. Chem. **43**, 1046 (1930).
(12) Gronwall, T. H., LaMer, V. K., and Sandved, K.: Physik. Z. **29**, 358 (1928).
(13) Guggenheim, E. A.: Phil. Mag. [7] **19**, 588 (1935).
(14) Hall, R. E., and Harkins, W. D.: J. Am. Chem. Soc. **38**, 2658 (1916).
(15) Harned, H. S.: J. Am. Chem. Soc. **48**, 326 (1926).
(16) Harned, H. S., and Åkerlöf, G.: Physik Z. **27**, 411 (1926).
(17) Harned, H. S.: in H. S. Taylor's *Treatise on Physical Chemistry*, 2nd Edition, Vol. I, p. 803. D. Van Nostrand Co., New York (1931).
(18) Hausrath, H.: Ann. Physik [4] **9**, 522 (1902).
(19) Hückel, E.: Physik. Z. **26**, 93 (1925).
(20) Lannung, A.: Z. physik. Chem. **170A**, 134 (1934).
(21) Onsager, L.: J. Am. Chem. Soc. **58**, 1486 (1936).
(22) Pauling, L. J.: J. Am. Chem. Soc. **50**, 1036 (1928).
(23) Robinson, R. A., and Sinclair, D. A.: J. Am. Chem. Soc. **56**, 1830 (1934).
(24) Robinson, R. A.: J. Am. Chem. Soc. **57**, 1161 (1935).
(25) Robinson, R. A.: J. Am. Chem. Soc. **57**, 1165 (1935).
(26) Robinson, R. A., and Jones, R. S.: J. Am. Chem. Soc. **58**, 959 (1936).
(27) Robinson, R. A.: Personal communication.
(28) Scatchard, G.: Chem. Rev. **8**, 321 (1931).
(29) Scatchard, G.: Physik. Z. **33**, 22 (1932).
(30) Scatchard, G., and Prentiss, S. S.: J. Am. Chem. Soc. **54**, 2690 (1932).
(31) Scatchard, G., and Prentiss, S. S.: J. Am. Chem. Soc. **55**, 4355 (1933).
(32) Scatchard, G., and Prentiss, S. S.: J. Am. Chem. Soc. **56**, 807 (1934).
(33) Scatchard, G., and Prentiss, S. S.: J. Am. Chem. Soc. **56**, 1486 (1934).
(34) Scatchard, G., and Prentiss, S. S.: J. Am. Chem. Soc. **56**, 2314 (1934).
(35) Scatchard, G., and Prentiss, S. S.: J. Am. Chem. Soc. **56**, 2320 (1934).
(36) Scatchard, G., and Benedict, M. A.: J. Am. Chem. Soc. **58**, 837 (1936).
(37) Scatchard, G., Hamer, W. J., and Wood, S. E.: Unpublished.
(38) Wien, M.: Ann. Physik [4] **83**, 327 (1927).
(39) Wien, M.: Ann. Physik [4] **85**, 795 (1928).
(40) Wyman, J., Jr.: J. Am. Chem. Soc. **58**, 1482 (1936).