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THE ACTIVITY COEFFICIENTS OF IONS IN VERY DILUTE SOLUTIONS[1]

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1. Introduction

In the case of dilute solutions of non-electrolytes it is well known that we have a region in which the simple gas laws are applicable within the limits of experimental error. With increasing concentration this "ideal" region gradually changes over into a region in which deviations from the gas laws are manifested according to the individual nature of each substance. However, in the case of dilute solutions of electrolytes, we have in addition to these two regions, an intermediate region of particular importance. This intermediate region is characterized by a uniform divergence from the simple gas laws exhibited by any salt merely according to its valence type, but independent of its chemical nature in other respects.

The existence of such an ideal region, where salts, according to their valence type, show a uniform behavior, must be expected from the point of view of the theory of the complete dissociation of strong electrolytes. It has recently[3] been suggested that for this region the osmotic and activity coefficients, φ and f, respectively, are given for all uni-univalent salt by the thermodynamically correlated formulas

$$1 - \varphi = \alpha \sqrt{C} \qquad (1)$$

and

$$-ln\, f = 3\alpha \sqrt{C} \qquad (2)$$

where α is a universal constant, changing only a little with temperature, and c stands for the equivalent concentration. Introduction of the empirical value $\alpha = 0.32$ in these formulas shows that even at $c = 10^{-5}\,M$ the deviation of a uni-univalent salt from the simple gas laws, as meas-

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[3] Brönsted, (a) THIS JOURNAL, **44**, 938 (1922). See also Lewis and Randall, (b) *ibid.*, **43**, 1122 (1921), where a two constant empirical equation of the form; $-ln\, f = 3XC^n$ is given as the limiting law for dilute solutions, X and n being assigned different values for each salt under consideration. The authors add the interesting corollary that inasmuch as n (α in their notation) possesses values between 0.500 and 0.565 for uni-univalent salts, a square-root expression may be used as a close approximation to the truth for this type. For the higher valence types, however, they employ values of n as low as 0.364 so that their constants do not possess the physical significance we have attached to those in the square-root expression, used by us for all valence types.

ured by its activity coefficient, amounts to 0.1%. On the other hand, with increasing concentration individual deviations from the above formulas make their appearance between $c = 10^{-3}$ and $10^{-2}\,M$. It is no wonder therefore, that the establishment of the theory of the ideal region of electrolytes, in which the deviations from the gas laws depend merely upon the types, encounters difficulties of an experimental character on account of the high degree of dilution at which such experimental work has to be carried out.

When we bear in mind that the above-mentioned activity coefficient, f, is the stoichiometric activity coefficient,[4] that is, the activity of the substance in question divided by its stoichiometric molality, it seems very unlikely that a formula as simple as (2) would apply if, in addition to the electric forces between the ions, the displacement of the electrolytic equilibrium also had any effect upon the activity. The establishment of the general validity of the above formulas, therefore, would mean not only an important addition to our knowledge regarding thermodynamic properties of salt solutions, but also be a strong indication of the correctness of the assumption of the complete dissociation of strong electrolytes.

The experimental work of the present paper was taken up from this standpoint, with the purpose of furnishing new and more quantitative evidence regarding the ideal region of electrolytic solutions. A detailed report of this work will be found in the later chapters. It will be preceded by an extension of Equations 1 and 2 to salts of higher valence types, and by a brief exposition of the recent work of Debye and Hückel, which forms a most important step in the modern development of the theory of salt solutions.

2. Influence of the Valence

The influence of valence on the activity coefficient of ions has long been recognized. Thus Bjerrum[5] as early as 1918 suggested that the logarithm of the activity coefficient is directly proportional to the square of its valence. In the determination of the solubility of slightly soluble salts the effect of an added salt proved to depend very markedly on the valence of the ions involved.[6] From such measurements it is possible to get

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[4] Brönsted, This Journal, **42**, 763 (1920).

[5] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).

[6] Brönsted and Petersen, This Journal, **43**, 2265 (1921). Although we shall be concerned in this paper only with the effect of valence types on the thermodynamic properties of ions, mention should be made of the extensive work of A. A. Noyes and his collaborators on the conductivity of salt solutions carried out previous to the development of the theory of the complete dissociation of strong electrolytes and the activity concept. Their investigations showed that, at least, a rough proportionality could be obtained at a given concentration between the conductivity ratios Λ_v/Λ_∞ and the valence product of the ions of one type and those of another valence type. (Compare This Journal, **33**, 1436 (1911), where references to much of the earlier work are given.)

quantitative information of this influence. Considering, for instance, the solubility of sparingly soluble uni-univalent salts in 0.05 *M* salt solutions of the same type, we find on an average an increase of 20% from the value in pure water. We can therefore put $\log f_1 = -\log 1.20 = -0.079$ if the activity coefficient f_1 equals unity in pure water. Now for the tri-trivalent luteocobaltic hexacyano-cobaltiate the solubility in 0.05 *N* potassium chloride solution is 5.4 times as great as in pure water. The activity coefficient f_3 of the trivalent ion under the same supposition is therefore given by $\log f_3 = -\log 5.4 = -0.73$. Thus we obtain: $\frac{\log f_3}{\log f_1} = \frac{0.73}{0.079} = 9.2$, that is, the ratio of the logarithms of the two activity coefficients very nearly equals the square of the ratio of the corresponding valences.

Evidence from the available experimental material on solubilities seems to be in favor of the conclusion that the above result exemplifies a relatively general rule. If this is the case we can write

$$\frac{1}{z_1^2} \ln f_1 = \frac{1}{z_2^2} \ln f_2 = \ldots\ldots\ldots \tag{3}$$

where the ions having the valences z_1, z_2. . . . . and the corresponding activity coefficients f_1, f_2. . . . are present in the same solution of a uni-univalent salt. Equation 3 is expected to be exact only in the ideal region of concentration. It expresses how the activity of an ion changes with its valence, when the surrounding medium is kept constant.

Equation 3, however, affords only part of the solution of the problem before us. It remains to examine the influence of changing type of the surrounding solvent salt on the activity coefficient of a certain ion. Consideration of the varying and marked effect of the surroundings led Lewis and Randall[7] to the concept of the ionic strength, by means of which they attempted to give a general solution of this problem. They define the ionic strength as half the sum of the molar concentrations of each ion multiplied by the square of its valence. They have offered the generalization that in dilute solution the activity coefficient of a given electrolyte is the same in all solutions of the same ionic strength. Lewis and Randall did not offer a general relationship connecting the ionic strength and the activity coefficient but used various relationships for the various cases which they examined.

The conception of ionic strength is one of obvious importance. We shall adopt it for the present investigation, but with some restrictions. First, the principle of equal coefficients in solutions of the same ionic strength applies accurately only in the ideal region. Its thermody-

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[7] Lewis and Randall, (a) THIS JOURNAL, **43**, 1140 (1921); (b) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., **1923**, p. 364.

namic inconsistency at such concentrations, where the individual properties of the ions are of perceptible influence, has already been emphasized in an earlier communication.[8] Furthermore, it must be noted that *there seems to be experimental evidence for the presence, even at high dilution, of an electric type effect* which can be most simply described by the statement that in an unsymmetric solvent, for example, a solution of magnesium chloride, the activity coefficients of ions of the same valence but of opposite sign (for instance, a Ca^{++} and a SO_4^{--} ion) are different from one another. This phenomenon has been explicitly described in an earlier communication.[9]

The ionic strength μ in a solution of a simple salt is in accordance with the definition of Lewis and Randall given by $\mu = {}^1/_2(m_1z_1^2 + m_2z_2^2)$, where m_1 and m_2 are molarities, z_1 and z_2 valences of the two ions. Now remembering that the equivalent concentration c is given by

$$c = m_1z_1 = m_2z_2 \tag{4}$$

we obtain the following as a simpler definition of the ionic strength.

$$\mu = c\frac{z_1 + z_2}{2} \tag{5}$$

The ionic strength is thus seen to be identical with the equivalent concentration multiplied by the mean value of the valence of the two ions.

For a mixture of salts we can write

$$\mu = \frac{1}{2}(c_1z_1 + c_2z_2 + \ldots\ldots) \tag{6}$$

where $c_1, c_2 \ldots\ldots$ are the equivalent concentrations of all the ions present having the valences $z_1, z_2 \ldots\ldots$, respectively.

We are now clearly in a position to formulate the general equation for the activity coefficients in the ideal region on the basis of the validity of Equations 2 and 3 and the Lewis and Randall principle of ionic strength, and obtain

$$-ln\,f = 3\alpha z^2\sqrt{\mu} \tag{7}$$

which is valid for the activity coefficient of an ion of any valence z in a solution of the ionic strength, μ.

The activity coefficient of a salt, as defined by

$$ln\,f = \frac{\nu_1}{\nu}ln\,f_1 + \frac{\nu_2}{\nu_1}ln\,f_2 \tag{8}$$

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[8] Brönsted, (a) THIS JOURNAL, 44, 877 (1922); (b) 45, 2903 (1923). Ref. 7b, p. 368.

[9] Ref. 6, p. 2285. Thus it was found, for example, that the activity coefficient of luteocobaltic tetranitro-diammine cobaltiate is 60% higher in 0.01 *M* $MgCl_2$ than in 0.01 *M* Na_2SO_4. As at this concentration the individual effects, caused by the different chemical natures of the ions, are still very marked with ions of high valence it may be possible that also the electric type effect will disappear in the ideal region of concentration, but considering its concentration dependence this does not seem probable.

The question of electric type effect evidently deserves a careful study in the region of very dilute solutions. Until this has been done we must look with some reservation upon the principle of the ionic strength in its application to unsymmetric solutions.

where ν_1 and ν_2 are the number of cations and anions contained in one molecule of the salt, $\nu = \nu_1 + \nu_2$, and f_1 and f_2 the corresponding activity coefficients of the ions, is now easily computable, by introducing

$$\frac{\nu_1}{z_2} = \frac{\nu_2}{z_1} = \frac{\nu}{z_1 + z_2} \tag{9}$$

$$-ln\, f = 3\alpha z_1{,}z_2 \sqrt{\mu} \tag{10}$$

Finally for the osmotic coefficient φ we derive by means of the relation[10] between f and φ,

$$1 - \varphi = \alpha z_1{,}z_2 \sqrt{\mu} \tag{11}$$

These general relations for the thermodynamic properties of ideal salt solutions should be valid with the same proviso that we have taken with regard to the general principle of the ionic strength as mentioned above.

3. The Theory of Debye and Hückel

While the experimental work of this article was in progress an important paper by P. Debye and E. Hückel[11] has appeared in which the authors have derived general relations for the osmotic coefficients of strong electrolytes of any valence type from purely theoretical considerations. As far as we are aware, this theory approaches a complete solution of the problem of the strong electrolytes in very dilute solutions. Their results are not consistent with the earlier calculations of Milner[12] and Ghosh.[13]

We note, however, with great satisfaction that the theory leads to the same equations that have been developed by us, above, on a basis which is chiefly experimental.

We shall make no attempt to reproduce the lengthy mathematical derivation of Debye and Hückel but simply sketch some of the important steps and assumptions involved in their reasoning. The essential part of their work is the calculation of the potential energy *Ue* of the dissolved

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[10] $-ln\, f = 3\,(1 - \varphi)$. This follows from the square root dependence of *ln f* upon the concentration. See Ref. 4, pp. 765–766.

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

[12] Milner, *Phil. Mag.*, [6] **23**, 553 (1912); **25**, 742 (1913).

[13] Ghosh, *J. Chem. Soc.*, **113**, 149, 627, 790 (1918). Debye and Hückel point out that Ghosh's calculation of the electrostatic energy of an ionized electrolyte, upon which his further conclusions depend, is defective, due to the fact that he uses an expression for the average distance between ions which is applicable for crystals but not applicable for solutions where the neighboring ion may or may not be an unlike ion.

In this connection it may be mentioned that Kendall [This Journal, **44**, 719 (1922)] in discussing the incompatibility of Ghosh's postulate regarding the crystal-lattice arrangement of ions in solution with the postulate that the oppositely charged radicals of a salt molecule in solution form a completely saturated electrical doublet, has pointed out that any atom will be kept in a definite mean position in such a lattice by the electrical forces exerted between it and *all* of the surrounding atoms, and cannot, therefore, form a neutral doublet with any one of the 6 (in the case of NaCl) oppositely charged atoms in immediate proximity to it without destroying the whole basis of the crystal structure.

ions originating from their electric charges. While Milner in his attempt to solve the same problem, considered all the possible positions of the ions, applying to these the Boltzmann principle of probabilities, the treatment of Debye and Hückel is characterized by the introduction of an average potential in the ionic atmosphere surrounding an ion, which constitutes a marked simplification of the calculations. Since the potential and electric density are correlated by both the Boltzmann principle and the Poisson equation, the potential can be calculated and appears as a function of a characteristic distance $1/\kappa$ given by

$$\kappa^2 = \frac{4\pi e^2}{D\,k\,T} \Sigma\, n_i z_i^2 \tag{12}$$

where e is the charge of a univalent ion, k the Boltzmann gas constant per molecule, D the dielectric constant, T the temperature, n_i the *number* of *ions of the* i^{th} *sort per unit volume* and z_i the valence of this ion. The quantity $1/\kappa$, having the dimension of a distance and replacing the average distance between the ions in former theories, is the most important factor in the Debye-Hückel theory. For the electric energy the total number of dissolved ions N, where $N = \Sigma N_i$ the following formula is obtained.

$$Ue = \frac{-\Sigma\, N_i\, z_i^2}{2} \cdot \frac{e^2\,\kappa}{D} \tag{13}$$

expressing the energy as a function of the characteristic quantity κ. This formula is an approximation which is valid only for a high degree of dilution. We shall discuss their formula for more concentrated solutions in Part 4.

From the formula for the energy the expressions of the thermodynamic potential or similar functions as well as osmotic and activity coefficient are arrived at by familiar thermodynamic methods.[14] For the osmotic coefficient φ in a simple salt solution the expression obtained is

$$1 - \varphi = w\,\frac{e^2}{6D\,k\,T}\sqrt{\frac{4\pi E^2}{D\,k\,T} N\, \Sigma\, \nu_i} \tag{14}$$

where $N = \Sigma N_i$, w a "valence factor" determined by

$$w = \left[\frac{\Sigma \nu_i\, z_i^2}{\Sigma_i\, \nu}\right]^{\frac{3}{2}} \tag{15}$$

and ν_i *the number of ions of the* i^{th} *sort formed by dissociation of one molecule of the salt considered.* Introducing $\nu_i = \Sigma \nu_i$, the usual molal concentration m, and the numerical values of the constants, Equation 14 reduces to

$$1 - \varphi = 0.270\; w \sqrt{m\,\nu} \tag{16}$$

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[14] By utilizing the Planck function G, determined by $G = \int \frac{U}{T^2} dT$, the integration is carried out by making D in Equation 13 independent of temperature, which is certainly inconsistent with fact. It is mentioned by the authors, however, that the direct kinetic theory of the osmotic pressure agrees with the expression of G, thus obtained.

for aqueous solutions at 0°.

For the case of a salt consisting of *two kinds of ions* we can convert Debye and Hückel's expression (16) into a simpler form by inserting in this equation from (15)

$$w = (z_1z_2)^{\frac{3}{2}} \tag{17}$$

$$M\nu = \frac{z_1 + z_2}{z_1z_2}c \tag{18}$$

and Expression 6 for the ionic strength, c being the equivalent concentration. From this we obtain

$$1 - \varphi = 0.38\, z_1z_2 \sqrt{\mu} \tag{19}$$

in complete agreement with Equation 11 if we put $\alpha = 0.38$ instead of 0.32 as previously employed.

For the activity coefficient of an *ion* the formula derived by Debye and Hückel is

$$ln f_i = z_i^2 \frac{e^2 \kappa}{2DkT} \tag{20}$$

from a chemical standpoint perhaps the most useful expression in the theory. The activity coefficient of a *salt* then becomes

$$ln f = \frac{e^2 \kappa}{2DkT} \cdot \frac{\Sigma \nu_i z_i^2}{\Sigma \nu_i} \tag{21}$$

and leads again easily to the formula for $1-\varphi$, from the general equation corresponding to Equation 8 and Ref. 10.

Introduction of numerical values in (20) for 0° yields

$$-ln f_i = 1.14\, z_i^2 \sqrt{\mu} \tag{22}$$

for an ion, and

$$-ln f = 1.14\, z_1z_2 \sqrt{\mu} \tag{23}$$

for a salt composed of two ions. These equations are in complete correspondence with Equations 7 and 10, derived in Section 2 of the present article, except that the limited data previously available conformed most closely to an empirical value of 0.32 for α, while the value for α computed theoretically is 0.38 at 0°. These data were of necessity founded almost entirely upon freezing-point and electromotive-force measurements available in the literature. It is well known that both of these methods when used in highly dilute solution become somewhat uncertain owing to the marked effect which minute experimental errors can exert upon the calculated activity results.

On the other hand, the method of solubility change which we have used in obtaining the experimental data of this paper is singularly free from the sort of errors which beset the freezing-point and electromotive-force measurements for the same range of dilution, and the reader will note from a consideration of the slope of the theoretical curves of Figs. 2 to 5 that the present data conform more closely to the theoretical value of α than to the former empirical value. For this reason we have considered it sufficient to present in the tables only the deviations which the experimental data show in comparison with the values from the theoretical equations.

4. The Deviation Coefficients at Higher Concentration

The theory considered in Section 3 has dealt with "ideal salt solution" in which the dimensions of the ions were negligible in comparison with the characteristic distance $1/\kappa$. The complete theory of Debye and Hückel, however, does not confine itself to this ideal region, but attempts by means of some simplifying assumptions regarding the construction of the ions to account for the influence of their magnitude. It is not clear at present what these rather hypothetical ideas mean for the final results of the theory for higher concentrations. In spite of this it is of interest to compare the theoretical equations reached in this way with the empirical equation previously established. In Equation 16 for the osmotic coefficient, the influence of the size of the ions is manifested as a factor σ as follows,

$$1 - \varphi = 0.270\, w \sqrt{m \nu}\, \sigma \tag{24}$$

or if the nature of the salt is kept unchanged

$$1 - \varphi = \alpha \sqrt{c}\, \sigma \tag{25}$$

the factor σ being a function of κ as well as of the "apparent diameter" a of the ions involved.

When the value of σ is not too far from unity, it can be represented by

$$\sigma = 1 - \frac{3}{2} x + \frac{9}{5} x^2 - 2 x^3 + \ldots\ldots \tag{26}$$

where $x = \kappa a$. By sufficient dilution, therefore, one can put

$$\sigma = 1 - \frac{3}{2} \kappa a \tag{27}$$

or by introduction of (12)

$$\sigma = 1 + \zeta \sqrt{c} \tag{28}$$

where ζ is a constant depending upon the "diameter" of the ions a. This again inserted in (25) gives

$$1 - \varphi = \alpha \sqrt{c} + \beta c \tag{29}$$

where $\beta = \alpha\zeta$.

Equation 29, however, is identical with the equation established by Brönsted on a chiefly empirical basis.[15] It is characterized by the fact, that as the concentration approaches the ideal region the osmotic deviations become uniformly determined by the general equation (1), α being a universal constant, while at higher concentrations the deviations show a linear dependence of the concentration. The magnitude of this deviation is determined by the coefficient β, depending upon the nature of the salts in question.

While in the previous paper α was ascribed to the "primary" Milner-

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[15] Equation 4 of Ref. 3a.

effect, that is, the electric effect arising in the case of the ions being considered as mass points, the β coefficient of the linear member was assumed to be caused by several influences, particularly a "secondary" electric effect involved by the ions having a finite size and a hydration effect. As the latter is unquestionably a linear function of the concentration, it is important to obtain a theoretical verification of the linear influence of this secondary electric effect, as furnished by the Debye-Hückel theory, even if the underlying ideas in this case have not the same rigid character as for the ideal region where the dimensions of the ions can be neglected.

Equation 29 also requires a linear member in the activity equation; namely,[16]

$$-ln f = 3\,\alpha\sqrt{c} + 2\,\beta\,c \tag{30}$$

Finally, attention should be directed to the thermodynamic equation

$$\frac{\partial\, ln f_1}{\partial\, m_2} = \frac{\partial\, ln f_2}{\partial\, m_1}$$

recently developed by Bjerrum.[17] As shown by this author Equation 29 conforms with this thermodynamic requirement, while most other formulas hitherto proposed for the same purpose are inconsistent with it.

5. Solubility Relations in the Region of Dilute Solutions

The simplest and most useful method for testing Equation (2) in very dilute solution consists in determinations of the solubility of very sparingly soluble salts in solutions of other salts of varying concentration. The principle of this method has been described elsewhere.[4] On account of the importance of the solubility phenomena for the determination of activity coefficients we shall develop explicitly the general equations to govern the changes in solubility with changing concentration of the solvent on the basis of the above theory.

If in a saturated solution the ions of the saturating salt have the molalities, m_1 and m_2, the numbers of the ions ν_1 and ν_2 and the corresponding activity coefficients f_1 and f_2, then the equation

$$m_1^{\nu_1}\, m_2^{\nu_2}\, f_1^{\nu_1}\, f_2^{\nu_2} = \text{constant.} \tag{31}$$

holds thermodynamically at constant temperature. Since the solubility product P is given as $P = m_1^{\nu_1}\, m_2^{\nu_2}$ and the activity coefficient of the saturating salt as $f = f_1^{\frac{\nu_1}{\nu}} f_2^{\frac{\nu_2}{\nu}}$, Equation 3 can be written

$$P^{\frac{1}{\nu}} f = \text{constant.} \tag{32}$$

Introducing here the value of f from Equation 10 we obtain

$$P^{\frac{1}{\nu}}\, e^{-\,3\alpha\, z_1 z_2 \sqrt{\mu}} = \text{constant} \tag{33}$$

as the general solubility equation for the ideal region of concentrations.

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[16] Equation 10 of Ref. 3a.

[17] Bjerrum, *Z. physik. Chem.*, **104**, 406 (1923).

In the non-ideal region the linear member of Equation 30 must be taken into account and then instead of 3, we obtain

$$\frac{1}{P^{\nu}}e^{-3\alpha z_1 z_2\sqrt{\mu} - 2\beta c} = \text{constant.} \tag{34}$$

The two cases of hetero-ionic and homo-ionic solvents must be distinguished. In the first case the solvent salt and saturating salt have no ion in common and the two ion molalities are given by $m_1 = \nu_1 S$; $m_2 = \nu_2 S$, S being the molar solubility. The solubility product is, therefore,

$$P = S^{\nu}\nu_1^{\nu_1}\nu_2^{\nu_2} \tag{35}$$

In the case of a homo-ionic solvent, the second ion being common, we have $m_1 = \nu_1 S$; $m_2 = \nu_2 S + \frac{c}{z_2}$, where c is the equivalent concentration of the solvent and z_2 the valence of the common ion. In this case we obtain

$$P = (S\nu_1)^{\nu_1}\left(S\nu_2 + \frac{c}{z_2}\right)^{\nu_2} \tag{36}$$

By introduction of the values of P given by Equation 35 or 36 for hetero-ionic and homo-ionic solvents, respectively, in Equations 33 or 34, the general relations for calculating the solubility in terms of the concentration of the solvent are obtained. In the ideal region and for no ion in common the equation becomes

$$ln\ \frac{S}{S\infty} = 3\ \alpha z_1 z_2\ \sqrt{\mu} \tag{37}$$

where the constant in Equation 32 is defined by means of $S\infty$ representing the solubility which corresponds to infinite dilution. Defining the constant by means of the solubility S_0 in pure water we obtain

$$ln\ \frac{S}{S_0} = 3\ \alpha\ z_1 z_2\ (\sqrt{\mu} - \sqrt{\mu_0}) \tag{38}$$

where μ_0 is the ionic strength of the saturated solution, using pure water as solvent.

6. Experimental Part

Saturating salts suitable for our purpose must meet a number of criteria, namely; (*a*) they must be sufficiently insoluble so that one can work in highly dilute solution; (*b*) on the other hand, the salts must not be too insoluble else it will be difficult to obtain an accurate determination of the solubility; salts containing a large number of ammonia groups are best suited for this reason; (*c*) the ions of the solvent salts used must not form precipitates with the ions of the saturating salts used; (*d*) the saturating salts must be stable in aqueous solution at the temperature investigated and possess definite crystalline forms.

Needless to say, salts possessing all of these qualifications are not easy to find. In this paper we will present experimental data on four cobalt-ammines having solubilities in water ranging from 0.00049 to 0.00005 *M* which fulfil these requirements satisfactorily. Their formulas and names are to be found at the headings of Tables I to IV where their complete solubility relations in various solvents are tabulated. Tables V to VII contain some results previously obtained in this Laboratory but which were limited only to uni-univalent solvents. Table VIII contains calculations of the solubility relations of barium iodate, the original data for which were obtained by Harkins and Winninghof.[18]

The preparation of the saturated solutions was carried out in a large, specially constructed water-bath maintained at 15°. As the solubilities of the cobaltammine salts used as saturating salts in this investigation increase on the average about 5–10% per degree, it was necessary to maintain the temperature constant to 0.01°. To assist in maintaining a constant temperature, the relay (see Fig. 1) which operated the electric heating unit also directed a stream of cold tap water so that it flowed into the bath when the heating current was off and out of the bath into a waste pipe when the heating current was on. No fluctuations greater than 0.01° were ever observed with thermometers kept constantly near the top and near the bottom of the bath.

The four 1.5-liter glass bulbs (Fig. 1) were employed to hold the solvent liquid which flowed slowly through a layer of the solute contained in the tube leading from the bulb. A plug of cotton served as a support and filter for the solute salt. A salt column 10 cm. long allowed about 500 cc. of liquid to pass through into the collecting flask in 24 hours. This was sufficient for two or three ammonia determinations, depending upon the composition and solubility of the particular cobaltammine employed.

Experiments in which the rate of flow of the solute through the solvent was varied showed that this factor had no influence upon our results, which we take as evidence of saturation.

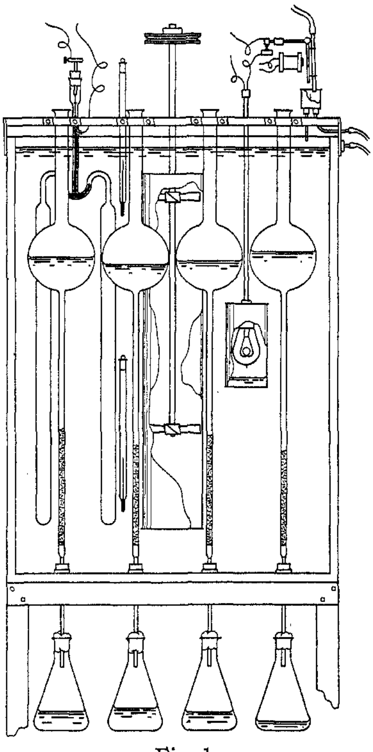
Fig. 1.

The cobaltammines were prepared by dissolving a soluble form of the constituent cation and anion[19] separately in a very large volume of water at 30° to 35°. For the purpose of obtaining crops of crystals of a desirable size, preliminary experiments were made to determine how dilute the cation and anion solutions should be to prevent visible crystallization of the final salt from occurring for some 20 or 30 minutes after mixing. Complete separation required at least one day.

We have found even under these conditions of preparation that the solubility of a fresh cobaltammine preparation decreases when the salt is first washed with water. Part of this decrease may be due to the elimination of minute crystals having a higher

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[18] Harkins and Winninghof, This Journal, 33, 1827 (1911).

[19] For more specific directions for preparing the particular cation or anion salts consult the handbook of Gmelin-Kraut, where references to the original work of Jörgenson and Werner and their co-workers are given.

solubility as well as the elimination of traces of extraneous salts which could influence the results. Continuous washing with water for a week yielded solubility values (s_0) which remained constant within the limits of analytical error throughout the course of the experiments.

This method[20] of obtaining the saturated solutions by use of the apparatus shown in Fig. 1 is much superior for the present purposes to the methods previously employed, as it enables one to carry out a complete series of experiments using different concentrations of salt solution as solvents and a single sample of saturating salt, thereby eliminating any chance of error due to minute differences in the physical properties of the saturating salt. In only one series was a second sample of saturating salt used. These results, all of which are confined to the effect of potassium sulfate and barium chloride on oxalo-tetrammine cobaltic dithionate (Table III) are followed by a question mark (?), as it was found that this second sample of salt continued to give a slightly higher solubility in water even after several weeks' washing. After the completion of the experiments it was found that the solubility in water had changed a little during the course of the experiments so that some of the results of this series may be in error by as much as 1%. The experiments marked with an exclamation point (!) were carried out on the original sample of oxalo-dithionate and are strictly comparable with the results on the other solvents. In the case of the other salts the solubilities in water showed no change during the course of the experiments.

When sufficient liquid had trickled through the solute, the liquid remaining in the bulb was sucked out and the bulb walls and saturating salt column thoroughly washed with the next solvent before samples were collected for analysis.

The analyses were performed by measuring a fixed quantity of the saturated solution, adding sufficient sodium hydroxide solution to make the final mixture about 0.1 *M* in alkali and distilling the ammonia, which is liberated on boiling, into a known quantity of 0.02044 *N* hydrochloric acid through a quartz condenser tube. Methyl red was used as indicator in making the titrations. Owing to the large number of equivalents of ammonia liberated per mole of cobaltammine it was possible to attain an accuracy of one or at most two parts per thousand in the determination of the ammonia liberated except perhaps in the case of the very insoluble luteo salt. (Table IV.)

7. Discussion of Results

In order to determine the activity coefficients in terms of $-\log f$, we have plotted the values of the solubility ratio, $\log s/s_0$, obtained directly from the analytical data by comparing the solubility in a given solvent with the solubility in pure water, against the square root of the ionic strength. We have not reproduced these plots as the reader will readily see that they are parallel but otherwise identical with the plots which we have given of $-\log f$ against the square root of the ionic strength, owing to the constant term $-\log f_0$ in the expression

$$-\log f = \log (s/s_0) - \log f_0 \qquad (39)$$

f_0 representing the activity coefficient of the salt when present as a saturated solution in what is otherwise pure water. The plots in Figs. 2 to 5 correspond to the data in Tables I to IV. Owing to the linear character of these curves and the marked insolubility of the salts, it is possible to

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[20] The same principle has been used previously by Brönsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

evaluate —log f_0 very accurately by performing graphically the resulting short extrapolation from the ionic strength of a saturated solution in otherwise pure water to infinite dilution. The ordinate where the log s/s_0 curve cuts the line of zero ionic strength gives the value of —log f.

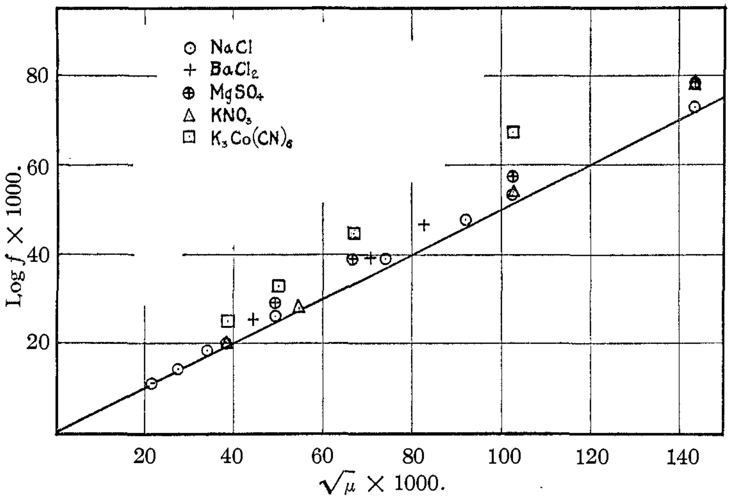

Fig. 2.—The relation of the activity coefficient f to the ionic strength μ for the uni-univalent salt oxalo-tetrammine-cobalto diammino-dinitro-oxalo-cobaltiate (oxalo-nitro—see Table I) in the presence of various solvent salts. The heavy line is theoretical equation 40; —log f = 0.50 $\sqrt{\mu}$.

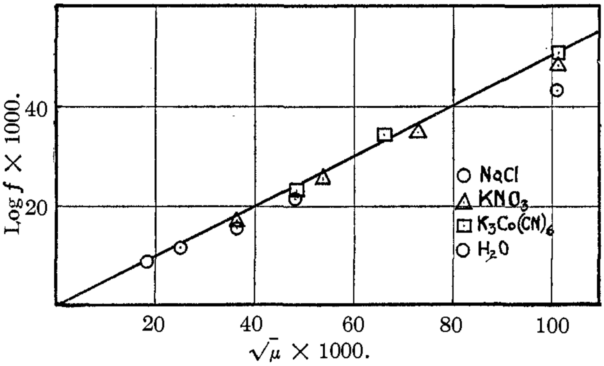

Fig. 3.—The relation of the activity coefficient f and the ionic strength μ for the uni-univalent salt thiocyanato-nitro (Table II). Theoretical equation (heavy line): —log f = 0.50 $\sqrt{\mu}$

In the columns headed "f calc." we have given the values of the activity coefficient which would be obtained from the use of the ideal equation ((23) in decadic logarithms)

$$-\log f = 0.50\, z_1 z_2 \sqrt{\mu} \qquad (40)$$

and have compared these values with those found by direct experiment as outlined above. The error in the activity coefficient is directly pro-

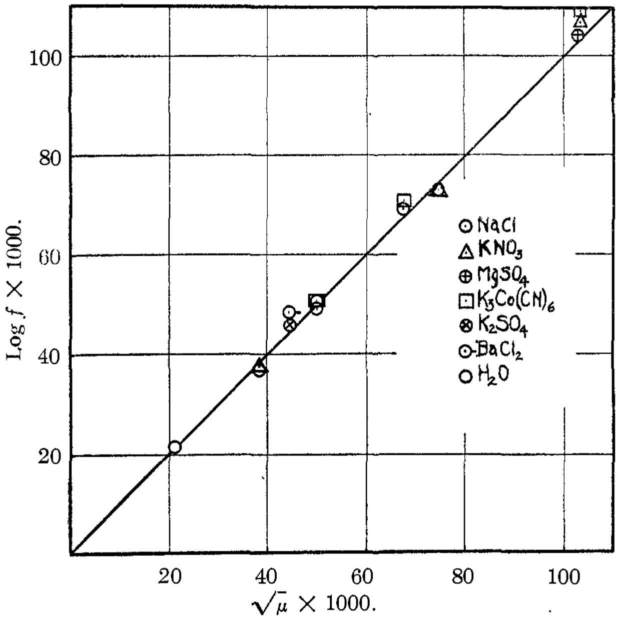

Fig. 4.—The relation between the activity coefficient f and the ionic strength μ for the uni-bivalent salt, oxalo-dithionato (Table III) in the presence of solvent salts of various types. The heavy line is the theoretical equation 40; $-\log f = 1.00\sqrt{\mu}$.

TABLE I

THE SOLUBILITY RELATIONS OF THE UNI-UNIVALENT SALT OXALOTETRAMMINECOBALTO-DIAMMINODINITROÖXALO COBALTIATE (OXALO-NITRO) $[Co(NH_3)_4C_2O_4][Co(NH_3)_2(NO_2)_2C_2O_4]$ IN VARIOUS AQUEOUS SOLVENTS

Solubility in water (S_0) = 0.0004900 M. —Log f (extrapolated) = 0.0115 (water). Probable error of final activity result less than 0.3%.

Conc. of solvent salt equivs./L	Solubility equivs. per l. × 10^4	μ	$\sqrt{\mu}$	Log $\frac{S}{S_0}$	—Log$f$ found	f found	f calc.	Diff.
			Solvent Water					
0.0000	4.900	0.0004900	0.0221	0.0000	0.0115	0.974	0.975	− 0.001
			Solvent NaCl					
.0003	4.935	.0007935	.0282	.0031	.0146	.967	.968	− .001
.0007	4.977	.0011970	.0346	.0068	.0183	.959	.961	− .002
.0010	5.000	.0015000	.0387	.0088	.0203	.954	.956	− .002
.0020	5.067	.0025070	.0500	.0147	.0262	.941	.944	− .003
.0050	5.220	.0055220	.0743	.0272	.0390	.914	.918	− .004
.0080	5.326	.0085260	.0924	.0363	.0478	.896	.899	− .003
.0100	5.396	.0105400	.1027	.0418	.0533	.885	.888	− .003
.0200	5.646	.0205600	.1434	.0616	.0731	.845	.848	− .003

			SOLVENT KNO_3					
.0010	5.000	.0015000	.0387	.0088	.0203	.954	.956	− .002
.0025	5.088	.0030090	.0549	.0164	.0279	.938	.939	− .001
.0050	5.218	.0055220	.0743	.0273	.0388	.915	.918	− .003
.0100	5.414	.0105400	.1027	.0433	.0548	.881	.888	− .007
.0200	5.725	.0205700	.1434	.0676	.0791	.834	.848	− .014
			SOLVENT $BaCl_2$					
.0010	5.059	.0020060	.0447	.0139	.0254	.943	.948	− .005
.0030	5.222	.0050220	.0709	.0277	.0392	.914	.922	− .008
.0050	5.375	.0080380	.0826	.0402	.0517	.888	.902	− .014
.0100	5.649	.0155650	.1245	.0617	.0732	.845	.867	− .022
.0200	6.093	.0307000	.1750	.0946	.1061	.783	.820	− .037
			SOLVENT $MgSO_4$					
.0010	5.102	.0025100	.0501	.0176	.0291	.935	.944	− .009
.0020	5.220	.0045220	.0672	.0275	.0390	.914	.925	− .011
.0050	5.446	.0105450	.1027	.0459	.0574	.876	.888	− .012
.0100	5.710	.0205710	.1435	.0664	.0779	.836	.848	− .012
			SOLVENT $K_3Co(CN)_6$					
.0005	5.055	.0015060	.0388	.0136	.0251	.944	.956	− .012
.0010	5.150	.0025150	.0502	.0216	.0331	.927	.944	− .017
.0020	5.289	.0045290	.0673	.0332	.0447	.902	.925	− .023
.0050	5.572	.0105600	.1028	.0558	.0673	.856	.888	− .032

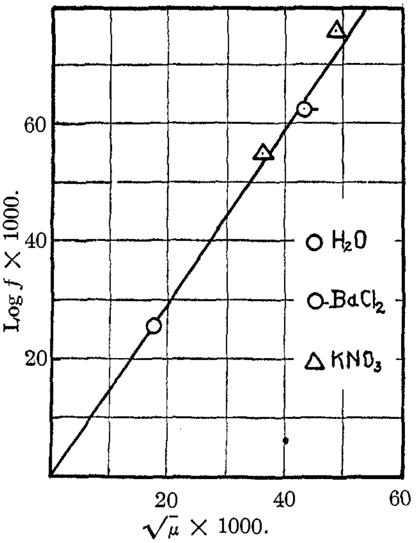

Fig. 5.—The relation of the activity coefficient f to the ionic strength μ for the tri-univalent salt, luteo-diammino-dinitro-oxalo-cobaltiate (Table IV) in the presence of various solvent salts. The heavy line is for the theoretical equation 40; $-\log f = 1.50\sqrt{\mu}$.

portional to the errors made in determining the solubility of the salt in a given solvent plus any constant error introduced by extrapolating the log s/s_0 curve to infinite dilution. It will be noted that all of the values of the activity coefficient in water so obtained agree within 0.1% of the calculated value except for the case of the much more soluble salt, oxalo-chromiate (Table VII), where the values differ by 0.3%.

Examination of the values of f (Cols. 7 and 8 of Tables I to VIII) and of the plots of $-\log f$ against the square root of the ionic strength (Figs. 2 to 4) shows that the concordance of the observed and calculated values leaves little to be desired toward substantiating Equation 23 (40) as the ideal law for the influence of inter-ionic forces upon the osmotic and activity coefficients of the ions. This becomes more evident when one considers the close approach of the experimental points to the numerically different theoretical equations obtained with saturating salts of different types; see Figs. 3, 4 and 5 where the slopes of the curves are in the ratio of 1:2:3. From this we may conclude that the α constant and the valence factor z_1z_2 which are involved in these cases are to be considered as established for highly dilute solutions, at least for the same order of reliability for which the dielectric constant D entering into the computation of α is known for 15°.

TABLE II

SOLUBILITY RELATIONS OF THE UNI-UNIVALENT SALT NITROTHIOCYANATOTETRAMMINECOBALTO-DIAMMINODINITROÖXALO COBALTIATE (THIOCYANATO-NITRO), $[Co(NH_3)_4(NO_2)(CNS)][Co(NH_3)_2(NO_2)_2C_2O_4]$, IN VARIOUS AQUEOUS SOLVENTS

Solubility in water (S_0) = 0.0003355 M. —Log f (extrapolated) = 0.0088 (water). Probable error of final activity result less than 0.3%.

Conc. salt equiv. per liter	Solubility equiv. per l. ×10⁴	μ	$\sqrt{\mu}$	Log $\frac{S}{S_0}$	—Log f	f found	f calc.	Diff.
				SOLVENT WATER				
0.0000	3.355	0.0003355	0.01831	0.0000	0.0088	0.980	0.979	+0.001
				SOLVENT NaCl				
.0003	3.377	.0006375	.0252	.0028	.0116	.975	.971	+ .004
.0010	3.405	.001340	.0366	.0065	.0153	.965	.959	+ .006
.0020	3.451	.002345	.0484	.0124	.0212	.952	.946	+ .006
.0100	3.627	.010363	.1015	.0340	.0428	.906	.890	+ .016
.0200	3.790	.020379	.1428	.0531	.0619	.867	.848	+ .019
				SOLVENT KNO_3				
.0010	3.418	.001342	.0366	.0081	.0169	.962	.959	+ .003
.0025	3.488	.002849	.0538	.0170	.0258	.942	.940	+ .002
.0050	3.572	.005357	.0732	.0257	.0345	.924	.919	+ .005
.0100	3.669	.010367	.1015	.0390	.0478	.896	.890	+ .006
				SOLVENT $K_3Co(CN)_6$				
.0010	3.464	.002346	.0484	.0141	.0229	.949	.946	+ .003
.0020	3.556	.004356	.0660	.0254	.0342	.925	.927	− .002
.0050	3.687	.010369	.1015	.0412	.0500	.891	.890	+ .001

The same may also be said to be true of the factor involving the ionic strength if we keep in mind the restrictions mentioned in Part 2.

Previous work[21] has shown that of the simple uni-univalent inorganic solvent salts investigated, potassium nitrate and sodium chloride have, on the whole, exhibited the widest variation in solvent power, so that one can expect that salts such as sodium nitrate and potassium chloride will show no greater deviations from the theoretical values than the minute ones exhibited by potassium nitrate and sodium chloride at high dilution in this work.

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[21] Ref. 8a, p. 888.

TABLE III

SOLUBILITY RELATIONS OF THE UNI-BIVALENT SALT, OXALOTETRAMMINECOBALTO DITHIONATE (OXALO-DITHIONATO) $[Co(NH_3)_4C_2O_4]_2[S_2O_6]$ IN SOLVENTS OF VARIOUS VALENCE TYPES

Theoretical equation: $-\text{Log } f = 0.498\ z_1z_2\sqrt{\mu}$. Solubility in water = 0.0001545 *M*. $-\text{Log } f$ (water extrapolated) = 0.0220. Error of final result less than 0.3%.

Salt added equiv. per l.	Solubility moles per l. × 10^4	Solubility equiv. per l. × 10^4	μ	$\sqrt{\mu}$	Log $\frac{S}{S_0}$ found	$-$Log f found	f found	f calc.	Diff.
SOLVENT WATER									
0.0000	1.545	3.090	0.000464	0.0215	0.0000	0.0220	0.951	0.952	−0.001
SOLVENT NaCl									
.0010	1.597	3.194	.001479	.0385	.0149	.0369	.918	.915	+ .003
.0020	1.645	3.290	.002494	.0500	.0277	.0497	.892	.892	± .000
.0050	1.737	3.474	.005521	.0744	.0513	.0733	.845	.843	+ .002
SOLVENT KNO_3									
.0010	1.603	3.206	.001489	.0385	.0164	.0384	.915	.915	± .000
.0050	1.737	3.474	.005521	.0744	.0513	.0733	.845	.843	+ .002
.0100	1.880	3.760	.010564	.1028	.0857	.1077	.780	.790	− .010
SOLVENT K_2SO_4									
.0006	1.614	3.228	.001384	.0372	.0193	.0413	.909	.918	− .009(?)
.0010	1.630	3.260	.001989	.0446	.0238	.0458	.900	.902	− .002(!)
.0010	1.650	3.300	.001995	.0447	.0289	.0509	.889	.902	− .013(?)
.0020	1.718	3.436	.003515	.0593	.0466	.0686	.854	.872	− .018(?)
.0030	1.775	3.550	.005033	.0709	.0608	.0828	.826	.849	− .013(?)
.0050	1.878	3.756	.008063	.0897	.0852	.1072	.781	.813	− .032(?)
SOLVENT $BaCl_2$									
.0010	1.641	3.288	.001992	.0446	.0266	.0486	.894	.902	− .008(!)
.0020	1.710	3.420	.003513	.0593	.0444	.0664	.858	.872	− .014(?)
.0050	1.862	3.724	.008059	.0898	.0814	.1034	.788	.813	− .025(?)
.0100	2.032	4.064	.015610	.1249	.1193	.1413	.722	.750	− .028(?)
SOLVENT $MgSO_4$									
.0010	1.652	3.304	.002496	.0500	.0296	.0516	.888	.892	− .004
.0020	1.723	3.446	.004517	.0672	.0478	.0698	.852	.857	− .005
.0050	1.866	3.732	.010560	.1028	.0826	.1046	.786	.790	− .004
SOLVENT $K_3Co(CN)_6$									
.0010	1.651	3.302	.002490	.0500	.0294	.0514	.889	.892	− .003
.0020	1.728	3.456	.004158	.0673	.0491	.0711	.849	.857	− .008
.0050	1.889	3.778	.010570	.1028	.0878	.1098	.777	.790	− .013

TABLE IV

SOLUBILITY RELATIONS OF THE TRI-UNIVALENT SALT LUTEODIAMMINODINITROÖXALO COBALTIATE (LUTEO DINITRO) $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2C_2O_4]_3$ AT 15°

Theoretical equation: $-\text{Log } f = 1.49\sqrt{\mu}$; $S_0 = 0.00005041$ *M*. $-\text{Log } f$ (extrapolated) = 0.0260 (water). Error of final result less than 0.5%.

Salt added equiv. per l.	Solubility moles × 10^4	μ × 10^4	$\sqrt{\mu}$	Log $\frac{S}{S_0}$	$-$Log f found	f found	f calc.	Diff.
SOLVENT WATER								
0.0000	0.5041	3.025	0.0174	0.0000	0.0260	0.942	0.942	±0.000
SOLVENT KNO_3								
.0010	.5389	13.23	.0364	.0290	.0550	.881	.881	− .001
.0020	.5661	23.39	.0483	.0504	.0764	.839	.846	− .007
SOLVENT $BaCl_2$								
.0010	.5484	18.29	.0427	.0366	.0626	.866	.863	+ .003

However, when we come to examine the individual results for the higher valence solvent salts we meet with a few cases where the deviations exceed our limits of probable error in highly dilute solution, and at least one example which may be attributed to the influence of an unsymmetric solvent. We refer particularly to the case of the uni-trivalent solvent

TABLE V

SOLUBILITY RELATIONS OF THE UNI-UNIVALENT SALT CROCEO-COBALTIATE, $[Co(NO_2)_2(NH_3)_4][Co(NO_2)_4(NH_3)_2]$, AT 20°

Concn. of salt added	Solubility equiv. per 1. × 10^4	μ	$\sqrt{\mu}$	Log $\frac{S}{S_0}$	—Log f found	f found	f calc.	Diff.
SOLVENTS KNO_3, NaCl, KCl								
0.0000	3.70	0.000370	0.0192	0.0000	0.0098	0.978	0.978	±0.000
.0010	3.78	.001378	.0372	.0090	.0188	.958	.958	± .000
.0020	3.83	.002383	.0480	.0149	.0247	.945	.946	− .001

TABLE VI

SOLUBILITY RELATIONS OF THE UNI-UNIVALENT SALT CROCEO-CHROMIATE, $[Co(NH_3)_4(NO_2)_2][Cr(NH_3)_2(CNS)_4]$, AT 20°

SOLVENTS KNO_3, NaCl, KCl								
.0000	1.43	.000143	.0120	.0000	.0059	.986	.986	± .000
.0010	1.46	.001146	.0339	.0109	.0164	.963	.962	+ .001

TABLE VII

SOLUBILITY RELATIONS OF THE UNI-UNIVALENT SALT OXALO-CHROMIATE, $[Co(NH_3)_4(C_2O_4)][Cr(NH_3)_2(CNS)_4]$, AT 20°

SOLVENTS KNO_3, NaCl, KCl								
.0000	13.7	.00137	.0370	.0000	.0170	.961	.958	+ .003
.0010	13.9	.00239	.0489	.0047	.0217	.951	.945	+ .006
.0020	14.0	.00340	.0583	.0583	.0268	.940	.934	+ .006

TABLE VIII

CALCULATIONS ON SOLUBILITY RELATIONS OF BARIUM IODATE, $Ba(IO_3)_2$. DATA TAKEN FROM TABLE GIVEN BY LEWIS AND RANDALL, REF. 7B, P. 375.

$S_0 = 0.000790\ M. \quad -\text{Log} f = 0.996\sqrt{\mu}$

Solvent salt equiv. per liter	μ	$\sqrt{\mu}$	Log $\frac{S}{S_0}$	—Log f found	—Log f calc.	f found	calc.	Diff
SOLVENT WATER								
0.0000	0.00237	0.0487	0.0000	0.0487	−0.0487	0.894	0.894	0.000
SOLVENT $Ba(NO_3)_2$								
.0010	.00482	.0697	.0259	.0746	.0695	.841	.853	− .008
.0025	.00896	.0946	.0527	.1014	.0940	.792	.805	− .013
.0100	.0310	.1760	.1255	.1742	.175	.668	.668	± .000
.025	.0759	.2752	.2276	.2763	.274	.530	.532	− .002
SOLVENT KNO_3								
.002	.00444	.0666	.0116	.0603	.0663	.870	.858	− .012
.010	.01274	.113	.0629	.1116	.1122	.773	.772	+ .001
.050	.0528	.230	.233	.282	.2320	.535	.586	− .051

potassium cobalticyanide, $K_3Co(CN)_6$, upon the solute oxalonitro (see Fig. 2 and Table I), where the activity coefficient differs from the theoretical value by as much as 1.2% at an ionic strength of 0.0015. That this effect cannot be due to a peculiarity of the cobalticyanide ion $Co(CN)_6^{---}$ alone, but is more probably to be ascribed to an interaction between this ion and the complex ions of the saturating salt is evident when we consider Fig. 3 and Table II where potassium cobalticyanide gives satisfactory agreement with another uni-univalent solute—thiocyanato-nitro. It is possible that the explanation of these more special minor effects will be found to be due to the interaction between the residual fields of force of such ions originating from an unequal distribution of electric charges within the complex ion, as well as from their size and construction in other respects, as was pointed out in Part IV.

In conclusion we wish to express our indebtedness to the donors of the William Bayard Cutting Traveling Fellowship of Columbia University for the grant which permitted one of us (V. K. L.) to engage in this work.

Summary

1. The thermodynamically correlated expressions given previously for the concentration dependence of the osmotic and activity coefficients of uni-univalent electrolytes have been extended to include salts of higher valence types, on the assumption that these coefficients are determined in highly dilute solution solely by inter-ionic electrostatic forces. By introducing the concept of ionic strength, under certain restrictions, the relations are extended to include mixtures of electrolytes of different valence types.

2. The general equations applicable for the ideal region are: $1-\varphi = \alpha z_1 z_2\sqrt{\mu}$, and $-ln\ f = 3\alpha z_1 z_2\sqrt{\mu}$, where φ and f refer to the osmotic and activity coefficients, respectively; z_1, z_2 are the valences of the ions of the salt in question; μ is the ionic strength of the solution defined simply as the sum of the equivalent concentrations of each binary salt present in the mixture multiplied by the mean value of the valences of their respective ions; α is a constant, involving the dielectric constant of the solvent and the temperature.

3. It is shown that these ideal equations, as well as those applicable for the more concentrated non-ideal region, where an additional linear term is necessary to account for the individual properties of the ions, follow as a direct consequence of the independent theoretical considerations of P. Debye and E. Hückel.

4. Experimental data verifying the general ideal equations are given. The experiments involve measurements on the change of solubility of sparingly soluble electrolytes due to the presence of added electrolytes of various valence types for concentrations extending from 0.02 *M* to 0.00005 *M*.

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