At ionic strengths above 0.01 *M* the results deviate from the limiting equation expressing the theory at very small concentrations in the direction of too large values of the activation, as has been found with almost all substances previously investigated. Moreover, the deviations differ considerably in the case of the different added salts. The magnitude of the variations of the mean activation ($\sqrt{\alpha_{Ag}\,\alpha_{IO_3}}$) at an ionic strength of 0.08 *M* ($\sqrt{\Sigma(cz^2)} = 0.4$) is as follows: potassium chlorate, 0.762; potassium nitrate, 0.744; potassium sulfate, 0.699; magnesium sulfate, 0.743; theory, 0.701.

Summary

The solubility of silver iodate has been determined at 75° in pure water (where it is 0.000840 *M*) and in the presence of potassium perchlorate, nitrate and sulfate, and of magnesium sulfate and barium nitrate, at concentrations ranging from 0.0002 to 0.1 *M*. The results conform, up to an ionic strength of 0.01 *M*, almost completely with the limiting equation of Debye and Hückel, and supplement the earlier work of Brönsted and La Mer in affording a particularly good verification of the ion-attraction theory at very small concentrations. Not only is the predicted functional relation between activation and concentration shown to be correct, but also the numerical coefficient of the equation is that required by the theory. At higher ionic strengths the observations show the usual deviations in the direction of too large mean activation values; thus, at an ionic strength of 0.08 *M* in the presence of potassium perchlorate, nitrate and sulfate, and of magnesium sulfate, these deviate from the value 0.701 given by the limiting expression for zero concentration by 8.7, 6.1, —0.3 and 6.0%, respectively.

Since these experiments were made at 75°, while the earlier ones were at room temperature, they afford specifically a confirmation of the theoretical effect of varying the temperature and of the concomitant variation of the dielectric constant in the case of the solvent water.

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[CONTRIBUTION FROM THE NELA RESEARCH LABORATORY]

THE ELECTROSTATIC VIRIAL OF STRONG ELECTROLYTES

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The thesis that "strong electrolytes" are almost completely dissociated in dilute aqueous solution, and that the failure of proportionality to concentration of osmotic pressure and of electrolytic conductivity is to be attributed to electrostatic forces between the ions has been defended by so many authors that even an enumeration is impracticable in a brief note.[1] From the standpoint of *a priori* plausibility, it may be pointed out that

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[1] Compare Milner, *Phil. Mag.*, 25, 743 (1913).

the application of the usual criteria for discriminating between physical and chemical phenomena would point unmistakably to a physical explanation of the "undissociated part" of strong electrolytes in dilute aqueous solution, since the "degree of dissociation," by any given method of measurement and expression, shows an independence of atomic (or radical) weight, or place in the periodic system, which is quite unknown in really chemical properties. On the other hand, the dependence of the "degree of dissociation" on the valence product of the electrolyte concerned, that is to say, on the product of the electrostatic charges of the ions produced, is almost incontrovertible proof that the effect under consideration is of electrostatic origin. From the quantitative standpoint the calculations of Milner[2] and of Ghosh showed at any rate that the electrostatic virial is of the right order of magnitude to account for the observed "degree of dissociation" of strong electrolytes. More recently, Debye and Hückel[3] have derived expressions for the osmotic pressure and electrolytic conductivity of strong electrolytes which with but a single arbitrarily assignable constant—the effective ionic radius—agree within the error of experiment with measurements in even fairly concentrated solutions. On the theoretical side, these authors have left unanswered two questions bearing on the validity of their equations.

Milner's earlier figure for the electrostatic virial[2] is approximately two-thirds that found by Debye and Hückel,[3] and neither they nor Noyes[4] offer any explanation of the discrepancy. Moreover, all these authors make calculations in which the dielectric constant is treated as independent of temperature, although all of them recognize that it is not independent and speculate on the reason why this false assumption does not lead to erroneous results.[5] A study of their derivations has led to the apparently inescapable conviction that both of these discrepancies are due to a confusion of thermodynamic quantities.

All the authors considered start with an expression represented by the letter U for the energy of an ion as an electrostatic condenser in terms of κ (or D) the dielectric constant of water. But the measured dielectric constant of a liquid is proportional to the electrical energy obtainable from a condenser charged (and discharged), at constant temperature and pressure, to (and from) a given potential. It tells nothing about the total energy U of the condenser; what it measures is the free energy (at constant pressure), F.

From ΔF can be calculated ΔA, and from this the defect in osmotic pressure, without requiring any knowledge of temperature coefficients

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[2] Milner (a) *Phil. Mag.*, **23**, 551-78 (1912); (b) Ref. 1, pp. 742-751.

[3] Debye and Hückel, *Physik. Z.*, **24**, 185-206, 305-325 (1923).

[4] Noyes, THIS JOURNAL, (a) **46**, 1080-97, (b) 1098-1116 (1924).

[5] See also Gross and Halpern, *Physik. Z.*, **26**, 403-7 (1925).

at all. *For simplicity the symbols ΔA, ΔU, ΔF and ΔH will be made to stand for the departures from perfect gas conditions; and similarly ΔP will be the difference of the osmotic pressure from that given by the gas law.* Since "A" is being used for "work content," Noyes's coefficient "A" will be represented by the letter "b." The notation is otherwise that of Noyes.[4]

$$\Delta F = -\frac{b\nu^2\sqrt{\Sigma(c\nu^2)}}{\mathrm{K}^{1.5}\,T^{0.5}} \qquad (1)^6$$

$$\Delta A = -\frac{1}{c}\int_0^c \Delta F\,\mathrm{d}\,c = -\frac{b\nu^2\sqrt{\Sigma(\nu^2)}}{c\,\mathrm{K}^{1.5}\,T^{0.5}}\int_0^c c^{0.5}\,\mathrm{d}\,c \qquad (2)$$

$$= -\frac{b\nu^2\sqrt{\Sigma(\nu^2)}}{c\,\mathrm{K}^{1.5}\,T^{0.5}}\left(\frac{2}{3}\,c^{1.5}\right) = -\frac{2}{3}\,\frac{b\nu^2\sqrt{\Sigma(c\nu^2)}}{\mathrm{K}^{1.5}\,T^{0.5}} \equiv \frac{2}{3}\,\Delta F$$

But the difference, ΔP, of the osmotic pressure from that calculated by the perfect gas law, for an electrolyte giving two ions of equal valence, ν, is related to ΔA by the equation:

$$\mathrm{d}\,(2\Delta A) = -\Delta P\,\mathrm{d}\,V \text{ whence } \Delta P = -\frac{\mathrm{d}\,(2\Delta A)}{\mathrm{d}V} \qquad (3)$$

since V is molecular volume, $V \equiv 1/c$ and

$$\Delta P = \frac{\mathrm{d}}{\mathrm{d}V}\left(\frac{4}{3}\,\frac{b\nu^2\sqrt{2\nu^2}}{\mathrm{K}^{1.5}\,T^{0.5}}\,V^{-0.5}\right) = -\frac{2}{3}\,\frac{b\nu^2\sqrt{2\nu^2}}{\mathrm{K}^{1.5}\,T^{0.5}}\,V^{-1.5} \qquad (4)$$

$$= -\frac{2}{3}\,\frac{bc\nu^2\sqrt{2c\nu^2}}{\mathrm{K}^{1.5}\,T^{0.5}}$$

which is identical with the "virial" term in Noyes's[7] expression for osmotic pressure.

With regard to Milner's expression, Noyes[8] points out that its ratio to the Debye and Hückel formula is approximately $^2/_3$. The departure is no more than can be accounted for by the error in extrapolating from "m = 16" to "$m = \infty$," concerning which Milner himself says:[9] "the extrapolation of these curves to the axis is certainly a rather violent one, but it may be done with some confidence by observing the following points." In particular, the ratio is high for small values of "h" (low concentrations), but Milner's extrapolation for the smallest value of "h" seems forced.[10] It is very probable that a more accurate extrapolation[11] would have given exactly two-thirds of the Debye and Hückel value for $-\Delta F$[12], in which case Milner's value is numerically identical with $-\Delta A$.

[6] Except for writing $-\Delta F$ instead of ΔU, this is Noyes's Equation 15, Ref. 4 a, p. 1085.

[7] Ref. 4 a, p. 1092, Equation 31.

[8] Ref. 4 a, p. 1087.

[9] Ref. 2 a, p. 577.

[10] The lines for h = 0.109 of the plot on p. 577.

[11] Anyone who has studied the method of extrapolation used by Milner will be moved to admire Milner's diligence, but hardly tempted to try to increase the accuracy of the extrapolation by carrying the calculation to higher values of "m."

[12] Called by them, as already explained, $-\Delta U$.

Without attempting a formal proof that Milner's procedure[11] leads to $-\Delta A$, it may be pointed out that Milner gives[13] reasons for expecting the result to be numerically less than $-\Delta F$:

> "If V_p were only independent of ν, the arithmetical calculation would be much simpler. In order to obtain numerical values of the average virial, so that a curve showing the way in which it varies with the concentration can be plotted, I have contented myself with a calculation from an approximation to (38) for the virial contribution, which is explained and justified in the following paragraph." ...." and secondly, the mean virial of the arrangement will not be exactly the same as it would be on a random distribution, because the inter-ionic forces as well as affecting the chance of a given arrangement of signs, will also affect the mean distances of the ions. We shall here, however, neglecting the second of these effects in comparison with the first, assume that the mean virial of the arrangement is still given by $\Sigma_{\nu = 1}^{m} \pm whu_\nu$ in the modified distribution."

Now, the change in "the mean distances of the ions" is the occasion for the difference between $-\Delta A$ and $-\Delta F$ (in the case considered by Milner, namely, when K, the dielectric constant, is independent of temperature $-\Delta U = -\Delta F$). Consequently, a calculation in which "the mean distances of the ions" are not allowed to vary might be expected to give $-\Delta A$.

It remains to reconcile the formula of Debye and Hückel with the second-law equation

$$\mathrm{d}\left(\frac{-\Delta A}{T}\right) = \frac{\Delta U}{T^2}\,\mathrm{d}T \tag{5}$$

It appears to be almost universally admitted that the derivation of Debye and Hückel would be correct for a liquid whose dielectric constant, κ, had no temperature coefficient; and, further, that the values of ΔA and ΔF ought not to depend on the temperature coefficient of κ. If both these statements are true, Equation 2 for ΔA is general and the general equation for ΔU can be found by performing the differentiation called for by Equation 5.

$$\Delta A = -\frac{2}{3}\,\frac{b\nu^2\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\,T^{0.5}} \tag{2}$$

$$\begin{aligned} \mathrm{d}\left(\frac{-\Delta A}{T}\right) &= +\frac{2}{3}\,b\nu^2\sqrt{\Sigma(c\nu^2)}\;\mathrm{d}\,(\kappa^{-1.5}\;T^{-1.5}) \\ &= \frac{2}{3}\,b\nu^2\sqrt{\Sigma(c\nu^2)}\;(-1.5\,\kappa^{-2.5}\,T^{1.5}\,\mathrm{d}\kappa - 1.5\,\kappa^{-1.5}\,T^{-2.5}\mathrm{d}T) \qquad (6) \\ &= \frac{\Delta U}{T^2}\,\mathrm{d}T \end{aligned}$$

whence

$$\Delta U = -\frac{b\nu^2\sqrt{\Sigma c\nu^2}}{\kappa^{1.5}\;T^{0.5}}\left(\frac{\mathrm{d}\;ln\;\kappa}{\mathrm{d}\;ln\;T} + 1\right) \tag{7}$$

This equation differs from Equation 15 of Noyes[14] in two respects, the reversal of the convention as to the sign of ΔU, and the presence of the

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[13] Ref. 2 a, pp. 571–572.

[14] Ref. 4 a, p. 1085.

factor $\left(\frac{\mathrm{d}\,ln\,\kappa}{\mathrm{d}\,ln\,T}+1\right)$, a factor which would disappear (by becoming unity) for a liquid whose dielectric constant was independent of temperature.

The best available measurements, over a wide range of temperature, of the dielectric constant of water are those of Lili Kockel,[15] which between 10° and 100° agree within the error of experiment with the equation

$$\kappa = 400{,}000\ T^{-1.5} \tag{8}$$

Below 8°, as might have been expected, the relation is less simple.

Differentiating Equation 8:

$$\mathrm{d}\,ln\,\kappa/\mathrm{d}\,lnT = -1.5 \tag{9}$$

whence Equation 7 becomes

$$\Delta U = +\frac{1}{2}\,\frac{b\nu^2\sqrt{\Sigma(c\nu^2)}}{\kappa^{1.5}\,T^{0.5}} \tag{10}$$

In other words, when account is taken of the temperature coefficient of the dielectric constant of water, a value for ΔU results which is half as large as, and opposite in sign to, that given by the original Debye and Hückel equation. ΔH is similarly altered, but the expressions for ΔF, ΔA and ΔP are unchanged.

Summary

1. Since the customary methods of measuring the dielectric constant of water involve measurements of the electric work obtainable by discharging at constant pressure a condenser filled with water, a virial term for the energy of strong electrolytes in aqueous solution, derived from κ, the dielectric constant of water, should be denoted by ΔF (free energy at constant pressure), not ΔU (total internal energy).

2. Only if the dielectric constant is independent of temperature are these two thermodynamic functions equal. In general, the expressions for ΔU and likewise for ΔH must be multiplied by the factor, $1 + \mathrm{d}\,ln\,\kappa/\mathrm{d}\,ln\,T$. According to the best available data, the value of this factor for water, between 10° and 100°, is —0.5.

3. Evidence, but not proof, is given that Milner's method of calculating the virial gives neither ΔU nor ΔF, but ΔA (work content = Helmholtz's free energy). For an inverse square force, $\Delta A = {}^2/_3\,\Delta F$.

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[15] Kockel, *Ann. Physik* [4] **77,** 417–448 (1925). Instead of Equation 8, the author gives, p. 433, the exponential, $\epsilon = 87.9\ e^{-0.0047t}$, whose average deviation from the data is twice that of (8).

So far as absolute magnitude is concerned these results are dependent on Isnardi's value for the dielectric constant of toluene at 22°. The results of W. F. Powers and J. C. Hubbard [*Phys. Rev.*, [2] **15,** 535–536 (1920)] and of Jezewski [*J. phys.*, [6] **3,** 293–308 (1922)], both by absolute methods, are several per cent. larger than those of Kockel at the same temperatures. An increase in the *coefficient* of (8) would leave (9) unchanged and would, therefore, have no effect on the *coefficient* of Equation 10. It would, however, by increasing $\kappa^{1.5}$, diminish the *numerical* value of ΔU, ΔH, ΔA, ΔF and ΔP, and correspondingly increase the calculated value of the "activation," (Noyes, Ref. 4 b, p. 1099).

4. This agrees with the observation of Noyes that Milner's virial is $^2/_3$ that of Debye and Hückel.

5. The osmotic pressure can be calculated from ΔA and hence from ΔF, without a knowledge of the temperature coefficient of the dielectric constant of water.

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THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN GLYCEROL-WATER MIXTURES

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Comparatively few measurements of the electromotive force of concentration cells in other than aqueous solutions have been made. In the main these have been limited to cells with lithium chloride in a number of different alcohols and to hydrochloric acid in ethyl alcohol and alcohol-water mixtures.[1] In the present paper are given the results of measurements of the electromotive forces at 25° ± 0.01° of cells of the type, $H_2 | HCl\ (M) | AgCl | Ag$, in which the solvents used were 1 and 5 mole-per cent. of glycerol.

Apparatus, Materials and Procedure

The cell was of the usual H-shaped type into one arm of which the silver chloride electrode was inserted while the other bore the platinum electrode together with an outlet tube for the hydrogen. At the base of this latter arm was a pointed inlet tube through which the hydrogen passed in small bubbles over the platinized platinum electrode.

The silver-silver chloride electrodes were made in the manner described by Noyes and Ellis,[2] the silver being formed from silver oxide as was done by Lewis.[3] The silver chloride was formed on the electrode by making it the anode in a 0.75 *M* hydrochloric acid solution for five hours with a current of 0.004 ampere. A number of different sets of electrodes were made throughout the course of the investigation. The hydrogen electrodes consisted of platinized platinum foil and were remade after every third or fourth determination.

The hydrochloric acid was prepared by diluting by about one-half a high grade acid and redistilling. The middle fraction was diluted with distilled water and the concentration determined by gravimetric analysis. The glycerol used was a high grade product and no attempt was made to further purify it. Its water content was determined by measurements of its density. The solutions were made up in each case by adding to a weighed amount of the redistilled hydrochloric acid sufficient distilled water

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[1] Pearce and Mortimer, This Journal, **40,** 509 (1918). Pearce and Hart, *ibid.*, **44,** 2411 (1922). Danner, *ibid.*, **44,** 2832 (1922). Harned and Fleysher, *ibid.*, **47,** 82 (1925). Nonhebel and Hartley, *Phil. Mag.*, [6] **50,** No. 298, 729 (1925).

[2] Noyes and Ellis, This Journal, **39,** 2532 (1917).

[3] Lewis, *ibid.*, **28,** 166 (1906).