From these data, it is, of course, impossible to say how far the Debye–Hückel limiting law involving perchlorates and nitrates will hold for activity coefficients. However, in light of the fact that a constant value of d results in agreement of experiment and theory for the chlorides and bromides up to $0.1 N$, it is reasonable to assume that the limiting law would hold equally well for the perchlorates and nitrates.

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The Application of Onsager's Theory of Conductance to the Conductances and Transference Numbers of Unsymmetrical Electrolytes

By J. L. Dye and F. H. Spedding

Consideration of the transference number behavior of unsymmetrical electrolytes in aqueous solution led to an examination of the mathematical development of Onsager's theory of conductance. A mathematical treatment of Onsager's theory of conductance is described, which employs graphical methods to evaluate integrals which were only approximately evaluated by Onsager. The approximate methods, while satisfactory for 1-1 electrolytes, are unable to explain the transference number behavior of unsymmetrical electrolytes. The new treatment of the theory was applied to the conductances and transference numbers of $CaCl_2$, $NdCl_3$ and $ErCl_3$. The agreement between theory and experiment was greatly improved for both transference numbers and conductances of these unsymmetrical electrolytes.

Introduction

In a theoretical study of the processes of diffusion and electrical conduction in electrolytic solutions, Onsager[2] developed equations which quantitatively describe the changes in conductance with concentration in sufficiently dilute solutions. Because the theory was developed for the individual ionic species in the solution, the results were also applicable to the transference numbers of the constituent ions. The theory predicted the transference number to be a linear function of the square root of the concentration in dilute solutions. This has actually been found to be the case for most electrolytes, and the slope of the resultant straight line agrees quite well with the predicted slope for 1-1 electrolytes. It has been pointed out, however,[3-5] that unsymmetrical electrolytes for which the transference numbers have been measured exhibit slopes which differ by as much as a factor of one-fifth from the slope predicted by the Onsager equation.

Because of this dependence upon charge type, it was deemed advisable to re-examine the mathematical development of the conductance equation. The change in the conductance of an electrolytic solution with concentration may be said to be due to two factors, which are called the "time of relaxation effect" and the "electrophoretic effect." The electrophoretic effect normally makes the larger contribution to the conductance. If the fundamental assumptions of Onsager's treatment of conductance are assumed to be correct, it can be shown that for ions of high charge an exponential expansion and subsequent neglect of high order terms in the usual treatment of the electrophoretic effect, is invalid even at quite low concentrations. In attempting to include the complete integral, however, the equation could not be put into an analytical form, and certain integrals were evaluated graphically. The results are compared with experimental values of the transference numbers and conductances.

Development of the Method

From the treatment of the electrophoretic effect upon conductance given by Onsager[2] one may obtain the electrophoretic correction to the conductance to be

$$|\Delta\lambda_j| = \frac{96,500}{450\eta} \int_{a_j}^{\infty} r \left[\sum_{i=1}^{s} (n_{ji} - n_i) \right] dr \qquad (1)$$

in which n_{ji} is the concentration of the ith kind of ion at a distance r from any j ion and is given by the Boltzmann distribution to be approximately

$$n_{ji} = n_i \exp \left[-\frac{e_i \psi_j^0}{kT} \right] \qquad (2)$$

in which ψ_j^0 is the electrostatic potential at a distance r from the jth ion and was found by Debye and Hückel to be

$$\psi_j^0 = \left[\frac{e_j e^{\kappa a_j}}{D(1 + \kappa a_j)} \right] \left[\frac{e^{-\kappa r}}{r} \right] \qquad (3)$$

The quantities in these equations are defined by

η is the viscosity of the solvent
e_i is the charge on the ith ion and includes the sign of the charge on the ion
k is the Boltzmann constant
D is the dielectric constant of the solvent
a_j is the mean distance of closest approach of the ions to the j ion

$$K^2 = \frac{4\pi e^2}{DkT} \sum_{j=1}^{s} n_i Z_i^2 \qquad (4)$$

s is the total number of kinds of ions in the solution, and e is the charge on the electron

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) (a) L. Onsager, Physik. Z., 28, 277 (1927); (b) L. Onsager and R. M. Fuoss, J. Phys. Chem., 36, 2689 (1932).

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publ. Corp., New York, N. Y., 1950, p. 165.
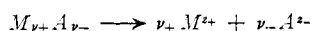
(4) L. G. Longsworth and D. A. MacInnes, This Journal, 60, 3070 (1938).

(5) F. H. Spedding, P. E. Porter and J. M. Wright, ibid., 74, 2778 (1952).

Combining 1, 2 and 3 gives for the electrophoretic correction to the conductance

$$|\Delta\lambda_j| =$$

$$\frac{96,500}{450\eta} \int_{a_j}^{\infty} r \left\{ \sum_{i=1}^{s} n_i e_i \left[\exp\left(\frac{-e_i e_j e^{K a_i e^{-Kr}}}{DkT(1 + Ka_j)r} \right) - 1 \right] \right\} dr$$

$$(5)$$

For an electrolyte which dissociates into ν ions by the scheme

$$M_{\nu_+} A_{\nu_-} \longrightarrow \nu_+ M^{z+} + \nu_- A^{z-}$$

and having a mean distance of closest approach of the ions, a, equation 5 may be specialized to

$$|\Delta\lambda_+| = M \int_{Ka}^{\infty} \rho \left\{ \exp\left[-|z_+|^2 P \frac{e^{-\rho}}{\rho} \right] - \exp\left[|z_+ z_-| P \frac{e^{-\rho}}{\rho} \right] \right\} d\rho \quad (6)$$

and

$$|\Delta\lambda_-| = M \int_{Ka}^{\infty} \rho \left\{ \exp\left[-|z_-|^2 P \frac{e^{-\rho}}{\rho} \right] - \exp\left[|z_+ z_-| P \frac{e^{-\rho}}{\rho} \right] \right\} d\rho \quad (7)$$

in which

$$\rho = Kr$$

$$M = \frac{96,500 DkT}{1800 \pi e \eta(|z_+| + |z_-|)}$$
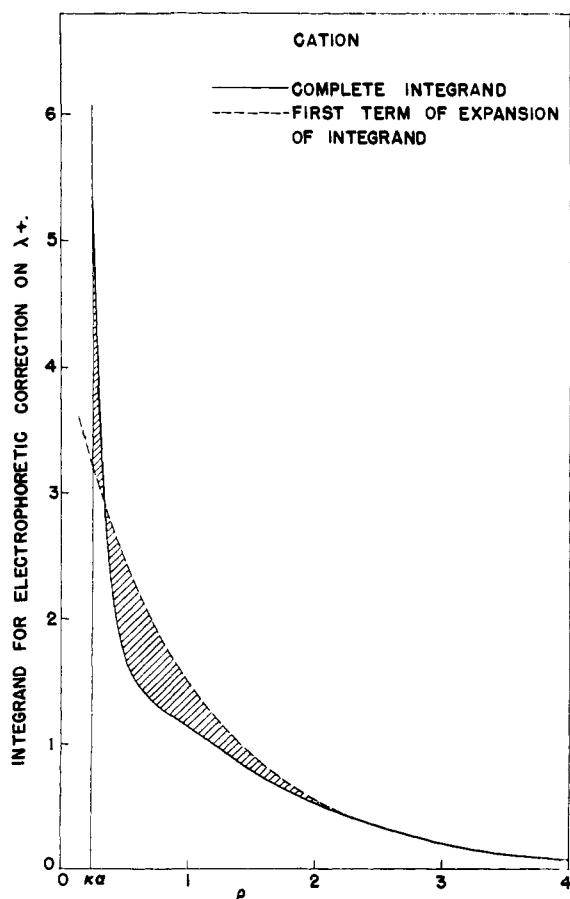
$$P = \frac{Ke^{Ka} \epsilon^2}{DkT(1 + Ka)}$$

Fig. 1.—Comparison of the integrands of the ordinary and extended equations for the electrophoretic correction on the conductance of 0.00333 M NdCl$_3$ at 25°.

and for this system

$$K^2 = \frac{4\pi\epsilon^2 N C_m}{10^3 DkT} [\nu_+ z_+{}^2 + \nu_- z_-{}^2]$$

in which

N is the Avogadro number
C_m is the concentration of the salt in moles per liter

We may let the integrand of equations 6 and 7 be represented by G_+ and G_-, respectively. The electrophoretic correction can then be determined at any specified concentration and a value, by a graphical integration of a plot of G_+ against ρ, and G_- against ρ, from Ka to infinity. It is to be noted that M is dependent upon the charge type of the electrolyte, and P is dependent also on the value of a, the mean distance of closest approach, and the concentration of the solution. Typical plots of G_+ against ρ and G_- against ρ are shown for 0.00333 M neodymium chloride ($a = 5.49 \times 10^{-8}$ cm.) in Figs. 1 and 2. For comparison purposes, plots of the integrands of the usual Onsager equation also are included. These plots of the usual equation include the complete first term of the expansion of the integrand not neglecting $â$.
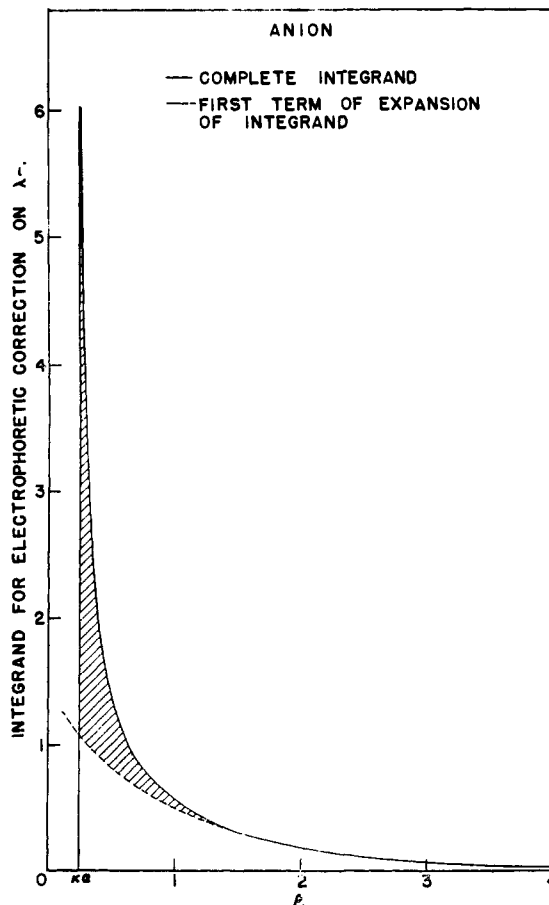

Fig. 2.—Comparison of the integrands of the ordinary and extended equations for the electrophoretic correction on the conductance of 0.00333 M NdCl$_3$ at 25°.

One can obtain the area under the curve from a large value of ρ to infinity analytically instead of graphically because $e^{-\rho}/e$ becomes very small for
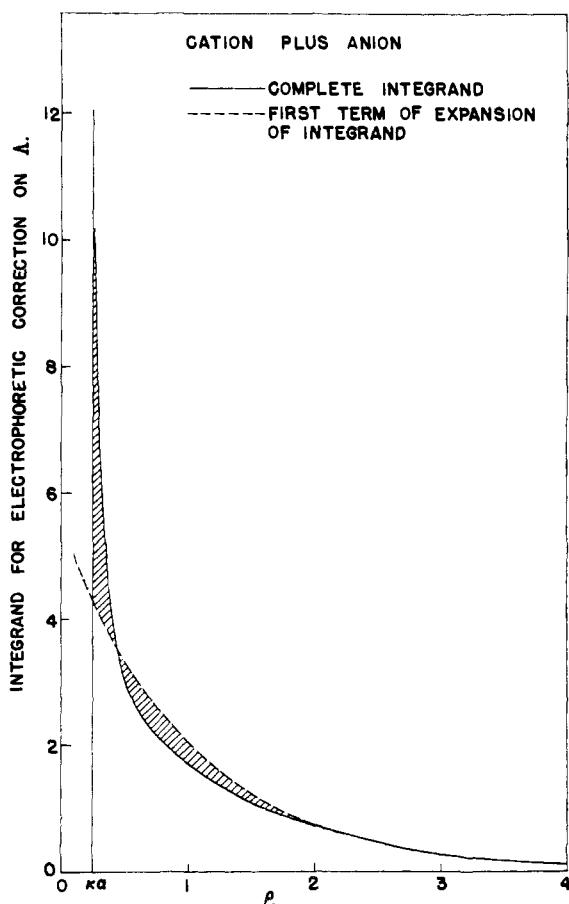
Fig. 3.—Comparison of the integrands of the ordinary and extended equations for the electrophoretic correction on the conductance of 0.00333 M NdCl₃ at 25°.

Fig. 4.—Comparison of theoretical and observed transference numbers of erbium chloride at 25°.

large values of ρ. Let F_j be the area under the curve G_j from a large value of ρ, say B, to infinity. Then F_j is given by

$$|F_j| = MP[|z_j|^2 + |z_j z_i|]e^{-B} \qquad (8)$$

This value of the integral from B to infinity is added to the integral from Ka to B which is determined graphically.

It is not necessary to perform a new graphical integration for each value of a used in this treatment. To determine the electrophoretic correction at a value of a different from that used in obtaining the graph, one uses the first graphical integration but with a different lower limit and at a slightly different concentration. This concentration is determined from K in the expression for P. For the case of 3–1 electrolytes

$$P = 7.135 \times 10^{-8} (e^{Ka}/(1 + Ka)) \qquad (9)$$

The same value of P that was used in the original graphical integration is used to solve for K by successive approximations, using the new value of a, and equation 9. The integral from the old lower limit K'a' to the new lower limit Ka, may be determined graphically.

The expressions for $\Delta\lambda_+$ and $\Delta\lambda_-$ due to the electrophoretic effect may be combined with the "time of relaxation" corrections to obtain the individual ionic conductances, λ_+ and λ_-, from
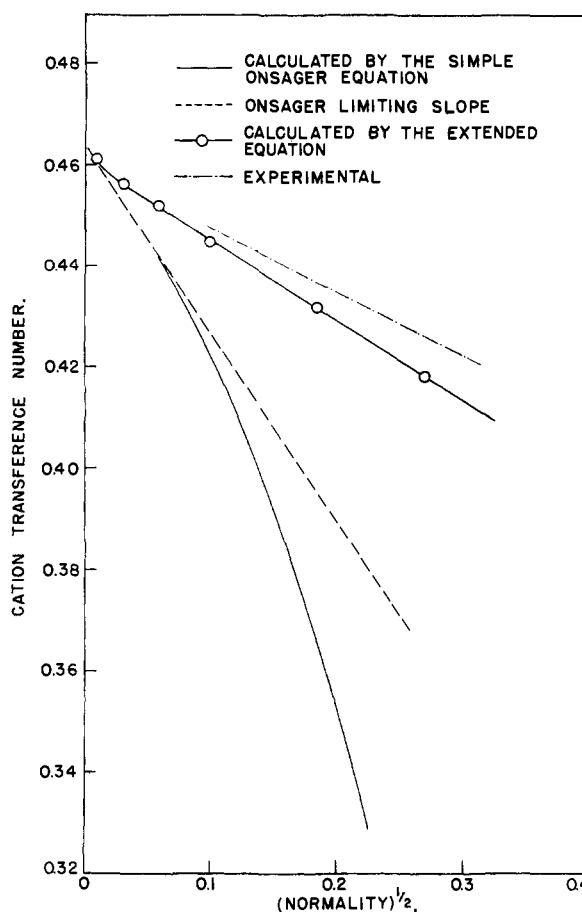
which Λ and T_+ can be obtained. The theoretical quantities determined by the method can thus be compared with experiment.

Comparison with Experiment

The values of λ_+, λ_-, Λ and T_+ for NdCl₃, ErCl₃ and CaCl₂ were calculated by the method outlined above, using values of a obtained from activity coefficient measurements. The values of a for NdCl₃ and ErCl₃, were taken from data obtained in this Laboratory.[6] Transference and conductance data for comparison purposes were also obtained in this Laboratory.[6] The value of a for calcium chloride is listed as 4.575×10^{-8} cm. by McLeod and Gordon.[7] Transference data for calcium chloride were obtained from measurements by Allgood, LeRoy and Gordon[8] and Longsworth.[9] Conductivity data for calcium chloride were obtained from measurements by Shedlovsky and Brown.[10]

Tables I and II give the values of the conductances and transference numbers of NdCl₃, ErCl₃ and CaCl₂ calculated by this method as well as those calculated using the Onsager equation as it is

(6) F. H. Spedding and J. L. Dye.

(7) H. G. McLeod and A. R. Gordon, THIS JOURNAL, **68**, 58 (1946).

(8) R. W. Allgood, D. S. LeRoy and A. R. Gordon, J. Chem. Phys., **13**, 466 (1945).

(9) L. G. Longsworth, THIS JOURNAL, **57**, 1185 (1935).

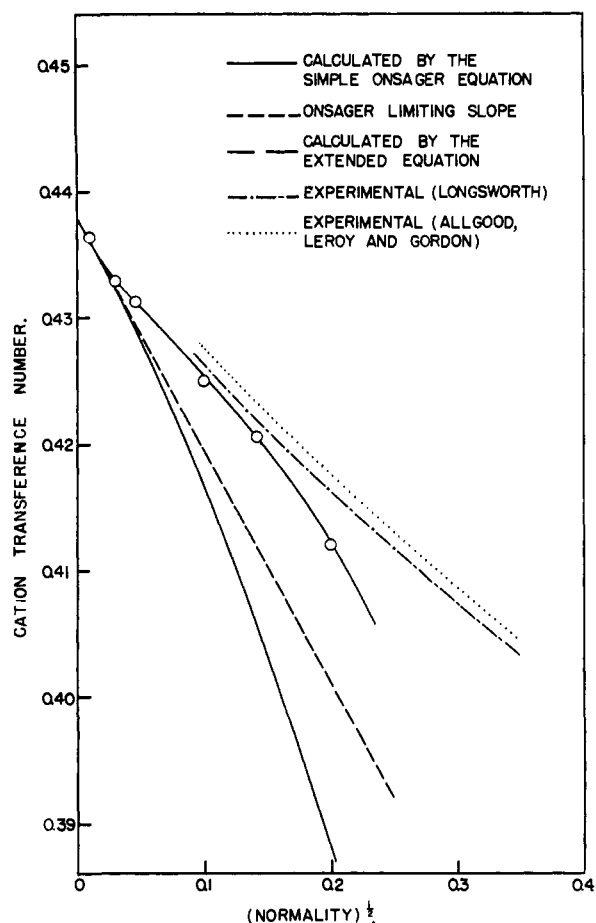(10) T. Shedlovsky and A. S. Brown, ibid., **56**, 1066 (1934).

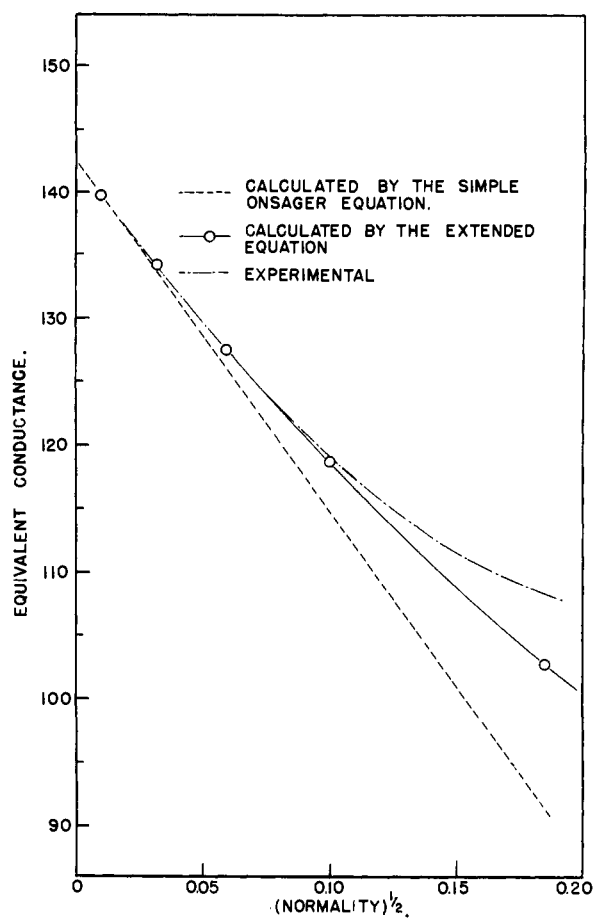Fig. 5.—Comparison of theoretical and observed transference numbers of calcium chloride at 25°.

ordinarily applied. The smoothed experimental values are also listed as well as the percentage deviations of the calculated values from experiment. The table for calcium chloride transference numbers gives the average of the values obtained by Allgood, LeRoy and Gordon,[8] and Longs-

TABLE I

COMPARISON OF THEORETICAL AND OBSERVED CONDUCTANCES OF NEODYMIUM CHLORIDE, ERBIUM CHLORIDE AND CALCIUM CHLORIDE AT 25°

Salt	Normality	Measured conductance	Calculated conductance Onsager	Calculated conductance Extended	Deviation, % Onsager	Deviation, % Extended
NdCl₃	0.00009294	143.1	142.91	143.05	0.14	0.03
	.0003340	137.1	136.88	137.37	0.16	.20
	.003507	130.4	129.14	130.53	1.00	.10
	.01002	122.1	117.72	121.05	3.6	.80
	.03506	109.9	93.35	103.87	15.0	5.5
	.07520	102.1	69.06	89.50	32.3	12.3
ErCl₃	.00009291	139.7	139.64	139.77	0.04	0.05
	.0009993	134.0	134.22	133.59	0.33	.16
	.003489	127.5	126.03	127.72	1.2	.17
	.009945	119.3	114.84	118.76	3.8	.42
	.03423	108.2	91.37	102.73	15.5	1.1
	.07257	99.6	68.15	89.15	31.6	10.2
CaCl₂	.0001000	134.1	134.06	134.08	0.03	0.01
	.0009000	130.6	130.53	130.76	.05	.12
	.002114	128.0	127.71	128.09	.24	.07
	.01000	120.3	118.16	119.38	1.7	.76
	.02000	115.6	110.85	113.49	4.1	1.7
	.04000	110.3	100.50	105.47	8.9	4.3

Fig. 6.—Comparison of theoretical and observed equivalent conductances of erbium chloride at 25°.

worth.[9] The transference numbers as calculated and measured for ErCl₃ and CaCl₂ are plotted in Figs. 4 and 5. The calculated and observed conductances of ErCl₃ are plotted in Fig. 6.

TABLE II

COMPARISON OF THEORETICAL AND OBSERVED TRANSFERENCE NUMBERS OF NEODYMIUM CHLORIDE, ERBIUM CHLORIDE AND CALCIUM CHLORIDE AT 25°

Salt	Normality	T_+ measured	T_+ calculated Onsager	T_+ calculated Extended	Deviation, % Onsager	Deviation, % Extended
NdCl₃	0.00009294	....	0.4731	0.4738	...	..
	.0003340	....	.4655	.4695	...	..
	.003507	....	.4551	.4657	...	..
	.01002	0.4650	.4370	.4592	4.8	1.2
	.03506	.4542	.3833	.4469	14.2	1.6
	.07520	.4440	.2924	.4339	32.6	2.3
ErCl₃	.00009291	....	.4605	.4610	...	..
	.0009993	....	.4524	.4563	...	..
	.003489	....	.4411	.4522	...	..
	.009945	.4471	.4217	.4451	5.7	0.45
	.03423	.4366	.3658	.4318	16.2	1.1
	.07257	.4262	.2723	.4182	36.17	1.9
CaCl₂	.0001000	....	.4361	.4364	...	..
	.0009000	....	.4322	.4329	...	..
	.002114	....	.4289	.4313	...	..
	.01000	.4271	.4167	.4245	2.4	0.60
	.02000	.4226	.4060	.4206	3.9	0.50
	.04000	.4167	.3850	.4120	7.6	1.1

Discussion of Results

It may seem inconsistent to retain the complete exponential in this treatment, while using the value

for the electrostatic potential which was obtained by neglecting higher terms in an expansion of the same exponential when solving the Poisson–Boltzmann differential equation. The Poisson–Boltzmann equation in its complete form is known to be inconsistent, however, and one can only hope that the potential function obtained by a solution of the consistent part of the equation is close to the true answer. The close fit of activity coefficient data to the theory of Debye and Hückel, derived on the basis of this assumption, seems to substantiate it as a good first approximation.

The true distribution of charge is given by

$$\sum_{i=1}^{s} n_{ji}e_i = \sum_{i=1}^{s} e_i n_i e^{-W_i/kT}$$

where n_{ji} is the concentration of i ions in the neighborhood of a j ion. Here W_i is the true extra energy an i ion obtains at the point in space considered. In the treatment of Debye and Hückel and also in this paper the approximation is made that

$$W_i \approx e_i \psi_i^0$$

Because of the close fit of activity coefficient data to the theory of Debye and Hückel, this approximation is believed to be more valid than it appears to be from observation of the Poisson–Boltzmann equation, and so $e_i \psi_j^0$ is used in the treatment of the electrophoretic effect as if it were the same as W_i. The agreement of the final result with both conductance and transference data seems to add weight to this premise.

Figures 4, 5, 6 and Tables I and II show that the new calculated values for the transference numbers agree with experiment much better than those calculated using the Onsager equation, while the fit of conductance data is also improved. The individual ionic conductances using this method result in quite different values than are obtained using the abbreviated equation, even at low concentrations where the Onsager equation begins to give the correct total conductance. The reason for this may be seen by comparing Figs. 1, 2 and 3.

Figure 3 is a plot of the integrand G of the sum of the ionic conductances, compared with the integrand of the ordinary Onsager equation, while Figs. 1 and 2 are similar plots for the cation and anion conductances only. The areas under the two curves for the total conductance are approximately equal because the shaded areas almost cancel each other. It is seen from Figs. 1 and 2 that no such complete cancellation occurs for the individual ionic constituents.

It is of interest to note that the calculation of a for the rare earth nitrates from conductance data by Spedding and Jaffe,[11] using the extended equation described above, gives a value of about 4.5 Å. for a, while the usual Onsager equation including a gives a value of about 2 Å. The value of 4.5 Å. for a is in accord with the physical meaning of a.

The original Onsager equation explains the transference number behavior of 1–1 electrolytes quite well. This is because the low charges on the ions result in small exponents in the integrands of equations 6 and 7, and also because, for symmetrical electrolytes, both the simple and the extended equation demand equal contributions to the conductance from the cation and anion.

The calculations described in this paper are of value because they show that the underlying assumptions made by Onsager are valid at higher concentrations than was previously thought to be the case. It will be necessary to know the extent of validity of the present physical assumptions before an extension of the present theories of conductance can be made. It would be desirable to develop mathematical methods to obtain the exact solutions of the Debye–Hückel and basic Onsager equations to determine the concentrations at which the present assumptions break down.

AMES, IOWA

(11) F. H. Spedding and S. Jaffe, THIS JOURNAL, **76**, 884 (1954).