repeated until all the variations of X and T have been satisfied.

TABLE III

PEAK CURRENT AS A FUNCTION OF ΔT

$\Delta T \times 10^4$	i_p(μamp.)	Δi_p[a]	% error[b]
20.00	0.7440	0.1412	26.0
10.00	.8121	.0731	8.26
5.000	.8479	.0373	4.21
2.500	.8664	.0188	2.12
1.250	.8758	.0094	1.06
0.6250	.8805	.0047	0.53
0.3125	.8829	.0023	0.26
0.1563	.8841	.0011	0.13
0	.8852[c]	0	0

[a] Difference between peak current at indicated value of ΔT and peak current at $\Delta T = 0$. [b] $(\Delta i_p/0.8852) \times 100\%$. [c] Extrapolated.

This calculation is very time consuming and tedious and is not practical unless computer facilities are available.[17] This is particularly so since the accuracy of the method depends on using small values of ΔT to reduce the error. The convergence of the calculations for decreasing values of ΔT was checked using the standard set of experimental and kinetic parameters (Table III).

As a compromise between accuracy and excessive machine time, a value of $\Delta T = 0.3125 \times 10^{-4}$ was used in this work. The results can be considered accurate within about 0.3%.

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[17] This problem was programmed for the IBM type 704 with the help of Mr. Lee F. Thompson of this Laboratory. It was Mr. Thompson's ability and patience which made this work possible.

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[CONTRIBUTION NO. 1525 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY

Conductance of Dilute Solutions of 1-1 Electrolytes[1]

BY RAYMOND M. FUOSS

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The conductance of solutions of 1-1 electrolytes decreases with increasing concentration because the mobility of the ions is decreased due to the action of long range interionic forces and because the concentration of free ions decreases due to association increasing with concentration. A conductance equation based on these effects is derived; it is applicable to 1-1 electrolytes in solvents of dielectric constant greater than about 15, at concentrations up to that corresponding to $\kappa a \approx 0.2$ (a = ionic diameter, κ = Debye–Hückel parameter). In solvents of high dielectric constant, the equation reduces to Onsager's limiting tangent while in solvents of low dielectric constant, it transforms into the classical Ostwald dilution law. In the intermediate range of dielectric constant, previously inaccessible to theoretical analysis, the equation describes conductance data in terms of three molecular parameters: the limiting conductance, the ion size and the association constant. Methods of applying the equation to experimental data are described.

The theory of the conductance of symmetrical electrolytes in dilute solutions now appears to be substantially complete; various parts of the derivation of the final equation are, however, scattered among a number of different publications.[2-11] The purpose of this paper is to present a summary derivation for the case of 1-1 electrolytes, unobscured by mathematical details, and to describe the analysis of conductance data by means of the theory.

Specific conductance, the experimentally observable quantity, is given by the ratio of current density to field strength X and is therefore proportion to $\Sigma n_i e_i u_i$, where n_i is the number of ions of species i per unit volume and e_i and u_i are, respectively, their charge and mobility. The equivalent conductance Λ is defined as the ratio of 1000 times the specific conductance to the concentration c in equivalents per liter. Consequently

$$\Lambda \sim \Sigma \gamma_i u_i \tag{1}$$

where γ_i is the fraction of the ions of species i which actually contribute to transport of charge at a given concentration. The Debye–Hückel–Onsager theory assumes that γ_i equals unity and ascribes the decrease of Λ with increasing concentration to a decrease in mobility arising from the electrostatic forces between the ions. The mobility is found to be

$$u_i = (u^0{}_i - \Delta u_i)(1 + \Delta X/X) \tag{2}$$

where $u^0{}_i$ is the limiting mobility at infinite dilution, Δu_i is the electrophoretic counter-velocity[12,13] of the solvent and ΔX is the braking relaxation field[14,15] which an ion creates by its motion. The asymmetry in the atmosphere of a moving ion also produces a virtual osmotic force ΔP which slightly increases conductance,[9] and finally a correction must in general be made for the increase in static viscosity of the solution due to the presence of the ions.[5] Since both $u^0{}_i$ and Δu_i are inversely proportional to viscosity, (2) becomes

$$u_i = (u^0{}_i - \Delta u_i)(1 + \Delta X/X + \Delta P/X)/(1 + Fc) \tag{3}$$

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where Fc equals 5/2 times the volume fraction of solute.[16]

Real ions occupy space and like any other molecules, occasionally collide. Due to electrostatic attraction between opposite charges, the dwell time of a pair of ions which have collided will be greater than that for two uncharged particles. During the time that two ions remain in contact, neither ion can contribute to transport of charge, and neither ion is to be counted as the member of the atmosphere of other ions because the pair present only a dipole field to distant ions. For symmetrical electrolytes, $\gamma_1 = \gamma_2$ and the identifying subscript can be dropped. By a device invented by Boltzmann, it can be shown[8] that

$$K_A c\gamma^2 f^2 = 1 - \gamma \qquad (4)$$

where K_A is a constant and f is the mean activity coefficient, given by[17]

$$-\ln f = \kappa e^2/2DkT(1 + \kappa a) \qquad (5)$$

The dynamic equilibrium between pairs of ions in contact and those at large distances from other ions thus follows the formal algebra of the classical thermodynamic law of mass action. Symbolically, then, the conductance of symmetrical electrolytes is expressed by the equation

$$\Lambda = \gamma(\Lambda_0 - \Delta\Lambda)(1 + \Delta X/X + \Delta P/X)/(1 + Fc) \qquad (6)$$

The theoretical evaluation of the various terms in (6) proceeds as follows. First, a model is chosen to represent the electrolytic system. The simplest model which includes the minimum number of properties which are necessary for a theoretical treatment consists of charged spheres of diameter a to represent the ions and a continuum to represent the solvent. (The impossibility of determining single ion activities requires that both anions and cations be represented by spheres of the same size; it obviously would be pointless to complicate the algebra by introducing two diameters a_1 and a_2 if experiment can only give the center to center distance of two ions at contact.) Using this model, the Navier–Stokes equation can be integrated,[4,10] to give the velocity field which is created in an electrolytic solution when the ions are in motion under the influence of an external electrical field. The final result is

$$\Delta\Lambda = \beta c^{1/2}/(1 + \kappa a) \qquad (7)$$

for the electrophoretic term in the conductance. Here β is the Onsager coefficient[12,13]

$$\beta = \sigma \mathfrak{F} e\kappa/3\pi\eta_0 c^{1/2} \qquad (8)$$

where $\sigma = (299.79)^{-1}$ converts electrostatic units to practical ones, $\mathfrak{F}$ is the Faraday equivalent, e is the electronic charge, κ is the Debye–Hückel parameter and η_0 is solvent viscosity.

In the absence of an external field, the ionic atmospheres are spherically symmetric; a perturbation in the distribution appears when the ions are subjected to an external field. Theoretical investigation of the asymmetry leads to a fourth-order differential equation; its integration[2,4] gives the asymmetry potential which produces the relaxation effect. A rather complicated function of κa is found for ΔX; for the case of dilute solutions, defined for present purposes as those for which $\kappa a < 0.2$, this function can be adequately approximated to give

$$-\Delta X/X = \alpha c^{1/2}(1 - \Delta_1 + \Delta_2) + \Delta X_v/X \qquad (9)$$

where

$$\alpha c^{1/2}(\Delta_1 - \Delta_2) = (\kappa^2 a^2 b^2/12)\,[0.9074 + \ln \kappa a + g(b) + \kappa a\,(0.7620 - 0.7071 g)] \qquad (10)$$

and

$$-\Delta X_v/X = [\kappa^2 ab/6\pi\eta(\omega_1 + \omega_2)]\,[0.2543 + 0.25 \ln \kappa a + 1/6b] \qquad (11)$$

The leading term of (9) is the Onsager limiting value[16] for the relaxation effect in the conductance

$$\alpha c^{1/2} = e^2\kappa/6DkT(1 + \sqrt{2}) \qquad (12)$$

The parameter b, introduced by Bjerrum,[18] is defined as

$$b = e^2/aDkT \qquad (13)$$

and g is a function of b

$$g(b) = (1 + 2b)/b^2 \qquad (14)$$

The reciprocal friction coefficients ω_1 and ω_2 in (11) translate into limiting single ion conductances when (11) is substituted into (6). In the final conductance equation, the term of order $\kappa^3 a^3$ in (10) is dropped, because its coefficient is very small, going through zero at $b = 2.266$. The retention of this term up to the point in the derivation represented by equation 10 was a necessary consequence of the expansion of the exponential integrals which appear in the explicit form of the relaxation field. The approximate cancellation in (0.7620–0.7071g), which permits dropping the term at this stage, only becomes apparent when higher terms from the exponential integrals are combined with terms from other sources.[11]

Finally, for the osmotic term ΔP, the value

$$\Delta P = Xec[(b - 1)/b^3][\kappa^2 a^2 b^2/12c] \qquad (15)$$

was found[9] by integrating the virtual force field around the reference ion, which is produced by its impacts with other ions.

When (7), (9) and (15) are substituted in (6), the result, after rearrangement, is

$$\Lambda = \gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma \log c\gamma + Jc\gamma)/(1 + Fc) \qquad (16)$$

where

$$S = \alpha\Lambda_0 + \beta$$
$$E = E_1\Lambda_0 - E_2$$
$$E_1 = 2.3026(\kappa^2 a^2 b^2/24c)$$
$$E_2 = 2.3026(\kappa ab\beta/16c^{1/2})$$
$$J = \sigma_1\Lambda_0 + \sigma_2$$
$$\sigma_1 = (\kappa^2 a^2 b^2/12c)[h(b) + 0.9074 + \ln(\kappa a/c^{1/2})]$$
$$\sigma_2 = \alpha\beta + (11\beta\kappa a/12c^{1/2}) - (\kappa ab\beta/8c^{1/2})[1.0170 + \ln(\kappa a/c^{1/2})]$$
$$h(b) = (2b^2 + 2b - 1)/b^3$$
$$F = \pi NR^3/300 = 6.308 \times 10^{21} R^3$$

The Einstein coefficient F above is the value for a salt with one ion much larger than the other (*e.g.*, Bu_4NBr); if both ions are large (*e.g.*, $Bu_4N \cdot BPh_4$), $F = 12.62 \times 10^{21} R^3$ where R is the average hydrodynamic radius. The accompanying table summarizes the useful combinations of parameters which appear in (16); the numerical values of the universal constants used in the calculation were those recommended[19] in 1952. For convenience,

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TABLE I

NUMERICAL VALUES OF CONSTANTS AT 25°

$$\begin{aligned}
\alpha &= 159.35/D^{3/2}\\
\beta &= 4.7779/\eta D^{1/2}\\
E_1 &= 2.5559 \times 10^5/D^3\\
E_2 &= 1122.3/\eta D^2\\
ab &= 560.37 \times 10^{-8}/D\\
\kappa/c^{1/2} &= 2.9127 \times 10^8/D^{1/2}\\
\kappa^2a^2b^2/12c &= 2.2200 \times 10^5/D^3\\
11\ \beta\kappa/12c^{1/2} &= 12.757 \times 10^8/\eta D\\
\kappa ab\beta/8c^{1/2} &= 974.8/\eta D^2\\
2\ \beta'' &= 708.85/D^{3/2}\\
0.4343\ e^2/kT_{25} &= 243.3 \times 10^{-8}
\end{aligned}$$

the coefficient $2\beta''$ in $-\log f^2 = -2\beta''c^{1/2}\gamma^{1/2}$ is also included.

We now shall consider the application of (16) to conductance data. The equation[20] contains three arbitrary constants, Λ_0 explicitly, and a (through J) and K_A (through γ) implicitly. The problem is to derive values for these constants from a measured set of Λ, c values. If ionic association is negligible, γ may be replaced by unity, and (16) reduces to

$$\Lambda_\eta = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc \qquad (17)$$

where

$$\Lambda_\eta = \Lambda(1 + Fc) \qquad (18)$$

The auxiliary variable Λ_η can be computed if viscosity data are available, because

$$F = [(\eta - \eta_0)/\eta_0 - S_\eta c^{1/2}]/c \qquad (19)$$

where S_η is the Falkenhagen–Dole coefficient[21]

$$S_\eta = (\beta/320)(\Lambda_0/\ \lambda_1^0\lambda_2^0)\{1 - 0.6863[(\lambda_1^0 - \lambda_2^0)/\Lambda_0]^2\} \qquad (20)$$

If the single ion conductances are nearly the same, (20) may be approximated by the simpler expression

$$S_\eta \approx \beta/80\Lambda_0 \qquad (21)$$

If viscosity data are not available, the Einstein term can be approximated by estimating R; alternatively, (18) is approximately

$$\Lambda_\eta \approx \Lambda + F\Lambda_0 c \qquad (22)$$

and (17) becomes

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Jc - F\Lambda_0 c \qquad (23)$$

Then the coefficient of the linear term $(J - F\Lambda_0)c$ must be separated into its components.[6] For simple inorganic salts, $F\Lambda_0 c$ is negligible, but it is clearly visible in the case of electrolytes with large ions such as the quaternary ammonium salts.

A preliminary value of Λ_0, obtained by extrapolation of Shedlovsky's function[22]

$$\Lambda'_0 = (\Lambda + \beta c^{1/2})/(1 - \alpha c^{1/2}) \qquad (24)$$

is used to compute S and E. Then

$$\Lambda'_\eta = \Lambda_\eta + Sc^{1/2} - Ec \log c \qquad (25)$$

is plotted against concentration; since

$$\Lambda'_\eta = \Lambda_0 + Jc \qquad (26)$$

we see that Λ_0 and J are determined as intercept and slope of the resulting straight line. (If the value of Λ_0 so obtained is significantly different from the preliminary value, S and E are recomputed and the extrapolation is repeated.) Finally, from a plot of J against a, the value of the ion size is interpolated.

When association is not negligible, equations 4 and 16 are combined to give

$$\Lambda_\eta = \Lambda_0 - S(c\gamma)^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_A c\gamma f^2 \Lambda_\eta \qquad (27)$$

and then we redefine Λ'_η as

$$\Lambda'_\eta = \Lambda_\eta + S(c\gamma)^{1/2} - Ec\gamma \log c\gamma \qquad (28)$$

New variables then are defined

$$\Delta\Lambda = \Lambda'_\eta - \Lambda_0 \qquad (29)$$

$$y = \Delta\Lambda/c\gamma \qquad (30)$$

$$x = f^2\Lambda_\eta \qquad (31)$$

which convert the conductance function to the linear form

$$y = J - K_A x \qquad (32)$$

and hence a plot of y against x evaluates J and K_A. In order to compute the variable y, values of γ and Λ_0 are needed. Now the terms in E and J are of opposite sign: if they are both neglected the conductance equation reduces to

$$\Lambda = \gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2}) \qquad (33)$$

the modified form of the Ostwald dilution law used formerly for analysis of conductance data.[23] Introduction of a variable z, defined by

$$z = S\Lambda_0^{-3/2}(c\Lambda)^{1/2} \qquad (34)$$

transforms (33) into

$$\gamma = \Lambda/\Lambda_0 F(z) \qquad (35)$$

The function $F(z)$ has been tabulated.[24] In order to use (32), a preliminary value of Λ_0, obtained by Walden's rule or by a free-hand extrapolation of the phoreogram, is used to compute S, E and z; then γ is obtained from (35) and Λ'_η and x are calculated. Trial values of Λ_0 are used in $\Delta\Lambda$ and y until the correct one is found; the "correct" one is the value which linearizes the y–x plot. Too small a trial value gives a curve which is concave up, while too large a value leads to a y–x plot which is concave down. Then in second approximation, γ is calculated by the equation

$$\gamma_2 = \Lambda_\eta/(\Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma \log c\gamma + Jc\gamma) \qquad (36)$$

where, on the right-hand side, the first approximation for γ from (35) and the values just obtained for Λ_0 and J are used. Then a second y–x plot is made.

The procedure can of course be considerably simplified if one of the constants is known.[25,26] For example, if the assocition constant is known, a plot of Λ_J against $c\gamma$, where

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(20) The equation differs from (18) of ref. 5 in the following details: (1) The terms in $c^{3/2}$ have been dropped. (2) J_1 is replaced by J and θ_1, θ_4 by σ_1, σ_2. In σ_1, $h(b)$ replaces $g(b)$ of θ_1, to include the term ΔP. In σ_2, 11/12 replaces 8/9 and 1.0170 replaces 0.8504; these small numerical changes resulted from the detailed study of the velocity field (ref. 10).

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$$\Lambda_J = \Lambda'_\eta + K_A c\gamma f^2\Lambda_\eta \tag{37}$$
$$= \Lambda_0 + Jc\gamma \tag{38}$$

evaluates Λ_0 and J; on the other hand, if J is known (from a known a-value), a plot of Λ_K against $c\gamma f^2\Lambda_\eta$ evaluates K_A

$$\Lambda_K = \Lambda'_\eta - Jc\gamma \tag{39}$$
$$= \Lambda_0 - K_A c\gamma f^2\Lambda_\eta \tag{40}$$

The first case occurs if the association constant satisfies the condition

$$K_A = K^0{}_A\, e^b \tag{41}$$

provided that $K^0{}_A$ is independent of solvent. Then values of K_A in solvents of high dielectric constant can be obtained by extrapolating on a $\log K_A - 1/D$ plot. In such solvents, association is slight, and the y–x plots are practically horizontal and hence useless for evaluating K_A. On the other hand, when the dielectric constant is small, the constant J becomes a small difference between two much larger quantities ($J = y + K_A x$, $y < 0$) and cannot be directly determined with any certainty. Then, assuming that a is independent of solvent composition, J can be computed, using the value obtained for a given salt in solvents of high dielectric constant, and K_A is obtained by use of (40) or as the slope of a plot of ($y + Jc\gamma$) against x.

As was mentioned above, the terms $Jc\gamma$ and $Ec\gamma \log c\gamma$ are of opposite sign, since $c\gamma < 1$ in any practical case. When the dielectric constant of the solvent is less than about 20, the term in K_A completely dominates the J and E terms, because K_A varies exponentially as D^{-1} while J and E are essentially algebraic functions of D. Also, for this range of dielectric constant, J and E can be fairly well approximated by their first terms

$$E \approx E_1\Lambda_0,\ J \approx \sigma_1\Lambda_0 \tag{42}$$

because the second terms are smaller than the first for any dielectric constant, and increase relatively slowly with decreasing dielectric constant. Hence

$$J \approx \kappa^2 a^2 b^2 \Lambda_0 k_J/12c \tag{43}$$

and k_J is a numerical constant in the range 2 to 3. Likewise

$$E \approx 2.303\kappa^2 a^2 b^2 \Lambda_0/24c \tag{44}$$

and in the usual working range of concentration, $\log c$ varies slowly from about minus 4 or 5 to minus 2 or 3. Hence

$$E \log c \approx -\kappa^2 a^2 b^2 \Lambda_0 k_E/12c \tag{45}$$

where k_E is a quasi-constant also in the range 2 to 3. Therefore the simultaneous neglect of both terms in replacing (27) by (33), the device used above in first approximation for γ, is justified.

A final comment concerning the range of applicability of (27) is needed. The integration of the equation of continuity, which leads to the relaxation field, yields an unwieldy collection of transcendental and algebraic terms. This function of κa can be simplified to a usable form by series expansion, but the expansion in turn becomes awkward to use if too many terms are retained. Therefore only terms up to order $c^{3/2}$ were retained in order to avoid an inconveniently long series. Numerically, this approximation is reliable only over the range $0 \leqslant \kappa a \leqslant 0.2$ and obviously (27) should never be applied to data for higher concentrations than correspond to $\kappa a \approx 0.2$. This cut-off has physical justification on two counts: (1) for $\kappa a > 0.2$, ions are on the average so near each other that the Debye model of a continuous space charge (ion atmosphere) becomes unrealistic and (2) in the equation of continuity which was integrated, terms which would lead to terms in the conductance of order $c^{3/2}$ were dropped. The limit $\kappa a \approx 0.2$ is practically useful in the design of conductance experiments, in that it states the highest concentration which is worth measuring, if the goal of the research is a reduction of the data to molecular parameters.

The general equation 27 has two limiting forms which have long been familiar: at low concentrations in solvents of high dielectric constant, it reduces to the Onsager limiting tangent, while in solvents of low dielectric constant, it reduces to the Ostwald dilution law. It therefore permits analysis of conductance data in any solvent (down to the range where triple ions and higher clusters must also be considered.[27]) In smenocolytic solvents,[28] or for salts[29] with very large ions in solvents of intermediate dielectric constant, the phoreogram usually lies above the Onsager tangent (anabatic) and conductance data can only give Λ_0 and a. In smenogenic solvents, on the other hand, association controls, and the data give only Λ_0 and K_A; in fact, if the dielectric constant is low enough, only the ratio Λ_0^2/K_A can be evaluated from conductance data. In the intermediate range, the data evaluate all three constants, Λ_0, a and K_A.

As the dielectric constant decreases, a continuous transition in the appearance of the conductance curve is observed: first, it drops below the Onsager tangent and becomes concave-down (catabatic). Usually this behavior indicates the onset of association (although some cases are known where the $c \log c$ term is numerically larger then Jc, and hence here a catabatic curve is also obtained, even when K_A is negligibly small). With further decrease in D, an inflection point appears in the working range of concentrations, due to the appearance of the product in (6): γ decreases from unity initially as the first power of c and asymptotically approaches zero while the mobility terms decrease initially as $c^{1/2}$. In the inflection range, the curve simulates linearity, of course; this behavior explains the (erroneous) statements that conductance curves "obey a square root law, but with a slope larger than the theoretical." With further decrease in D, the $\Lambda - c^{1/2}$ curves become very steep; here a $\log \Lambda - \log c$ plot is preferable. A slope of minus one-half on the latter scale means that the ion-ion pair equilibrium controls the behavior of the solute. Equation 27 thus bridges the former gap between systems with negligible association and those with marked association and provides a mathematical description of the transition.

NEW HAVEN, CONN.

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