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CONDUCTANCE OF STRONG ELECTROLYTES AT FINITE DILUTIONS

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The equivalent conductance Λ of strong electrolytes in solvents of high dielectric constant approaches linearity in the square root of concentration in the limit of infinite dilution. At finite dilutions, the conductance curve is concave upwards. The slope of the limiting tangent has been computed theoretically by Onsager^{1, 2} in terms of ionic charge, dielectric constant D and viscosity η of the solvent, absolute temperature T , universal constants, and one arbitrary constant, the limiting conductance Λ_0 of the solute. It has been surmised that the course of the actual conductance curve is a consequence of the finite size of real ions and of terms higher than linear in the charge of the reference ion; these were neglected in the derivation of the limiting law. It is the purpose of this communication to derive a conductance equation which is valid for nonzero concentrations. One additional arbitrary constant, the ion size a , suffices to reproduce experimental data up to about 0.1 normal for strong 1-1 electrolytes in water.

Briefly summarized, the derivation proceeds as follows: We start with the general equation of continuity³ which specifies the concentration of ions of one species in the vicinity of ions of other species in a solution of electrolyte which has reached a steady state under the influence of an external force (here, an electric field). The equation is first solved, neglecting terms of higher order, but using ions of finite size rather than point charges as the model. This first-order solution is then returned to the higher-order terms in the equation of continuity. Solution of the resulting perturbation problem gives the desired expression for the relaxation effect in the mobility to terms of order c and $c \log c$. On combining this result with the previous value³ of the electrophoresis calculated to the same order, the final conductance function is obtained.

Consider a solution containing N_i ions of charge e_i in a total volume V , where $i = 1, 2, \dots, s$. Locate two elements of volume dV_1 and dV_2 by vectors \mathbf{r}_1 and \mathbf{r}_2 , drawn from an arbitrary origin, as shown in Figure 1. If we know that a j -ion is in dV_1 , the concentration of i -ions in dV_2 will not equal $n_i = N_i/V$, the gross average, but will be $n_{ji}(\mathbf{r}_1, \mathbf{r}_{21})$, due to electrostatic and hydrodynamic interaction of the several ions. Let \mathbf{v}_{ji} represent the (mean) velocity of an i -ion in dV_2 when a j -ion is in dV_1 . Then, in terms of the symmetrical density functions

$$f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_j n_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_i n_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) = f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}), \quad (1)$$

the general equation of continuity

$$\text{div}_1 (f_{ij}v_{ij}) + \text{div}_2 (f_{ji}v_{ji}) = 0 \quad (2)$$

must be satisfied. In the conductance problem, (1) becomes simply

$$f_{ji}(r_{21}) = n_j n_{ji}(r_{21}) = n_i n_{ij}(r_{12}) = f_{ij}(r_{12}), \quad (3)$$

because the distribution depends only on relative and not on absolute location. We retain the idealized picture of the solvent as a viscous dielectric continuum in which the motion of the ions obeys Brownian motion kinetics; inertial effects are assumed

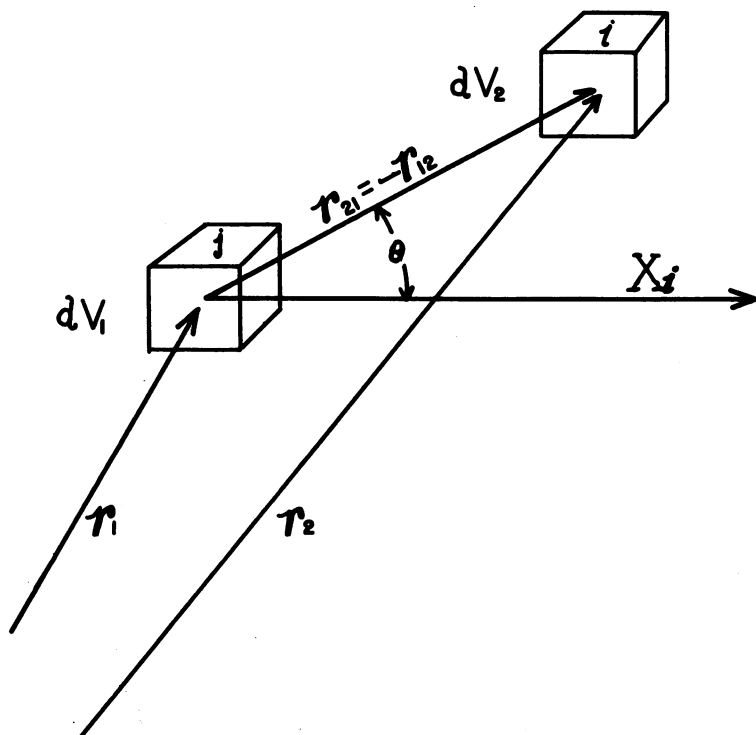


FIG. 1.—Definition of vectors

negligible. Accordingly, the pertinent properties of an ion of species j are its coefficient of friction $1/\omega_j$ and its electric charge e_j . In an electrical field X acting in the direction of the positive x -axis, the velocity of an isolated ion is therefore

$$v^{\circ}_j = X e_j \omega_j \mathbf{i}. \quad (4)$$

At finite concentrations, electrostatic interaction causes each ion to surround itself by an "atmosphere" carrying a compensating average charge density. Debye and Hückel⁴ computed the distribution of this shielding charge for the static case and obtained the familiar limiting result

$$\psi^{\circ}_j(r) = \frac{e_j e^{-\kappa r}}{Dr} \quad (5)$$

for the average potential of the electrostatic field surrounding a point ion. Motion of the ions in an external electric field distorts the charge distribution, so that the above potential must be replaced by

$$\psi(r) = \psi^\circ(r) + \psi'(r).$$

The density functions (3) likewise consist of radial and unsymmetrical parts.

In previous work, it was assumed that atmospheric charge densities of neighboring ions could be superimposed; careful investigations have shown that this is a good approximation in the computation of ψ° . We have satisfied ourselves that this use of the superposition principle introduces only quite small errors (of the order of κ^2) in our final results. Accordingly, we assume for the force on an i -ion in dV_2

$$\mathbf{K}_{ji} = X e_i \mathbf{i} - e_i \nabla_2 \psi'_i(a) - e_i \nabla_2 \psi_j(r_{21}). \quad (6)$$

This force contributes to the mean velocity of an ion according to (4). The Brownian motion produces an average velocity equal to $-\omega_i kT \nabla_2 \ln f_{ji}(r_{21})$. Finally, the local motion of the solvent is modified by the presence of another ion (with its atmosphere) in the vicinity. The resultant flow field $\mathbf{v}_i(r_{21})$ was computed by Debye and Hückel;⁵ we have used an alternative derivation which permits the boundary conditions to be stated in terms of the potential in all but a small part of the function. Hence, except for this small term (of order c in the final conductance equation) involving the Stokes radius, the hydrodynamic terms in the relaxation field contain the same parameter a as the electrostatic ones.⁶ Combining the various contributions to the velocity \mathbf{v}_{ji} of an i -ion in the vicinity of a j -ion, we obtain

$$\mathbf{v}_{ji}(r_{21}) = \mathbf{v}_i(r_{21}) + \omega_i [\mathbf{K}_{ji} - kT \nabla_2 \ln f_{ji}(r_{21})], \quad (7)$$

with a similar expression for $\mathbf{v}_{ij}(r_{12})$. We then substitute (6) in (7) and the result in (2). The divergence terms ($\text{div } \varphi \mathbf{A} = \mathbf{A} \cdot \text{grad } \varphi + \varphi \text{ div } \mathbf{A}$) are expanded, noting that $\nabla \cdot \mathbf{v}_i = 0$. Functions are reduced to those of one variable $r = r_{21} = -r_{12}$ according to the operational rules $\nabla_2 = -\nabla_1 = \nabla$; $\nabla_1 \cdot \nabla_1 = \nabla_2 \cdot \nabla_2 = \Delta$. Potentials are assumed to be of the form

$$\psi_j(r_{21}) = \psi^\circ_j(r) + \psi'_j(r), \quad (8')$$

$$\psi_i(r_{12}) = \psi^\circ_i(r) - \psi'_i(r), \quad (8'')$$

and the distribution functions are decomposed similarly:

$$f_{ji}(r_{21}) = f^\circ_{ji}(r) + f'_{ji}(r) = f_{ij}(r_{12}) = f^\circ_{ij}(r) - f'_{ij}(r). \quad (9)$$

The field strength is assumed to be below that at which any Wien effect is observable, so that $\psi' \sim X$, $f' \sim X$. In the above expansion, all terms in X^2 are therefore dropped; furthermore, the functions of spherical symmetry cancel each other because $\mathbf{v}_{ji} = \mathbf{v}_{ij} = 0$ when $X = 0$. The result of the above manipulation is

$$\begin{aligned} (e_i \omega_i - e_j \omega_j) X \mathbf{i} \cdot \nabla f^\circ_{ji}(r) - kT (\omega_i + \omega_j) \Delta f'_{ji}(r) - f^\circ_{ji} (e_i \omega_i \Delta \psi'_j - e_j \omega_j \Delta \psi'_i) - \\ (e_i \omega_i \nabla \psi'_j - e_j \omega_j \nabla \psi'_i) \cdot \nabla f^\circ_{ji} - f'_{ji} (e_i \omega_i \Delta \psi^\circ_j + e_j \omega_j \Delta \psi^\circ_i) - \\ (e_i \omega_i \nabla \psi^\circ_j + e_j \omega_j \nabla \psi^\circ_i) \cdot \nabla f'_{ji} + [e_i \omega_i \nabla \psi'_i(a) - e_j \omega_j \nabla \psi'_j(a)] \cdot \nabla f^\circ_{ji} - \\ (\mathbf{v}_i - \mathbf{v}_j) \cdot \nabla f^\circ_{ji} = 0. \quad (10) \end{aligned}$$

One boundary condition (impenetrability) arises from the requirement that the radial component of the relative velocity of any two ions in contact must vanish. Thus the sum

$$f_{ij}(\mathbf{v}_{ij} \cdot \mathbf{r}_{12}) + f_{ji}(\mathbf{v}_{ji} \cdot \mathbf{r}_{21})$$

has to vanish at $r = a$. With the convention $\mathbf{r}_{21} = \mathbf{r} = -\mathbf{r}_{12}$, this condition becomes

$$[(f_{ij}\mathbf{v}_{ij} - f_{ji}\mathbf{v}_{ji}) \cdot \mathbf{r}]_{r=a} = 0. \tag{11}$$

Let \mathbf{Y} represent the flow vector in the above bracket; then, by a calculation parallel to that which led to (10), we obtain

$$\begin{aligned} \mathbf{Y} = & (e_i\omega_i - e_j\omega_j)f'_{ji}\mathbf{X}\mathbf{i} - kT(\omega_i + \omega_j)\nabla f'_{ji} - f'_{ji}(e_i\omega_i\nabla\psi'_j - e_j\omega_j\nabla\psi'_i) - \\ & f'_{ji}(e_i\omega_i\nabla\psi^\circ_j + e_j\omega_j\nabla\psi^\circ_i) + f'_{ji}[e_i\omega_i\nabla\psi'_i(a) - e_j\omega_j\nabla\psi'_j(a)] - \\ & (\mathbf{v}_i - \mathbf{v}_j)f^\circ_{ji}, \end{aligned} \tag{12}$$

where $(\mathbf{Y} \cdot \mathbf{r}) = 0$ at $r = a$.

It will be more convenient to use the boundary condition in the form

$$Z(a) = 0, \tag{13}$$

where

$$Z(r) = \frac{(\mathbf{Y} \cdot \mathbf{r})}{x}. \tag{14}$$

The following operations are used in expanding (14): $\mathbf{i} \cdot \mathbf{r} = x$, $x/r = \cos \theta$; $\mathbf{i} \cdot \nabla f^\circ(r) = \partial f^\circ / \partial x$; $\nabla f^\circ(r) \cdot \nabla \psi'(r) = (df^\circ/dr) (\partial \psi' / \partial r) = (df^\circ/dr) [\partial(\psi' / \cos \theta) / \partial x]$; $\mathbf{r} \cdot \nabla f'(r) = r \partial f' / \partial r = x d(f' / \cos \theta) / dr$; $\mathbf{r} \cdot \nabla \psi^\circ(r) = r d\psi^\circ / dr$; $(\mathbf{v} \cdot \mathbf{r}) / x = v_r / \cos \theta$; $\mathbf{v} \cdot \nabla f^\circ(r) = v_r df^\circ / dr$. The result, after specializing to $s = 2$, is

$$\begin{aligned} Z(r) = & (e_1\omega_1 - e_2\omega_2)Xf^\circ_{21} - kT(\omega_1 + \omega_2) \frac{d}{dr} \left(\frac{f'_{21}}{\cos \theta} \right) - f^\circ_{21} \left\{ e_1\omega_1 \frac{d}{dr} \left(\frac{\psi'_2}{\cos \theta} \right) - \right. \\ & \left. e_2\omega_2 \frac{d}{dr} \left(\frac{\psi'_1}{\cos \theta} \right) \right\} - \frac{f'_{21}}{\cos \theta} \left(e_1\omega_1 \frac{d\psi^\circ_2}{dr} + e_2\omega_2 \frac{d\psi^\circ_1}{dr} \right) + f^\circ_{21} \left\{ e_1\omega_1 \frac{d}{dr} \left(\frac{\psi'_1}{\cos \theta} \right) - \right. \\ & \left. e_2\omega_2 \frac{d}{dr} \left(\frac{\psi'_2}{\cos \theta} \right) \right\} - (v_{1r} - v_{2r}) \frac{f^\circ_{21}}{\cos \theta}. \end{aligned} \tag{15}$$

Similar substitutions are made in (10), and from the Poisson equations

$$\Delta\psi'_j = - \left(\frac{4\pi}{D} \right) \sum_i \frac{f'_{ji}e_i}{n_i} \tag{16}$$

we obtain, on specializing to $s = 2$,

$$\Delta\psi'_1 = - \frac{4\pi f'_{12}e_2}{Dn_1} = \frac{4\pi f'_{21}e_2}{Dn_1} \tag{16'}$$

and

$$\Delta\psi'_2 = - \frac{4\pi f'_{21}e_1}{Dn_2}. \tag{16''}$$

These equations serve to eliminate the potentials from a number of terms. In one of the inhomogeneous terms, the Debye-Hückel approximation

$$\Delta\psi^{\circ}_j = \kappa^2\psi^{\circ}_j \quad (17)$$

is used; here

$$\kappa^2 = \left(\frac{4\pi}{DkT}\right)(n_1e_1^2 + n_2e_2^2). \quad (18)$$

The final result is the equation of continuity translated into a form ready for integration:

$$\begin{aligned} (e_1\omega_1 - e_2\omega_2)X \left(\frac{\partial f^{\circ}_{21}}{\partial x}\right) - kT(\omega_1 + \omega_2)\Delta f'_{21} + \left(\frac{4\pi f^{\circ}_{21}f'_{21}}{D}\right)\left(\frac{e_1^2\omega_1}{n_2} + \frac{e_2^2\omega_2}{n_1}\right) - \\ \left\{e_1\omega_1 \frac{\partial}{\partial x} \left(\frac{\psi'_2}{\cos\theta}\right) - e_2\omega_2 \frac{\partial}{\partial x} \left(\frac{\psi'_1}{\cos\theta}\right)\right\} \frac{df^{\circ}_{21}}{dr} - \kappa^2 f'_{21} (e_1\omega_1\psi^{\circ}_2 + e_2\omega_2\psi^{\circ}_1) - \\ \left(e_1\omega_1 \frac{d\psi^{\circ}_2}{dr} + e_2\omega_2 \frac{d\psi^{\circ}_1}{dr}\right) \frac{\partial}{\partial x} \left(\frac{f'_{21}}{\cos\theta}\right) + \left\{e_1\omega_1 \frac{\partial}{\partial x} \left(\frac{\psi'_1}{\cos\theta}\right) - \right. \\ \left. e_2\omega_2 \frac{\partial}{\partial x} \left(\frac{\psi'_2}{\cos\theta}\right)\right\} \frac{df^{\circ}_{21}}{dr} - (v_{1r} - v_{2r}) \left(\frac{df^{\circ}_{21}}{dr}\right) = 0. \quad (19) \end{aligned}$$

Investigation⁶ of (19) shows that the last five terms are of higher order in κ ($\sim c^{1/2}$) than the first three. We therefore define $F_{21}(r) = h_{21}(r) \cos\theta$ as the solution of

$$\begin{aligned} (e_1\omega_1 - e_2\omega_2)X \left(\frac{\partial f^{\circ}_{21}}{\partial x}\right) - kT(\omega_1 + \omega_2)\Delta F_{21} + \\ \left(\frac{4\pi f^{\circ}_{21}F_{21}}{D}\right)\left(\frac{e_1^2\omega_1}{n_2} + \frac{e_2^2\omega_2}{n_1}\right) = 0, \quad (20) \end{aligned}$$

subject to the boundary condition that the corresponding terms of (15) vanish at $r = a$:

$$\begin{aligned} \left[(e_1\omega_1 - e_2\omega_2)X f^{\circ}_{21} - kT(\omega_1 + \omega_2) \left(\frac{dh_{21}}{dr}\right) - \right. \\ \left. f^{\circ}_{21} \left\{ e_1\omega_1 \left(\frac{d\Phi_2}{dr}\right) - e_2\omega_2 \left(\frac{d\Phi_1}{dr}\right) \right\} \right]_{r=a} = 0. \quad (21) \end{aligned}$$

Here $\Phi_j(r) \cos\theta = \Psi_j(r)$, where $\Delta\Psi_j = -(4\pi/Dn_j)\sum_i F_{ji}e_i$; in other words, Ψ_j and F_{ji} are our previous ψ'_j and f'_{ji} , but subject to boundary conditions for non-zero radius instead of for the vanishing radius which was previously used.

Since the potentials are determined by fourth-order differential equations, we need three more boundary conditions: they are $\Psi(\infty) = 0$, $(\partial\Psi/\partial r)_{r=\infty} = 0$ and $\Psi(a-0) = \Psi(a+0)$. The latter leads to

$$\left(r \frac{\partial\Psi}{\partial r} - \Psi\right)_{r=a} = 0. \quad (22)$$

Falkenhagen and coworkers⁷ solved (20) using the same boundary conditions for

potential as those listed above, and using the Eigen-Wicke⁸ distribution, but they chose a rather arbitrary fourth condition. Their result differs from ours by terms of order κ^2 . In expanding (20) and (21), we use the Debye-Hückel approximation⁴ for the unperturbed potentials around ions of finite size

$$\psi^{\circ}_j = \left(\frac{e_j e^{-\kappa r}}{Dr} \right) \left[\frac{e^{\kappa a}}{(1 + \kappa a)} \right] \quad (23)$$

and the corresponding value for the distribution function

$$f^{\circ}_{21} \approx n_1 n_2 \left(1 - \frac{e_1 e_2 e^{-\kappa r}}{\mu D k T} \right), \quad (24)$$

where

$$\mu = (1 + \kappa a) e^{-\kappa a}. \quad (25)$$

The following abbreviations

$$\gamma^2 = q^2 \kappa^2 = \left(\frac{4\pi}{DkT} \right) \frac{n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2}{\omega_1 + \omega_2} \quad (26)$$

and the Bjerrum parameter

$$b = - \frac{e_1 e_2}{a D k T} > 0 \quad (27)$$

also aid in a compact formulation of the result.

The relaxation field ΔX is given by

$$-\Delta X = \text{grad}_x \Psi(a). \quad (28)$$

Solution of (20), followed by solution of the corresponding Poisson equation and adjustment to the boundary conditions, gives finally,⁶ on substitution in (28),

$$\frac{\Delta X}{X} = \frac{e_1 e_2 q^2 \kappa}{3 D k T (1 + q)} \frac{1 + (1 + q)(1 - [1 + \kappa a]/b)(\kappa a/2)}{(1 + \kappa a)(1 + q \kappa a + q^2 \kappa^2 a^2/3)}. \quad (29)$$

For convenience in later formulations, we write (29) in the form

$$\frac{\Delta X}{X} = \frac{e_1 e_2 q^2 \kappa (1 - \Delta_1)}{3 D k T (1 + q)} = -\alpha (1 - \Delta_1). \quad (30)$$

It is immediately obvious that (29) differs from our earlier result by terms of order κ^2 , which means that (29) will give c -terms in the conductance function. Now the five terms of (19) which we neglected above also give terms of order κ^2 ; still more important, they lead, in addition, to transcendental terms whose limiting behavior is like that of $(\kappa a \ln \kappa a)$. It is clear, then, that a conductance function, self-consistent to terms of order c , must also include the contributions of these orders from the neglected five terms. Furthermore, the latter terms in turn give rise to still higher terms, but consistency requires that only terms $O(\kappa a)$ and $O(\kappa a \ln \kappa a)$ be retained in the numerators of these quantities. Accordingly, we set

$$f'_{ji} = F_{ji} + g_{ji} \quad (31)$$

and

$$\psi'_j = \Psi_j + p_j \quad (32)$$

in the second and third terms of (19) and in the corresponding terms of the Poisson equation. In the leading (initial) inhomogeneous term, we carry one more term of the power series (24). Elsewhere, the approximation $f'_{ji} \approx F_{ji}$, $\psi'_j \approx \Psi_j$ is used. A similar procedure is followed in the velocity boundary condition. The result, after dropping higher terms and cancellation of terms of order κ which vanish by virtue of (20) and (21), is

$$\begin{aligned} \frac{n_2 e_1 e_2^2 \gamma^2 X}{8\pi D(\mu k T)^2} \frac{\partial}{\partial x} \left(\frac{e^{-2\kappa r}}{r^2} \right) - \Delta g_{21} + \gamma^2 g_{21}(r) - \frac{e_1 e_2 \gamma^2 e^{-\kappa r} F_{21}}{\mu D k T r} + \\ \frac{n_2 e_2 \gamma^2}{4\pi \mu k T} \frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) \frac{\partial \Phi}{\partial x} - \frac{e_1 e_2 \kappa^2 e^{-\kappa r} F_{21}}{\mu D k T r} - \frac{e_1 e_2}{\mu D k T} \frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) \frac{\partial h_{21}}{\partial x} - \\ \frac{n_2 e_2 \gamma^2}{4\pi \mu k T} \frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) \left(\frac{\partial \Phi}{\partial x} \right)_a + \frac{n_1 n_2 e_1 e_2 (v_{1r} - v_{2r})}{\mu D \kappa^2 T^2 (\omega_1 + \omega_2)} \frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) = 0, \quad (33) \end{aligned}$$

and

$$\begin{aligned} Z'(r) = \frac{-n_2 e_2 \gamma^2 X e^{-\kappa r}}{4\pi \mu k T r} - \frac{d}{dr} \left(\frac{g_{21}}{\cos \theta} \right) + \frac{n_2 e_2 \gamma^2 e^{-\kappa r}}{4\pi \mu k T r} \frac{d\Phi}{dr} - \\ \frac{e_1 e_2 h_{21}}{\mu D k T} \frac{d}{dr} \left(\frac{e^{-\kappa r}}{r} \right) + \frac{n_2 \gamma^2 D}{4\pi e_1} \left(\frac{d\Phi}{dr} \right)_a - \frac{v_{1r} - v_{2r}}{\omega_1 + \omega_2} \frac{n_1 n_2}{k T \cos \theta}. \quad (34) \end{aligned}$$

No subscript is written on Φ in the above equations because $\Phi_1 = \Phi_2$. Solution of (33) subject to (34) vanishing at $r = a$ and to the appropriate boundary conditions for potential, followed by manipulation parallel to that which led to (29), gives a rather complicated expression⁶ which simplifies considerably for symmetrical electrolytes (where $n_1 = n_2$, $e_1 = -e_2$, $q^2 = 1/2$).

The final result is

$$-\frac{\Delta X}{X} = \alpha(1 - \Delta_1 + \Delta_2) + \frac{\beta \Delta_3'}{\Lambda_0}$$

where α is the coefficient derived by Onsager² for the point charge model, Δ_1 is the change in $\Delta X/X$ produced by introducing finite ion size, Δ_2 is the change due to the electrostatic perturbation terms summarized in (33), β is the electrophoresis coefficient² and Δ_3' derives from the relaxation field due to the flow produced at the location of the reference ion by its neighbors. In order to be consistent with the order of terms retained in the original differential equation, terms of order $\kappa^2 a^2$ and higher in the numerators of the various Δ 's are dropped: the final values are:

$$\Delta_1 = \frac{(1+q)\kappa a}{2p_3(1+\kappa a)} \left(1 + \frac{1}{b} \right) \quad (35)$$

$$\Delta_2 = \frac{b(1+q)\kappa a}{p_2 p_3 (1+\kappa a)^2} \left\{ \frac{11\sqrt{2}+3}{24} - \frac{T_0}{2} (1+\kappa a + 2q\kappa a) + \frac{T_1}{8} (1+\kappa a + q\kappa a) + \frac{7T_2}{8} (1+q\kappa a) \right\} - \frac{(1+q)\kappa a}{2p_2(1+\kappa a)^2} \quad (36)$$

$$\Delta_3' = \frac{-b\kappa a}{p_2(1 + \kappa a)^2} \left\{ \frac{35 - 6\sqrt{2}}{192} - \frac{T_0}{8} (1 + \kappa a + q\kappa a) + \frac{T_1}{32} (1 + \kappa a) + \frac{7T_2}{32} \right\} + \frac{11\kappa a}{96p_2(1 + \kappa a)^2} \quad (37)$$

where $p_1 = (1 + \kappa a + \kappa^2 a^2/2)$, $p_2 = (1 + q\kappa a + \kappa^2 a^2/4)$, $p_3 = (1 + q\kappa a + \kappa^2 a^2/6)$, $T_0 = \text{Tr}(\kappa a)$, $T_1 = \text{Tr}[(1 + q)\kappa a]$ and $T_2 = \text{Tr}[(2 + q)\kappa a]$. We are compiling tables of numerical values of the above functions.⁶

The transcendental function which appears in (37) is

$$\text{Tr}(x) = e^x \int_x^\infty \frac{e^{-t}}{t} dt. \quad (38)$$

In the limit of very small values of x , $\text{Tr}(x) \approx -0.5772 - \ln x$, but this expansion is useless in the range of concentrations where $\alpha\Delta_2\Lambda_0\sqrt{c}$ is experimentally observable.⁹

For symmetrical electrolytes, the $\text{Ei}(2\kappa a)$ term in our previous³ equation (4.2.10) vanishes in the electrophoretic correction to conductance, and the original¹ electrophoresis term β need only be divided by $(1 + \kappa a)$ to give a result consistent in order of κ with our new relaxation term (35). The final conductance equation can therefore be summarized by the following formula:

$$\Lambda = \Lambda_0 - \alpha(1 - \Delta_1 + \Delta_2)\Lambda_0\sqrt{c} - \beta(1 + \Delta_3)\sqrt{c} \quad (39)$$

where $\Delta_3 = \Delta_3' - \kappa a/(1 + \kappa a)$; all the terms which involve hydrodynamic effects are thus grouped together.

A comparison of (39) with experimental data is shown in Figure 2, where Shedlovsky's values¹⁰ for the conductances of the alkali halides are shown as the open circles. By plotting values of Λ , calculated by (39) and Shedlovsky's values of limiting conductances, at $c = 0.05$ for a series of selected values of a , a value for a can be interpolated which reproduces the experimental value of Λ at this concentration. Then values of conductance at other concentrations were computed, using the interpolated value of a ; these are plotted as solid circles in Figure 2. The agreement appears to be well within the experimental error of about 0.03 Λ -units. The a -values found are as follows: LiCl, 4.31×10^{-8} ; NaCl, 4.20×10^{-8} and KCl, 4.23×10^{-8} . These seem quite reasonable, considering that all errors and approximations are absorbed in this single arbitrary constant. Our equation can be fitted to data at higher concentrations, but we do not believe that it has physical reality for $\kappa a > 0.3$, because not only do still higher terms from (2) begin to become significant, but also other physical complications which we have completely ignored begin to play a part. For example, as Eigen and Wicke⁸ first pointed out, the fact that an ion and a solvent molecule cannot simultaneously occupy the same place becomes important.

Our present derivation shows that the upward curvature of the conductance curves of strong electrolytes can be accounted for theoretically merely by a refinement of the earlier calculation; the only change required in the physical model is the replacement of point charges by charged spheres. This, in turn, means that more realistic values of association constants can now be calculated from conduct-

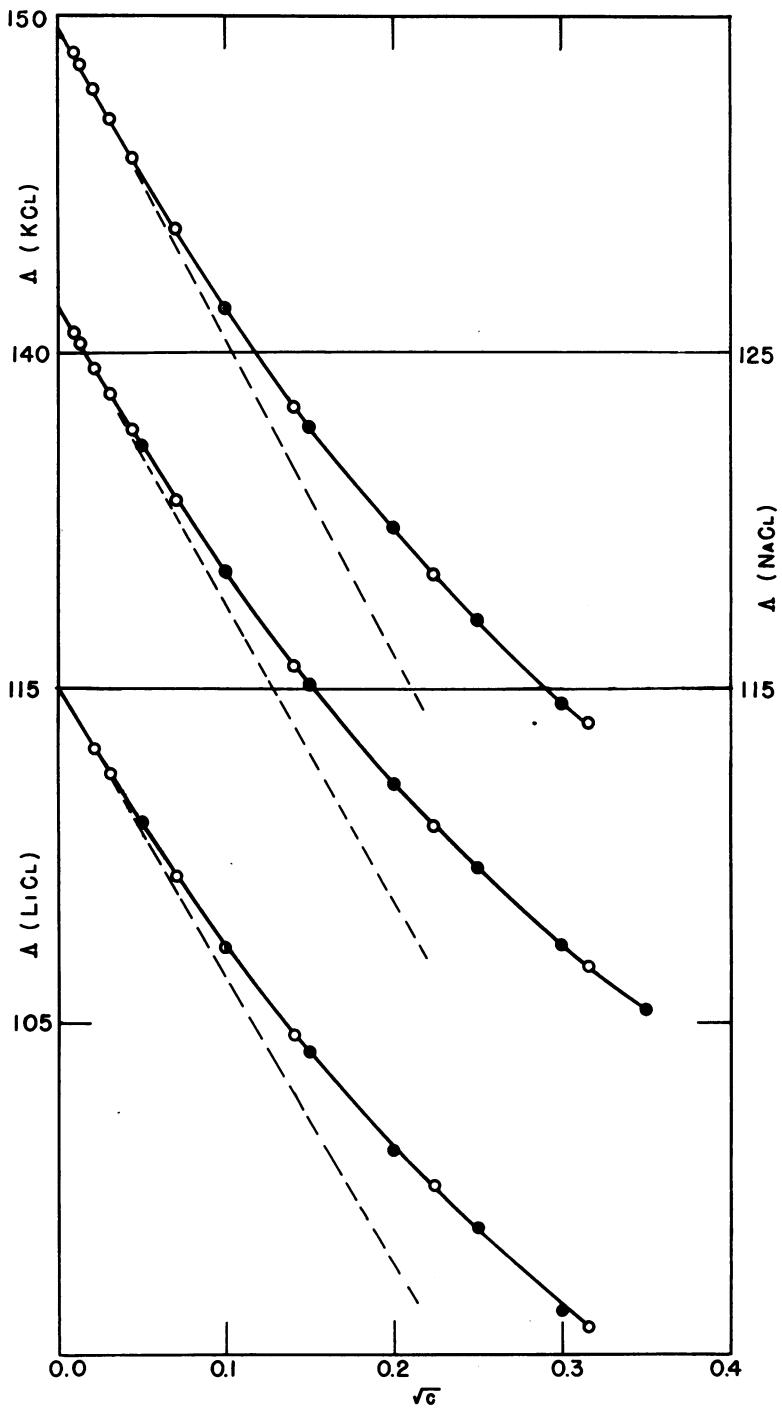


FIG. 2.—Comparison of experimental (*open circles*) and calculated (*solid circles*) values of conductance of the alkali halides

ance data than was previously possible in those cases where the fraction of ions associated is small. Work on this problem and on the case of unsymmetrical electrolytes is in progress.

* Contribution No. 1275.

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⁵ P. Debye and E. Hückel, *Ibid.*, **24**, 305, 1923.

⁶ We plan to present the details of this computation later.

⁷ H. Falkenhagen, M. Leist, and G. Kelbg, *Ann. Physik*, 6th ser., **11**, 51, 1952.

⁸ M. Eigen and E. Wicke, *Naturwissenschaften*, **38**, 453, 1951.

⁹ R. M. Fuoss, *J. Phys. Chem.*, **58**, 682, 1954.

¹⁰ T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1411, 1932.

AN INTERACTION BETWEEN ALLELES AT THE *Rh* LOCUS IN MAN WHICH WEAKENS THE REACTIVITY OF THE *Rh*₀ FACTOR (*D*^u)

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Occasionally bloods are found which, when tested with different anti-*Rh*₀ (anti-*D*) sera, give some but not all the serological reactions expected from the presence of the *Rh*₀ (*D*) factor, or the intensity of such reactions is consistently weaker than the average. Owing to the clinical importance of the *Rh*₀ factor, on which the condition of *Rh*-positivity or *Rh*-negativity depends, such "intermediate variants" (Wiener¹), usually symbolized as *D*^u (Stratton²) or *Rh*₀^u (Wiener³), represent a difficult problem for blood-grouping laboratories. For a review of the subject we refer to Race and Sanger.⁴

From a genetical point of view, a number of family investigations, actually not very large (Stratton and Renton;⁵ Dunsford;^{6,7} Race, Sanger, and Lawler⁸), have led to the conclusion that the *D*^u variants are to be regarded as products of mutation of the *D* allele and are thus inherited like the other *Rh* blood factors. Owing to the fact that often the *D*^u variants in members of the same family show identical serological peculiarities, while they may differ broadly between different families, a series of *D*^u alleles has been supposed. This view received additional indirect support from the knowledge that generally blood groups behave as a direct, not mediate, product of the determining gene and are little influenced by other environmental or genetical agents.

While the interpretation given by the British authors is certainly true in some and may be true in the majority of *D*^u cases, other genetical interpretations cannot be disregarded.