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Deviations from Ohm's Law in Weak Electrolytes

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(Received May 29, 1934)

The effect of an external electric field on the electrolytic dissociation is computed kinetically from the equations for Brownian motion in the combined Coulomb and external fields. The result is an increase of the dissociation constant, by the factor $K(X)/K(0) = F(b) = 1 + b + (1/3)b^2 + \dots$, where the parameter b is proportional to the absolute value of the field intensity, and inversely proportional to the dielectric constant. In water at 25°, $F(b) = F(1) = 2.395$ for a field of 723 kilovolt/cm, while in benzene, the same increase of the dissociation constant is obtained for a field of only 21 kilovolt/cm. The theory is quantitatively confirmed by the deviations from Ohm's law which have been observed for solutions of weak electrolytes in water and in benzene. For solutions of salts in acetone, and for solid electrolytes such as glass, mica, celluloid, etc., the observed increments of conductance are smaller than those expected from the theory, but still of the predicted

type and order of magnitude. The kinetic constants of dissociation and recombination can be computed separately on the assumption that the recombination proceeds as rapidly as the mutual approach of two ions due to the Coulomb attraction. The derivation is equivalent to that of Langevin, and leads to the same result. In the Langevin case, the coefficient of recombination is independent of the field; that of dissociation is increased by the factor $F(b)$. Slower reactions may occur when a (chemical) rearrangement of the ion pairs is involved. In the most general case, it is necessary to consider the successive reversible reactions $ions \rightleftharpoons pairs \rightleftharpoons molecules$, where the former takes place with the Langevin velocity; only the reaction rate $pairs \rightarrow ions$ depends on the field. On the basis of this picture, the saturation phenomena observed in dielectrics are discussed in relation to the field effect.

INTRODUCTION

IN recent years, it has been definitely established that the conductance of electrolytes increases with the intensity of the field, so that Ohm's law has only a limited range of validity.¹

For the case of strong electrolytes, this effect has been successfully interpreted as a destruction of the "ionic atmosphere." The initial effect is proportional to the square of the field intensity, and for very strong fields the equivalent conductance approaches a limiting value, which is not greater than the limiting equivalent conductance for small concentrations. Weak electrolytes, on the other hand, show much enhanced deviations from Ohm's law; the conductance increases linearly over a considerable range of the field intensity, and the limit of the increase, if any, corresponds to complete dissociation of the total amount of electrolyte present.²

It has been considered an open question whether the prevailing theory for the electrostatic interaction of the ions could account for this increased dissociation of weak electrolytes, and several explanations have been offered. Without entering into the possible merits and defects of these various approaches to the

problem, I shall present a result which has been computed on the basis of the interionic attraction theory, and discuss its significance. The agreement with the available measurements of conductance in strong fields may be considered satisfactory. In addition, the theory allows some predictions concerning the rates of dissociation and recombination of the ions, and the considerations involved by this question are extended with equal ease to the case of high field intensities.

The computed relative increase of the dissociation constant is given by the formula

$$K(X)/K(0) = J_1(4(-\beta q)^{1/2})/2(-\beta q)^{1/2} \\ = 1 + 2\beta q + \frac{(4\beta q)^2}{2!3!} + \frac{(4\beta q)^3}{3!4!} + \dots, \quad (1)$$

where

$$q = -e_1 e_2 / 2DkT > 0; \\ 2\beta = |X(e_1 \omega_1 - e_2 \omega_2)| / kT(\omega_1 + \omega_2). \quad (2)$$

Here, e_1 and e_2 denote the charges of the ions, X the intensity of the field (in electrostatic units), D the dielectric constant of the solution, k Boltzmann's constant, $kT\omega_i$ the coefficients of diffusion, and $e_i\omega_i$ the velocities of electrolytic migration in a field of one e.s.u. = 300 volt/cm. The most remarkable feature of (1) is the proportionality with the absolute value of the field. This paradoxical *linear law* is borne out by the

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¹ M. Wien, *Phys. Zeits.* **29**, 751 (1928).

² M. Wien, *Phys. Zeits.* **32**, 545 (1931).

experiments for all but the lowest field intensities, where deviations occur due to an effect that has been neglected in the derivation of (1). A complete theory would eliminate the discontinuity which (the differential quotient of) the function (1) possesses for $X=0$, in a manner dependent on the concentration; the result (1) of the approximate theory is *independent of the concentration*.

KINETIC THEORY OF THE DISSOCIATION EQUILIBRIUM

The formula (1) is derived from a detailed study of the mutual approach and parting of pairs of ions; we shall assume that these events are governed by the laws of Brownian motion. It will be necessary to make a somewhat arbitrary distinction between "free" and "bound" ions (i.e., in molecules); we may adopt Bjerrum's³ convention, that a pair of ions at a distance $r < q$ are considered as "bound" to each other. Our considerations will apply primarily to cases where the concentration of "free" ions is sufficiently small, so that the Debye-Hückel "radius" $1/\kappa$ of the ionic atmosphere is much greater than the "effective range" q of the ions; i.e.,

$$\kappa q = -\kappa e_1 e_2 / 2DkT \ll 1, \quad (3)$$

with Bjerrum's convention

$$\kappa^2 = 4\pi(n_1 e_1^2 + n_2 e_2^2) / DkT, \quad (4)$$

where n_1 and n_2 denote the concentrations of "free" ions. The effects of interionic forces in *strong electrolytes* are of the order κq ; the condition (3) implies that these effects are small. In *weak electrolytes*, the electrostatic (and other) forces may still cause considerable "association" of ions into "bound" pairs, even when κq is small. As pointed out by Bjerrum, this process is practically governed by the mass-action law, no matter what are the forces that keep the pairs together. Here we are interested in the modification of the mass-action equilibrium by an external electric field.

Let us first examine briefly the structure of the ionic atmosphere in a case of the type (3). When no external field is present (equilibrium), the density of ions of the species i in the neighborhood of ions of the species j is given by the

formula

$$n_{ji}(r) = n_i \exp(-w_{ji}(r)/kT), \quad (5)$$

where $w_{ji}(r)$ is the potential of the average force between two ions i and j , with the understanding that both ions should be "free" or (for $r < q$) bound to each other. According to Bjerrum,

$$w_{ji}(r) = \frac{e_i e_j \exp(\kappa q - \kappa r)}{D(1 + \kappa q)r} \quad \text{for } r > q, \quad (6)$$

and

$$w_{ji}(r) = e_i e_j / Dr \quad \text{for } r < q, \quad (7)$$

approximately. In Bjerrum's theory, (7) contains a correction of the order $\kappa q kT$, which may be neglected under the assumption (3). The total concentration of "bound" pairs equals

$$\nu_{ji} = \nu_{ij} = n_j \int_a^q n_{ji}(r) 4\pi r^2 dr, \quad (8)$$

where a denotes the "diameter" (the least distance of approach) of the ions i, j . It is important that in the case of typical weak electrolytes, and quite generally in solvents of *low dielectric constant*, the main contribution to (8) arises from distances r that are but slightly greater than a . The upper limit of the integral in (8) is fixed by an arbitrary convention due to Bjerrum, but if the limit q were replaced by $q/2$ or by $2q$, the difference would be negligible for our purposes, as for his.

We take the opportunity to point out one peculiar characteristic of the Eqs. (6) and (7). The factor $\exp(-\kappa r)$ in (6) is due to the gradual screening off of the electric field of an ion by the surrounding space charge; without this factor, Eq. (5) would lead to an infinite total space charge. Nevertheless, under the assumption (3) it is possible to neglect the factor $\exp(-\kappa r)$ up to some distance $r' > q$; in fact, this distance may be chosen so as to fulfill the condition

$$q \ll r' \ll 1/\kappa, \quad (9a)$$

and we may extend (7) up to the distance r' :

$$w_{ji}(r) = e_i e_j / Dr \quad \text{for } r < r', \quad (9b)$$

without appreciable error. This method of approximation is very well adapted to the purpose in hand; because the phenomenon of incomplete

³ N. Bjerrum, Kgl. Danske Vid. Selskab, Math. -fys. medd. 7, 9 (1926).

dissociation depends mainly on the innermost part (7) of the field of an ion, while the region beyond the limit given by (9) is of no importance whatever.

The customary procedure in the theory of *strong* electrolytes is to replace formula (5) by the abbreviated Taylor series

$$n_{ji}(r) \sim n_i(1 - w_{ji}(r)/kT). \quad (10)$$

This approximation is good where $w/kT \ll 1$, that is for large distances r ; for small distances it is poor and leads to absurd consequences (n_{ji} negative for $w > kT$). The approximation expressed by (8) and (9) has the opposite characteristics: It is good for small distances, in fact wherever w/kT is appreciable, but it would lead to absurd results if extended to all distances ($r' = \infty$). For the purpose of convenient computation, we shall nevertheless remove the outer boundary r' in (9) to infinity, and it will turn out that we still obtain intelligible results for the significant region of small distances r ; only the disastrous effects due to the infinite total charge in the distant part of the "ionic atmosphere" must be disregarded.

In the presence of an external electric field \mathbf{X} the Boltzmann Eq. (5) is no longer applicable, because we are not dealing with a true equilibrium. We must now develop a kinetic theory for the electrolytic dissociation and the recombination of the ions; we shall base this theory on the laws of Brownian motion. The general procedure in applying the equations of Brownian motion to the problem of two particles is well known.⁴

We now consider a distribution-function

$$f_{ji}(\mathbf{r}) = f_{ij}(-\mathbf{r}) = n_j n_i(\mathbf{r}) = n_i n_j(-\mathbf{r}), \quad (11)$$

where the distance \mathbf{r} must be regarded as a vector, because now the direction is important. The mean relative velocity of two ions j and i at a distance $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ from the former to the latter is

$$\begin{aligned} \mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r}) &= \omega_i(e_i \mathbf{X} + \mathbf{k}_{ji}(\mathbf{r})) \\ &\quad - kT \text{grad}_2 \log f_{ji}(\mathbf{r}) - \omega_j(e_j \mathbf{X} + \mathbf{k}_{ij}(-\mathbf{r})) \\ &\quad - kT \text{grad}_1 \log f_{ij}(-\mathbf{r}), \end{aligned} \quad (12)$$

where $\mathbf{k}_{ji}(\mathbf{r})$ and $\mathbf{k}_{ij}(-\mathbf{r})$ denote the average of the ionic forces on the ions in this position, and the stationary condition is

$$\begin{aligned} \partial f / \partial t &= -\text{div}_2 (f_{ji}(\mathbf{r}_2 - \mathbf{r}_1) \mathbf{v}_{ji}(\mathbf{r}_2 - \mathbf{r}_1)) \\ &\quad - \text{div}_1 (f_{ij}(\mathbf{r}_1 - \mathbf{r}_2) \mathbf{v}_{ij}(\mathbf{r}_1 - \mathbf{r}_2)) \\ &= \text{div}_2 (f_{ji}(\mathbf{r}) \{ \mathbf{v}_{ij}(-\mathbf{r}) - \mathbf{v}_{ji}(\mathbf{r}) \}) = 0. \end{aligned} \quad (13)$$

On account of the difference between the ionic atmospheres of the ions j and i , there is, in general, no simple relation between $\mathbf{k}_{ji}(\mathbf{r})$ and $\mathbf{k}_{ij}(-\mathbf{r})$. However, if we assume (3), then the screening effect of the atmosphere is negligible in the region of interest, as shown above for the equilibrium case; with a strong field \mathbf{X} the approximation is even better, because the field tends to sweep the atmosphere away from the ion. For simplicity, we put $r' = \infty$ in (9); then \mathbf{k}_{ji} and \mathbf{k}_{ij} possess everywhere the same potential $w_{ji}(r)$:

$$\begin{aligned} \mathbf{k}_{ji}(\mathbf{r}_2 - \mathbf{r}_1) &= \mathbf{k}_{ji}(\mathbf{r}) = -\text{grad}_2 w_{ji}(r), \\ \mathbf{k}_{ij}(\mathbf{r}_1 - \mathbf{r}_2) &= \mathbf{k}_{ij}(-\mathbf{r}) = -\text{grad}_1 w_{ji}(r), \end{aligned} \quad (14)$$

where w is simply the Coulomb potential (9), and (12) becomes

$$\begin{aligned} f_{ji}(\mathbf{r})(\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})) &= (e_i \omega_i - e_j \omega_j) \mathbf{X} f_{ji}(\mathbf{r}) \\ &\quad - (\omega_j + \omega_i) \{ f_{ji}(\mathbf{r}) \text{grad} (e_j e_i / Dr) \\ &\quad + kT \text{grad} f_{ji}(\mathbf{r}) \}. \end{aligned} \quad (15)$$

We now choose a frame of reference such that the x axis is parallel to the external field \mathbf{X} , with the potential $-Xx$, and assume

$$Xe_j > 0; \quad Xe_i < 0.$$

Then with the notation (2), and dropping the indices for f , the mean relative velocity \mathbf{v} of the two ions in a given configuration is given by

$$\begin{aligned} f(\mathbf{r}) \mathbf{v}(\mathbf{r}) &= f(\mathbf{r})(\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})) \\ &= kT(\omega_j + \omega_i)(-\text{grad} f \\ &\quad + f \text{grad} ((2q/r) + 2\beta x)). \end{aligned} \quad (16)$$

The stationary condition (13) takes the form

$$\text{div} (f \text{grad} ((2q/r) + 2\beta x)) - \text{div} \text{grad} f = 0, \quad (17)$$

which, since the field of the potential $(2q/r) + 2\beta x$ is divergence-free, may be written

$$\text{div} \text{grad} f = (\text{grad} f \cdot \text{grad} ((2q/r) + 2\beta x)). \quad (18)$$

In accordance with (16), the net rate of entry of (pairs of) ions into the interior of any closed surface S in the $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ space equals

⁴ M. v. Smoluchowski, Phys. Zeits. 15, 593 (1916); Onsager, Phys. Zeits. 28, 277 (1928); Onsager and Fuoss, J. Phys. Chem. 36, 2689 (1932), Section 2.

$$\int (\partial f / \partial t) dv = (\omega_j + \omega_i) kT \int (\text{grad}_n f - f \text{grad}_n ((2q/r) + 2\beta x)) dS, \quad (19)$$

where grad_n denotes the normal component of the gradient at the surface S .

Now if the phenomenon of incomplete dissociation can be dealt with entirely by Bjerrum's picture, our task is to solve the partial differential Eq. (18)⁵ with the boundary conditions:

$$f = n_j n_i \quad \text{for } r = \infty, \quad (20)$$

and $fv_r = 0$, (radial component of the flow); that is according to (16):

$$\begin{aligned} \text{grad}_r f &= f \text{grad}_r ((2q/r) + 2\beta x) \\ &= f(2\beta \cos \Theta - 2qr^{-2}) \quad \text{for } r = a. \end{aligned} \quad (21)$$

For the purpose of computation, the boundary condition (21) is unduly complicated, but the limit of a solution fulfilling (21) for $a=0$ is relatively simple. We shall actually apply a boundary condition for $r=0$ which will lead directly to this limiting solution.

If the formation of undissociated molecules involves special configurations and possibly the passage of a potential barrier, then the boundary condition (21) for small distances must be modified accordingly. The result (1) for the dissociation constant will not be materially affected by this complication, but the time required to establish equilibrium may be increased, because the passage of a potential barrier may be the slowest step involved in the process.

Rather than to search directly for a solution of (18) fulfilling both the boundary conditions (20) and (21), we shall compute separately the parts of f that correspond to the two processes of dissociation and recombination, so as to obtain the rate constants KA and A in the chemical kinetic equation

⁵ The general solution of this equation has the form:

$$f = r^{-\frac{1}{2}} e^{(q/r) + \beta x} \sum_n T_n(\cos \Theta) F_n(\frac{1}{2} i \log(\beta r^2/q)).$$

Here, T_n denotes the n th wave function of a dumb-bell dipole rotator in an electric field, and F_n a linear combination of the corresponding Mathieu functions of indices $\pm \frac{1}{2}$; $r^{-\frac{1}{2}} F_n$ is a single-valued transcendental function of r . The functions F_n and T_n are related by a Laplace transformation. The general properties of these functions will be the subject of a separate treatise.

$$\begin{aligned} dv_{ji}/dt &= -dn_j/dt = -dn_i/dt \\ &= An_j n_i - KA v_{ji}. \end{aligned} \quad (22)$$

The state of complete dissociation we shall represent by the random distribution, which conforms to (18). Thus

$$f(\mathbf{r}) = n_j n_i = \text{const.}, \quad (23)$$

whence, by (19), the rate of recombination becomes

$$\begin{aligned} An_j n_i &= kT(\omega_j + \omega_i) \int n_j n_i ((2q/r^2) \\ &\quad - 2\beta \cos \Theta) r^2 \sin \Theta d\Theta d\varphi \\ &= 8\pi q kT(\omega_j + \omega_i) n_j n_i. \end{aligned} \quad (24)$$

Here, (r, Θ, φ) denote polar coordinates. For a binary electrolyte, $e_1 = -e_2 = e$, we obtain simply

$$A = 4\pi\Lambda/D = 4\pi(e_1^2\omega_1 + e_2^2\omega_2)/D, \quad (25)$$

where Λ denotes the conductance per molecule in e.s.u.

When the field X (and hence β) vanishes, the undissociated molecules are according to (5), (9) and (23) represented by the part

$$f(r) = (v_{ji}/K(0))(e^{2q/r} - 1) = n_j n_i (e^{2q/r} - 1), \quad (26)$$

of the distribution-function, which by itself satisfies (18). This distribution corresponds to a stationary flow from a source at the origin, of the magnitude (24) but in the outward direction. It is possible to show that (26) is the only solution of (18) that satisfies the following set of boundary conditions: that $f=0$ for $r=\infty$, that there is a source of the given yield at the origin, and that the flow from the origin through any space angle is finite.

For $X \neq 0$, the solution of (18) under these same boundary conditions involves elaborate analysis. However, the unique result can be expressed by a definite integral in terms of known functions, as follows

$$\begin{aligned} f(r, \Theta) &= gr^{-1} e^{-\beta r + \beta r \cos \Theta + (2q/r)} \\ &\quad \times \int_{s=0}^{s=2q} J_0((-8\beta s)^{\frac{1}{2}} \cos \frac{1}{2}\Theta) e^{-s/r} ds, \end{aligned} \quad (27)$$

where $J_0(z) = \sum (-)^n (z^{2n}/2^{2n} n!)$ denotes the ordinary Bessel function of order zero. For small values of r , the upper limit of the integral in (27) may be replaced with very good approxi-

mation by ∞ , which yields

$$f(r, \Theta) \sim g e^{2q/r} e^{2\beta r \cos \Theta}, \quad (28)$$

whereby the error is of the order

$$g(\beta q)^{-1} \exp(4(\beta q)^{1/2}) \quad (29)$$

when βq is large, otherwise of the order g , and may be neglected whenever

$$\exp((2q/r) - 4(\beta q)^{1/2}) \gg 1. \quad (30)$$

By means of (28), we can easily establish the relation between the undetermined factor g and the total number of "undissociated" ion pairs. As before in discussing (8), we disregard the region $r > q$. For the region of small r , which contains practically all the "bound" pairs, we admit the approximation (28) and go one step further in that we replace the factor $\exp(2\beta r \cos \Theta)$ by unity.⁶ We then have practically the same distribution as in the equilibrium case (26), where $1 \ll \exp(2q/r)$, and by comparison,

$$v_{ji} = gK(0). \quad (31)$$

It remains to evaluate the rate of dissociation that corresponds to the distribution (27). For this purpose, the complete function (27) must be substituted in (19); if the integral in (27) be written

$$\int_0^{2q} = \int_0^\infty - \int_{2q}^\infty,$$

it turns out that only the second term on the right contributes to the flow (19). Most easily by specialization to small r , one obtains

$$\begin{aligned} -K(X)A v_{ji} &= \int (\partial f / \partial t) dv \\ &= -8\pi q k T (\omega_j + \omega_i) g J_1(4(-\beta q)^{1/2}) / 2(-\beta q)^{1/2}. \end{aligned}$$

By comparison with (24) and (31), we see that the rate constant for the dissociation is increased by the factor

$$\begin{aligned} AK(X)/AK(0) &= K(X)/K(0) \\ &= J_1(4(-\beta q)^{1/2}) / 2(-\beta q)^{1/2}, \quad (32) \end{aligned}$$

verifying (1), while the rate constant A for the recombination (cf. (24)) is not affected by the field.

⁶ The corresponding error in $K(X)/K(0)$ is measured approximately by the factor $2\beta a / \sinh(2\beta a)$; an error of the same order has probably been made already by neglecting the hydrodynamic interaction of the ions.

CRITIQUE OF APPROXIMATIONS

Our principal result, given by Eq. (32), may be considered a consequence of the boundary condition (21) for the limiting case $a=0$. In this case, too, the condition (30) for allowing the approximation (28) is ideally fulfilled. In order to estimate the effect of changing the boundary condition for small r , e.g., by another choice of a in (21), we observe that the approximate distribution (28) corresponds to a *local Maxwell-Boltzmann equilibrium* for small r , in the combined Coulomb and external field.⁷ Hence the distribution (28) fulfills not only the boundary condition (21) for every value of a , but (at least for binary electrolytes⁷) any possible alternative condition as well. Since it is only the difference (29) between the distribution (27) and the equilibrium distribution (28) that must be modified in order to fit a particular boundary condition for small r , we may expect that the error of (28) will not be of much greater order of magnitude than (29). Indeed, if the differential Eq. (18) is assumed valid for all distances $r=a$, with arbitrary boundary conditions for $r < a$, and provided that the Coulomb field at contact is stronger than the external field, i.e.,

$$1 - a(\beta/q)^{1/2} = h > 0, \quad (33)$$

then it can be shown that the relative error of (28) for $r=a$ is at most of the order

$$(q^2/a^2 h) \exp(-2h^2 q/a). \quad (34)$$

Therefore, as long as (34) is small, the boundary condition for small r is immaterial and our idealization of the interior region contributes but a small error to the result (32). In (34), a is of molecular dimensions and does not vary greatly from one case to another.

The variation of β is limited by the available intensities of electric fields, which do not exceed 500 kv/cm, to the range $0 < \beta < 10^7 \text{ cm}^{-1}$. The most important quantity that enters into (34) is the length q , which depends on the valence type of the electrolyte and on the dielectric constant of the solvent. For uni-univalent elec-

⁷ When the charges of the ions are unequal, i.e., $e_1 + e_2 \neq 0$, a true equilibrium in the external field is impossible on account of the resultant net force $(e_1 + e_2)X$ on the ion pair. Nevertheless, the ambiguity due to this force is only of the same order of magnitude as the correction discussed in footnote 6, and therefore of slight importance.

trolytes in water at ordinary temperatures, with $D=80$, we find $q=3.5\times 10^{-8}$ cm, while for similar electrolytes in acetone, $q=14\times 10^{-8}$ cm, and in benzene, $q=125\times 10^{-8}$ cm.

From this analysis, we must be prepared to find considerable deviations from (32) in solvents of high dielectric constant like water and, to a lesser extent, acetone. Still, we know that in such solvents, the only *weak electrolytes* are those for which a very close approach of the ions can occur and if a is computed from the dissociation constant according to Bjerrum's theory,³ then for any weak electrolyte in any solvent

$$\exp(2q/a) \gg 1.$$

The weight that can be given to this reassuring consideration depends on the actual laws of motion for small distances between the ions. Rather than to utilize unlimited opportunities for interesting conjecture, it seems proper to wait until adequate experimental material can guide the theory, if one should be required.

For distances r that are substantially greater than molecular and ionic dimensions, the laws of motion are known with practical certainty; but the exact equations which result lead to excessive mathematical difficulties. Our fundamental equation (18), which we were able to solve, represents several simplifications of the physical picture. We shall discuss the nature of these approximations, and estimate their effects.

First of all, we must admit that in formulating the equations for ionic motion, the hydrodynamic interaction was neglected. Except for structure-dependent terms of the order $1/r^3$, this interaction decreases the mutual mobility of the ions,

$$\omega_1 + \omega_2,$$

by the amount

$$1/2\pi\eta r, \quad (\eta = \text{viscosity}),$$

in the direction connecting the two ions, and by half this amount in any perpendicular direction. It is very difficult to estimate how much this effect will modify the distribution (27) and the result (32) for the dissociation constant. So much seems certain, that the correction will be inversely proportional to $\omega\eta$, that is proportional to the Stokes "radius,"

$$\rho = 1/6\pi\eta\omega.$$

Moreover, in case $q=0$ (one ion neutral), the hydrodynamic interaction does not disturb the uniform distribution which results from (23) alone, while (27) vanishes. Therefore, the hydrodynamic correction is probably proportional to some power of q . Every power of ρ or q must be multiplied by β to make the result dimensionless, so that we obtain the following estimate for the order of the hydrodynamic correction:

$$\begin{aligned} K(X)/K(0) &= F(2\beta q) + O(\beta^{n+1}\rho q^n) \\ &= 1 + 2\beta q + \cdots + O(\beta^{n+1}\rho q^n). \end{aligned}$$

This correction increases with the intensity of the field. For high field intensities it may become important in any solvent, but even so, it ought not to change the order of magnitude of the principal effect.

Finally, we have to discuss the shielding of the Coulomb forces due to the Debye-Hückel "ionic atmosphere," which has been neglected so far. When no external field is present, this shielding decreases the work required to separate a pair of ions by the amount

$$-kT \log \Pi(\gamma) = 2\kappa q kT,$$

where κ is the mean inverse distance of the shielding charge. The factor $\Pi(\gamma)$ is called the activity coefficient product, and is usually written

$$\gamma_1\gamma_2/\gamma_{12} = \Pi(\gamma).$$

It enters as a correction to the mass-action law when the concentration of free ions becomes appreciable, in the form

$$c_1c_2/c_{12} = K_c = K_0/\Pi(\gamma),$$

where K_c is called the "stoichiometric" or apparent dissociation constant for the concentration in question, and K_0 the "true" dissociation constant.

We shall show next that for high field intensities, that is when

$$\beta \gg \kappa,$$

the value of $K(0)$ to be employed in (32) is the true dissociation constant K_0 , and not K_c . The reason is that, as seen from (27), the modification of the distribution due to the external field proceeds by peeling off the excess density of ions from the outside inwards to a distance of the order $1/\beta$ in all directions except $\Theta=0$. The only effect of the ionic atmosphere is to

reduce the concentration gradients for distances of the order $1/\kappa$. Now if the external field is strong enough to break down the concentration gradients for all distances $r > 1/\beta$, where $1/\beta \ll 1/\kappa$, then the shielding charge in the ionic atmosphere can have no further effect.

Conversely, the field requires a leverage of the length $1/\beta$ to modify the distribution; because over a path of this length, the work of the field is comparable to kT . When $\kappa \gg \beta$, then the atmospheric shielding levels the concentrations for all distances r that afford sufficient leverage for the field. In this case, it is the effect of the field that becomes very small.

The conclusions from these considerations can be summarized as follows:

$$\begin{aligned} K(X) &= K_0 F(2\beta q) + O(\kappa^2 q / \beta) = K_0 (1 + 2\beta q + \dots) \\ &\quad + O(\kappa^2 q / \beta), \quad \text{when } \beta \gg \kappa; \\ K(X) &= K_c + O(\beta^2 q / \kappa) = K_0 (1 + 2\kappa q + \dots) \\ &\quad + O(\beta^2 q / \kappa), \quad \text{when } \beta \ll \kappa. \end{aligned} \quad (35)$$

The estimated orders of the corrections are probable conjectures.

When κq and $\kappa \rho$ are appreciable, it is also necessary to allow for the effect of the "atmosphere" on the migration of the free ions, and for the modification of this action by the field, that is the "ordinary" Wien effect as observed for strong electrolytes. This correction does not affect the dissociation equilibrium itself, but only the relation between the free ion concentration and the conductance of the solution.

A computation of these effects for small β has been given by Joos and Blumentritt.⁸ A computation of all terms of the orders q and ρ = Stokes radius, homogeneous of the first order in κ and β , is in progress.⁹ The results for very strong fields are simple: the asymmetry of the ionic atmosphere becomes negligible, but a part of the "electrophoresis" remains. For binary electrolytes, the conductances in weak and in strong fields are

$$\begin{aligned} \Lambda &= \Lambda_0 - (A\Lambda_0 + B)(c)^{\frac{1}{2}}, \quad \beta = 0; \\ \Lambda &= \Lambda_0 - (B/2^{\frac{1}{2}})(c)^{\frac{1}{2}}, \quad \beta \gg \kappa. \end{aligned} \quad (35a)$$

⁸ M. Blumentritt, Ann. d. Physik [5] 1, 195 (1929).

⁹ For an approximate treatment of this problem see H. Falkenhagen, Phys. Zeits. 32, 353 (1931).

The constants A and B are the same for all binary electrolytes of the same valence.

DISCUSSION OF THEORETICAL RESULTS

The increase of the dissociation constant due to the field is measured by the parameter

$$\begin{aligned} b = 2\beta q &= \frac{z_1 \omega_1 + z_2 \omega_2}{\omega_1 + \omega_2} \frac{|X| \epsilon^3}{2Dk^2 T^2} \\ &= \frac{z_1^2 z_2^2 (\Lambda_1 + \Lambda_2)}{z_2 \Lambda_1 + z_1 \Lambda_2} \cdot \frac{9.636 V}{DT^2}, \end{aligned} \quad (36)$$

where z_1 and z_2 are the valences of the ions, Λ_1 and Λ_2 the equivalent conductances, ϵ the electronic charge, X the field in e.s.u., and V the field measured in volt/cm. For uni-univalent electrolytes, (36) reduces to the simple result,

$$b = 9.636 V / DT^2. \quad (37)$$

The function (1) can be computed from the power series

$$\begin{aligned} K(X)/K(0) = F(b) &= 1 + b + \frac{b^2}{3} + \frac{b^3}{18} \\ &\quad + \frac{b^4}{180} + \frac{b^5}{2700} + \frac{b^6}{56700} + \dots \end{aligned} \quad (38)$$

or, for large values of b , from the asymptotic expansion

$$\begin{aligned} F(b) &\sim (2/\pi)^{\frac{1}{2}} (8b)^{-3/4} e^{(8b)^{\frac{1}{2}}} \\ &\times \left\{ 1 - \frac{3}{8(8b)^{\frac{1}{2}}} - \frac{15}{128.8b} - \frac{105}{1024((8b)^{\frac{1}{2}})^3} - \dots \right\}, \end{aligned} \quad (39)$$

where, for $b \geq 3$, the remainder of the series is less than $1/130b^2 < 10^{-3}$.

The increase of the concentration c_i of free ions due to the altered dissociation constant is given by the mass-action law. For binary electrolytes this law takes the form

$$c\alpha^2/(1-\alpha) = K = K_0 F(b), \quad (40)$$

where c denotes the total concentration of electrolyte, and $\alpha = c_i/c$ the degree of dissociation. The increase of the conductance λ is proportional to the displacement of the dissociation equilibrium:

$$\lambda/\lambda_0 = c_i/c_{i0} = \alpha/\alpha_0.$$

It is seen from (40) that the displacement due to a given change of K depends on the initial degree of dissociation, α_0 .

The change of K with the field for binary electrolytes depends only on one individual characteristic, the valence (cf. Eq. (36)). We shall see that the uniformity, thus predicted by the theory, is indeed borne out by experience. In spite of its simplicity, this law has remained undiscovered because previous workers have only paid attention to the variation of λ with the field, and have failed to properly allow for the effect of α .¹⁰

In discussing the influence of α , we shall limit ourselves to binary electrolytes. Further complications are to be expected in mixed electrolytes and in cases of step-wise dissociation, but the binary case is the most important, and will suffice for illustration.

In general, α/α_0 decreases with increasing α_0 . It is instructive to specialize (40) for small values of b . If we neglect all terms of the order b^2 and higher in (38) and in (40), we get

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\alpha}{\alpha} = \frac{(1-\alpha)}{(2-\alpha)} \frac{\Delta K}{K} = \frac{(1-\alpha)}{(2-\alpha)} b. \quad (41)$$

When the dissociation is nearly complete, the change due to the field is proportional to the remaining fraction, $1-\alpha$, of undissociated electrolyte. In the other extreme, $\alpha \ll 1$, the effect approaches a maximum which is given for all values of b by the simple formula,

$$\begin{aligned} \lambda/\lambda_0 &= \alpha/\alpha_0 = (K/K_0)^{\frac{1}{2}} = (F(b))^{\frac{1}{2}} \\ &= 1 + \frac{1}{2}b + \frac{1}{24}b^2 + \dots \end{aligned} \quad (42)$$

The function $(F(b))^{\frac{1}{2}}$ is represented graphically in Fig. 1.

Formula (42) applies whether the molecules and the ions are simple or complex, as long as all kinds of ions have the same charge (± 1 or ± 2 , etc.), and the total number of ions is small compared to the number of molecules. This is

¹⁰ It is but fair to point out that in many cases, reliable determinations of α are lacking. The qualitative effect of α has been recognized by Schiele, *Ann. d. Physik* [5] 13, 811 (1932).

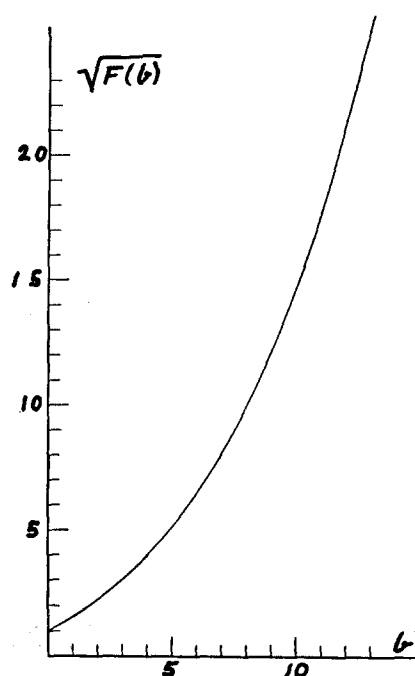


FIG. 1.

important for the application to solvents of low dielectric constant, where complexity is the rule, but the ionized fraction of the solute is always small.¹¹

The characteristic parameter b is proportional to the cube of the valence, and inversely proportional to the dielectric constant of the solvent. It is illuminating to compare extremes among solvents. For uni-univalent electrolytes in water at 25°C, with $D = 78.57$, we get

$$b = 1.384 \times 10^{-6} V, \quad (43)$$

but in benzene, with $D = 2.280$, at the same temperature,

$$b = 47.5 \times 10^{-6} V. \quad (44)$$

Since in either medium, the strongest practically obtainable fields are about the same, of the order 5×10^5 volts/cm, the greatest effect that can be obtained in water is approximately

$$\begin{aligned} \lambda(X)/\lambda(0) &= c_i(X)/c_i(0) \\ &= (F(b))^{\frac{1}{2}} = (F(0.7))^{\frac{1}{2}} = 1.37, \end{aligned}$$

while in benzene, for $X = 5 \times 10^5$ volts/cm,

¹¹ Kraus and Fuoss, *J. Am. Chem. Soc.* 55, 21 (1933); Fuoss and Kraus, *ibid.* 55, 2387 (1933).

$$\lambda(X)/\lambda(0) = c_i(X)/c_i(0) \\ = (F(b))^{\frac{1}{2}} = (F(23.7))^{\frac{1}{2}} = 121.$$

Even in water, however, very large effects could be expected if it were possible to dissolve a weak electrolyte of high valence type.

When an electric field is applied suddenly to a solution, some time will pass before the new dissociation equilibrium becomes established. The approach to equilibrium is described by the mass-action law (22). The recombination constant A , which determines the reaction velocity, is equal to our theoretical value (24) whenever the mutual approach of the ions is the slowest step in the reaction; otherwise it is smaller. For a binary electrolyte, the solution of (22) can be written in the form,

$$(\alpha - \alpha_0)/(\alpha + \alpha_0/(1 - \alpha_0)) = Ce^{-t/\tau}, \quad (45)$$

where α denotes the degree of dissociation at the time t , α_0 the steady value of α , C is an integration constant, and the time-lag equals

$$\tau = (1 - \alpha_0)/(2 - \alpha_0)n\alpha_0 A.$$

For binary electrolytes, our computed maximum A takes the very simple form (25), and if we may adopt this value, we get the interesting result

$$\tau = \frac{1 - \alpha_0}{(2 - \alpha_0)n\alpha_0 A} = \frac{(1 - \alpha_0) D}{(2 - \alpha_0) 4\pi\lambda}, \quad (46)$$

where $1/\lambda$ denotes the specific resistance of the solution, measured in electrostatic units, i.e., seconds ($1 \text{ sec.} = 9 \times 10^{11} \text{ ohm cm.}$). When $\alpha_0 \ll 1$, the time-lag is simply

$$\tau = D/8\pi\lambda. \quad (46a)$$

This is substantially the same as the time needed for any readjustment of charges in an electrolytic conductor. For example, suppose that a pair of charges $\pm e$ be introduced on a pair of ideal electrodes, so arranged that practically all the force lines run between the electrodes. Without any further restrictions, the time needed for neutralization or shielding of the charges will be:

$$\text{capacity} \times \text{resistance} = D/4\pi\lambda,$$

i.e., twice that given by formula (46a). The relaxation of the Debye-Hückel "ionic atmos-

phere" is a similar process, and the time involved is of the same order of magnitude.

In formulas (45), (46) and (46a), α_0 and λ refer to the steady state in a field of intensity X , and both α_0 and λ increase with X . Hence *the time-lag decreases with increasing field intensity*. This consequence of the theory is important for the application to saturation in strong fields. The saturation current may increase more rapidly with the field intensity than the conductance.

EXPERIMENTAL VERIFICATION

The increased conductances due to strong electric fields have been measured for a number of substances, in several solvents. The following have been selected as a fair sample: Acetic and chloroacetic acids in aqueous solution,¹⁶ cobalt chloride in acetone,¹⁹ and picric acid in benzene containing some alcohol.²¹

Acetic and chloroacetic acids are among those electrolytes whose dissociation constants in aqueous solution have been determined with great precision. We shall base our computations on the conductance data of MacInnes and Shedlovsky,¹² who give $K = 1.753 \times 10^{-5}$ for acetic acid at 25° , and those of Saxton and Langer,¹³ who give $K = 1.396 \times 10^{-3}$ for chloroacetic acid at the same temperature. The values found by electromotive force measurements at 25° are $K = 1.754 \times 10^{-5}$ for acetic acid¹⁴ and $K = 1.378 \times 10^{-3}$ for chloroacetic acid.¹⁵ Incidentally, the latter sources^{14, 15} give data over ranges of temperature from 0° to 60° and from 0° to 40° , respectively.

Unfortunately, Schiele does not specify the concentrations of acids used in his experiments, nor the temperatures, but only the conductances of his solutions. Probably, the temperatures were not far from 25° , perhaps 5 or 10 degrees lower. In the absence of better directions, the added labor involved by computation for some temperature different from 25° , even if slightly more plausible, was not considered worth while.

¹² MacInnes and Shedlovsky, J. Am. Chem. Soc. **54**, 1429 (1932).

¹³ Saxton and Langer, J. Am. Chem. Soc. **55**, 3638 (1933).

¹⁴ Harned and Ehlers, J. Am. Chem. Soc. **55**, 652 (1933).

¹⁵ Donald D. Wright, J. Am. Chem. Soc. **56**, 314 (1934).

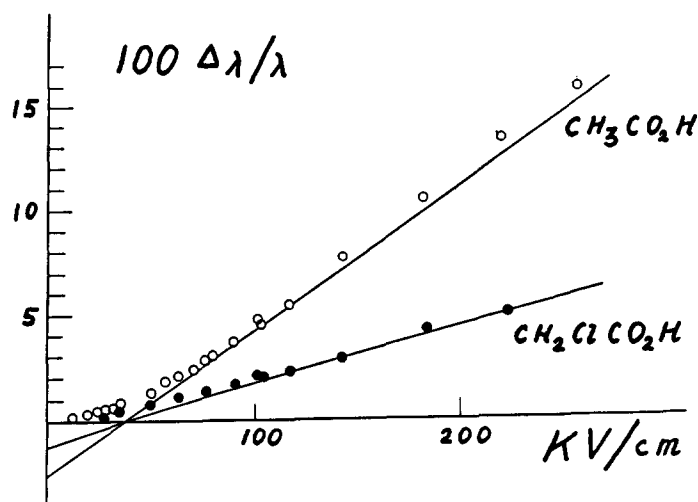


FIG. 2.

The overall error that arises from our overestimate of the temperature is probably of the order 0.3%. Since the sensitivity in Schiele's measurements was of the order 0.03%, a later revision of our calculations to the correct temperatures may be justified. It must be borne in mind, however, that in the experiments where Schiele found a reasonably large effect, the field intensities could not be determined with an accuracy comparable to the sensitivity for small differences of resistance.

Schiele did not measure directly the entire increase of the conductance due to the field, but instead, the difference between the conductances of weak electrolytes and a strong acid, HCl, as a function of the field intensity. This procedure practically eliminates the error due to heating and in addition, the "general" Wien effect of the free ions. In the cases which we have selected, two electrolytes of the same valence type and nearly equal conductances were compared. In consequence, the compensation of the general Wien effect was particularly good, within 0.03% as estimated from formula (35a). This means that we make no appreciable error when we attribute the differential effects measured by Schiele for monobasic acids entirely to the increased ionization of the weak acids.

In Fig. 2, Schiele's¹⁶ measurements for acetic acid and for chloroacetic acid are compared with

the computed concentrations of free ions. The calculation is based on a *stoichiometric* dissociation constant $K(X) = K_0 F(b)$. For $X=0$, this computed dissociation constant is in error by the factor³

$$\gamma^2 = \exp(-2\kappa q / (1 + \kappa q))$$

due to the weakening of the interionic attraction by the "atmosphere." With increasing field intensity, the effect of the atmosphere is eliminated. The agreement between theory and experiment is most striking, all the more when one considers that the computation of the theoretical curves involves no adjustable constants.

The discrepancies between theory and experiment in Fig. 2 are within the limits of uncertainty of this comparison, and perhaps of the measurements. The difference between the two acids depends entirely on the degree of dissociation. Other acids investigated by Schiele fit equally well into the picture. Propionic acid behaves almost exactly like acetic, as it should. Phosphoric acid, conductance 2×10^{-4} , shows a small effect, 1.8 percent at 260 kv/cm, which agrees quantitatively with Nims' result,¹⁷ $K = 8 \times 10^{-3}$ at 20°, for the first dissociation constant; the second dissociation is negligible.

For weak bases, Schiele¹⁸ found somewhat smaller effects than expected from the theory. On the other hand, the effect found for NaOH

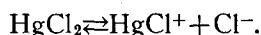
¹⁶ J. Schiele, Ann. d. Physik [5] 13, 811 (1932).

¹⁷ Nims, J. Am. Chem. Soc. 56, 1110 (1934).

¹⁸ Schiele, Phys. Zeits. 34, 60 (1933).

was surprisingly high, in fact, equal to that of $\text{Ba}(\text{OH})_2$. This strange coincident could perhaps be explained by the absorption of CO_2 from the air; it would not be safe to draw conclusions until this question has been settled.

In view of the approximations which we have discussed before, we must be prepared to find appreciable deviations from our theoretical formula for the highest field intensities. It is a bit surprising that the acids in water agree as well as they do. This may be due to the small Stokes' radius, in which case the slower ions of the bases might lead to greater deviations. However, it would be easier and even more interesting to investigate a weak salt, so as to get a still greater hydrodynamic effect. A possible suggestion is mercuric chloride, which dissociates according to the scheme



A strong salt, for example NaCl , could be used for comparison. Since weak salts may be liable to greater time-lags than acids, the effect of time should be investigated.

Some di- and tribasic acids, among them sulfuric, tartaric and ferricyanic acids, also were investigated by Schiele. In these cases, the differential effects against HCl is partly due to the general Wien effect, and partly to the increased dissociation. For this reason, and in view of the inaccurate data on the dissociation of the acids in question, it is not practicable at present to use these cases for a test of the theory. The general trend of the results seems to be in accord with the theory.

In applying the data of F. Bauer¹⁹ for the Wien effect in acetone we meet with similar difficulties. Bauer was more interested in the general Wien effect of free ions, than in the increased dissociation of weak electrolytes. In the cases where he extended his experiments to the highest field intensities that he could get, his main purpose was to determine the upper limit of the general Wien effect. For weak electrolytes he then found very large effects, which gave little indication, if any, of approaching a limit. As outstanding examples he mentions, in the

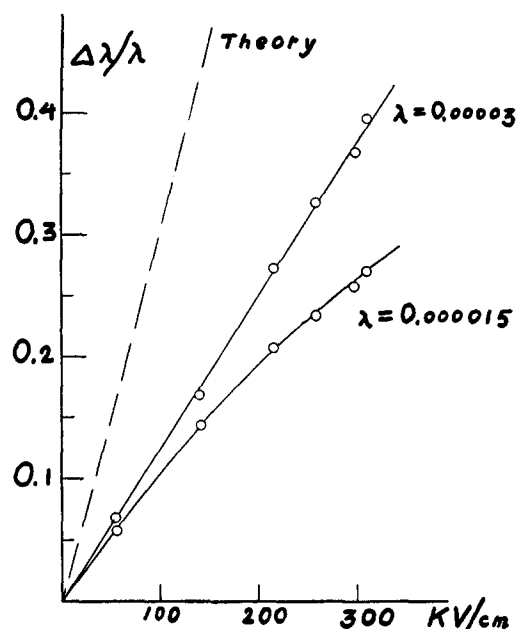


FIG. 3.

order of increasing effects, LiBr , CoCl_2 and $\text{Co}(\text{NO}_3)_2$. The results for the last named substance are not given in his article, except by a qualitative description. The next best case from our point of view is CoCl_2 . Adequate data for the dissociation of this salt are not available. Bauer describes measurements but fails to publish the complete results. In Fig. 3, the solid curves and the points represent Bauer's data for the Wien effect of CoCl_2 in acetone, while the theoretical curve (dashes) has been computed on the assumptions $\alpha \ll 1$; $\gamma^2 = 1$, which necessarily lead to an overestimate of the effect. The predicted effect is evidently large enough to account for Bauer's results. In fact, a prediction based on reasonable estimates of α and γ still leads to values which are somewhat greater than those observed by Bauer. The discrepancy might arise from errors in our estimates of α and γ , or else from the time-lag of the dissociation equilibrium, which would then have to be considerably greater than our theoretical minimum (46a). The latter explanation finds support in Bauer's remarks about the time-effect, and with the data given in his Fig. 4. Unfortunately, the interpretation of these data remains ambiguous, for Bauer failed to specify the conductances of the solutions in connection with the time-lag.

¹⁹ F. Bauer, Ann. d. Physik [5] 6, 253 (1930).

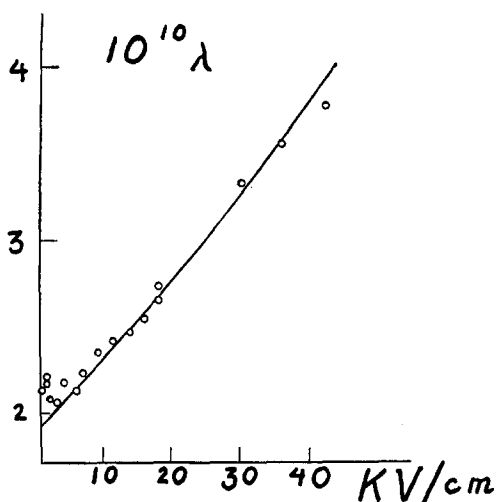


FIG. 4.

In solvents of very low dielectric constant, such as benzene, the application of the theory is no longer complicated by the variation of the degree of dissociation α , which is always very small. Moreover, in most cases the activity coefficients will be practically equal to unity; in benzene, only a few very good electrolytes provide exceptions.^{11, 20} We therefore expect the great majority of conducting solutions in solvents of low dielectric constant to exhibit the simple variation of conductance with the field intensity, which is described by our formula (42). When the dielectric constant is as low as that of benzene, a field of less than 40 kv/cm will suffice to double the conductance.

This class of conductors includes the liquid insulators used in electrotechnics. It is common knowledge that the conductance of a transformer oil increases with the field intensity. However, most investigators have failed to separate the opposing effect of saturation, so that their results are by no means direct measurements of the conductance. Only A. Gemant²¹ made successful efforts to find "semiconducting" solutions that would lend themselves more readily to a quantitative study of the field effect. In order to obtain reproducible results, he replaced the transformer oil by a mixture of

benzene and ethyl alcohol for solvent, with picric acid as electrolyte. By the addition of phenol or mineral oil in moderate amounts, the temperature coefficients of the conductances could be adjusted to zero. Thanks to the higher conductance of his solutions as compared to transformer oil, the saturation of the current was negligible in his experiments, at least if the time-lags for his electrolytes are of the order given by our minimum estimate (46). Gemant used a steady direct current, and derived the resistances of his solutions from measurements of voltage and current.

The dielectric constants of Gemant's solutions have not been measured, but they can be estimated with reasonable certainty from available data on solutions of ethyl alcohol in benzene.²² For a solution containing 1 percent picric acid, 5 percent ethyl alcohol and 1 percent mineral oil, of conductance $\lambda = 2 \times 10^{-10}$, the estimated dielectric constant is $D = 2.71$ at 20° . For another solution, which contained 1 percent picric acid, 8 percent ethyl alcohol and 3 percent mineral oil, of conductance $\lambda = 4 \times 10^{-9}$, our estimate is $D = 3.03$ at 20° . Both estimates involve extrapolation of Stranathan's data,²³ which only cover concentrations of ethyl alcohol up to 4.3 percent.

In Figs. 4 and 5, Gemant's data for the two solutions referred to are compared with the theoretical formula (42). Both the magnitude and the general type of the effect conform approximately to the theory. The agreement in Fig. 4 is almost as good as for Schiele's data in aqueous solutions, Fig. 2. However, both figures 4 and 5 indicate a flattening out of the experimental curves for low field intensity, which cannot be explained by the present theory. While some flattening of the curves due to the effect of the atmospheres should indeed be expected, the observed effects seem much too large. The concentrations of free ions can be estimated from the conductances, if reasonable assumptions about the equivalent conductances Λ are allowed. For the case represented in Fig. 5, $\Lambda = 40$ is hardly an overestimate. On this basis,

²⁰ Kraus and Vingee, J. Am. Chem. Soc. **56**, 511 (1934).

²¹ A. Gemant, *Elektrophysik der Isolierstoffe*, p. 78, Springer, Berlin, 1930.

²² J. Stranathan, Phys. Rev. **31**, 653-71 (1928).

²³ A. Gemant, *Elektrophysik der Isolierstoffe*, p. 80, Springer, Berlin; Phys. Zeits. **29**, 289 (1928).

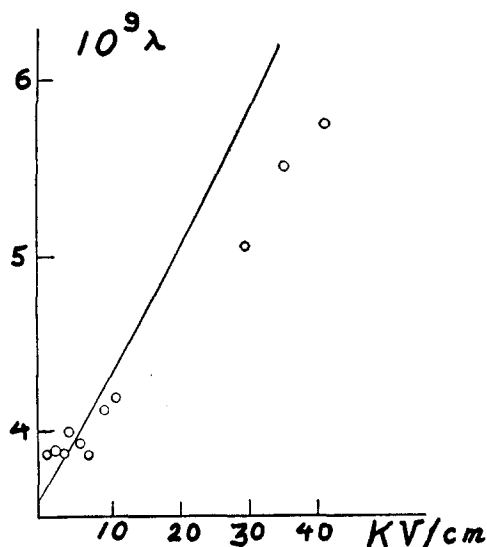


FIG. 5.

the concentrations of free ions would be 10^{-7} , and the activity coefficient would be $\gamma=0.95$. The value of λ for $X=0$, computed by the theory from the three highest points, is 3.17×10^{-9} ; the given activity coefficient would raise this value to 3.34×10^{-9} , but by no means up in the neighborhood of 4×10^{-9} , as indicated by the data.

In one other respect, the present theory fails to agree with Gemant's results. Since the theory predicts an increase of electrolytic dissociation, the resultant increase of the conductance should be independent of the direction. Gemant²³ made special arrangements to measure the conductance perpendicularly to a strong field, and found that the transverse conductance increased much less with the field intensity than the longitudinal, if at all.

On the whole, the verification of the theory is satisfactory. In some instances, the numerical agreement is excellent, and with one exception, an effect of the predicted order of magnitude has been observed. The only qualitative discrepancy is Gemant's failure to find a substantial transverse effect.²³ The discrepancies cannot be interpreted without further experimental evidence.

APPLICATIONS TO SOLID ELECTROLYTES

Most ionic solids possess an intrinsic conductance, which is ordinarily electrolytic. In addition, a photoconductance induced by sun-

light or by natural γ -radiation may be present. The intrinsic conductance is characterized by its regular variation with the temperature. Its electrolytic mechanism can often be established by the verification of Faraday's law for suitable temperatures, or by the evidence of polarization. For part of the time at least, the mobile ions must occupy abnormal positions in the structure of the solid. If a process of exchange takes place regularly between the mobile and the normal ions, perhaps something like the process,



which takes place in pure water, then the solid will behave like a weak electrolyte. If the mobile ions should arise from permanent faults in the lattice, then the solid electrolyte would be weak or strong, according to the frequency of recombination of the ions. There is no conclusive evidence that strong solid electrolytes exist.

There is no reason why the present theory for the dissociation of weak electrolytes in strong fields could not be applied to solids, except that for highly anisotropic crystals, the quantitative relation between conductance and field intensity might be different.

It was first shown by H. H. Poole²⁴ that solid dielectrics exhibit deviations from Ohm's law. Poole demonstrated this effect in fields of the order 10^6 volt/cm for glass, mica, shellac and celluloid (Kodak film). He could describe his results fairly well by the formula,

$$\log_{10} \lambda = A - B|X|.$$

His values of B range from 1.2×10^{-6} for mica to 3.80×10^{-6} for celluloid. In the case of glass, but not in the case of mica, the constant B was found to decrease with increasing temperature.

H. Schiller and N. Albrecht²⁵ found similar results for glass, mica and gypsum. In their experiments with glass, considerable polarization was evident. For mica, which will stand up in very strong fields if thin enough, Poole's formula was found valid only for a limited range of field intensities. In the range $10^6 < X < 3 \times 10^6$ volt/cm, $\log \lambda$ increases less rapidly with the field than for $X < 10^6$ volt/cm. A field of the in-

²⁴ H. H. Poole, *Phil. Mag.* **32**, 112 (1916); *ibid.* **34**, 204 (1917); *ibid.* **42**, 488 (1921).

²⁵ H. Schiller, *Ann. d. Physik* [4] **81**, 32 (1926).

tensity 3×10^6 volt/cm increases the conductance of mica by a factor of more than a thousand.

The effects found by these investigators were not quite as large as those predicted by the present theory, but of the expected order of magnitude. The agreement is comparatively good for very high field intensities, which tend to suppress polarization and time-lags. The deviations from Poole's formula observed by Schiller are in the direction expected by the theory, cf. our asymptotic formula (39).

Finally, it may be pointed out that Poole's values for his characteristic parameter B were about inversely proportional to the dielectric constant of the materials, which may be taken as a crude verification of our theoretical prediction $b \sim 1/D$ (formula (37)).

As yet, the deviations from Ohm's law in solids have not been explored to any great extent. It would be advantageous to eliminate the complicating effect of polarization. This could probably be achieved by appropriate choice of electrodes, such as silver electrodes for the investigation of silver halides, or *alkali metal electrodes* for glasses and other alkali silicates.

TIME-LAGS AND POLARIZATION

In many cases it is important to know not only the dissociation constant as a function of the field intensity, but the actual reaction velocities of electrolytic dissociation and recombination as well.

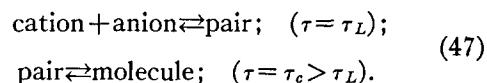
We have shown that the time required for the mutual approach and departure of the ions determines a certain maximum value (Eqs. (24) and (25)) for the kinetic coefficient constant of recombination. For binary electrolytes, the corresponding minimum time-lag for adjustment of the dissociation equilibrium is given by Eq. (46),

$$\tau = \tau_L = \frac{(1 - \alpha_0) D}{(2 - \alpha_0) 4\pi\lambda}.$$

This minimum time of adjustment we shall call the Langevin time-lag, because the underlying theory of ionic recombination was first derived by Langevin.²⁶ When the steady degree of disso-

ciation α_0 is very small, the Langevin time-lag equals half the Maxwell time-lag, $\tau_M = D/4\pi\lambda$, for the readjustment of charges in a conductor.

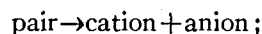
The mutual approach of two ions will not in all cases complete the recombination, which may involve a molecular rearrangement of the pair. If the time needed for this rearrangement is smaller than the Langevin time-lag, then it is of no importance. Otherwise, we have to consider two reversible reactions with different time-lags:



When $\tau_c < \tau_L$, all the molecules may be counted as ion pairs. The Langevin time-lag τ_L depends on the degree of dissociation α_0 of the ion pairs, and on the conductance λ in the steady state. Both of these depend on the intensity of the electric field (although, when $\alpha_0 \ll 1$, only the change of λ matters). As a result, the Langevin time-lag decreases with increasing field; when $\alpha_0 \ll 1$, the relation between the two is

$$\tau_L = D/8\pi\lambda(X) = D/8\pi\lambda(0)(F(b))^{1/2}. \quad (48)$$

The chemical time-lags, τ_c , will not be affected by the field. *Only one of the four reactions represented in the scheme (47) is affected by the field, namely the dissociation:*



the kinetic constant of this reaction is increased by the factor $F(b)$.

It is reasonable that cases of the type (47) should exist, and some experimental indications have been found, although there is no certain evidence of chemical time-lags from measurements of conductance in strong fields. Two conditions must be satisfied in order that the chemical time-lag can be measured. First, the concentration of molecules must obviously be at least comparable to the concentration of free ions. Secondly, *the concentration of free ions must be at least comparable to the concentration of ion pairs.* Otherwise, even a large displacement of the equilibrium between ions and pairs will not

²⁶ Langevin, Ann. chim. phys. **28**, 433 (1903), applied his theory to ionized gases. See Herzfeld, Phys. Rev. **34**,

791 (1929); ibid. **37**, 287 (1931), for applications to dielectrics.

materially disturb the equilibrium ratio between pairs and molecules, and the subsequent adjustment of the latter will involve changes too slight to be detected. The condition for detecting chemical time-lags by saturation currents is somewhat milder: The rate of removal of free ions must be comparable to the rate of conversion of molecules into pairs.

In Schiele's measurements (Fig. 2), the electric fields were applied for time intervals of the order 10^{-6} sec., about the shortest admissible in view of the Langevin time-lag for acetic acid of conductance $\lambda = 2 \times 10^{-4}$. We calculate

$$\tau_L = 1.7 \times 10^{-8} \text{ sec.}$$

Since Schiele's conductances agree with the theoretical steady values, any chemical time-lag involved in the dissociation of acetic, chloroacetic and phosphoric acids in water must likewise be of the order a few times 10^{-8} sec. or less. The slightly lower field effects found by Schiele for bases might be due to greater time-lags (between 10^{-6} and 10^{-7} sec.); but as we have pointed out, it does not appear certain that sufficient precautions were taken to exclude carbon dioxide in his experiments with bases.

It would be worth while to investigate by this method the possible time-lags in the dissociation of other electrolytes as well. The dissociation of weak salts ought to be slower, in general, than the proton exchange involved in the dissociation of acids and bases.

For solutions in acetone, F. Bauer¹⁹ made some interesting observations of time-lags. He worked with conductances in the range

$$0.000015 < \lambda < 0.0004;$$

the corresponding Langevin time-lags for sparingly dissociated electrolytes lie in the range

$$2 \times 10^{-9} < \tau_L < 4 \times 10^{-8} \text{ sec.}$$

The data represented in Bauer's Fig. 4 indicate time-lags of the order 10^{-7} sec. for cobalt chloride, and two or three times greater for mercuric chloride.

In liquid and solid electrolytic semiconductors, the Langevin time-lag can range from fractions of a second to the order of an hour. However, as I have pointed out in discussing the conductance of such substances, in most experiments the field effect and the polarization

have not been separated. It will therefore be necessary to discuss the interaction of the two effects.

The observed polarizations are of the order of kilovolts, and are probably analogous to the saturation phenomena in gases. When the electrodes furnish no ions, which is frequently the case, the total current cannot exceed the rate of production of ions by dissociation of molecules (ion pairs) in the interior of the dielectric. For a given rate of dissociation, the saturation current is evidently proportional to the volume.

The removal of ions starts at the electrodes: The region near the cathode becomes depleted of anions, and *vice versa*. As long as the current remains considerably below that necessary for complete saturation, the concentrations of both ions midway between the electrodes will be maintained by the normal kinetic equilibrium of dissociation and recombination. Near the electrodes, the dissociation must exceed the recombination by an amount that equals the rate of removal of ions. Therefore, the thickness of each electrode layer will be proportional to the intensity of the field, unless the field itself affects the rate at which the dissociation takes place. The electrode layers contain space charges, which intensify the fields near the electrodes. The resultant excess potential drop appears as a "polarization." For transformer oils, the excess fields near the electrodes have been demonstrated by Whitehead and Marvin,²⁷ and the space charges by A. Gemant.²⁸

There also is evidence of genuine polarization from some of the experiments performed by Whitehead and Marvin, in which a considerable increase of the conductance was observed after reversal of the current. The quick appearance of the carriers would seem to exclude the possibility that they were formed after the current was reversed. Hence, the only reasonable explanation for the increased conductivity is the accumulation of undischarged ions in the immediate vicinity of the electrodes. Since the layer involved ought to be very thin in the case of strong fields, the polarization is not likely to become greater than a few volts. However, the local

²⁷ Whitehead and Marvin, A. I. E. E. Trans. **48**, 299 (1929), *ibid.* **49**, 647 (1930). See also Herzfeld.²⁶

²⁸ A. Gemant, Elektrotech. Zeits. **54**, 468 (1933).

field in the polarization layer might become quite considerable, and could possibly play a part in the breakdown of dielectrics.

For the interpretation of certain experiments on the initial conductance of dielectrics, it might be worth while to consider the adsorption of ions by the electrodes due to the electrostatic image force. This effect would tend to increase the equilibrium concentration of ions, and to accelerate the separation of ion pairs in a layer of the thickness $q \sim 10^{-6}$ cm near the electrodes. The effect would be greater, the smaller the distance of closest approach between the ions and the metal. In order to interpret any part of the charging current curves found by Whitehead and Marvin as due to adsorption, it is necessary to assume a least distance of approach smaller than 3×10^{-8} cm. The current of adsorbed ions ought to exhibit a Schottky effect, which might account for the observed increase of the initial conductance with field intensity.

The experiments of Whitehead and Marvin are outstanding in the detailed study of individual factors, such as time-lags, and in the consistent limitation to relatively weak fields. Thanks to the latter precaution, the increase of the dissociation constant due to the field in their experiments could not have exceeded fifty percent (for 10^4 volt/cm), except in the cases where the fields were locally enhanced by space charges. Therefore, their investigation represents a rather clear-cut study of the saturation phenomena, without serious complications due to the field effect.

In most other investigations recorded in the literature, the experimenters sought one of the effects, and apparently measured a combination of both. The task of separating the factors that enter into the results then becomes rather hopeless. Hence, it seems proper to discuss only the most pertinent simple deductions that can be made from the present theory, and to draw tentative general conclusions from the available mass of data.

In applying the scheme (47) to liquids of dielectric constant less than 3, we must bear in mind that at equilibrium, even when the concentration of free ions is as low as 10^{-10} mol/l, the concentration of ion pairs will almost certainly be large in comparison. This conservative

inference from the data of Kraus and Fuoss¹¹ is another example of the valuable general information that can be gained by studying solutions of known electrolytes in well purified solvents.

We now recognize that when a considerable chemical time-lag exists, the saturation phenomena will develop through two essentially different stages.

At first, the ions removed by electrolysis will be replaced by dissociation of ion pairs at the Langevin rate. The modifications of the field by space charges will be moderate (a factor of the order 2), as long as the concentration of ion pairs is nowhere greatly reduced. However, after the electrode regions have been depleted of ion pairs, the subsequent production of ions in these regions will be determined by the slower transformation of molecules, and the electrode layers will expand accordingly. The conditions in this second stage permit the development of much greater fields, so that even the concentration of cations near the cathode and that of anions near the anode will be greatly lowered due to their high velocities.

With this general picture in mind, certain predictions can be made regarding the magnitude of the saturation current. First, if there is a chemical time-lag $\tau_c > \tau_L$, and the saturation current is measured after the ion pairs have been removed by electrolysis, then the current will be found independent of the field intensity. On the other hand, if there is no appreciable chemical time-lag, or if the saturation current is measured before any great fraction of the ion pairs have been electrolyzed, then we shall expect the saturation current to increase with field intensity X , in the ratio

$$i_{\text{sat}}(X)/i_{\text{sat}}(0) = K(X)/K(0) = F(b). \quad (49)$$

For comparison, the conduction current in the case of no saturation increases with the field intensity as

$$i = X\lambda(X) = X\lambda(0)(F(b))^{1/2} \sim b(F(b))^{1/2}.$$

It is seen from Fig. 1, that for $b > 4$, the ratio $(F(b))^{1/2}/b$ increases with the field intensity. Accordingly, for a field intensity that corresponds to a value of b somewhat less than 4, the thickness of the space charge layer will reach a

maximum. The field in question should be of the order 70 kv/cm for transformer oil, and 200 kv/cm for glass.

The data given by Toriyama²⁹ for the conductance of transformer oil indicate that the saturation current may indeed increase very rapidly with the field intensity. The effects found by Toriyama were somewhat larger than could be accounted for by the theory (assuming univalent ions); the cause of the discrepancy would have to be determined before definite conclusions could be drawn.

Where the saturation current is found to increase with the field intensity, it should be possible to find evidence of the Langevin time-lags. Where the saturation current is independent of the field intensity, the distribution of space charges ought to correspond to a greater, chemical time-lag.

In a given experiment, some electrolytes may show a Langevin time-lag, others a chemical

time-lag. Whether a given electrolyte will show one or the other, will depend on two properties that cannot in general be predicted, namely, the ratio τ_c/τ_L and the reserve concentration of ion pairs. Incidentally, the pair concentration and τ_L will depend on the concentration of ions, the latter inversely as the conductance. The chemical time-lag ought not to depend on the concentration unless the electrolyte is polymerized, or cluster ions are formed. It must be pointed out, however, that cluster ions may form at surprisingly low concentrations.¹¹

As yet, time-lags or saturation currents have not been measured for electrolytes of known constitution in solvents of low dielectric constants. By such methods, it should be possible to determine the mobilities of suitable free ions in benzene and similar solvents, where there is no hope that we should ever be able to extrapolate conductance curves. Moreover, the investigation of these phenomena in known electrolytes would greatly aid their application to the study of semiconductors of unknown constitution.

²⁹ Y. Toriyama, *Archiv f. Electrotech.* **19**, 31 (1927).

Caesium Nitrate and the Perovskite Structure

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1. The crystal structure of dysanallyte has been verified. 2. The crystal structure of CsNO_3 has been determined. 3. The so-called perovskite structure as a type of cubic symmetry is based on a mineral which is very probably not cubic but is orthorhombic. 4. The term "perovskite structure" should be discontinued.

THE authors' interest was first directed to the perovskite structure when a powder diffraction pattern of CsNO_3 was found to suggest cubic symmetry (Fig. 1) while the weak birefringence, as shown by the polarizing microscope, indicated some other symmetry.

Wyckoff¹ discussed the assignment of crystals, giving a pattern of this kind, to the so-called perovskite structure and expressed his doubt that these crystals were really isometric. Barth² made the first structure determination of pe-

rovskite and reported the mineral to be orthorhombic, $a : b : c = 0.9881 : 1 : 1.4078$, and the space group to be V_h ¹⁹. Barth² also determined the structure of dysanallyte to be cubic with $a_0 = 3.826$. The authors of this paper were able to check Barth's work on dysanallyte, using a sample from Magnet Cave, Arkansas (see Table I).

The authors were unable to obtain a sample of perovskite but, in view of Table I, saw no reason to doubt Barth's work. It therefore seemed worthwhile to make a complete structure analysis of CsNO_3 , since the "perovskite structure" was in question and the structure of CsNO_3 had never been determined.

¹ R. W. G. Wyckoff, *Structure of Crystals*, Chemical Catalogue Company, New York, 1931.

² T. Barth, *Norsk. Geology Tidsskr.* **8**, 201 (1925).