The Diffusion of an Electrolyte Solution in a Superimposed Electric Field

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A diffusion effect in electrolyte solutions, arising from an outer field being superimposed in the diffusion direction, is discussed and, in a special case, related to the field characteristics and to the kinetics of the ionization equilibrium.

A s is well known, the diffusion of salts in solution is accompanied by a macro-
scopic electric field, which changes with the nature of the concentration
gradient and during the diffusion process. This field, and the ionic migration
in it, is characteristic of the gradient diffusion of electrolytes. Phenomena
within the gradient, obtained by superimposing an outer electrical field, are
naturally considered in connection with the theory of electrophoresis [1], owing
to the importance of knowing what happens to the gradient itself (such as
sharpening or broadening effects) and of knowing how to define the migration
of a boundary. It is in this case the question of a constant outer field. The
literature concerning this case is rather large.

In the present article we will investigate the possible ability of the super-
imposed field to increase the diffusion coefficient of one component of the
solution. Such an effect can be foreseen for both alternating current and direct
current. In section 3 we will briefly systematize some different reasons for the
occurrence of such an electrodiffusion phenomenon, irrespective of whether the
order of magnitude is sufficient for an experimental demonstration or not.
In sections 1 and 2 we will enter into the quantitative aspect, although only in
a special case. We will assume the system to be free of thermal convections,
the appearance of which sets a serious limit for the measurements and must be
decisive for the choice of experimental conditions.

1. GENERAL PRINCIPLES

Owing to the fact that gegenions, which play no direct role in the above-
mentioned electrodiffusion phenomenon possess the disadvantage of increasing
the Joule heat, the theory is exemplified by a case with only one single electro-

lyte component *. In the simplest case, this is a weak electrolyte AB. In the ionization equilibrium the constituents A and B are present either as ions or as uncharged AB. This forms a statistical basis for a diffusion effect since the ions are not simply moving up and down as in a completely ionized, simple electrolyte. (This latter is theoretically true only if the statistical changes in the mobility of the ions are neglected. These changes appear to be too rapid for a measurable effect in ordinary cases.)

In the kinetical equilibrium $AB = A^+ + B^-$, an ion has a certain average life-time T. This may not always be the same for the two kinds of ions, $T^+ \neq T^-$. For the present we will assume that the undissociated state AB has a sufficiently long average life-time, with a statistical dispersion large enough, to make the duration of the ionic state of each single A (and B), even for short time intervals, randomly distributed on the time axis of the alternating field.

In the experiments it is not necessary to use a concentration gradient — we can instead measure the self-diffusion using isotopic labelling. Some of the possible systems (see section 3) will give an effect *only* in self-diffusion. In self-diffusion we have, with some exceptions, the disadvantage of a very small density gradient, which may cause difficulties owing to the Joule heat and convection risk **. We will, therefore, assume a real concentration gradient. This complicates the theory because of the Nernst diffusion potential.

Assuming a concentration gradient of the salt as in a differential measurement of the diffusion coefficient, we arrange electrodes at the top and bottom of the diffusion cell or use a technique as in electrophoresis work. Applying an alternating electrical field upon the gradient column, an ion A^+ will move a distance l_+ in one direction, the length of which may depend on the life-time of the ion, on the phase condition at the moment of appearance of the ionic state and on the frequency of the electric field. In addition, l_+ of course depends on the mobility of the ion and on the field strength. After an average time T^+, the ion disappears. In the next ionic state of the same A, the field direction may be the same or opposite, the correlation of phase of the electrical field at the moments of disappearance and reappearance of the ion being supposed to be low according to our suppositions. Under these circumstances, the action of the field will result in a macroscopical net displacement of the ion and the ion constituent A, and therefore also of the substance AB as a component. Thus we have an electrical diffusion effect in addition to the ordinary diffusion.

Assuming ideal statistical conditions, the electrical diffusion effect upon the cations may be expressed by a one-dimensional diffusion coefficient according to *** (see for instance the recent article [2])

$$D^+ = \nu \, l_+^2/2 \qquad\qquad (1)$$

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* Two solute components is in itself a wider field for practical application. Using a real concentration gradient (mutual diffusion as distinct form self-diffusion), this case will not give an ideal gaussian gradient curve, which means a complication in the evaluation of the experiments.

** The porous disc method is often used, *e. g.* to avoid convections, but would eventually involve troubles from the Joule heat in the membrane and an electroosmotic diffusion effect which is of interest in itself but undesired as a source of error.

*** The number factor 2 is deduced assuming steps of equal length.

where ν is the number of steps per unit time. From eqn. (1) it is seen that the length of the steps (and therefore also the duration of the steps) is more important than the number of steps/sec., since the former appears as a square. As a matter of fact, the kinetical process, and the current frequency as well, has to be comparatively slow if the electro-diffusion shall compete measurably with the ordinary diffusion.

The choice of characteristics of the superimposed field is optional from both theoretical and practical viewpoints. A certain generality and simplicity is achieved by choosing a square field as in Fig. 1.
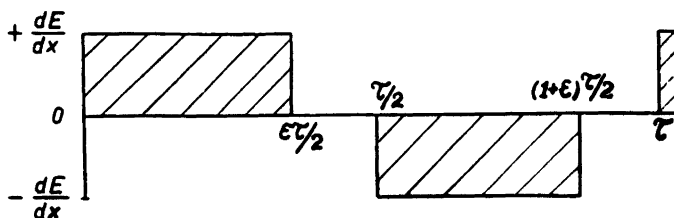

Figure 1.

The period length is τ sec and ε is the fraction of the half-period during which current is conveyed. The reason for choosing $\varepsilon \neq 1$ is that ε is an interesting variable for the magnitude of the diffusion effect. The possibility is also foreseen of using the current-free interval to measure the conductance of the diffusion column, in order to get an exact measure of the average temperature in the column.

It seems that, under certain conditions of current and kinetical characteristics, the regularity of the current variations gives rise to a lower diffusion effect than that which would be obtained if the superimposed field is given a random nature. There is no doubt that such can be experimentally arranged.

We will here treat two extreme cases, the theory for which is elementary. In both cases we assume as above that the uncharged state for A and B is of a comparatively long duration $T°$ and that the statistical dispersion of $T°$ is broad enough to eliminate any correlation between the consecutive phases (on the time axis of the field) with which an ion appears. In this way we also practically exclude the possibility that the ion can appear twice or more during the same period of the current.

The life-time of the ion being T, the two cases we are going to treat are a) $T < \varepsilon\tau/2$ and b) $\varepsilon\tau/2 < T$, $\varepsilon \ll 1$. The latter case corresponds to sudden current shocks, as experimentally used when studying the Wien-effect of electrolytes. In both cases τ is intermediate between T and $T + T°$, which means a kind of broad resonance between the field and the pulsation of the electrolyte.

$$\text{a) } T < \varepsilon\tau/2.$$

The length of each step is $l = \pm Tu$, $\pm u$ being the velocity of the ion in the field dE/dx. The number of ionic states/sec. is $1/(T+T°)$. Of these states

a fraction ε leads to a step, so that the number of steps/sec. is $\nu = \varepsilon/(T+T^\circ)$. Thus eqn. (1) gives for the electrodiffusion of the cations

$$D^+ = \frac{(T^+u^+)^2\varepsilon}{2(T^+ + T^\circ)} \tag{2}$$

The frequency $1/\tau$ is not directly contained in this formula, compare however the discussion of eqn. (5).

$$\text{b)} \quad \varepsilon\tau/2 < T, \quad \varepsilon \lll 1.$$

The step length is $l = \pm \varepsilon\tau u/2$, i. e. the duration $\varepsilon\tau/2$ of the step multiplied by the velocity $\pm u$. The number of steps/sec. is the product of the number of $+$ or $-$ shocks $2/\tau$/sec. and the probability $T/(T+T^\circ)$ that a step shall be taken at a certain current shock. Thus $\nu = 2T/\tau(T+T^\circ)$ and, for cations

$$D^+ = \left(\frac{u^+\varepsilon}{2}\right)^2 \frac{T^+ \tau}{T^+ + T^\circ} \tag{3}$$

In order to compare cases a) and b), the D^+-values are divided by the Joule effect w watt/cm^3 in each case, which ratio ought to be decisive for the possibility of measuring the effect. This effect is $w = \varepsilon\varkappa(\mathrm{d}E/\mathrm{d}x)^2$, the conductance being denoted by $\varkappa$. The measurements are supposed to be made upon exactly similar diffusion columns, one according to eqn. (2) and the other according to eqn. (3). The allowed potential gradients are different in these cases, and therefore also the velocities u^+. Considering also that $u^+ = U^+\mathrm{d}E/\mathrm{d}x$, where U^+ denotes the ionic mobility, we obtain

$$(D^+/w)_{\text{eqn. (2)}} / (D^+/w)_{\text{eqn. (3)}} = T^+ / \tfrac{1}{2} \varepsilon\tau \tag{4}$$

Here $\varepsilon \tau$ belongs to the conditions of eqn. (3), for which we have assumed $\varepsilon\tau/2 < T^+$. Thus this case is comparatively unfavourable according to eqn. (4).

From eqn. (2) we obtain

$$D^+ / w = (T^+U^+)^2 / 2 \varkappa (T^+ + T^\circ) \tag{5}$$

showing that the result is independent of the field characteristic ε. (τ does not enter this formula. However, the greater τ is, the greater must $T^+ + T^\circ$ be according to our suppositions.)

2. DIFFUSION THEORY

The diffusion effect on the two kinds of ions has to be combined with the ordinary diffusion of the ions and undissociated part, due regard being paid to the diffusion potential. For this purpose we first need an expression for the

diffusion of a weak electrolyte A_pB_q, with mole concentration C and degree of dissociation α according to

$$A_pB_q \underset{k'}{\overset{k}{\rightleftharpoons}} pA^{z+} + qB^{z-}; \quad pz^+ = qz^- \tag{6}$$
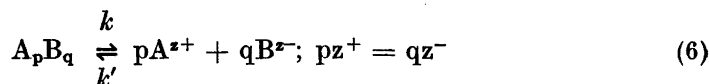
$$C\,(1-\alpha) \quad pC\alpha \quad qC\alpha$$
$$(pC\alpha)^p \,(qC\alpha)^q = KC(1-\alpha) \tag{7}$$

neglecting for the present the activity coefficients. We will calculate the diffusion coefficient D_{12} using the general expression [3] for the components 1 and 2

$$D_{12} = RTN_1 B_{12} \,/\, \Phi_2; \quad B_{12} = \partial \ln a_2 \,/\, \partial \ln N_2 \tag{8}$$

The mole fraction N_1 of the solvent is sufficiently near 1 in the dilute solutions considered here. Φ_2 is the molar friction of the solute, a_2 its activity.

It has been previously shown [3,4] that if a component in solution exists in different forms or molecular sizes, the molar friction Φ of the component depends upon the molar frictions Φ_i of the different species according to

$$\frac{1}{\Phi} = \sum \frac{n\nu_i}{\Phi_i} \tag{9}$$

where ν_i is the fraction of the component which is present in the form i and n is the degree of association ($n = 2$ for double molecules etc.). The molecular weight of the c o m p o n e n t (necessary for defining Φ) shall correspond to $n = 1$.

Since in our present, simple case with only two kinds of ions, the ions must follow one another in the stoichiometric proportion, eqn. (6) corresponds to a simple conversion, the forms of the electrolyte being A_pB_q with the friction Φ° and $(pA^{z+} + qB^{z-})$ with the friction $\Phi^\pm$. For the friction of the solute Φ_2 we obtain from eqn. (9) simply

$$\frac{1}{\Phi_2} = \frac{1-\alpha}{\Phi^\circ} + \frac{\alpha}{\Phi^\pm} \tag{10}$$

This determines Φ_2 of eqn. (8). We will now proceed to determine B_{12} and may use the concentration of the undissociated part as a measure of the activity of the solute; $a_2 = C(1-\alpha)$. Eqns. (7) and (8) give

$$B_{12} = \frac{p + q}{p + q - \alpha\,(p + q - 1)} \tag{11}$$

This is quite plausible, $\alpha = 0$ giving $B_{12} = 1$ (ideal solute) and $\alpha = 1$ giving $B_{12} = p + q$ (ideal solute of $p + q$ ions per mole salt). The desired expression is then for the very dilute solution ($D_{12} \rightarrow D_2$)

$$D_2 = \frac{RT\,(p + q)}{p + q - \alpha\,(p + q - 1)} \left(\frac{1 - \alpha}{\Phi^\circ} + \frac{\alpha}{\Phi^\pm} \right) \tag{12}$$

This expression will now be extended to include the specific electrodiffusion effect. For this purpose it is preferable to use the complete expressions for the stationary motion as functions of forces and frictions. The contribution k^+ of the electrodiffusion to the diffusion force must first be calculated. In the diffusion theory, this force per mole solute, is the gradient in the chemical potential, $k_2 = -RT\partial\ln a_2/\partial x$. Confining our calculation to a dilute component of concentration c_2, eqn. (8) may be written $D_2 = (-RT\partial\ln a_2 \,/\, \partial x) \,/\, (-\varPhi_2\partial\ln c_2/\partial x)$ and from this

$$k_2 = -D_2\,\varPhi_2\partial\ln c_2/\partial x \tag{13}$$

For the cations, eqn. (2) is now assumed (the sign $\varDelta$ distinguishes electrodiffusion from ordinary diffusion)

$$\varDelta\,D^+ = \tfrac{1}{2}\,\frac{(T^+u^+)^2\varepsilon}{T^+ + T^\circ} \tag{14}$$

The concentration is, according to eqn. (6), p$C\alpha$. Further, the velocity $u^+ = U^+\mathrm{d}E \,/\, \mathrm{d}x$, U expressing mobility. The electrical force per gram-ion is $-z^+F\,10^7\mathrm{d}E \,/\, \mathrm{d}x$ ($F = 1$ faraday). From this, since the ratio of force to velocity equals the friction,

$$\varPhi^+ = z^+F\,10^7 \,/\, U^+ \tag{15}$$

Denoting by L the magnitude

$$L^+ = \tfrac{1}{2}\,\frac{\left(T^+\dfrac{\mathrm{d}E}{\mathrm{d}x}\right)^2}{T^+ + T^\circ}\,F\,10^{\,7} \tag{16}$$

we finally get the diffusion force per gram-ion k^+ from equation (13) (D_2 in this case being $\varDelta D^+$, $c_2 = \mathrm{p}C\alpha$ and $\varPhi_2 = \varPhi^+$) and by analogy also k^-

$$\begin{aligned}k^+ &= -L^+U^+z^+\partial\ln C\alpha \,/\, \partial x \\ k^- &= -L^-U^-z^-\partial\ln C\alpha \,/\, \partial x\end{aligned} \tag{17}$$

Let v°, v^+, and v^- be the linear velocities of AB, A^+, and B^-, respectively. Considering also the forces originating from the l o c a l potential gradient $\mathrm{d}E'/\mathrm{d}x$ in the diffusion column, and denoting, as in eqn. (12), the molar friction of AB by $\varPhi^\circ$, we obtain by equalizing the forces,

$$v^\circ\,\varPhi^\circ = -RT\frac{\partial\ln C(1-\alpha)}{\partial x} \tag{18}$$

$$v^+\,\varPhi^+ = -RT\frac{\partial\ln C\alpha}{\partial x} - L^+U^+z^+\,\frac{\partial\ln C\alpha}{\partial x} - z^+F10^{\,7}\,\frac{\mathrm{d}E'}{\mathrm{d}x} \tag{19}$$

$$v^-\,\varPhi^- = -RT\frac{\partial\ln C\alpha}{\partial x} - L^-U^-z^-\,\frac{\partial\ln C\alpha}{\partial x} + z^-F10^{\,7}\,\frac{\mathrm{d}E'}{\mathrm{d}x}$$

We have $pz^+ = qz^-$ and, the resulting electricity transport being zero, $pz^+Cav^+ = qz^-Cav^-$. From this, $v^+ = v^-$, and this velocity is denoted v. Expressing the ionic friction in terms of the electrochemical mobilities (eqn. (15)), the following is obtained by elimination of dE'/dx from the eqns. (19)

$$F \ 10^{\ 7} \left(\frac{1}{U^+} + \frac{1}{U^-}\right) v = -\left[RT\left(\frac{1}{z^+} + \frac{1}{z^-}\right) + (L^+U^+ + L^-U^-)\right]\frac{\partial \ln Ca}{\partial x} \quad (20)$$

Calculating the total flow of A_pB_q as a component, according to $J_2 = v^\circ C(1-\alpha) + vCa$, we get from eqns. (18) and (20)

$$J_2 = -\left\{\frac{RT}{\varPhi^\circ}\frac{\partial C(1-\alpha)}{\partial C} + \frac{RT\left(\frac{1}{z^+} + \frac{1}{z^-}\right) + (L^+U^+ + L^-U^-)}{F \ 10^{\ 7}\left(\frac{1}{U^+} + \frac{1}{U^-}\right)}\frac{\partial Ca}{\partial C}\right\}\frac{\partial C}{\partial x} \quad (21)$$

Since eqn. (21) is Fick's first law, the expression within the brackets is the total diffusion coefficient D_2. The equilibrium expression (7) provides

$$\frac{\partial C(1-\alpha)}{\partial C} = \frac{(p+q) \ (1-\alpha)}{p+q-\alpha \ (p+q-1)} \quad (22)$$

and similary for $\partial Ca/\partial C$. Inserting in eqn. (21) we arrive at

$$D_2 = \frac{RT(p+q)}{p+q-\alpha \ (p+q-1)}\left[\frac{1-\alpha}{\varPhi^\circ} + \frac{\alpha\left(\frac{1}{z^+} + \frac{1}{z^-}\right)}{(p+q)F10^{\ 7}\left(\frac{1}{U^+} + \frac{1}{U^-}\right)}\right] +$$
$$+ \frac{\alpha}{p+q-\alpha \ (p+q-1)}\frac{L^+U^+ + L^-U^-}{F \ 10^{\ 7}\left(\frac{1}{U^+} + \frac{1}{U^-}\right)} \quad (23)$$

The analogy with eqn. (12) is evident. The last term of eqn. (23) is the contribution ΔD of the superimposed field to the diffusion coefficient of the electrolyte. Thus by eqn. (16)

$$\Delta D = \frac{\frac{1}{2}\alpha\varepsilon\left(\frac{dE}{dx}\right)^2}{p+q-\alpha \ (p+q-1)}\frac{\frac{(T^+)^2U^+}{T^+ + T^\circ} + \frac{(T^-)^2U^-}{T^- + T^\circ}}{\frac{1}{U^+} + \frac{1}{U^-}} \quad (24)$$

We have assumed a real (but small) concentration gradient and thus dE/dx is not exactly constant over the diffusion column. Measuring instead, with isotopic labelling, say AB against A*B, the theory (for the diffusion of the A constituent) is simpler but shall not be given here.

In order to complete our intention of indicating a theory for a simple case, consider the equilibrium scheme of eqn. (6). It is the question of determining average life-times (T°, T^+ and T^-) of the uncharged and the ionic states from the kinetics of the dynamical equilibrium. In a monomolecular reaction, the lifetime of a particle is the inverse of the specific reaction constant k. Assuming an uncomplicated monomolecular reaction, we simply obtain $T^\circ = 1/k$. For the reverse reaction we observe that the process of disappearance of an A^{z+} ion is not limited to a reaction with the ions existing at a certain (zero) time point. Since any A^+ and B^- ion (of equilibrium concentration) can take part, the disappearance of A^{z+} also occurs according to a monomolecular scheme

$$\frac{1}{p}\ \frac{dA^{z+}}{dt} = k'\ (pC\alpha)^{p-1}(qC\alpha)^q(pC\alpha - A^{z+}) \qquad (25)$$

This equation describes the disappearance of the cations which exist at a certain zero time while the equilibrium is maintained. Since p of A^{z+} must disappear simultaneously for the formation of A_pB_q, each elementary reaction includes the disappearance of a number of the original A^{z+} ions which, on an average, is proportional to the relative content of these amongst the total amount. It seems however that this is accounted for in eqn. (25). It may in this connection be pointed out that the problem is not identical with the rate of disappearance of labelled ions from an original mixture of them with unlabelled salt. In the latter problem, labelled ions successively reappear by dissociation of the molecules formed, a process which is irrelevant to the question of the life-time of an ion, with which we are here concerned.

A complete theory has to consider an eventual exchange reaction, say according to the scheme

$$A_pB_q + (A^{z+})^* \rightarrow A_{p-1}(A^*)B_q + A^{z+} \qquad (26)$$
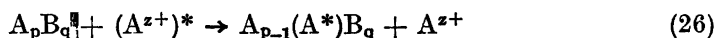
by which the life-time of the ion, and of the undissociated state of A, are diminished.

Special reaction mechanisms might modify the statistical nature of the kinetics. The same is true in the case of an equilibrium between different states of the salt or a formation of double molecules etc.* — From eqn. (25) we obtain

$$T^+ = T^- = 1/(k'p^pq^q(C\alpha)^{p+q-1}) \qquad (27)$$

The common life-time being denoted by $T^\pm$, this leads to

$$\frac{(T^\pm)^2}{T^\circ + T^\pm} = \frac{\alpha^2}{k(1-\alpha)};\ \left(\frac{T^\pm}{T^\circ + T^\pm} = \alpha\right)^{**} \qquad (28)$$

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* This may modify the statistical distribution, for short time-intervals, of the life-times. This distribution may be quite abnormal and it may not be self-evident that the calculated kinetical average life-time is identical with the average life-times which are contained in the electro-diffusion eqns. (2) and (24), as is assumed here.

** This expression is directly obtained from $T\pm/T^\circ =$ the ratio of the ion concentration (divided by the stoichiometric factor) and the concentration of the undissociated state.

Applying this result, eqn. (24) reads

$$\Delta D = \frac{\frac{1}{2}\, \alpha^{\,3}\, U^{+} U^{-} \varepsilon}{k\,(1-\alpha)\,[\text{pq}\alpha]} \left(\frac{\mathrm{d}E}{\mathrm{d}x}\right)^{2} \tag{29}$$

$$[\text{pq}\alpha] \equiv \text{p} + \text{q} - \alpha\,(\text{p} + \text{q} - 1)$$

From the experimental point of view, the current heat is a critical magnitude. Introducing the electrical effect $w = \varepsilon \varkappa \left(\dfrac{\mathrm{d}E}{\mathrm{d}x}\right)^{2}$ watt/cm^3 and the ionic conductances $\Lambda_0^{+} \simeq FU^{+}$, eqn. (29) transforms to

$$\Delta D = \frac{\frac{1}{2}\, \alpha^{\,3}\, w}{(1-\alpha)\,[\text{pq}\alpha]k} \,\frac{\Lambda_0^{+}\Lambda_0^{-}}{F^{\,2}\,\varkappa} \tag{30}$$

We will from now on assume $\text{p} = \text{q} = 1$ and $z = 1$. A modification may be attained by considering $\Lambda \simeq \alpha(\Lambda_0^{+} + \Lambda_0^{-}) = 1\,000\ \varkappa/C$. Eliminating $\varkappa$ and introducing the equilibrium constant K gives

$$\Delta D = \frac{500\ K\ (w/C)}{k(2-\alpha)CF^2}\,\frac{\Lambda_0^{+}\,\Lambda_0^{-}}{\Lambda_0^{+} + \Lambda_0^{-}} \tag{31}$$

The reason for using w/C is that the permitted Joule heat w increases with the density gradient of the column, which latter may be chosen greater with increasing concentration of the salt. Thus, according to eqn. (31), the order of magnitude of a measurable diffusion effect for a given electrolyte in our case varies inversely to the molarity of the salt. Another expression for a numerical estimation is

$$\Delta D = \frac{500\alpha^{\,2}\ (w/C)}{(1-\alpha)\ (2-\alpha)kF^2}\,\frac{\Lambda_0^{+}\,\Lambda_0^{-}}{\Lambda_0^{+} + \Lambda_0^{-}} \tag{32}$$

obtained from eqn. (31) by eliminating K.

For the present we will prefer the formula

$$\Delta D = \frac{500\alpha^{4}w}{(1-\alpha)^2\ (2-\alpha)KkF^2}\,\frac{\Lambda_0^{+}\,\Lambda_0^{-}}{\Lambda^{+} + \Lambda_0^{-}} \tag{33}$$

for an estimation of the electrodiffusion effect, in order to use the value $w = 0.2$ watt/cm^3 which is sometimes given as a maximum value in electrophoresis work at the temperature (approx. 4° C) of the maximum density of water. Our requirements for undisturbed diffusion ought to be greater than those in general electrophoretic work, but on the other hand the cooling of the cell has been considerably improved in our work, so we may use this value as an upper limit. Assuming $\alpha = 1/3$, $K = 10^{-3}$, and the Λ-factor $= 40$ (international units), we get $\Delta D = 2/3 \cdot 10^{-5}/k$ cm^2/sec. Since $2 \cdot 10^{-5}$ is the

order of magnitude of the diffusion coefficients of common electrolytes in water, the calculation shows that $k = 1/3$ / sec., *i. e.* $T° = 3$ sec., would give a diffusion effect of about 100 %. The molarity is, in this example $C = 0.006$.

With regard to the current to be used (see eqn. (28) the period length is in this example between $T° = 3$ sec. and $T° + T^± = 4.5$ sec. The conditions $T^± < \varepsilon\tau / 2$ and $T^± + T° > \tau$ lead to $\varepsilon > 2\alpha$, independent of k.

These calculations refer to eqn. (2), case a) above, as it was introduced in eqn. (14). The case b), eqn. (3), leads to the expressions

$$\Delta D = \frac{250\alpha\varepsilon\tau(w/C)}{(2-\alpha)\ F^{\,2}} \frac{\Lambda_0^+\ \Lambda_0^-}{\Lambda_0^+ + \Lambda_0^-} \tag{34}$$

and

$$\Delta D = \frac{250\alpha^{\,3}\ \varepsilon\tau w}{(2-\alpha)\ (1-\alpha)\ KF^2} \frac{\Lambda_0^+\ \Lambda_0^-}{\Lambda_0^+ + \Lambda_0^-} \tag{35}$$

From these equations it is seen that the use of current shocks leads to an electrodiffusion effect, which is i n d e p e n d e n t of the kinetics of the dynamical equilibrium. This result of the calculation can be seen directly, since sudden shocks do not give an indication of life-times which are comparatively long. The reaction rate is, however, contained in the assumptions regarding order of magnitudes, which were made in case b). A numerical estimate shows clearly that a measurable effect may be obtained also under these conditions.

3. RANGE OF SYSTEMS

If the magnitude or sign of the electric charge of at least one of the constituents changes, then an electrodiffusion effect is possible. The same is true if the mobility of an ionic constituent varies with time, *e. g.* in the case of linear macromolecular ions or longchain polyelectrolytes. The mobility is in this case a function of the actual form of the ion. Other causes are: random changes in solvation, in the instantaneous properties of the medium or in the interionic forces. The reversible formation of micelles and other colloids, the formation of complexes, electron transfers, ampholytes and protolytic systems in general, and exchange reactions within the electrolyte or with an additional component, also belong to this field. An effect upon an added nonelectrolyte or upon the solvent is possible, if this component is bound to ions or reversibly dissolved (solubilized) in micelles. An interesting case may prove to be that of carbon dioxide, say according to the scheme $CO_2 + OH^- = HCO_3^-$. The diffusion of acids, with an equilibrium between *pseudo-* and *aci*-form, belongs to the category theoretically discussed above, since we may here find the delayed kinetics which are necessary in order to provide the region of measurable conditions.

A special field is represented by the presence of a solid structure, such as diffusion in an ion exchange column, in a gel or in an adsorbent.

4. COMPLETIVE REMARKS

Experiments in a special cell, cooled by water to approximately 4° C, have shown that reproducible measurements may be made at somewhat higher electric effects than the figure 0.2 watt/cm^3 given above. We have delayed publication, awaiting experimental evidence of the special effect in question. The publication of Mysels [5,1], in which the principles are the same, although in part rather differently outlined, has now caused the publication of this article.

The connection with the kinetics of the dynamical equilibrium is of interest and may, in special cases, lead to determinations which are difficult to obtain with simpler or more direct methods. It is of special value to obtain an insight into statistical details of the kinetics, which are not revealed by other methods, if this proves to be possible.

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