

times obtained, however, after a factor of 25, in a direction which would be compatible with the presence of two types of oxygen atoms. Even though we feel that this curvature is most likely due to errors in the graphical analysis of the curves, we cannot be certain that the plots are linear over a factor of more than 25 to 30.

Therefore, the participation (to an important extent) of excited oxygen atoms cannot be ruled out because the observed linearity is over an insufficient range. However, from the linearity over the first factor of 25–30 in $\log(I_{tr}/I_{tr}^0)$, we can say the following: (1) if $k_{1a} > 2k_{1b}$, then initially $O(^3P)/O(^1D) > 3$, and our experimental value is approximately 25% (or less) lower than k_{1a} ; (2) if $k_{1b} > 2k_{1a}$, then initially $O(^1D)/O(^3P) > 3$, and our experimental value is approximately 25% (or less) lower than k_{1b} ; (3) if $O(^3P)/O(^1D)$ is initially approximately unity, then (a) k_{1a} is less than about $1.8k_{1b}$, and our experimental value is approximately midway between k_{1a} and k_{1b} , or (b) k_{1b} is less than about $1.8k_{1a}$, and our experimental value is approximately midway between k_{1a} and k_{1b} .

One can see that the above statements are valid by making test plots of two simultaneous ozone growth

curves, using various values for k_{1a}/k_{1b} and $O(^3P)/O(^1D)$, and adding together the curves due to reactions 1a and 1b. One can then see the extent of nonlinearity expected.

The most reliable value of k_{1a} , as determined¹⁸ by the steady-state flow method already described, appears to be $1.3 \pm 0.3 \times 10^8 M^{-2} \text{ sec.}^{-1}$. On the basis of this we can rule out (2) and (3b) above as being possibilities. From (1), our experimental value predicts that $k_{1a} = 0.83 \times 10^8$ to about $1.0 \times 10^8 M^{-2} \text{ sec.}^{-1}$, and (3a) predicts from our experimental value that $k_{1a} \simeq 1.0 \times 10^8 M^{-2} \text{ sec.}^{-1}$. Within the uncertainty allowed by either (1) or (3a), therefore, there is agreement between the value of k_{1a} obtained from our experiments and the value of $1.3 \pm 0.3 \times 10^8 M^{-2} \text{ sec.}^{-1}$, although our results favor the lower extreme of the latter.

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Chronopotentiometric Diffusion Coefficients in Fused Salts

I. Theory^{1a}

Richard W. Laity^{1b} and James D. E. McIntyre

Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey. Received February 11, 1965

The significance of the chronopotentiometric diffusion coefficient D_{ch} of an ion in a fused salt solvent is elucidated by developing rigorous equations that relate this quantity to other transport properties of the system ("ordinary" diffusion coefficient and transference numbers). It is shown that when sufficiently small concentrations are employed D_{ch} becomes substantially identical with both ordinary and self-diffusion coefficients. A new method is proposed for taking account of the double layer charging current in determining the "transition time" to be used in the calculation of D_{ch} from experimental chronopotentiograms.

Chronopotentiometry is an experimental procedure in which the potential of an electrode is observed as a function of time during passage of a constant current sufficiently large to produce concentration polarization with respect to a species undergoing electrochemical reaction. In addition to being an analytical tool, the technique has been used to measure a transport parameter usually referred to as the "ionic" diffusion coefficient. Here this will be called the "chronopotentiometric" diffusion coefficient. Its relation to other

transport parameters, particularly "ordinary" and "self-diffusion" coefficients, has not been elaborated elsewhere. By developing equations that accurately describe variations of concentration and potential with time in terms of unambiguously defined parameters, the present work will show the physical significance of the chronopotentiometric diffusion coefficient of an electroactive ion in a molten salt solvent.

The Instantaneous Flux. A Rigorous Diffusion-Migration Equation. In any experiment involving ionic migration through a concentration gradient, correct mathematical treatment requires the use of electrochemical potentials as the "thermodynamic forces" on ionic species.² A particularly simple set of equations for this purpose is provided by the friction coefficient formalism.^{3,4} In applying this approach to steady-state problems in an ionic diffusion layer,⁵ the product of concentration times friction coefficient that appears throughout the phenomenological equations was previously expressed in the form $X_k r_{ik}$, where X_k is a kind of mole fraction in which each ionic and molecular species is treated as a separate com-

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ponent. It is more convenient in the present work to express concentrations in moles per unit volume. Thus the fundamental equations for a system composed of N ionic and/or neutral species at uniform temperature and pressure are written

$$-\nabla\bar{\mu}_i = \sum_{k=1}^N R_{ik}c_k(v_i - v_k) \quad (i, k = 1, 2, \dots, N) \quad (1a)$$

$$R_{ik} = R_{ki} \quad (1b)$$

where $\nabla\bar{\mu}_i$ is the gradient of electrochemical potential of species i , v_i and v_k are ionic velocities, c_k is the concentration in gram formula wt./cm.³, and R_{ik} is the corresponding friction coefficient (joule cm./mole of i mole of k). In a mixture of two binary fused salts with one ion in common this becomes

$$-\nabla\bar{\mu}_1 = R_{12}c_2(v_1 - v_2) + R_{13}c_3(v_1 - v_3) \quad (2a)$$

$$-\nabla\bar{\mu}_2 = R_{12}c_1(v_2 - v_1) + R_{23}c_3(v_2 - v_3) \quad (2b)$$

$$-\nabla\bar{\mu}_3 = R_{13}c_1(v_3 - v_1) + R_{23}c_2(v_3 - v_2) \quad (2c)$$

where the Onsager reciprocal relations 1b have already been applied. If ionic species 1 is transformed at an electrode to a new species soluble in the melt, these equations must be modified and another equation added to describe completely the transport properties of the resulting system. However, if species 1 is being removed by electrolysis from the mixture, the three equations (2) will suffice. Our attention will be restricted to the latter case.

An expression for the flux J_1 in terms of the current density i and concentration gradient ∇c_1 can be derived from eq. 2a-c. Let species 1 and 2 have charges of the same sign. If we adopt the convention that the *chemical* potential of the salt composed of ions 1 and 3 is written⁴

$$\mu_{13} = z_3\bar{\mu}_1 + z_1\bar{\mu}_3$$

where z_1 and z_3 are the absolute values of the ionic charges, then on combining eq. 2a and 2c with the electroneutrality condition

$$z_1c_1 + z_2c_2 = z_3c_3$$

we obtain the gradient of this potential.

$$-\nabla\mu_{13} = (z_3R_{12} + z_2R_{13})c_2v_1 - (z_3R_{12} + z_1R_{23})c_2v_2 - (z_2R_{13} - z_1R_{23})c_2v_3 \quad (3)$$

If species 1 and 2 are taken to be cations, the net current density i is given by⁶

$$i = -F(z_1c_1v_1 + z_2c_2v_2 - z_3c_3v_3) \quad (4)$$

Equation 3 can now be rearranged to give

$$v_1 - v_3 = -\frac{z_2}{z_1^2c_1R_{23} + z_2^2c_2R_{13} + z_3^2c_3R_{12}}\nabla\mu_{13} - \frac{z_3R_{12} + z_1R_{23}}{z_1^2c_1R_{23} + z_2^2c_2R_{13} + z_3^2c_3R_{12}}\frac{i}{F} \quad (5)$$

This expression is rigorously correct, but cumbersome to work with. It contains the interionic friction coefficients R_{12} , R_{13} , and R_{23} whose values are not available

(6) For convenience in applications involving the presence of an electrode, we have taken the current to be positive when the velocities of the cations are negative; *i.e.*, cations approach the origin from the positive x direction. A negative sign is therefore written before the parentheses in eq. 4.

for most fused salt mixtures. Considerable simplification can be effected by identifying the particular combinations of friction coefficients that appear on the right-hand side of (5) with conventional transport parameters.

Relations of the type needed have been given previously for the friction coefficients r_{ik} , defined on the mole fraction basis.^{4b} Here, we can develop analogous expressions by inserting the definitions of conventional parameters into eq. 5. Thus, when a mixture of uniform composition ($\nabla\mu_{13} = 0$) is electrolyzed, the current i_{13} carried by species 1 relative to species 3 is given by

$$i_{13} = -(v_1 - v_3)c_1z_1F \quad (6)$$

and can be used to define a "transference number" t_{13} equal to i_{13}/i . From (5) it follows that

$$t_{13} = \frac{z_1c_1(z_3R_{12} + z_1R_{23})}{z_1^2c_1R_{23} + z_2^2c_2R_{13} + z_3^2c_3R_{12}} \quad (7)$$

Similarly, the thermodynamic mutual diffusion coefficient D_{12}' is defined by^{4b}

$$v_1 = -(D_{12}'/RT)\nabla\mu_{13} \quad (8a)$$

with the restrictions

$$i = 0 \text{ and } c_1v_1 + c_2v_2 = 0 \quad (8b)$$

Putting restrictions 8b into (5) and comparing the result with (8a) shows that

$$D_{12}' = \frac{z_3c_3RT}{(c_1 + c_2)(z_1^2c_1R_{23} + z_1^2c_2R_{13} + z_3^2c_3R_{12})} \quad (9)$$

Substitution of (7) and (9) into (5) now gives

$$v_1 - v_3 = -\frac{z_2(c_1 + c_2)}{z_3c_3}\frac{D_{12}'}{RT}\nabla\mu_{13} - \frac{t_{13}i}{z_1c_1F} \quad (10)$$

an expression containing no friction coefficients. To remove the necessity of having thermodynamic data available, we can make use of the ordinary diffusion coefficient D_{12} , which is related to D_{12}' by

$$D_{12} = D_{12}'(1 + d \ln \gamma_{13}/d \ln X_{13})$$

where γ_{13} is the activity coefficient of the *salt* and X_{13} its mole fraction. Now since

$$d\mu_{13} = RT d \ln a_{13} = RT(d \ln \gamma_{13} + d \ln X_{13})$$

it follows that

$$\frac{D_{12}'}{RT}\nabla\mu_{13} = D_{12}\nabla \ln X_{13} \quad (11)$$

It is desirable to have all concentrations expressed in dimensions of moles per unit volume. Recalling the convention adopted here in defining the mole, we can write

$$X_{13} = c_1\bar{V}/z_3 \quad (12)$$

where \bar{V} is the volume of mixture containing a total of 1 mole of salt. Now letting J_{13} represent the flux of ion 1 relative to ion 3, it follows from (10) with (4), (11), and (12) that

$$J_{13} = -\left(1 + \frac{z_2 - z_1c_1}{z_3c_3}\right)\left(1 + \frac{d \ln \bar{V}}{d \ln c_1}\right)D_{12}\nabla c_1 - \frac{t_{13}i}{z_1F} \quad (13)$$

Equation 13 is an exact relationship governing the flux of cation 1 at any point in a system of this type under any conditions of concentration gradient and current density, provided there are no convection currents. The corresponding equation when 1 and 2 are anions would have the sign of the last term on the right reversed.

Time Dependence of Concentration in Chronopotentiometry. In order to take the divergence of eq. 13 it is necessary to know the concentration dependence of the coefficients of ∇c_1 and i . Clearly these depend on the specific system under consideration, so that in order to give a general treatment it is necessary to assume a characteristic or idealized behavior. Here we will choose the simplest assumptions consistent with reasonable behavior of the transport properties of a system dilute with respect to one of the cations (species 1). We define

$$D_{13} = \left(1 + \frac{z_2 - z_1 c_1}{z_3 c_3}\right) \left(1 + \frac{d \ln \bar{V}}{d \ln c_1}\right) D_{12} \quad (14a)$$

$$\theta_{13} = t_{13}/c_1 \quad (14b)$$

and assume that both D_{13} and θ_{13} are independent of concentration in the range of interest. Putting definitions 14 into eq. 13 and taking the negative divergence of both sides (restricting the flux to the x direction) now gives

$$-\nabla J_{13} = \frac{\partial c_1}{\partial t} = D_{13} \frac{\partial^2 c_1}{\partial x^2} + \frac{\theta_{13} i \partial c_1}{z_1 F \partial x} \quad (15)$$

The classical treatment of the growth of concentration polarization due to electrochemical removal of an ionic species starts with a statement of "Fick's second law"

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2}$$

in which the significance of the "ionic" diffusion coefficient D_1 is not specified. Equation 15 is seen to be a more rigorous version of Fick's second law in which the nature of the diffusion coefficient is specified (by eq. 14a) and a term is included that reflects the presence of the applied field. To determine the significance of the latter in chronopotentiometry, we will retain the second member on the right in applying eq. 15 to this experiment.

We wish to determine the concentration c_1 at the surface of a planar electrode (normal to the x direction) at any time t after a constant current i starts removing species 1 from solution in the absence of convection currents. The initial condition is

$$c_1 = c_1^b \quad (t = 0, 0 \leq x) \quad (16a)$$

due to the uniform composition of the solution. The boundary conditions are

$$\begin{aligned} J_1 &= -i/z_1 F \\ J_2 &= 0 \end{aligned} \quad (t \geq 0, x = 0) \quad (16b)$$

where the total number of electrons transferred in the electrolysis reaction is taken equal to the charge on species 1, since only this cation can "cross" the solution-electrode interface.⁷

(7) It will be recalled that species 3 has been taken as the velocity reference in eq. 15, and hence in (16b) where it defines the velocity of

Equation 15 can be simplified by a transformation of variables. Substituting

$$c_1^* = (c_1^b - c_1) \exp\left(\frac{I^2 t}{4D_{13}} + \frac{Ix}{2D_{13}}\right)$$

where $I = \theta_{13}/z_1 F$ gives

$$\frac{\partial c_1^*}{\partial t} = D_{13} \frac{\partial^2 c_1^*}{\partial x^2} \quad (17)$$

Application of the Laplace transformation

$$\overline{c_1^*}(x, \sigma) = \int_0^\infty e^{-\sigma t} c_1^*(x, t) dt$$

and the appropriate initial and boundary conditions for c_1^* reduces the partial differential equation (17) to the ordinary differential equation

$$D_{13} \frac{d^2 \overline{c_1^*}}{dx^2} = \sigma \overline{c_1^*} \quad (18)$$

Solving (18) for the case $x = 0$ and carrying out the inverse transformations gives an expression for the concentration c_1^s at the electrode surface at any time t in a solution whose bulk concentration is c_1^b

$$c_1^s = c_1^b - t_{23} E / \theta_{13} \quad (19a)$$

where $t_{23} = (1 - c_1^b \theta_{13})$ is the transference number of species 2 in the bulk melt (*i.e.*, outside the diffusion layer)

$$E = 2a\sqrt{t/\pi} \exp(-a^2 t) + \operatorname{erf}(a\sqrt{t}) + 2a^2 t \operatorname{erfc}(-a\sqrt{t}) \quad (19b)$$

and

$$a = \theta_{13} i / 2z_1 F \sqrt{D_{13}} \quad (19c)$$

The symbols erf and erfc refer to the error function and its complement, respectively.

$$\operatorname{erf} \omega = \frac{2}{\sqrt{\pi}} \int_0^\omega \exp(-z^2) dz$$

$$\operatorname{erfc} \omega = 1 - \operatorname{erf} \omega$$

Significance of the Chronopotentiometric Diffusion Coefficient. We have pointed out that the concept of "ionic" diffusion coefficient is introduced in the classical treatment of chronopotentiometry as the unspecified quantity D_1 appearing in Fick's second law. It is later made operational by identifying it with a combination of experimental parameters⁸

$$D_1 = \left(\frac{2i}{z_1 F c_1^b}\right)^2 \frac{\tau}{\pi} \equiv D_{\text{ch}} \quad (20)$$

where τ is the "transition time," *i.e.*, the time required for c_1^s to become zero (negligible compared with c_1^b). Equation 20 can be taken as the definition of the chronopotentiometric diffusion coefficient D_{ch} .

the electrode surface as zero at $x = 0$. When the two salts have unequal equivalent volumes, the reference coordinates move in the coordinate system of the laboratory at points further out ($x > 0$), but remain fixed at $x = 0$.

(8) Note that we are considering only the case in which cation 1 is completely discharged at the electrode. Hence we have used z_1 in eq. 20 where it is customary to use n , the number of electrons transferred in whatever electrochemical reaction occurs.

In our treatment the value of τ can be obtained implicitly from eq. 19.

$$0 = c_1^b - (t_{23}/\theta_{13})\left\{2a\frac{\tau}{\pi}\exp(-a^2\tau) + \operatorname{erf}(a\sqrt{\tau}) + 2a^2\tau \operatorname{erfc}(-a\sqrt{\tau})\right\} \quad (21)$$

Now in order to determine the significance of the chronopotentiometric diffusion coefficient D_{ch} , we note from eq. 19c and 20 that

$$a\sqrt{\tau} = \frac{\sqrt{\pi}\theta_{13}c_1^b}{4} \sqrt{\frac{D_{\text{ch}}}{D_{13}}}$$

Substitution of this expression (or its square) into eq. 21 wherever a power of $a\sqrt{t}$ appears gives D_{ch} implicitly in terms of the bulk concentration c_1^b and the transport parameters D_{13} and θ_{13} . The equation thus obtained is rigorously correct, but rather complicated. To obtain greater insight, certain approximations are useful.

When the argument ω is 0.05 or less, the functions in eq. 19b and 21 are given to within 0.1% or better by

$$\begin{aligned} \operatorname{erf} \omega &= 2\omega/\sqrt{\pi} \\ \operatorname{erfc} \omega &= 1 - 2\omega/\sqrt{\pi} \\ \exp(-\omega^2) &= 1 - \omega^2 \end{aligned}$$

Under these conditions E can be calculated from

$$E = 2a\sqrt{t/\pi}(2 + a\sqrt{t\pi} + a^2t) \quad (22)$$

and substituted into (19a) to obtain $c_1^s(t)$. The transition time is again given implicitly when c_1^s is set equal to zero.

$$0 = c_1^b - (2t_{23}i/z_1F)\sqrt{\frac{\tau}{D_{13}\pi}} \left\{ 1 + \frac{\theta_{13}^2}{4z_1F} \sqrt{\frac{\pi\tau}{D_{13}}} + \frac{\theta_{13}^2 i \tau}{8D_{13}z_1^2 F^2} \right\} \quad (23)$$

The range of validity of (22) and (23) for a typical fused salt system can be estimated by taking $\theta_{13} \approx 50 \text{ cm.}^3/\text{mole}$ and $\sqrt{D_{13}} \approx 5 \times 10^{-3} \text{ cm. sec.}^{-1/2}$ equiv./mole. The approximations are found to be accurate within 0.1% provided $i\sqrt{t} \leq 1 \text{ amp. sec.}^{1/2} \text{ cm.}^{-2}$. This provision will be satisfied for all t up to the transition time, according to (23), at any initial concentration c_1^b up to about 2 M , i.e., $2 \times 10^{-3} \text{ mole/cm.}^3$, at which point the last two terms inside the braces have attained the values 0.10 and 0.045, respectively. In the limit, as $t_{23} \rightarrow 1$, i.e., as $c_1^b \rightarrow 0$, eq. 23 can be rearranged to give

$$D_{13} = \left(\frac{2i}{z_1Fc_1^b}\right)^2 \frac{\tau}{\pi} \quad (24)$$

Comparing (24) with (20) and (23), we therefore conclude that the measured chronopotentiometric diffusion coefficient can be considered identical with the parameter D_{13} whenever the neglect of the last two terms of (23) is warranted by the accuracy of the experiment. The discrepancy is calculated to be less than 0.2% at concentrations below 0.04 M but increases to about 11% at 2 M . To obtain a much more

accurate relationship ($\pm 0.2\%$) between D_{ch} and D_{13} for the range 0.04 to 2 M , it is only necessary to preserve the transference correction factors of (23) in eliminating $i\sqrt{\tau}$ between this equation and eq. 20.

Since $c_1/c_3 \leq 0.002$ and $d \ln \bar{V}/d \ln c_1$ is expected to be even smaller at concentrations below $c_1^b = 0.04 M$, it follows from eq. 14a that the chronopotentiometric diffusion coefficient can be equated directly to the ordinary or interdiffusion coefficient D_{12} even for mixtures of different charge type ($z_1 \neq z_2$) in this concentration range. This in turn is equal to the self-diffusion coefficient D_{11} in very dilute solutions.^{4b} At higher concentrations the expressions developed here permit a rigorous evaluation of D_{13} (but not D_{11}) from chronopotentiometric and transference data for systems conforming to our assumptions that both D_{13} and θ_{13} remain concentration independent. It seems unlikely, however, that such restrictive assumptions will apply quantitatively to most systems above 0.04 M . Thus, unless specific solutions of eq. 15 are developed that take account of actual concentration dependences of D_{13} and θ_{13} in particular systems, the use of chronopotentiometry for determining transport properties of fused salt mixtures can be applied unambiguously only to the very dilute range in which $D_{\text{ch}} = D_{12}$.

Effect of Electrical Migration. In the foregoing section it was seen that the effect of the final term in our rigorous analog of Fick's second law (eq. 15) on the interpretation of chronopotentiometric data is relatively small in dilute solutions. Its component in eq. 23 is a correction factor which is a quadratic function of the initial concentration c_1^b (since $i\sqrt{\tau}$ is directly proportional to c_1^b). Thus at $c_1^b = 0.04 M$, electrical migration of the electroactive ion may be said to contribute about 0.2% to the observed transition time, while at $c_1^b = 2 M$ the value of $\sqrt{\tau}$ is increased by 5.5% and hence τ itself by 11% as a result of migration.

Although the almost negligible effect of migration seems to be taken for granted in the literature of chronopotentiometry, it was not so obvious to us at the outset of this work. At the first moment the current is turned on, the ionic flux must be due entirely to migration. The contribution from diffusion "grows in" as the electrode becomes increasingly concentration polarized, but the run is terminated just as the concentration gradient reaches its maximum value. The fraction of τ over which migration is significant would be difficult to estimate without the equations developed here.

Gradient of Electrical Potential. To describe quantitatively the variation of the measured potential with time, it is first necessary to develop an expression for the potential difference between the electrode at which the ion of interest is discharging (indicator electrode) and a reference electrode placed some distance away in the melt. Although the latter is normally a reversible electrode, the potential of the former is determined by both thermodynamic and kinetic aspects of the reaction taking place and cannot be strictly reversible to the electroactive ion. Especially in fused salts, however, the amount of "activation polarization" is usually very small. In any case, this part of the total polarization depends primarily on the current density

and thus should remain constant during a chronopotentiometric run. Its presence will be ignored in the remainder of this paper, the potential of the indicator electrode being taken the same as that of an electrode reversible to the electroactive ion at the same point in the melt.

For convenience we may also take the reference electrode reversible to ion 1. (Its potential can be related to the potential of any other reference electrode by standard thermodynamic methods.⁹) The potential of each electrode is then determined by the electrochemical potential of species 1 in the adjacent melt, the observed e.m.f. being⁹

$$\epsilon = (\bar{\mu}_1^s - \bar{\mu}_1^r)/z_1F \quad (25)$$

where the superscripts s and r refer to the electrolyte at the surfaces of the indicator and reference electrodes, respectively.

To evaluate the electrochemical potential difference in eq. 25, the right-hand side of eq. 2a must be rewritten in such a way that it can be integrated with respect to distance. First, solve eq. 4 for v_2 and substitute into (2a). Setting v_3 equal to zero throughout, we can now replace v_1 by the right-hand side of eq. 5 to obtain $\nabla\mu_{13}$ and i . Again the coefficients are complicated combinations of friction coefficients that can be identified with conventional transport parameters directly from the definitions of the latter. One of these identifications is the same expression for t_{13} that was found previously in eq. 7, the identity of the two expressions being a consequence of the Onsager reciprocal relations 1b. The other is a relation between the equivalent conductances Λ and the friction coefficients R_{ik} .

$$\frac{\Lambda}{F^2} = \frac{z_1^2 c_1 R_{23} + z_2^2 c_2 R_{13} + z_3^2 c_3 R_{12}}{z_3 c_3 (c_1 R_{12} R_{13} + c_2 R_{12} R_{23} + c_3 R_{13} R_{23})}$$

With these simplifications the expression for the gradient of electrochemical potential becomes

$$\nabla\bar{\mu}_1 = \frac{c_3}{z_2 c_2} t_{23} \nabla\mu_{13} + \frac{z_1 F}{z c_3 \Lambda} i \quad (26)$$

Equation 26 is an important relationship. Taken along with eq. 13 it provides us with a complete set of rigorous interrelations among the electrical and chemical potential gradients, the current density, and the flux of ion 1 at any point.

Variation of Potential with Time. In chronopotentiometry we are only concerned with the potential difference between two points and can restrict eq. 26 to one dimension. Integration along a line connecting the two electrodes then gives

$$\epsilon = \int_{\mu_{13}^r}^{\mu_{13}^s} \frac{c_3}{z_1 z_2 c_2 F} t_{23} d\mu_{13} + \int_{x=0}^{x=l} \frac{i}{z_2 c_3 \Lambda} dx \quad (27)$$

where l is the length of the line, and the potential difference ϵ is defined by (25). The two members on the right of eq. 27 can be thought of as the contributions of electrode potential and IR drop, respectively.

In dilute solution the second integrand in eq. 27 is almost independent of the small concentration changes

that occur in chronopotentiometry. We can treat it as a constant to obtain its contribution to the total e.m.f.

$$\epsilon_{IR} = \frac{il}{z_3 c_3 \Lambda} = \frac{il}{\kappa} \quad (28)$$

where κ is the specific conductance. The reference electrode might be located anywhere from 0.1 to 10 cm. away from the indicator electrode. Taking $\kappa = 1 \text{ ohm}^{-1} \text{ cm.}^{-1}$ as a typical fused salt conductivity, we see that for a polarization current of 20 ma./cm.² the contributions of IR polarization at these extremes of electrode separation are 0.002 and 0.2 v., respectively. It should be emphasized, nevertheless, that the *change* in ϵ_{IR} during a chronopotentiometric run is independent of electrode separation (so long as the reference electrode remains outside the region of concentration variation), and is so small (less than 0.1 mv.) that it can safely be neglected in any consideration of observed potential variations in fused salts.

To evaluate the contribution of electrode potential ϵ_e to the total value of ϵ in eq. 27, the thermodynamic behavior of the specific salt system must be known. We can get a general picture, however, by making use of the fact that the variation of activity coefficient in fused salt systems at low concentrations is likely to be negligible. In chronopotentiometry this justifies the approximations

$$\begin{aligned} d\mu_{13} &\approx RT(z_3 d \ln c_1 + z_1 d \ln c_3) \\ &\approx RT z_3 d \ln c_1 \end{aligned}$$

The first integral of eq. 27 is further simplified by the two additional dilute solution approximations $t_{23} \approx 1$ and $z_2 c_2 \approx z_3 c_3$, yielding a simple Nernst expression for the contribution of electrode potential

$$\epsilon_e = -\frac{RT}{z_1 F} \ln c_1^s / c_1^r \quad (29)$$

Since the concentration around the reference electrode c_1^r is the same as the bulk concentration c_1^b , the total e.m.f. during removal of species 1 at current i from a solution at concentration c_1^b can now be expressed as a function of time by substituting the value of c_1^s from eq. 19a into 29 and adding eq. 28. Approximating E in (19a) by the first term on the right in eq. 22 gives

$$\epsilon = -\frac{RT}{z_1 F} \ln \left(1 - \frac{2i\sqrt{t/\pi D_{13}}}{z_1 F c_1^b} \right) + \frac{il}{\kappa} \quad (30)$$

Equation 30 shows that chronopotentiometry at reversible electrodes in very dilute fused salt systems gives the familiar "wave" when ϵ is plotted against t . It can be put into more commonly used form by substituting the value of τ from eq. 24 to give

$$\epsilon = -\frac{RT}{z_1 F} \ln \left(1 - \sqrt{\frac{t}{\tau}} \right) + \frac{il}{\kappa} \quad (31)$$

Effect of Double Layer Charging. Any treatment of chronopotentiometry in which the electrolysis current density i_e is set equal to the total current density i_T suffers from the fact that the latter quantity includes also the current i_d required to charge the double layer to ever increasing potentials. The electrolysis current density in a practical experiment is thus a function of time given by

$$i_e = i_T - i_d \quad (32)$$

(9) R. W. Laity in "Reference Electrodes. Theory and Practice," D. J. G. Ives and G. J. Janz, Ed., Academic Press Inc., New York, N. Y., 1961, p. 524 ff.

where i_T is a constant and i_d a variable that changes most rapidly near the extremities of the run. To use the results of the previous sections to calculate accurate diffusion coefficients from experimental chronopotentiograms, it is therefore necessary to apply some sort of "correction" to the observed value of i or τ . Delahay and Berzins¹⁰ described a method of correcting τ in such a way that i in eq. 20 could be set equal to i_T . Their procedure was criticized by Reinmuth¹¹ because it implied that τ is a linear function of i_e . Instead, Reinmuth advocated an empirical approach which had been found to give constant values of $i_T\sqrt{\tau}$ in aqueous electrolytes at fixed concentration. These workers have been concerned primarily with kinetic and analytical applications of chronopotentiometry. The purpose of this section is to attempt to provide a simple, rational basis for analyzing chronopotentiograms in such a way that the quantities used in eq. 24 may be expected to give reliable values of D_{13} .

A typical chronopotentiogram is shown in Figure 1, the heavy solid line representing the variation of potential with time. Its shape can be rationalized in terms of the relative importance of i_e and i_d in each region. After establishment of the initial IR drop, the potential rises rapidly along AB. The current in this region consists entirely of the "charging current" required to bring the indicator electrode to the potential at which discharge of species 1 begins.

The electrode reaction then accelerates so rapidly that most of the current is due to electrolysis by the time C is reached. There usually follows an interval CD in which the curve is nearly linear, after which the potential begins to rise more rapidly until i_e reaches the limiting value corresponding to $c_1^b \approx 0$ at E. Beyond this point the decrease in electrolysis current (due to the widening diffusion layer) is so slow that the curve is essentially linear until the onset of another electrode reaction.

Now if we assume that the *effective capacitance* defined by dividing the slope $d\epsilon/dt$ of AB into the corresponding current density i_T remains constant throughout the run, then the charging current at any subsequent point can be determined by comparing the slope at that point with the initial slope. Subtraction of i_d from i_T at each point gives a complete record of the variation in i_e with time during the run. It is apparent from the shape of the curve that i_e is a rather complicated function of time. Nevertheless, as long as the initial concentration c_1^b is sufficiently low (less than 0.04 M) to make the "migration current" term in eq. 13 negligibly small, we can use expressions already derived in the literature (for "chronopotentiometry with programmed current") to calculate D_{13} from experimental chronopotentiograms.

The simplest method is to approximate the curve BCDE by a sequence of straight lines. Along each line i_d is constant. Since i_T is also constant, it follows from eq. 32 that i_e can be approximated by a sequence of step functions. An equation relating the diffusion coefficient to experimental parameters for such a current program has been given by Testa and Reinmuth.¹² Its use can be illustrated for the simple

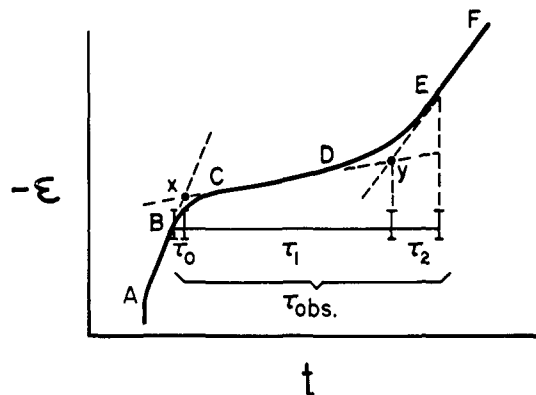


Figure 1. A typical chronopotentiogram.

construction indicated by the dashed lines in Figure 1. Here the approximately linear portion of the chronopotentiogram CD has been extended in both directions to intersect at points x and y with extrapolations of the linear traces that occur immediately before B and after E. At the abscissas of these intersections the total interval τ_{obsd} can be divided into segments τ_0 , τ_1 , and τ_2 . The slopes corresponding to these intervals are designated S_0 , S_1 , and S_2 . Application of the Testa and Reinmuth equation to this example gives

$$\frac{z_1 F c_1^b \sqrt{\pi D_{13}}}{2i_T} = \left(1 - \frac{S_1}{S_0}\right) \sqrt{\tau_1 + \tau_2} - \left(\frac{S_2}{S_0} - \frac{S_1}{S_0}\right) \sqrt{\tau_2} \quad (33)$$

By comparison with eq. 24, the right side of eq. 33 is seen to be an "effective" value of the square root of τ , *i.e.*, an approximation of the value that would be observed if the electrolysis current were maintained at i_T throughout the run. A better approximation of this quantity can of course be obtained by using a larger number of segments. The general expression for a construction with $n + 1$ segments (numbered 0 to n) is

$$(\sqrt{\tau})_{\text{eff}} = \frac{1}{S_0} \sum_{j=1}^n (S_{j-1} - S_j) \sqrt{\sum_{k=j}^n \tau_k} \quad (34)$$

By taking the limit as n goes to infinity, eq. 34 can be expressed in the integral form

$$(\sqrt{\tau})_{\text{eff}} = -\frac{1}{S_0} \int_{t=0}^{t=\tau_{\text{obsd}}} \left(\frac{dS}{dt}\right)_t (\tau_{\text{obsd}} - t)^{1/2} dt$$

where $(dS/dt)_t$ is the value of $d^2\epsilon/dt^2$ at time t . For practical purposes this form is less useful than eq. 34, which permits calculation of $(\sqrt{\tau})_{\text{eff}}$ directly from experimental chronopotentiograms to any degree of accuracy consistent with the data. Using the square of this quantity for τ in eq. 24 then gives D_{13} with corresponding accuracy. It should be recalled, however, that this treatment is confined to systems with essentially reversible electrodes in the concentration range for which use of the Sand equation (20) can be justified when i_e is constant. Furthermore, it is possible that errors may arise from inaccuracy of our initial assumption that the effective capacitance maintains its initial

(10) P. Delahay and T. Berzins, *J. Am. Chem. Soc.*, **75**, 2486 (1953).
 (11) W. Reinmuth, *Anal. Chem.*, **33**, 485 (1961).

(12) A. Testa and W. Reinmuth, *ibid.*, **33**, 1324 (1961).

value throughout the run. Such errors would lead to internal inconsistencies in data taken at different concentrations and/or current densities. Except in cases where specific adsorption of the electroactive ion is important in determining effective capacitance, these errors could be avoided by calculating a capacitance

at each potential from experimental observation of $d\epsilon/dt$ at the same charging currents in the absence of the electroactive species.

A subsequent communication will illustrate the application of these results to experimental studies of Ag^+ in molten NaNO_3 .

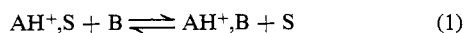
Ion-Solvent Interaction. The Interaction of a Phosphine Oxide and a Quaternary Ammonium Ion

W. R. Gilkerson and J. B. Ezell

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina. Received April 29, 1965

*The effect of added triphenylphosphine oxide on the conductances of methyltri-*n*-butylammonium perchlorate and iodide in *o*-dichlorobenzene and of the perchlorate in ethylene chloride has been investigated at 25°. The results are interpreted in terms of cation-phosphine oxide complex formation. The addition of the phosphine oxide to the cation lowers the limiting equivalent conductance of the salts 15–17%. Viewing the addition of phosphine oxide to the cation as involving a displacement of a solvating solvent molecule from the cation, the association constants for the complex in the two solvents are used as measures of specific cation-solvent interaction to account for the differences observed for ion-pair dissociation constants in the two almost isodielectric solvents.*

Previous reports^{1,2} from this laboratory represented studies of the effects of addends such as amines on the conductances of tertiary ammonium salts in *o*-dichlorobenzene (ODCB) and chlorobenzene. These effects were interpreted in terms of nucleophilic displacement of S by B, from the cation, AH^+ (eq. 1), where S



represents a solvating solvent molecule and B represents a molecule of addend. We assumed that the limiting equivalent conductance, Λ_B^0 , of the hypothetical salt, $\text{AH}^+\text{B}, \text{X}^-$, where X^- is the corresponding anion, was approximately equal to Λ_0^0 , the limiting equivalent conductance of the salt, AH^+X^- , in the solvent in question. This assumption was forced upon us since the salt, tri-*n*-butylammonium picrate typically, was such a weak electrolyte in the solvents used that independent values of limiting equivalent conductances could not be obtained by the usual extrapolation procedures.

The present work was initiated to test the validity of the foregoing assumption. The salts chosen, methyltri-*n*-butylammonium perchlorate and iodide, were selected because they are strong enough electrolytes in ethylene chloride,³ and thus presumably in ODCB,

that good values of Λ^0 can be obtained by extrapolation. The addend, triphenylphosphine oxide (TPPO), was chosen by trial. The amines used in prior work had little or no effect on the conductance of the fully quaternized salt. A clue pointing to the associating capabilities of phosphoryl compounds was furnished principally by the observation of Elliott and Fuoss⁴ that in tricresyl phosphate as solvent, the ion-pair dissociation constant of tri-*n*-butylammonium picrate was almost as large as that for the tetrasalt. Further, similar compounds are used extensively as solvent extraction agents for salts and acids,⁵ presumably through strong interaction of the phosphoryl oxygen group and the cation.

Our choice of ODCB and ethylene chloride (EC) as solvents was based on prior work^{1,2} in these media in this laboratory.

Experimental

Methyltri-*n*-butylammonium perchlorate was prepared from the iodide by metathesis with silver perchlorate in alcohol solution. The product was recrystallized from alcohol, m.p. 169° (lit.³ m.p. 159°). The salt was dried *in vacuo* at room temperature for 24 hr. prior to use. The iodide was prepared as previously.¹ Triphenylphosphine oxide (Columbia Organic Chemicals Co.) was dissolved in benzene, extracted with aqueous sodium bicarbonate, and washed with distilled water. The benzene was evaporated and the recovered TPPO was recrystallized from a benzene-hexane mixture. The TPPO was dried *in vacuo* at 90° for 24 hr., m.p. 154–155°. ODCB (Allied Chemical Co., Solvay Process Division) and EC (Columbia Organic Chemicals Co.) were treated as described previously.¹ The specific conductance of the ODCB was $1-2 \times 10^{-11}$ mho/cm., while that of EC was 1×10^{-10} mho/cm. The conductance bridge, cells, and experimental procedure have been described elsewhere.¹ All measurements were carried out at 25.00°.

(1) E. K. Ralph, III, and W. R. Gilkerson, *J. Am. Chem. Soc.*, **86**, 4783 (1964).

(2) W. R. Gilkerson and E. K. Ralph, III, *ibid.*, **87**, 175 (1965).

(3) L. F. Gleysteen and C. A. Kraus, *ibid.*, **69**, 451 (1947).

(4) M. A. Elliott and R. M. Fuoss, *ibid.*, **61**, 294 (1939).

(5) See R. M. Diamond and D. G. Tuck in "Progress in Inorganic Chemistry," Vol. 2, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 171 ff.