DIFFUSION KINETICS:

DISCUSSION

A Formulation of the Problem of Evaluating the Concentration Polarization in Transient State Analysis by S. V. Gorbachev

Yu. A. Chizmadzhev. I would like to make several remarks concerning inaccuracies in the paper of S. V. Gorbachev. My central point has to do with the difference between the boundary condition proposed in this work and that which has been applied in numerous other papers on concentration polarization. This new condition is based on Faraday's Law and has the following form:

$$\frac{iU_a}{nF} = D\left(\frac{\partial c}{\partial x}\right)_\delta - \delta \frac{\partial c(\delta,t)}{\partial t}. \qquad (1)$$

It is to be understood that the concentration appearing in this equation is that measured at the delta point. Thus, equation (1) is not a boundary condition, strictly speaking. The customary boundary condition is obtained if the delta of this equation is allowed to approach zero. The author does not do this, but carries equation (1) into the form:

$$-\frac{\partial c^\delta}{\partial t} = \frac{iU_a}{nF}\frac{1}{2\sqrt{Dt}}. \qquad (2)$$

This relation is solved with the usual initial condition $c_{t=0} = c_0$. The solution can be written as:

$$c_0 - c(\delta,t) = \frac{2iU_a}{nF\sqrt{2D}}\sqrt{t}. \qquad (3)$$

Here, again, c is to be taken at the point δ and at the time t. Such a solution calls for a boundary condition of the form $\mu(t) = c(0,t)$, rather than $\mu(t) = c(\delta,t)$. Thus transition to the limit, $\delta \rightarrow 0$ has been made, even though this point is passed by in silence. The resulting expression for the concentration differs from the familiar one by a coefficient which is approximately equal to 2. This is to be explained by the fact that S. V. Gorbachev's expression

$$\delta = \alpha\Delta(t), \qquad (4)$$

is incorrect. This equation does not take account of concentration changes occurring in the δ layer over time t as a result of the action of surface sources at the electrode.

I. Koryta. The conditions prevailing in polarography are those under discussion here. It can be proven that the condition

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \text{const}$$

is entirely correct. This is confirmed by the validity of the Illkovich equation. The appearance of any of physical law in one effect gives reason for expecting that the same law will apply to other, essentially similar, effects. Furthermore, Delahay has proven that the relation

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \text{const}$$

is also independent of time in polarography or ordinary electrolyses at constant current strength.

Certain Experiments in a Study of Convective Diffusion by A. I. Fedorova et al.

S. V. Gorbachev. I will not consider mathematical details. The principal point is that of discarding the boundary condition

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \text{const},$$

which is not consistent with experiment.

It has been said here that this boundary condition has been confirmed experimentally in Prague. But the Prague work dealt with polarography in electrolytes where the concentration of the current-determining substance is usually of the order of $10^{-3} - 10^{-5}$ M and the concentration of the supporting electrolyte, possibly 2 – 0.5 M. For all practical purposes the current-determining ion does not migrate in such case, the entire migration being due to the background ions. The result is a pure diffusion which would be treated by the usual theoretical methods, such as of Sands. I believe that this is incorrect. But I am convinced that the error involved will be quite small, i.e., that the theory is not very good but gives fairly satisfactory agreement with experiment.

It has been claimed that I have set δ equal to zero, but this is not so. I consider that δ, represents the depth of the ion exchange layer. This depth is not known. But it can be shown readily that this quantity falls out of the calculation. The equation is insensitive to variation of δ over the interval from $10^{-7} - 10^{-4}$.

I would like to turn attention to the following problem. When activation energies are plotted against potentials, numerous cases are met in which the resulting curve falls smoothly and approaches a horizontal line asymptotically, passage to a condition in which concentration polarization is the limiting step being indicated. On the other hand, comparison shows the energy of activation corresponding to this horizontal segment to be only one-half as large as that measured directly from viscosities. A. V. Izmailov has demonstrated that activation energies at constant $\Delta\varphi$ calculated from the familiar equation

$$\lg i = \frac{A}{2.3RT} + B \quad \text{or} \quad \left(\frac{\partial \ln i}{\partial T}\right)_{\Delta\varphi} = \frac{A}{RT^2}$$

refer to single electron processes, so that energies of activation obtained in work on divalent ions should be exactly twice as large as energies of activation based on viscosities. It is of interest that this gives still another method for determining the number of electrons participating in the elementary act of electrolysis.

In concluding I would like to point out that the efforts of the theoreticians to obtain a highly precise equation for concentration polarization give the electrochemist a mathematical apparatus which is cumbersome in describing simple effects, and difficult to apply in discussing really complex processes. I consider the paper of Kaishev and Stranskii to be interesting just because these authors rejected the apparent accuracy of highly complex basic equations, and at the same time, were able to discuss the truly serious problems.

A. N. Frumkin. A. V. Izmailov's idea of dividing the apparent energy of activation of a diffusion-controlled reaction by the number of electrons in order to bring the result into conformity with the true energy of activation for diffusion is not clear to me. The number of electrons would seem to bear no relation to the diffusion process. In general, activation energies calculated for processes under diffusional control have a definite physical meaning only when the mixing process is held constant. The report of A. I. Fedorova and her collaborators has shown that there is no difficulty in interpreting the activation energies obtained in such cases.

A Refractographic Study of Concentration Polarization in the Dissolution and Deposition of Metals by E. I. Grabova

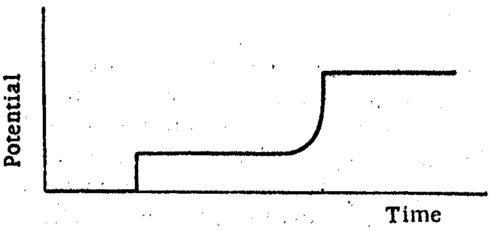
O. S. Ksenzhek. Delahay has recently proposed a method of polarography based on the Sands equation

$$c_t = c_0 - A\sqrt{Dt}.$$

Electrolysis at constant current strength involves a displacement of electrode potential as a result of concentration changes at the surface:

$$\Delta\varphi = \frac{RT}{nF}\ln\frac{c_0 - A\sqrt{Dt}}{c_0}.$$

The potential changes discontinuously when the numerator of the fraction in the logarithmic term becomes equal to zero. The graph shows potential plotted as a function of time. The time elapsing between the closing of the circuit and the appearance of the potential discontinuity (transition time) is fixed by the concentration and the ionic diffusion coefficients.



Polarogram at constant current strength.

Thus the Sands equation can serve as a basis for a method of quantitative analysis and there is no reason to doubt its validity.

One other remark. E. I. Grabova [S. V. Gorbachev, Zhur. Fiz. Khim. 30, 1151 (1956)] has measured the areas under curves showing concentration as a function of depth in solutions under concentration polarization. Her results were in apparent contradiction with Faraday's Law since the amount of material separating out of solution was not proportional to the time of electrolysis. Actually these results confirm the theory of concentration polarization rather than contradicting it, since the case in question was not one of electrolysis at constant current strength, as affirmed by S. V. Gorbachev, but at constant potential with a fixed concentration at the electrode. Here the amount of material separating out of solution should be proportional to the square root of the time of electrolysis. And this is exactly in line with the calculations of E. I. Grabova.

V. A. Myamlin. The claim is made in the report of S. V. Gorbachev that the boundary condition

$$j = D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \text{const} \qquad (1)$$

leads to contradictions. Let us consider how this conclusion was reached. Differentiation of equation (1) with respect to the coordinate gives $\partial^2 c/\partial x^2 = 0$. Since

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2},$$

it follows that

$$\frac{\partial c}{\partial t} = 0.$$

This simple result does not conform with experience. Where did error come in? It is easy to see that this occurred in the differentiation of equation (1). I venture to give an example in order to make this point entirely clear.

If the function c is taken to have the form:

$$c = ax + be^x,$$

then

$$\frac{\partial c}{\partial x} = a + be^{x}; \tag{2}$$

from which it follows that

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = a + b.$$

Following S. V. Gorbachev, we would have

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_{x=0} = 0;$$

since the derivative of a constant is zero. This is not correct, however, for equation (2) must first be differentiated and the substitution $x = 0$ then made. The correct expression for the second derivative is

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_{x=0} = b.$$

These considerations make it clear that boundary condition (1) does not entail the supposed contradiction.

Yu. A. Vdovin. The equation of diffusion with volume sources,

$$\frac{\partial c}{\partial t} = D\Delta c + f(x,t).$$

has been studied in the paper of S. V. Gorbachev. The density of these volume sources, $f(x,t)$, is the number of ions being produced or consumed per unit volume per unit time at the point x and the instant t. These volume sources are supposed to be responsible for the process of electrolysis.

A steady current of density i passed through an electrolyte for a time t will impoverish the electrolyte by:

$$Q_t = \frac{iU_a}{nF}\ t.$$

On this basis, the volume source density was assigned the form

$$f(x,t) = \frac{iU_a}{nF}$$

in the paper of S. V. Gorbachev. Nevertheless, it is incorrect to account for electrolysis in terms of volume sources, since the production and consumption of ions occurs only on the electrode surfaces. Ions are neither produced nor consumed in the body of the solution and there the density of the volume sources is equal to zero. This density could differ from zero if volume reactions of some kind were in progress in the electrolyte, but then the expression for the density would have an entirely different form. Thus, the electrolysis involves only surface sources with a density iU_a/nF. The presence of these sources is accounted for correctly by combining the boundary conditions with the diffusion equation

$$\frac{\partial c}{\partial t} = D\Delta c.$$

The fact that iU_a/nF cannot represent the volume source density follows immediately from dimensional analysis. This quantity has the dimensions

$$\left[\frac{iU_a}{nF}\right] = \frac{[c]}{[T]}\,[L],$$

just as must be the case for the surface source density, whereas the dimensions of the volume source density are given by

$$[f(x,t)] = \frac{[c]}{[T]}\,.$$

Thus the function

$$f(x,t) = \frac{iU_a}{nF}$$

has been incorrectly applied in the paper of S. V. Gorbachev and the results obtained there are unacceptable. In particular, the dimensions are not correct.

S. V. Gorbachev. I believe that the question under discussion to-day is one which is quite elementary. It comes down to this; that we take the basic Fick equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

introduce the initial condition

$$c = (x,t = 0) = c_0,$$

to which no one objects, and then the boundary condition

$$i = k\left(\frac{\partial c}{\partial x}\right)_{x=0} = \text{const.}$$

The question is whether this boundary condition is valid. Opinions on this point could differ as long as experimental data were lacking. But now we have data indicating that this condition is incorrect and there is, therefore, no longer room for discussion.

Existing solutions of this problem are based on an incorrect condition and for that reason stand in need of reconsideration.

I would like to turn attention to the interesting results obtained on $CuSO_4$ solutions, especially those of E. I. Grabova. The concentration gradient at the electrode falls almost to zero when crystallization occurs. I recall that V. G. Levich wrote in criticizing my paper that the current flow must cease when $\left(\frac{\partial c}{\partial x}\right)_{x=0} = 0$. The current flow does not cease, however.

E. I. Grabova. Concentration polarization is very fundamental to industrial processes. However, we do not yet have equations which can be applied to predict the concentration distribution established in large electrolytic cells over periods of time measured in hours. Even for periods of the order of minutes, the equation of V. G. Levich gives too great an excess of salt in the body of electrolyte. V. G. Levich explains this by saying that the equation is no longer applicable over periods which are so long that the effect of convection begins to make itself felt. The reproducibility of the experimental results (up to 2%) shows, however, that convection had been eliminated.

The equation of S. V. Gorbachev is in agreement with experiment but it is very cumbersome. Thus there is the need for other equations which would be more simple.

In deriving such equations it is necessary to realize that electrolysis is not a case of pure diffusion and that its description through Fick's Second Law alone is very difficult.

DISCUSSION

A. N. Frumkin. The work of E. I. Grabova failed to observe those conditions which are prerequisite for the elimination of natural convection. It is very difficult to avoid natural convection in experiments extending over several hours and the measures adopted in this direction by E. I. Grabova were quite inadequate. It is well known that the difficulties associated with natural convection have given rise to experimental techniques in electrochemistry such that observable changes in concentration can be obtained from current flow over periods of the order of seconds. In addition, supersaturation of the layer of electrolyte surrounding the electrode led to crystallization of the dissolved salt ($CuSO_4$) in the experiments of E. I. Grabova, and her results cannot be compared with the theory of concentration polarization since this was developed for the case in which the entire alteration in solution composition is determined by electrolysis and transfer. These experimental data of E. I. Grabova are the only argument which S. V. Gorbachev can advance against the criticisms of his theory by Yu. A. Chizmadzhev, V. A. Myamlin, and Yu. A. Vdovin, and these criticisms must, therefore, be considered as valid.

The Measurement of the Concentration of the Potential Determining Ions in the Electrolyte Surrounding an Electrode by G. P. Dezider'ev and S. I. Berezina

A. L. Rotinyan. I would like to make several remarks on the paper of G. P. Dezider'ev and S. I. Berezina.

The tables presented by these authors indicate the possibility of obtaining alkali in the layer surrounding the cathode during the electrolysis of pure H_2SO_4. Such results were obtained only because the author's acid solutions were not pure, but were contaminated by cations of some sort. On the other hand, their results cannot be accounted for on this ground alone. Other assumptions must be made. Their method for determining the pH of the layer surrounding the cathode actually measures an electromotive force which includes the diffusional discontinuity of potential arising from the difference in H^+ ion concentration at the surface and in the body of the solution. In a pure solution this term can have a magnitude of several pH units. The pH of the layer surrounding the cathode will be diminished when correction is made for this factor.

In addition it would seem that nickel-hydrogen or platinum-hydrogen electrodes would not be reversible at the instant of closing the circuit and thus would give pH values which are too high. In any event, pH values for the layer surrounding the cathode such as reported by these authors have never been obtained by other methods.

G. P. Dezider'ev. It is well known that the ion concentrations at the electrodes, the total ion concentration in solution, the limiting current density, and the actual current density are related by the following equation:

$$c_S = c_0 \left(1 - \frac{i}{i_d}\right) .$$

With approach to limiting conditions, the concentration at the electrode becomes more and more nearly equal to zero and the pH rises to 10, 12, 14, or even higher. The resulting pH values are fixed by the presence of contaminants; these we eliminated as far as possible and their amount can be taken into account. Of course, it is impossible to entirely eliminate these substances.

A. L. Rotinyan has tested our work by using the glass electrode and seeking for concentration changes several seconds after initiating passage of the polarizing current. The changes observed by us cannot be detected by this method.

GENERAL DISCUSSION

O. B. Khachaturyan. We have discovered an interesting relation during a study of the electrochemical kinetics of ionic charge exchange in reversible systems in solution.

Our study of the relation between composition and rate of electrolysis in the ferri-ferro cyanide system has shown the constant potential curves to pass through maxima. These maxima are displaced along the composition axis with increasing polarization potential, the displacement being toward an increase in the reduced component in the case of a cathodic process, and toward an increase in the oxidized component in the case of an anodic process. The temperature also affects the maxima on the constant potential curves, these being much more pronounced at 80° than at 25°.

We have applied the method of polytherms, which has been outlined in detail in the literature, to this study, showing concentration polarization to be the limiting step when there is 1 : 1 ratio of oxidized to reduced forms with the rate of charge exchange limited by diffusion of matter from the body of the solution to the electrode.

Our data are in good agreement with those of the literature.

Starting from the diffusional character of the process in question, we have derived the following equation:

$$I = \frac{x}{\gamma}\left(1 - \frac{c}{(c - x)\,e^{m} + x}\right),$$

in which γ is an empirical constant, c is the over-all concentration of the solution, x is the amount of the oxidized or reduced component, I is the current strength, and m is given by

$$m = \frac{\Delta\epsilon\, nF}{RT},$$

this permits the whole family of curves at fixed composition to be constructed from the current strength and the potential. The limiting step in the process of electrolysis can be determined by comparison with the experimental curve (see Fig. 7 on page 67). The values which we have calculated for this system (full curve) are in good agreement with the experimental data (circled points), thus again confirming the diffusional nature of the process.

A. N. Frumkin. The basic idea of the report of O. B. Khachaturyan seems to be correct. It should be pointed out, however, that the appearance of a minimum electrode polarizability with approach to equality of concentrations of oxidant and reductant in a reversible oxidation-reduction system is well known to electrochemists. Thus superposition of an oscillating potential of fixed amplitude in the alternating current polarography of a reversible process at the half-wave potential results in a maximum current strength which fully reflects the minimum polarizability referred to in the work in question.