PHYSICAL CHEMISTRY

A. V. GORODYSKII and Academician of the Academy of Sciences of the Ukrainian SSR Yu. K. DELIMARSKII

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Abstract

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THE EQUATION OF NONSTATIONARY DIFFUSION

TO A STATIONARY ELECTRODE

At present it is accepted ($^{1-3}$) that the diffusion of a reacting substance to a stationary electrode is determined by the following two conditions, formulated by Cottrell (^{4}) and by MacGillavry and Rideal (^{5}): 1) before the current is switched on, the concentration c_0 of the reacting substance is the same throughout the mass of the electrolyte; 2) at the surface of the electrode the ion concentration is equal to zero at any time t after the current is switched on. In other words, for linear diffusion

$$c(x,0) = c_0; \tag{1}$$

$$c(t,0) = 0; \tag{2}$$

for spherical diffusion

$$c(r,0) = c_0 \tag{3}$$

$$c(r_0,t) = 0 \tag{4}$$

(x and r are coordinates, r_0 is the radius of the spherical electrode).

According to these conditions, the solution of the general diffusion equation

$$\frac{\partial c}{\partial t} = a\Delta c \tag{5}$$

gives, for linear diffusion,

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{c_0}{\sqrt{\pi a t}}; \tag{6}$$

and, for spherical diffusion,

$$\left(\frac{\partial c}{\partial r}\right)_{r=r_0} = \frac{c_0}{\sqrt{\pi a t}} + \frac{c_0}{r_0}, \tag{7}$$

where a is the diffusion coefficient.

Conditions (1), (2) and (3), (4) do not take into account convection of the electrolyte and determine the diffusion process only in the case where stirring is eliminated. Therefore equations (6) and (7) agree with experimental data only for immobile (gelatinized) solutions ([2]) or only for short intervals of time after the current is switched on, when convection is insignificant ([2,3,6]). Under ordinary electrolysis conditions, however, after the circuit is closed the current strength at the electrode falls with time to a certain established value and thereafter remains constant ([2,3,6,7]), contrary to equations (6) and (7).

From this fact it follows that the process of diffusion of the reacting substance to the electrode reaches, in time, a certain stationary state with a constant concentration gradient of the diffusing substance at the electrode surface. In this case, i.e. upon attainment of the stationary diffusion regime, there is evidently established a constant thickness of the diffusion layer, at the outer boundary of which a practically constant concentration c_0 is maintained. This conclusion is in agreement with the theory of con-

Levich's convective diffusion ([8,9]), according to which, in the steady-state regime, the principal changes in the concentration of the diffusing substance occur practically linearly within a certain diffusion layer. Hence there follows an additional boundary condition for the diffusion of the reacting substance to an immobile electrode: at some distance l or $\rho - r_0$ from the electrode, the concentration of the reacting substance is maintained constant, equal to c_0. In other words, for linear diffusion

$$c(l, t) = c_0; \tag{8}$$

for spherical diffusion

$$c(\rho, t) = c_0. \tag{9}$$

From conditions (8), (9), however, it does not follow that a constant thickness of the diffusion layer is maintained in the process of nonstationary diffusion. The point is only that, at some distance from the electrode, the concentration of the diffusing substance practically does not fall below the initial concentration, which occurs, apparently, as a consequence of the natural convection of the diffusing substance.

Corresponding to conditions (1), (2), (8) and (3), (4), (9), the solution of equation (5) by means of the Laplace integral gives, for linear diffusion,

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{c_0}{l}\left[1 + 2\sum_{k=1}^{\infty}\exp\left(-\pi^2 k^2 \frac{at}{l^2}\right)\right], \tag{10}$$

and for spherical diffusion

$$\left(\frac{\partial c}{\partial r}\right)_{r=r_0} = \frac{c_0}{r_0} + \frac{c_0}{\rho - r_0}\left[1 + 2\sum_{k=1}^{\infty}\exp\left(-\pi^2 k^2 \frac{at}{(\rho - r_0)^2}\right)\right]. \tag{11}$$

The derived relationships were tested by us on current-time curves for the deposition of mercury on an immobile mercury spherical cathode and for the deposition of silver on an immobile silver plane cathode, and also on data obtained by other authors (2,3,7). In doing so, no forced stirring of the electrolyte was used, since we were primarily interested in the case of natural convection and diffusion. For the analysis of the experimental data we used the following approximate equations for the diffusion current, derived on the basis of equations (10) and (11), neglecting all terms of the series $\sum \exp\left[-\pi^2 k^2 at/l^2\right]$ except the first:

$$i = i_\infty + nFa\,\frac{c_0}{l}\,2\exp\left(-\frac{\pi^2 at}{l^2}\right) \tag{12}$$

(linear diffusion);

$$i = i_\infty + nFa\,\frac{c_0}{\rho - r_0}\,2\exp\left(-\frac{\pi^2 at}{(\rho - r_0)^2}\right) \tag{13}$$

(spherical diffusion). Here i_∞ is the current density at $t = \infty$, i.e., the steady-state current density; i is the diffusion-current density.

In the first case

$$i_{\infty(\text{linear})} = nFa\,\frac{c_0}{l}. \tag{14}$$

In the second,

$$i_{\infty(\text{spheric})} = nFa\left(\frac{c_0}{r_0} + \frac{c_0}{\rho - r_0}\right). \tag{15}$$

Equations (12) and (13) are reduced to the form

$$t = A - B\ln(i - i_\infty), \tag{16}$$

Fig. 1. Current-time curves. I –deposition of mercury on a mercury cathode, $U = 12.5$ mV; II –deposition of silver on a silver cathode, $U = 175$ mV; III –oxidation of $\mathrm{Fe(CN)}_6^{4-}$ ions at a platinum anode (2), electrode F; IV –deposition of zinc on a platinum cathode (2), $U = 1.20$ V.

Figure 1: Fig. 1. Current-time curves. I –deposition of mercury on a mercury cathode, $U = 12.5$ mV; II –deposition of silver on a silver cathode, $U = 175$ mV; III –oxidation of $\mathrm{Fe(CN)}_6^{4-}$ ions at a platinum anode (2), electrode F; IV –deposition of zinc on a platinum cathode (2), $U = 1.20$ V.

where, for linear diffusion,

$$A = \frac{l^2}{\pi^2 a} \ln\left(2nF\frac{c_0}{l}\right), \qquad B = \frac{l^2}{\pi^2 a}; \tag{17}$$

for spherical diffusion,

$$A = \frac{(\rho - r_0)^2}{\pi^2} \ln\left(2nF\frac{c_0}{(\rho - r_0)}\right), \qquad B' = \frac{(\rho - r_0)^2}{\pi^2 a}. \tag{18}$$

The current-time curves were recorded by us automatically on the photographic drum of a polarograph at constant voltages on the electrodes. When the circuit was closed, the spot of the mirror galvanometer sharply deviated from zero and then slowly moved in the opposite direction, tracing out the current-time curve.

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Equations (12), (13), (16) correspond to equations (10), (11) the better, the larger the value of t. At $t = 0$, equations (10), (11) in general have no physical meaning. In practice, however, in order to achieve good convergence

equation (16) with equations (10), (11) requires a time of the order of 1 sec., i.e., the time of the initial throw of the galvanometer spot.

The curves $i = f(t)$ obtained by us and by other authors were investigated in the coordinates t, $\lg(i - i_\infty)$ (examples of the curves are given in Fig. 1). The values of i_∞ were determined from the curves under study. In all the cases investigated by us, a linear dependence of t on $\lg(i - i_\infty)$ was observed, which confirms the validity of equation (16) and of the assumptions we adopted. The quantities A and B in all cases did not depend on the voltage applied to the electrodes.

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Institute of General and Inorganic Chemistry
Academy of Sciences of the USSR

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