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Abstract

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THEORY OF IRREVERSIBLE PROCESSES OCCURRING AT A SPHERICAL ELECTRODE

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The method of investigating the kinetics of electrode processes by using a hanging (stationary) mercury drop, along with the dropping-electrode method, is becoming increasingly important. Its chief advantage over the latter is that it eliminates a number of side effects (for example, the effect of electrolyte depletion, the capillary-pressure effect) that hinder the use of the dropping electrode for exact quantitative determinations. At the same time, the diffusion conditions at a stationary drop are considerably simpler and make it possible to take spherical diffusion into account also in irreversible processes. This has so far not been accomplished for the dropping electrode, although it is known that the correction for spherical diffusion in the latter case is of the order of 10–30%. The purpose of the present work is to calculate the dependence of the current on time, under potentiostatic conditions, for irreversible electrode processes occurring at a spherical electrode and for electrode processes preceded by a rapid chemical reaction in solution.

1. In an irreversible electrode process of the type $\mathrm{Ox} + ne_0^- \rightleftarrows \mathrm{Red}$, occurring at a constant potential on a spherical electrode of diameter a, the diffusion conditions are described by the system of equations

$$\frac{\partial C_{\mathrm{Ox}}(r,t)}{\partial t} = D_{\mathrm{Ox}}\left[\frac{\partial^2 C_{\mathrm{Ox}}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\mathrm{Ox}}(r,t)}{\partial r}\right]; \qquad (1)$$

$$\frac{\partial C_{\mathrm{Red}}(r,t)}{\partial t} = D_{\mathrm{Red}}\left[\frac{\partial^2 C_{\mathrm{Red}}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\mathrm{Red}}(r,t)}{\partial r}\right]; \qquad (2)$$

$$t = 0, \quad r > a: \qquad C_{\mathrm{Ox}}(r,0) = C^0, \quad C_{\mathrm{Red}}(r,0) = 0; \qquad (3)$$

$$t > 0,\ r = a: \quad D_{\mathrm{Ox}}\frac{\partial C_{\mathrm{Ox}}(r,t)}{\partial r} = R_1 C_{\mathrm{Ox}}(a,t) - k_2 C_{\mathrm{Red}}(a,t) = -D_{\mathrm{Red}}\frac{\partial C_{\mathrm{Red}}(r,t)}{\partial r}, \qquad (4)$$

where C_{Ox} and C_{Red} are concentrations. Boundary condition (4) means that at the electrode surface ($r = a$) the flux of substance Ox is equal to the difference between the rate of conversion of Ox into Red and the rate of regeneration of Ox as a result of the reverse reaction. At the same time this flux is equal in magnitude, but opposite in direction, to the flux of the product Red. R_1 and R_2 are the rate constants of the forward and reverse reactions, depending on the electrode potential. For $D_{\mathrm{Ox}} = D_{\mathrm{Red}} = D$, the diffusion conditions for Ox and Red are identical, and

$$C_{\mathrm{Red}}(r,t) = C^0 - C_{\mathrm{Ox}}(r,t). \tag{5}$$

(This a priori assertion is proved by the solution of equations (1)-(4).) In this case the boundary condition (4) for C_{Ox} is transformed into

$$\left(\frac{\partial C_{\mathrm{Ox}}(r,t)}{\partial r}\right)_{r=a} = h\left[C_{\mathrm{Ox}}(a,t) - C_1\right] \tag{6}$$

and for C_{Red} into

$$\left(\frac{\partial C_{\mathrm{Red}}(r,t)}{\partial r}\right)_{r=a} = h\left[C_{\mathrm{Red}}(a,t) - C_2\right], \tag{6a}$$

where

$$h = \frac{k_1 + k_2}{D}, \qquad C_1 = \frac{k_2}{k_1 + k_2}C^0 \quad \text{and} \quad C_2 = \frac{k_1}{k_1 + k_2}C^0.$$

Hence, for $C(r,t)$

one obtains (cf., for example, (^{1}))

$$C_{\mathrm{Ox}}(r,t) = C^0 - (C^0 - C_1)\frac{ha^2}{1+ha}\frac{1}{r}\left\{\operatorname{erfc}\frac{(r-a)}{2\sqrt{Dt}} - \right.$$
$$\left. - \exp\left[h'(r-a) + {h'}^2 Dt\right]\operatorname{erfc}\left[\frac{(r-a)}{2\sqrt{Dt}} + h'\sqrt{Dt}\right]\right\}; \tag{7}$$

$$C_{\mathrm{Red}}(r,t) = C_2\frac{ha^2}{1+ha}\frac{1}{r}\left\{\operatorname{erfc}\frac{(r-a)}{2\sqrt{Dt}} - \right.$$
$$\left. - \exp\left[h'(r-a) + {h'}^2 Dt\right]\operatorname{erfc}\left[\frac{(r-a)}{2\sqrt{Dt}} + h'\sqrt{Dt}\right]\right\}, \tag{7a}$$

where $h' = h + 1/a$.

Expression (7), if one takes into account that

$$C^0 - C' = \frac{k_1}{k_1 + k_2} C^0 = \frac{k_1}{Dh} C^0,$$

gives for the current:

$$i = nFAD \left(\frac{\partial C_{\mathrm{Ox}}(r,t)}{dr} \right)_{r=a} = nFAC^0 \frac{k_1 a}{1 + ha} \left[\frac{1}{a} + \exp(h'^2 Dt) \operatorname{erfc}\left(h' \sqrt{Dt} \right) \right]. \tag{8}$$

As $a \to \infty$, (8) becomes the expression for linear diffusion (^{2}). Equation (8) contains two unknown constants k_1 and h, which makes its use difficult.

A considerably simpler expression is obtained if, in (4), the reverse reaction $k_2 C_{\mathrm{Red}}(a,t)$ is neglected; this is permissible when the electrode potential is 50–60 mV more negative than the standard potential of the oxidation-reduction system. In this case the boundary condition (4) becomes

$$\left(\frac{\partial C_{\mathrm{Ox}}(r,t)}{dr} \right)_{r=a} = h C_{\mathrm{Ox}}(a,t). \tag{9}$$

The method of solution is the same as above, and for the current at $h = k_1/D_{\mathrm{Ox}}$ one obtains

$$i = D_{\mathrm{Ox}} nFAC_0 \left[\frac{h}{1 + ha} + \frac{h^2 a}{1 + ha} \exp(h'^2 D_{\mathrm{Ox}} t) \operatorname{erfc}\left(h' \sqrt{D_{\mathrm{Ox}} t} \right) \right]. \tag{10}$$

The interpretation of this expression is given below, after consideration of the second case.

2. As Koutecký showed (^{3}), the diffusion equations for the case of an electrode process preceded by a rapid chemical reaction in solution, for a dropping mercury electrode, can be reduced to the system of equations (1)–(4). This method will also be used here for the case of diffusion to a spherical stationary electrode.

Let us assume that the electrochemical process proceeds according to the scheme

$$\mathrm{B} \underset{\rho\sigma}{\overset{\rho}{\rightleftarrows}} \mathrm{A} \xrightarrow{+ne_0^-} \mathrm{Red},$$

i.e., that the electrochemically active substance A is in equilibrium with the electrochemically inactive substance B; ρ and $\rho\sigma$ are the rate constants of the forward and reverse reactions, and $\sigma = C_{\mathrm{B}}^0 / C_{\mathrm{A}}^0$ is the equilibrium constant. The diffusion conditions in this case are described by the system of equations

Fig. 1

Figure 1: Fig. 1

$$\frac{\partial C_{\mathrm{A}}(r,t)}{\partial t} = D_{\mathrm{A}}\left[\frac{\partial^2 C_{\mathrm{A}}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\mathrm{A}}(r,t)}{\partial r}\right] - \rho\left[C_{\mathrm{B}}(r,t) - \sigma C_{\mathrm{A}}(r,t)\right]; \tag{11}$$

$$\frac{\partial C_{\mathrm{B}}(r,t)}{\partial t} = D_{\mathrm{B}}\left[\frac{\partial^2 C_{\mathrm{B}}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\mathrm{A}}(r,t)}{\partial r}\right] - \rho\left[C_{\mathrm{B}}(r,t) - \sigma C_{\mathrm{A}}(r,t)\right]; \tag{12}$$

$$t = 0, \quad r > a: \qquad C_{\mathrm{A}}(r,0) = C_{\mathrm{A}}^0, \quad C_{\mathrm{B}}(r,0) = C_{\mathrm{B}}^0; \tag{13}$$

$$t > 0, \quad r = a: \qquad C_{\mathrm{A}}(0,t) = 0, \quad \frac{\partial C_{\mathrm{B}}(r,t)}{\partial r} = 0. \tag{14}$$

We shall assume that $D_A = D_B = D$. On adding (11) and (12) and substituting

$$\psi(r,t) = C_A(r,t) + C_B(r,t) \tag{15}$$

and on subtracting equation (11), multiplied by σ, from (12), substituting

$$\omega(r,t) = C_B(r,t) - \sigma C_A(r,t), \tag{16}$$

Fig. 1

we obtain a new system of equations

$$\frac{\partial \psi(r,t)}{\partial t} = D\left[\frac{\partial^2 \psi(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial \psi(r,t)}{\partial r}\right]; \tag{17}$$

$$\frac{\partial \omega(r,t)}{\partial t} = D\left[\frac{\partial^2 \omega(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial \omega(r,t)}{\partial r}\right] - l\omega; \tag{18}$$

$$t = 0, \quad r > a: \qquad \varphi(r,0) = \psi^*, \quad \omega(r,0) = 0; \tag{19}$$

$$t > 0, \quad r = a: \qquad \psi(a,t) = \omega(a,t), \quad \frac{\partial \omega(r,t)}{\partial r} = -\sigma\frac{\partial \psi(r,t)}{\partial r}. \tag{20}$$

Analogously to (3), it can be shown that, for values of the argument $lt \gg 1$, the time derivative in equation (18) may be neglected, and thus a second-order differential equation for ω may be obtained. The solu-

of this equation under the boundary conditions (19) and (20) has the form

$$\omega(r,t) = \omega(a,t)\frac{a}{r}\exp\left[-\sqrt{\frac{l}{D}}(r-a)\right], \tag{21}$$

whence

$$\left(\frac{\partial\omega(r,t)}{\partial r}\right)_{r=a} = -\left[\sqrt{\frac{l}{D}} + \frac{1}{a}\right]\omega(a,t) \tag{22}$$

or, according to (20),

$$\left(\frac{\partial\psi(r,t)}{\partial r}\right)_{r=a} = \frac{1}{\sigma}\left[\sqrt{\frac{l}{D}} + \frac{1}{a}\right]\psi(a,t). \tag{23}$$

The solution of equation (17) under the boundary conditions (19) and (23) is identical with (7) for $C_1 = 0$ and $h = \frac{1}{\sigma}\left[\sqrt{\frac{l}{D}} + \frac{1}{a}\right]$. The current is determined by $D(\partial C_A/\partial r)_{r=a}$; the latter, according to (15) and (14), is equal to $D(\partial\psi/\partial r)_{r=a}$. Consequently:

$$i = nFA(1+\sigma)C_A^0 D\left[\frac{h}{1+ha} + \frac{h^2 a}{1+ha}\exp({h'}^2 Dt)\,\mathrm{erfc}(h'\sqrt{Dt})\right]. \tag{24}$$

The equation obtained is identical in form with (10).

3. From the experimentally found dependence of the current on time, one can determine the constant characterizing the rate of the electrode process. For this purpose it is convenient to express equation (10), respectively (24), in terms of the dimensionless parameters $y = i/n \pm 4\pi aDC$, $\tau = Dt/a$, and $\alpha = 1/h'a$:

$$y = (1-\alpha)\left(1 + \frac{1-\alpha}{\alpha}\exp\frac{\tau}{\alpha^2}\,\mathrm{erfc}\,\frac{\sqrt{\tau}}{\alpha}\right). \tag{25}$$

The dependence of y on $\sqrt{\tau}$ (which represents the dependence of the current i on $\sqrt{t}$ at a definite reduced scale) is shown graphically in Fig. 1 for various values of α. The value of the parameter α, which contains the rate constant of the electrode process, can be determined from experimental data with the aid of the nomogram in Fig. 1. For this it is sufficient to have the value of the current i at a definite instant t after the beginning of the process. To calculate y and τ from these values, it is sufficient to know only the diffusion coefficient, whose value can be obtained from other parallel measurements (for example, measurements of the limiting diffusion current).

To determine α, one may, of course, also use the curve $i - \sqrt{t}$, which should be plotted in the coordinate system of Fig. 1 at the corresponding reduced scale. Obtaining a curve that does not intersect the theoretically calculated curves (which corresponds to a constant value of α over the measurement interval) is evidence of the correctness of the assumed mechanism.

From the value of α it is easy to determine the value of the rate constant from one of the equations: a) for an irreversible electrode process

$$k_1 = \frac{D}{a}\frac{1-\alpha}{\alpha};$$

b) for an electrode process with a preceding reaction

$$\rho = \frac{D}{a^2}\frac{\sigma^2}{1+\sigma}\left(\frac{1-\alpha}{\alpha}\right)^2.$$

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