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Abstract

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APPLICATION OF THE ROTATING DISK ELECTRODE TO THE STUDY OF KINETIC AND CATALYTIC PROCESSES IN ELECTROCHEMISTRY

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The development of the kinetics of electrochemical reactions in recent years has been marked by the beginning of a systematic study of such electrode reactions whose course is closely connected with accompanying chemical reactions in the bulk of the solution (kinetic and catalytic reactions). Until now, the systematic study of processes has been carried out with the aid of the dropping mercury electrode ([1]). For this instrument a general theory of catalytic and kinetic processes was developed ([1], [2]).

It will be shown below that the rotating disk electrode, as an instrument for studying kinetic and catalytic currents, has substantial advantages over the dropping electrode. Namely, in contrast to the dropping electrode, processes on the rotating disk occur under steady-state conditions. This circumstance makes it possible without difficulty to obtain calculation formulas for comparatively complicated cases of reactions. The existence of such formulas is a necessary prerequisite for studying the rates of chemical reactions. At the same time, the study of steady-state processes is also simpler from the experimental side. And finally, in the case of the disk there is the possibility of widely varying the experimental conditions, changing not only the pH of the solution, but also the rate of rotation of the disk.

We do not set ourselves the goal of covering the entire variety of different kinetic and catalytic processes. Using several examples, we shall explain the characteristic method of solving problems that arise in the study of kinetic and catalytic processes.

As a first example ([3]), let us consider a kinetic process having a quasi-monomolecular character and proceeding according to the scheme:

$$\begin{array}{cc} \text{bulk} & \text{electrode} \\ \mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{B} & \mathrm{A} \rightarrow \mathrm{C} \end{array}$$

The reaction has a quasi-monomolecular character in the sense that the rate constant of the reaction B → A may in this case depend on the concentration of some substance D present in the solution:

$$k_2 = k_2[\mathrm{D}].$$

In what follows we introduce the notation:

$$k_2 = \rho, \qquad k_1 = \rho\sigma, \qquad \text{where } \sigma = \frac{k_1}{k_2[\mathrm{D}]}.$$

If $C_1^{(0)}$ and $C_2^{(0)}$ are the concentrations of substances A and B, respectively, in the bulk of the solution and far from the electrode, then the equilibrium condition is written in the form

$$C_2^{(0)} - \sigma C_1^{(0)} = 0. \tag{1}$$

In this case the total concentration of the solution has the prescribed value:

$$C_1^{(0)} + C_2^{(0)} = C_0. \tag{2}$$

Let us now consider the equations for the concentration distribution near the reaction surface, which is the plane of the rotating disk. In contrast to the bulk of the solution, near the reaction surface the equilibrium will be disturbed, since at the surface itself substance A disappears as a result of the electrode reaction.

The strength of the volume sources for substances A and B can be written in the form

$$Q_1 = \rho C_2 - \sigma\rho C_1, \qquad Q_2 = -\rho C_2 + \sigma\rho C_1.$$

The equations of convective diffusion in the presence of volume sources can be written in the form

$$V\frac{dC_1}{dy} = D\frac{d^2C_1}{dy^2} + \rho(C_2 - \sigma C_1), \tag{3}$$

$$V\frac{dC_2}{dy} = D\frac{d^2C_2}{dy^2} - \rho(C_2 - \sigma C_1). \tag{4}$$

For formulas (3) and (4) we have used the specific feature of the rotating disk, the entire surface of which is equally accessible in the diffusion sense (provided edge effects are neglected), and the concentrations may be regarded as independent of the coordinates r, φ. In addition, to simplify the exposition we have assumed that the diffusion coefficients of particles A and B are equal to one another. In practice they often have very close values. The case of unequal diffusion coefficients has no fundamental difference from that considered below, but requires a longer exposition.

The boundary conditions at infinity are the relations (1) and (2). Let us also formulate the boundary conditions at the disk surface. We shall assume that the electrode reaction is very rapid, so that the concentration C_1 of substance A at the disk surface satisfies the condition

$$C_1 = 0 \quad \text{for } y = 0, \tag{5}$$

i.e., we shall restrict ourselves to the regime of limiting diffusion current.

Substance B neither disappears nor appears at the electrode. Therefore its concentration C_2 satisfies the condition

$$\frac{dC_2}{dy} = 0 \quad \text{for } y = 0. \tag{6}$$

To solve the system it is convenient to introduce new unknown functions

$$\varphi = \rho(C_2 - \sigma C_1), \qquad \psi = C_1 + C_2.$$

Simple transformations lead to the following equations for the functions ψ and φ:

$$V\frac{d\psi}{dy} = D\frac{d^2\psi}{dy^2}, \tag{7}$$

whence

$$\psi = a_1 \int_0^y \exp\left\{\int_0^t \frac{V(t')\,dt'}{D}\right\} dt + a_2, \tag{8}$$

$$V\frac{d\varphi}{dy} = D\frac{d^2\varphi}{dy^2} - \alpha\varphi, \tag{9}$$

where $\alpha = \rho(1 + \sigma)$ is denoted.

To solve equation (9), let us assume that the volume chemical reaction is rapid, so that the inequality always holds

$$V\frac{d\varphi}{dy} \ll \alpha\varphi. \tag{10}$$

Then, for φ one may write

$$\varphi = \text{const} \cdot \exp\left[-\sqrt{\frac{\alpha}{D}}\, y\right]. \tag{11}$$

With the aid of this expression for φ, from (5) and (6) one can obtain the boundary conditions for ψ in the form

$$\psi \to C_0 \quad \text{as } y \to \infty, \qquad \left(\frac{d\psi}{dy}\right)_{y=0} = \frac{1}{\sigma}\sqrt{\frac{\alpha}{D}}\,\psi.$$

Using the general solution of the boundary-value problem for ψ (4), we find the final form of the functions ψ and φ. The total reaction rate is given by the diffusion flux to the surface of the disk. Calculation with the aid of the relations obtained in work (4) gives

$$j = D\left(\frac{dC_1}{dy}\right)_{y=0} = D\left(\frac{d\psi}{dy}\right)_{y=0} = \frac{DC_0}{1.61\left(\frac{D}{\nu}\right)^{1/3}\sqrt{\frac{\nu}{\omega}}}\,\frac{1}{\left[1 + \frac{\sigma}{1.61}\sqrt{\frac{\omega}{\alpha}}\left(\frac{D}{\nu}\right)^{1/3}\right]}, \tag{12}$$

where ω is the angular velocity of rotation of the disk, and ν is the kinematic viscosity of the solution.

Introducing the intuitive concepts of the thickness of the diffusion layer δ' and the thickness of the kinetic layer δ_k (5), one may write j in the form

$$j = \frac{DC_0}{\delta'(1 + \delta_k/\delta')},$$

where $\delta_k = \sqrt{D/\alpha}$ and δ' has the value calculated in work (4). The condition of applicability of approximation (10) is obtained from an estimate of the terms of the next order of smallness. The calculation gives, instead of (10),

$$\frac{1}{8}\sqrt{\frac{\omega^2}{\alpha^3}\left(\frac{D}{\nu}\right)} \ll 1. \tag{13}$$

Inequality (10) may be interpreted visually if it is written in the form

$$\delta_k \ll \delta. \tag{14}$$

In Bulevskii' s work (^{6}) an analogous problem was considered. He, however, assumed that the liquid within the diffusion layer of constant thickness is immobile.

Let us now consider another typical example of a kinetic process (^{7}). Suppose that the homogeneous reaction is determined by the scheme

$$2A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

and thus has a bimolecular character. In this case the source density has the form

$$Q_1 = k_2 C_2 - k_1 C_1^2, \qquad Q_2 = \frac{1}{2}\left(k_1 C_1^2 - k_2 C_2\right).$$

The coefficient 1/2 means that, upon the disappearance of one molecule of substance A, 1/2 molecule of substance B arises.

In this case the distribution of the concentrations of substances A and B is determined by the equations

$$V\frac{dC_1}{dy} = D\frac{d^2C_1}{dy^2} + k_2C_2 - k_1C_1^2, \tag{15}$$

$$V\frac{dC_2}{dy} = D\frac{d^2C_2}{dy^2} - \frac{k_2C_2}{2} + \frac{1}{2}k_1C_1^2. \tag{16}$$

The boundary conditions at infinity may be written in the form

$$k_1C_1^{(0)} - k_2C_2^{(0)} = 0 \quad \text{as } y = \infty; \tag{17}$$

$$C_1^{(0)} + C_2^{(0)} = C_0. \tag{18}$$

The latter equality evidently expresses the condition of equilibrium. We shall assume that the rate constant of the reaction $B \to 2A$ is large in comparison with the rate constant of the reverse reaction, so that in the bulk of the solution the inequality holds

$$C_2^{(0)} \gg C_1^{(0)}.$$

Then boundary condition (18) can be written in the form

$$C_2^{(0)} \simeq C_0 \quad \text{as } y \to \infty. \tag{19}$$

Still restricting ourselves to the case of a very rapid electrode reaction, we may regard the boundary conditions at the disk surface as having the form (5) and (6).

To solve the system of equations (15) and (16), we introduce a new unknown function

$$\psi = C_1 + 2C_2,$$

which satisfies equation (7). Expressing C_2 through ψ and C_1, we can write (15) in the form

$$V\frac{dC_1}{dy} = D\frac{d^2C_1}{dy^2} + k_2\frac{\psi - C_1}{2} - k_1C_1^2. \tag{20}$$

Assuming that, as in the example of a monomolecular reaction considered above, the rate of the homogeneous chemical reaction is sufficiently large that the convective term in (20) may be neglected, and assuming that the variation of the function ψ occurs over the thickness of the diffusion layer δ', while the variation of C_1 occurs within the thickness of the kinetic layer δ_k, one can obtain the first integral of (20).

Using the integral (20), one can formulate the boundary conditions for ψ:

$$\psi \to 2C_0 \quad \text{as } y \to \infty; \tag{21}$$

$$\frac{d\psi}{dy} = k\psi^{3/4} \quad \text{at } y = 0, \tag{22}$$

where

$$k = \left(\frac{k_2^3}{k_1D^2}\right)^{1/4}\frac{1}{\sqrt[4]{18}}.$$

The solution of such a boundary-value problem was obtained earlier in work (4). The diffusion flux is equal to

$$j = D\frac{2C_0 - \psi_{y=0}}{1.61(D/\nu)^{1/3}\sqrt{\nu/\omega}}, \tag{23}$$

where $\psi_{y=0}$ satisfies the algebraic equation

$$\psi_{y=0}^{3/4} + \frac{D}{k\delta'}\left(\psi_{y=0} - 2C_0\right) = 0. \tag{24}$$

The condition for applicability of the formulas obtained is fulfillment of the inequality

$$\left(\frac{\omega}{\sqrt{k_1, k_2, C_0}}\right)^{3/2}\left(\frac{D}{\nu}\right)^{1/2} \ll 1. \tag{25}$$

In the case of the disk, analysis of more complicated cases—for example, the case of a slow electrode reaction—does not present great difficulty.

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