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V. Yu. FILINOVSKII, V. A. KIR' YANOV

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Abstract

Full Text

PHYSICAL CHEMISTRY

V. Yu. FILINOVSKII, V. A. KIR' YANOV

ON THE THEORY OF NONSTATIONARY CONVECTIVE DIFFUSION AT A ROTATING DISK ELECTRODE

(Presented by Academician A. N. Frumkin, February 3, 1964)

Nonstationary methods of investigation have in recent years been successfully applied to the study of the kinetics of electrode processes. However, in a number of cases, especially under polarization by a slowly varying voltage, chronopotentiometry, etc., interpretation of the experimental results is made difficult by the influence of natural convection. In this connection, in individual works an attempt has been made to use a rotating disk electrode in nonstationary measurements⁽³⁾.

A rigorous quantitative theory of stationary convective diffusion to the surface of a rotating disk was developed in the works of V. G. Levich⁽¹⁾. The study of nonstationary processes in such a system has been carried out either by the method of successive approximations⁽¹⁾, or qualitatively, by introducing a Nernst diffusion layer^(2,3). Both methods are applicable only for very limited time intervals.

In the present work, the description of the processes of nonstationary convective diffusion at a rotating disk has been carried out without introducing such simplifications, which makes it possible to follow the kinetics of the process up to the time at which the stationary regime is established. The proposed method also makes it possible to consider more complex cases of nonstationary diffusion at a rotating disk electrode.*

The transport equation for a reacting substance to the surface of a rotating disk has, for established flow of a viscous liquid, the form

$$\frac{\partial c}{\partial t} + v_y(y) \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}, \quad (1)$$

where $c(y, t)$ is the concentration of the reacting substance, $v_y(y)$ is the component of the liquid velocity normal to the disk, and y is the distance from the surface. For large values of the Schmidt number $Sc = \nu/D$, the velocity com-

ponent $v_y(y)$ can, with sufficient accuracy, be represented near the disk surface by the expression

$$v_y(y) = -0.51\sqrt{\omega^3/\nu}y^2, \quad (2)$$

where ω is the angular velocity of the disk and ν is the kinematic viscosity of the liquid.

For the convenience of subsequent calculations, instead of the variables y and t we introduce the dimensionless variables $x = y/\delta_d$, $\tau = Dt/\delta_d^2$, and the dimensionless concentration $g(x, \tau) = [c^0 - c(y, t)]/c^0$, where c^0 is the concentration in the bulk of the solution, and $\delta_d = 1.61(D/\nu)^{1/3}\sqrt{\nu/\omega}$ is the usual thickness of the diffusion boundary layer at the disk ⁽¹⁾.

In dimensionless variables, equation (1) takes the form

$$\frac{\partial g}{\partial \tau} = \frac{\partial^2 g}{\partial x^2} + \alpha x^2 \frac{\partial g}{\partial x}; \quad \text{here } \alpha = 2.128. \quad (3)$$

* In a recently published work ⁽⁵⁾, results are given of a numerical calculation of certain cases of nonstationary convective diffusion at a rotating disk electrode. In the corresponding cases, there is good agreement between the results of the present work and ⁽⁵⁾.

Let us first consider the case when the concentration on the surface of the disk is a certain prescribed function of time,

$$c(0, t) = f(t) \quad (4)$$

The boundary and initial conditions in this case are written as follows:

$$\begin{aligned} g \rightarrow 0 \quad \text{as } x \rightarrow \infty; \quad \tau \geq 0; \quad g(0, \tau) = \varphi(\tau) \quad \text{for } x = 0, \tau > 0; \\ g = 0 \quad \text{for } x \geq 0, \tau = 0, \end{aligned} \quad (5)$$

where $\varphi(\tau) = [c^0 - f(t)]/c^0$.

We perform the Laplace transform according to the formula

$$G(x, p) = p \int_0^\infty e^{-p\tau} g(x, \tau) d\tau. \quad (6)$$

The boundary-value problem posed is now reduced to the solution of the equation

$$pG = \frac{d^2G}{dx^2} + \alpha x^2 \frac{dG}{dx} \quad (7)$$

with boundary conditions

$$G \rightarrow 0 \quad \text{as } x \rightarrow \infty; \quad G = \Phi(p) \quad \text{for } x = 0, \quad (8)$$

where $\Phi(p)$ is the Laplace image of the function $\varphi(\tau)$.

We now transform equation (7) into an equation not containing the first derivative with respect to x , by means of the substitution

$$G(x, p) = \Psi(x, p) \exp\left(-\frac{\alpha x^3}{6}\right), \quad (9)$$

$$\frac{d^2\Psi}{dx^2} - \left(p + \alpha x + \frac{\alpha^2 x^4}{4}\right) \Psi = 0. \quad (10)$$

The boundary conditions (8) are preserved.

We shall be interested in the behavior of the solution of equation (10) near the electrode, i.e., for $x \ll 1$. In this region the solution of equation (10) is close to the solution of the equation

$$\frac{d^2\Psi_1}{dx^2} - (p + \alpha x)\Psi_1 = 0 \quad (11)$$

with boundary conditions

$$\Psi_1 \rightarrow 0 \quad \text{as } x \rightarrow \infty; \quad \Psi_1 = \Phi(p) \quad \text{for } x = 0. \quad (12)$$

Equation (11) is the well-known Airy equation, the general solution of which can be expressed in terms of Airy functions (*)

$$\Psi_1(x, p) = A_1 \text{Ai}\left(\frac{p + \alpha x}{\alpha^{2/3}}\right) + A_2 \text{Bi}\left(\frac{p + \alpha x}{\alpha^{2/3}}\right). \quad (13)$$

The constants A_1 and A_2 are determined from the boundary conditions (12)

$$\Psi_1(x, p) = \Phi(p) \frac{\text{Ai}[(p + \alpha x)/\alpha^{2/3}]}{\text{Ai}(p/\alpha^{2/3})}. \quad (14)$$

(It should be taken into account that $\text{Bi}(z)$ is an Airy function that grows exponentially as $z \rightarrow \infty$.)

The Laplace image of the flux of the substance diffusing to the surface of the disk is given by the following formula

$$\mathcal{L} \left[D \left(\frac{\partial c}{\partial y} \right)_0 \right] = -j^0 \left(\frac{\partial \Psi}{\partial x} \right)_0 \simeq -j^0 \Phi(p) \frac{\text{Ai}'(p/\alpha^{2/3})}{\text{Ai}(p/\alpha^{2/3})} \alpha^{1/3}. \quad (15)$$

Finding the inverse of the expression obtained in (15) is a very difficult mathematical problem. It can be substantially simplified if one uses the interpolation formula for the logarithmic derivative of the Airy function

$$\frac{\text{Ai}'(z)}{\text{Ai}(z)} \simeq -\frac{1+z}{\sqrt{1.877+z}}, \quad (16)$$

which is valid, with an accuracy up to 0.1%, over the entire range of variation of the real derivative z .

Performing the inverse Laplace transform, we obtain for the flux of substance to the electrode

$$j(\tau) = D \left(\frac{\partial c}{\partial y} \right)_0 = j^0 \frac{d}{d\tau} \int_0^\tau \varphi(\tau - \lambda) \left[\frac{e^{-3.10\lambda}}{\sqrt{\pi\lambda}} + 0.94 \operatorname{erf} \sqrt{3.10\lambda} \right] d\lambda, \quad (17)$$

where the function $\varphi(\tau)$ is determined from condition (5).

Let us consider the process of establishment of the steady-state regime for a prescribed constant concentration of the substance at the electrode ($c(0, t) = 0$). In this case, with the aid of (17), for the diffusion flux in ordinary variables we obtain

$$j(t) = j^0 \left[\frac{\exp(-3.10 Dt/\delta_d^2)}{\sqrt{\pi Dt/\delta_d^2}} + 0.94 \operatorname{erf} \sqrt{3.10 \frac{Dt}{\delta_d^2}} \right], \quad (18)$$

where $j^0 = Dc^0/\delta_d$ is the limiting diffusion flux to the surface of the rotating disk (1).

Relation (18) makes it possible to trace the kinetics of the establishment of the steady-state regime. At the initial moments of time (for $t \ll \delta_d^2/D$) the current has a purely diffusional character; convection is insignificant,

$$j(t) \simeq j^0 \frac{1}{\sqrt{\pi Dt/\delta_d^2}} = \frac{Dc^0}{\sqrt{\pi Dt}}. \quad (19)$$

For times $t \gg \delta_d^2/D$, the steady-state regime of convective diffusion is established,

$$j = 0.94 j^0. \quad (20)$$

The steady-state expression obtained agrees, to within 6%, with the limiting current to the surface of a rotating disk.

The characteristic time for establishment of the steady-state regime is the quantity

$$T = \delta_d^2/3.10D. \quad (21)$$

Let us consider processes of nonstationary diffusion for a prescribed flux of substance $D(\partial c/\partial y)_0 = u(t)$ at the rotating disk electrode. Such problems are characteristic of chronopotentiometric methods for studying the kinetics of electrode processes.

In contrast to the preceding problem, instead of the boundary conditions (5) one should write

$$g \rightarrow 0 \quad \text{as } x \rightarrow \infty, \quad \tau \geq 0; \quad \left(\frac{\partial g}{\partial x} \right)_0 = \omega(\tau) \quad \text{at } x = 0, \quad \tau > 0, \quad (22)$$

where $\omega(\tau) = -u(t)/j^0$.

The initial condition remains the same,

$$g = 0 \quad \text{for } x \geq 0, \quad \tau = 0.$$

To solve the formulated problem we shall use the method set forth above.

Having carried out the indicated transformations, we again obtain, for determining the Laplace transform of the concentration of the diffusing substance, the general solution (13). Now, however, the constants A_1 and A_2 are determined from the conditions

$$\Psi_1 = 0 \quad \text{as } x \rightarrow \infty; \quad \left(\frac{d\Psi_1}{dx} \right)_0 = W(p) \quad \text{at } x = 0, \quad (23)$$

where $W(p)$ is the Laplace transform of the function $\omega(\tau)$.

For the Laplace transform of the desired concentration we obtain the expression

$$\Psi_1(x, p) = \frac{W(p) \text{Ai} [(p + \alpha x)/\alpha^{2/3}]}{\alpha^{1/3} \text{Ai}' (p/\alpha^{2/3})}. \quad (24)$$

Fig. 1

Figure 1: Fig. 1

Usually, what is recorded experimentally is the electrode potential, which is determined by the concentration of the substance at the surface. Using the interpolation formula (16) proposed earlier for the logarithmic derivative of the Airy function, the concentration at the surface may be written in the following form:

$$g(0, \tau) = -\frac{d}{d\tau} \int_0^\tau w(\tau - \lambda) \left[1.07 \operatorname{erf} \sqrt{3.10\lambda} - 0.73e^{-1.65\lambda} \operatorname{erf} \sqrt{1.45\lambda} \right] d\lambda \quad (25)$$

In the case of electrolysis at constant current density j ,

$$c(0, t) = c^0 \left\{ 1 - \frac{j}{j^0} \left[1.07 \operatorname{erf} \sqrt{3.10 \frac{Dt}{\delta_d^2}} - 0.73e^{-1.65Dt/\delta_d^2} \operatorname{erf} \sqrt{1.45 \frac{Dt}{\delta_d^2}} \right] \right\}. \quad (26)$$

At the initial moments of time ($t \ll \delta_d^2/D$) the influence of convection is negligibly small. The corresponding limiting transition in (26) gives

$$c(0, t) = c^0 \left[1 - \frac{j}{j^0} \frac{2}{\sqrt{\pi}} \sqrt{\frac{Dt}{\delta_d^2}} \right] = c^0 - j \frac{2\sqrt{t}}{\sqrt{\pi D}}. \quad (27)$$

For $t \gg \delta_d^2/D$, formula (26) agrees, to an accuracy of 7%, with the expression for the surface concentration at a rotating disk electrode in the steady state,

$$c(0, t) = c^0 \left[1 - 1.07 \frac{j}{j^0} \right]. \quad (28)$$

The principal characteristic in chronopotentiometric investigations is the “transition time” T , which is determined from the condition $c(0, T) = 0$ or from the solution of the transcendental equation

$$\frac{j^0}{j} = 1.07 \operatorname{erf} \sqrt{3.10 \frac{Dt}{\delta_d^2}} - 0.73e^{-1.65Dt/\delta_d^2} \operatorname{erf} \sqrt{1.45 \frac{Dt}{\delta_d^2}}. \quad (29)$$

Fig. 1

Equation (29) can be easily studied for cases of large and small transition times T . The resulting dependence of the current density on the transition time agrees with that given by V. G. Levich¹ on the basis of qualitative considerations.

Figure 1 shows the dependence of $j\sqrt{T}$ on \sqrt{T} , which is usually investigated experimentally.

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Institute of Electrochemistry
Academy of Sciences of the USSR

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