DIFFUSION TO A UNILATERAL ELECTRODE IN A PLANE-PARALLEL CHANNEL WITH POISEUILLE FLOW

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1. An analysis of diffusion in a plane-parallel channel in the presence of a Poiseuille flow was made in [1, 2] for a two-sided slot electrode. It is interesting to consider also the transient and steady-state diffusion processes to an electrode situated on only one wall of the slot channel. Under current-limited conditions and in the presence of a constant Poiseuille flow an important characteristic of the steady-state diffusion process is the complete-absorption length L_0. To find L_0 we can use the asymptotic solution based on the theory of heat exchange in a channel consisting of a plane slot, one wall of which is thermally insulated and the other a good thermal conductor [3, 4]. In that case the density of the diffusion current j for a unilateral electrode can be expressed as:

$$j = (2Dc_0 / h)\,[1{,}09 \exp(-3{,}64Dz / v_0h^2) + 0{,}72 \exp(-35{,}4Dz / v_0h^2) + \ldots], \tag{1}$$

where D is the diffusion coefficient; h is the width of the channel; c_0 is the initial concentration of reacting material introduced into the channel by the Poiseuille current with a velocity v_0 in the center of the channel; the z axis is in the direction of the current and lies in the electrode plane; and the origin of the coordinates is located at the origin of the plate electrode.

The first term of Eq. (1) is dominant at distances which can be evaluated from the relative magnitudes of the first and second terms. The second term reaches 1% of the first when $z_0 = 0.13\ v_0h^2/D$. When $z > z_0$ it can be terminated at the first term with an error less than 1%. The diffusion current to the electrode of length L (with an error less than 1% if $L > z_0$) is then equal to:

$$I = Q_m - \Delta Q = hbc_0\bar{v} - b\int_L^\infty j\,dz = I_c[1 - 0.90 \exp(-3.64DL/v_0h^2)], \tag{2}$$

where Q_m is the amount of material introduced into the channel by the hydrodynamic current; ΔQ is the amount of unreacted ions leaving, beyond the electrode limits; b is the dimension across the electrode disc; $I_c = 2bhc_0v_0/3$ is the diffusion current of complete absorption; and $\bar{v} = 2v_0/3$. On the basis of Eq. (2) a leak coefficient of the plane uilateral electrode can be introduced:

$$k_1 = \Delta Q / Q_m = 0.90 \exp(-3.64DL / v_0h^2). \tag{3}$$

By substituting the previous value of z_0 in Eq. (3) we find that the error in calculating the diffusion current does not exceed 1% if the condition $\Delta Q/Q_m < 0.56$ is satisfied. Equation (3) makes it possible to calculate the complete absorption length L_0. Assuming, for example, that $k_1 = 0.01$, we find

$$L_0 = -(v_0h^2 / 3.64D) \ln (k_1 / 0.90) = 1.24v_0h^2 / D.$$

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The leak coefficient of a double-sided plane electrode is according to [1],

$$k_2 = 0.91 \exp(-11.3DL / v_0 h^2).$$

A comparison of k_1 with k_2 indicates that the intensity of absorption of the reacting material by the double-sided electrode is relatively high. For example, the length of complete absorption on a double-sided electrode when $k_2 = 0.01$ is $0.40\ v_0h^2/D$, i.e., one third of L_0.

Oleinik et al. [5] and Fish [6] obtained an approximation for the stationary diffusion current to a slot electrode assuming a plane (but not Poiseuille type) of velocity profile. Hence, the leak coefficient of a single-sided electrode is

$$k^* = 0.81 \exp(-3.70DL / v_0 h^2).$$

Thus, the agreement between k^* and the result of the calculation using the Poiseuille velocity profile is found to be significantly better than in the case of a double-sided electrode [1].

2. In examining the transient diffusion process we shall consider the electrode length L to be greater than the complete-absorption length L_0 ($k_1 \ll 1$). We can thus consider the electrode to be of infinite length. We shall find the transient diffusion current during a gradual change in that external perturbation which is the cause of the appearance of the hydrodynamic current. Since the relaxation time of the hydrodynamic process τ_ν is small in comparison with that of the diffusion process τ_D we shall consider that the hydrodynamic current velocity changes instantaneously from zero to the steady Poiseuille profile: $v(x) = (4v_0/h)(x - x^2/h)$. (The x axis is perpendicular to the walls of the channel.) It is thus assumed that the concentration distribution cannot change appreciably during the time τ_ν. With high values of the Péclet number, diffusion in the direction of flow can be ignored. We then obtain for the current-limited regime the following boundary-value problem

$$\partial c / \partial t + (4v_0 / h)(x - x^2 / h)\partial c / \partial z = D\partial^2 c / \partial x^2, \tag{4}$$

$$c|_{t=0} = 0; \quad c|_{z=0} = c_0; \quad \partial c / \partial x|_{x=0} = 0; \quad c|_{x=h} = 0, \tag{4'}$$

where c is the concentration of reacting material and t is the time. By changing to $Q(x, t) = \int_0^\infty c\,dz$ we find for Q

$$\partial^2 Q / \partial x^2 - D^{-1}\partial Q / \partial t = -4\pi\rho(x), \tag{5}$$

$$Q|_{t=0} = 0; \quad \partial Q / \partial x|_{x=0} = 0; \quad Q|_{x=h} = 0, \tag{5'}$$

where $\rho(x) = (v_0c_0/\pi Dh)(x - x^2/h)$. The solution can be written in the form given by Morse et al. [7].

$$Q(x,t) = \int_0^t dt' \int_0^h \rho(x') G(x,t|x',t')\,dx'. \tag{6}$$

Here $G(x, t|x', t')$ is the Green's function for Eqs. (5) and (5'):

$$G(x,t|x',t') = (8\pi D/h) \sum_{n=0}^{\infty} \cos k_n x \cdot \cos k_n x' \exp[-Dk_n^2(t-t')],$$

where $k_n = (2n + 1)\pi/2h = (2n + 1)k_0$ are the particular values of Eqs. (5) and (5'). From Eq. (6) we find for Q(x, t):

$$Q = (8v_0c_0/Dh^3) \sum_{n=0}^{\infty} k_n^{-5}[2(-1)^n - k_n h]\cos k_n x \cdot [1 - \exp(-Dk_n^2 t)].$$

Using Q we find the transient diffusion current to a single-sided plane electrode in the current-limited regime to be:

$$I(t) = -bD\partial Q/\partial x\Big|_{x=h} = (8v_0c_0b/h^3)\sum_{n=0}^{\infty} k_n^{-4}[2 - k_nh(-1)^n]\cdot[1-\exp(-Dk_n^2t)]. \tag{7}$$

When $t \to \infty$ the diffusion current of complete absorption I_c is established. The relative contribution of the first terms of these series in (Eq. 7), n = 0, n = 1, n = 2, to the steady-state current are respectively;

$$(I_0/I_c)_{t\to\infty} = 0.850; \quad (I_1/I_c)_{t\to\infty} = 0.164; \quad (I_2/I_c)_{t\to\infty} = -0.018.$$

Therefore, Eq. (7) can be rewritten in the form

$$I = I_c[1 - 0.85\exp(-2.47Dt/h^2) - 0.16\exp(-22{,}2Dt/h^2) + 0.02\exp(-61.6Dt/h^2) - \ldots]. \tag{8}$$

The second term in Eq. (8) begins to dominate the third and subsequent terms when $t > t_0$, where t_0 can be evaluated from the relative contribution of the second and third terms. The third term reaches 1% of the second when $t_0 \simeq 0.06h^2/D$. When $t > 0.06h^2/D$ the transient diffusion current is expressed, with an error less than 1%, by the equation

$$I = I_c[1 - 0.85\exp(-2.47Dt/h^2)]. \tag{8'}$$

Thus, the typical relaxation time of the diffusion process $\tau_D = h^2/(2.47\,D)$ for the single-sided electrode is 4 times as great as τ_D for a two-sided electrode [1] and is equal to $h^2/(9.9\,D)$.

An expression was obtained in [5] for the transient diffusion current to a slot electrode assuming a plane velocity profile. It follows from this that the diffusion current to a one-sided electrode is:

$$I^* = I_c[1 - 0.81\exp(-2.47Dt/h^2) - \ldots],$$

Thus it is clear that the index of the exponent which does not depend on the hydrodynamic velocity is the same as that in Eq. (8), while the preexponential factors differ appreciably less than in the case of a double-sided electrode [1].

3. When the rate of the hydrodynamic current changes randomly, but not too rapidly with the time, so that the current keeps its Poiseuille character for the whole time (τ_ν is small compared with the typical time for a change in the hydrodynamic velocity), the diffusion current can be expressed in the form of a Duhamel integral [2]:

$$I(t) = \int_0^t v_0(\tau) I_e'(t-\tau)\,d\tau, \tag{9}$$

where $v_0(t)$ is the variable hydrodynamic velocity in the center of the channel; $I_s(t)$ is the diffusion current produced by a single jump in the hydrodynamic velocity and is equal to I/v_0, where I is determined from Eq. (7); and $I_s'(t-\tau) = dI_s(z)/dz\,|_{z=t-\tau}$. Using Eq. (9) we consider the important particular case when the hydrodynamic velocity changes instantaneously from zero to the steady Poiseuille profile with a velocity of v_0^H in the center of the channel and then drops according to $v_0(t) = v_0^H\exp(-t/T)$ while the velocity profile retains its Poiseuille form. Here T is the characteristic time determined by the structural parameters of the system ($T \gg \tau_\nu$). Using Eqs. (7) and (9) the diffusion current is easily found to be

$$I(t) = (8c_0v_0^HbD/h^3)\sum_{n=0}^{\infty}[2 - k_nh(-1)^n][\exp(-t/T) - \exp(-Dk_n^2t)]/[k_n^2(Dk_n^2 - 1/T)]. \tag{10}$$

The diffusion process is characterized by a time constant $\tau_D = 1/(Dk_0^2) = h^2/(2.47\,D)$. If $T \gg \tau_D$ then for short times when $t \leq \tau_D$ the increase $I(t)$ is due to the transient diffusion process. The current $I(t)$ increases to the limiting stationary value I_c corresponding to v_0^H, after which it slowly decreases due to a decrease in the flow velocity. In this case the series in Eq. (10) takes the form:

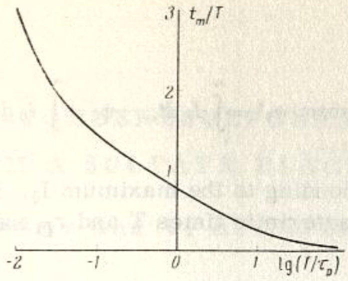

Fig. 1

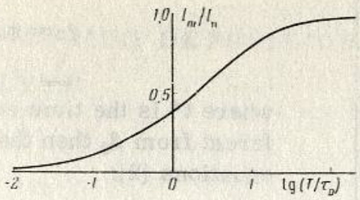

Fig. 2

$$I(t)=(8c_0v_0{}^{\text{H}}b/h^3)\sum_{n=0}^{\infty}k_n{}^{-4}[2-k_nh(-1)^n][\exp(-t/T)-\exp(-Dk_n{}^2t)];$$

and taking into account Eqs. (7) and (8) we find:

$$I(t)=I_c[\exp(-t/T)-0.85\exp(-2.47Dt/h^2)]. \tag{11}$$

In keeping with the evaluation of Eq. (8), Eq. (11) in our model involves an error of less than 1% when $t > 0.06h^2/D$.

When $T \ll \tau_D$, then at times short in comparison with T the increase I(t) is due to the increase in the area of the contact of the electrode with the enriched electrolyte introduced into the channel by the hydrodynamic flow, the velocity of which falls rapidly. The subsequent increase in I(t) is determined by the depletion of the solution due to diffusion towards the electrode. When T is comparable with τ_D or less than it, the relative magnitude of the term I_1 of Eq. (10) corresponding to n = 1 increases. To express approximately the diffusion current we can use $I(t) = I_0 + I_1$ where

$$I_0=(1.40c_0v_0{}^{\text{H}}bDT/h)\,[\exp[-t/T)-\exp(-2.47Dt/h^2)]\;/\;(2{,}47DT/h^2-1), \tag{12}$$

$$I_1=(2.42c_0v_0{}^{\text{H}}bDT/h)\,[\exp(-t/T)-\exp(-22.2Dt/h^2)]\,/\,(22{,}2DT/h^2-1). \tag{12'}$$

The time t_m corresponding to the maximum value of the expression $I(t) = I_0 + I_1$ is a function of the ratio T/τ_D. Figure 1 shows the curve of t_m/T against log (T/τ_D), while Fig. 2 shows the dependence of the corresponding values of the maximum diffusion current I_m/I_n on log (T/τ_D). The error Δ in the current approximation using Eqs. (12) and (12') is calculated from the equation for the rate of increase of the function $[I_0(t) + I_1(t)]\cdot\Delta$ and $\sum_{n=2}^{\infty} I_n(t)$ when t = 0, since in satisfying this equation the function $\sum_{n=2}^{\infty} I_n(t)$ for all t > 0 is majorized by the function $[I_0(t)+I_1(t)]\cdot\Delta$:

$$\Delta=\left\{\left(\sum_{n=2}^{\infty} dI_n/dt\right)\Big/\,[d(I_0+I_1)/dt]\right\}_{t=0}.$$

The error Δ is found to be independent of T/τ_D and is 5%.

4. By knowing the response of the system I(t) to gradual external perturbation we can find the magnitude of both the characteristic times of the system. The response of I(t) is conveniently characterized by the parameter $\beta = \Psi_m/\Psi$,

$$\text{where } \psi_m=\int_{t_m}^{\infty} I(t)\,dt, \quad \psi=\int_{0}^{\infty} I(t)\,dt.$$

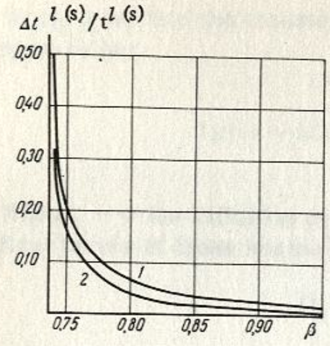

Fig. 3

Let us define

$$\beta_0 = \psi_0^*/\psi_0, \text{ where } \psi_0^* = \int_{t^*}^{\infty} I_0\,dt, \quad \psi_0 = \int^{\infty} I_0\,dt,$$

where t^* is the time corresponding to the maximum I_0. If β is slightly different from β_0 then the characteristic times T and τ_D satisfy the system of equations [2]:

$$\beta = (T - \tau_D)^{-1}[T \exp(-t^*/T) - \tau_D \exp(-t^*/\tau_D)],$$
$$t^* = T\tau_D(T - \tau_D)^{-1} \ln(T/\tau_D).$$

Here the larger (t^l) and the smaller, (t^s), characteristic times of the system correspond to a certain β and are obtained from the graph shown in Fig. 3 of [2]. Let us evaluate the error arising when $T > \tau_D$. It is easy to see that $\beta \equiv \psi_m/\psi = \beta_0\,[1-(\delta-\delta_1-\delta_2)/(1+\delta)]$,

$$\text{where } \delta = \Big(\int_0^{\infty}\sum_{n=1}^{\infty} I_n\,dt\Big)\Big/\psi_0, \quad \delta_1 = \Big(\int_{t_m}^{\infty}\sum_{n=1}^{\infty} I_n\,dt\Big)\Big/\psi_0^*, \quad \delta_2 = \Big(\int_{t_m}^{t^*} I_0\,dt\Big)\Big/\psi_0^*,$$

and I_n is the $(n+1)^{th}$ term of the series in Eq. (10).

Hence we find that $\Delta\beta = \beta - \beta_0 = \beta_0(\delta_1 + \delta_2 - \delta)/(1+\delta)$. In computing δ and δ_1 we can ignore the I_n terms corresponding to $n \geq 2$. The magnitude of δ does not depend on T and τ_D and is 0.192. In calculating the magnitude of δ_1 and δ_2 as functions of the ratio T/τ_D, we can use the graph of t_m/T (Fig. 1). Having found $\Delta\beta$ from the curve in Fig. 3 of [2], we can find the dependence of the relative errors $\Delta t^l/t^l$ and $\Delta t^s/t^s$ on the parameter β. The corresponding graphs for $\gamma > 1$ are shown in Fig. 3 (curve 1 corresponds to $\Delta t^l/t^l$ and curve 2 to $\Delta t^s/t^s$). It is clear that when $\gamma = 3.4$ ($\beta \approx 0.775$) the computational error is less than 10%.

LITERATURE CITED

1. E. Ya. Klimenkov, B. M. Grafov, V. G. Levich, and I. V. Strizhevskii, Élektrokhimiya, 5, 202 (1969).
2. E. Ya. Klimenkov, B. M. Grafov, V. G. Levich, and I. V. Strizhevskii, Élektrokhimiya, 6, 1024 (1970).
3. J. Schenk, Appl. Scient. Res., A5, Nos. 2-3, 241 (1955).
4. B. S. Petukhov, Heat Exchange and Resistance in Laminar Liquid Flow in Tubes [in Russian, Énergiya, Moscow (1967).
5. V. D. Oleinik and A. I. Linetskii, in Instrument Design [in Russian], No. 2, Tekhnika, Kiev (1966).
6. M. L. Fish, Chemitronic Instruments in Automation [in Russian], Tekhnika, Kiev (1967).
7. F. M. Morse and G. Fishbach, Methods in Theoretical Physics, Vol. 1, McGraw-Hill (1953).