RELAXATION OF A DIFFUSION PROCESS IN A CHANNEL IN THE PRESENCE OF A TIME-DEPENDENT HYDRODYNAMIC CURRENT

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1. The limiting electrical currents of an electrode occupying the interior surface of a channel depend substantially on the nature of the change in the convective delivery of reacting substance. In works devoted to heat exchange in a channel [1-5], only the simplest case where the Poiseuille hydrodynamic current in the channel does not change with time has been analyzed. Hence, it is not possible to use an analogy between the thermal and diffusion process (without having recourse to calculation) to obtain the resulting expressions for the time-dependent velocity of a hydrodynamic current. Taking the relaxation of the diffusion process in plane-parallel and cylindrical channels into account, leads to the following expressions for the limiting diffusion current corresponding to a gradual change in the velocity from zero to an established Poiseuille profile [6]:

$$I^p(t)=(8v_0c_0b/r_0^3)\sum_{n=0}^{\infty}k_n^{-4}[1-\exp(-Dk_n^2t)], \tag{1p}$$

$$I^c(t)=16\pi v_0c_0r_0^2\sum_{i=1}^{\infty}\mu_i^{-4}[1-\exp(-D\mu_i^2t/r_0^2)], \tag{1c}$$

where t is the time, v_0 is the value of the hydrodynamic velocity in the middle of the channel which is established due to rapid change, c_0 is the starting concentration of reacting substance, r_0 is the half-width of the channel in the planar case or the radius of the channel in the cylindrical case, b is the cross-sectional dimension of the plate of a planar electrode, D is the coefficient of diffusion, $k_n = (2n+1)\pi/2r_0$ (n = 0, 1, ...); μ_i are the Bessel null functions of the first type of null order J_0 (i = 1, 2, ...), and the "p" and "c" indices indicate the electrode form. (It is assumed that the electrode length is greater than the length of the complete absorption.)

Formulas (1p) and (1c) permit one to calculate the diffusion currents of an electrode in the case where the velocity of the hydrodynamic stream changes arbitrarily with time under the condition that the current itself is always of the Poiseuille type. This will be so if the relaxation time of the hydrodynamic process τ_ν is small in comparison with the characteristic time of the change in the hydrodynamic velocity. In this case, the diffusion current can be written in the form of a Duhamel [7] integral

$$I(t)=v_0(t)I_e(0)+\int_0^t v_0(\xi)I_e'(t-\xi)\,d\xi=\int_0^t v_0(\xi)I_e'(t-\xi)\,d\xi, \tag{2}$$

where $I_e(t)$ is the diffusion current caused by a single rapid change in the hydrodynamic velocity equal to $I^p(t)/v_0$ or $I^c(t)/v_0$; $I_e'(t-\xi)=dI_e(z)/dz|_{z=t-\xi}$.

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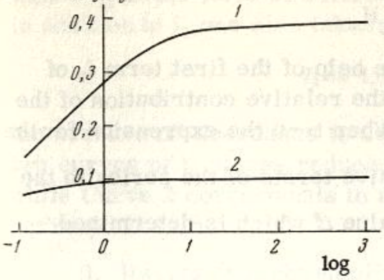

Fig. 1

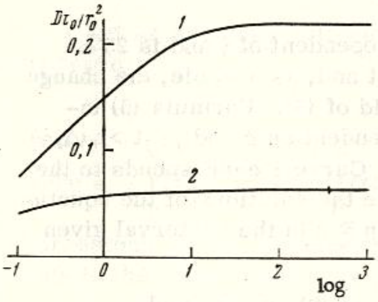

Fig. 2

Let us examine the special case which is important for applications where the hydrodynamic velocity changes instantaneously from zero to an established Poiseuille profile with a velocity in the middle of the canal of v_0^H and then decreases with time according to the exponential law $v_0(t) = v_0^H \exp(-t/T)$, where T is the characteristic time which depends on the construction parameters of the system ($T \gg \tau_\nu$). It is apparent that the response of the I(t) system to the $v_0(t)$ signal will initially increase and then decrease to zero; however, depending on the ratio between T and τ_D different processes will dominate on the portions of growth and increase of current. (τ_D is the characteristic time of the diffusion process.)

For the limiting diffusion current of an electrode occupying both walls of a plane-parallel channel at a distance $2r_0$ from each other, we obtain with the help of Eqs. (1p) and (2)

$$I = (8v_0^H c_0 bD/r_0^3)\sum_{n=0}^{\infty} k_n^{-2}(Dk_n^2 - 1/T)^{-1}[\exp(-t/T) - \exp(-Dk_n^2 t)]. \quad (3)$$

Because of the rapid convergence of series (3) the fundamental contribution to I gives the first term of the series I_0 corresponding to n = 0 and the characteristic time of the diffusion process is equal to $\tau_D = 1/Dk_0^2 = r_0^2/2.47\ D$. When $T \sim \tau_D$ both the transition diffusion process and the decrease with time of the hydrodynamic velocity for all t have a comparable effect on I. When $T \gg \tau_D$ the increase in I(t) is associated with the relaxation of the diffusion process which is established before the exponential attenuation of the hydrodynamic flow, which determines the subsequent decrease in I(t) with characteristic time T, shows up appreciably. However, if $T \ll \tau_D$ (but $T \gg \tau_\nu$), at small times $t \leq T$ the increase in I(t) is due to an increase in the contact area of the electrode with the concentrated electrolyte introduced into the channel of the hydrodynamic current, at times comparable to τ_D depletion of the electrolyte introduced into the channel begins to show up because of diffusion to the electrode, and the current decreases with characteristic time τ_D.

When $T_D \gg \tau_D$, series (3) takes on the form

$$I = (8v_0^H c_0 b/r_0^3)\sum_{n=0}^{\infty} k_n^{-4}[\exp(-t/T) - \exp(-Dk_n^2 t)].$$

Using the asymptotic formula for response to the rapid increase in the hydrodynamic velocity [6], we have

$$I = I_c^P[\exp(-t/T) - 0{,}99\exp(-t/\tau_D)], \quad (4)$$

where $I_c^P = (4/3)br_0c_0v_0^H$ is the steady current of complete absorption corresponding to v_0^H. On the basis of the estimate in [6] one can assume that expression (4) describes the diffusion current in the case where $T \gg \tau_D$ with an error of less than 1% when $t > 0.01\ r_0^2/D$.

The diffusion current can be approximately described by the first term I_0 of series (3) at any ratio between T and τ_D

$$I = 1{,}32 br_0c_0v_0^H (T/\tau_D)(e^{-t/T} - e^{-t/\tau_D})/(T/\tau_D - 1). \quad (5)$$

The maximum current is attained when $t = t^* = T\ln\gamma/(\gamma - 1)$ (where $\gamma = T/\tau_D$ and is equal to

$$I_{max} = 1{,}32 br_0c_0v_0^H \gamma^{-1/(\gamma-1)}. \quad (5')$$

When $\gamma = 1$ the expansion of the indeterminacy in (5) gives

$$I|_{\gamma=1} = 1{,}32 br_0c_0v_0^H (t/T)\exp(-t/T).$$

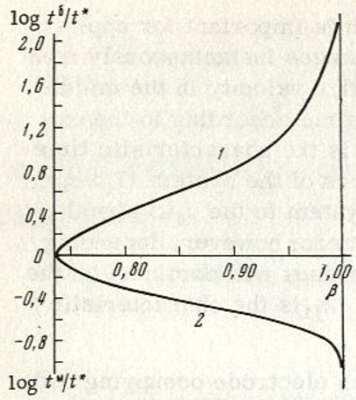

Fig. 3

The maximum of this expression is attained when $t = T$ and, as follows from (5'), is equal to $I_{max}|_{\gamma=1} = 0.49\, br_0 v_0 c_0^H$.

The error in the approximation with the help of the first term I_0 of series (3) increases with increasing t, since the relative contribution of the successive terms of the series increases. When $t \to 0$ the expression for the total contribution $\varphi(t) = \sum_{n=1}^{\infty} I_n$ of all the successive terms of the series to the contribution $I_0(t)$ converges to a maximum value Δ^* which is determined from the equality

$$\Delta^* = \left[\left(\sum_{n=1}^{\infty} dI_n/dt \right) \Big/ \, (dI_0/dt) \right]_{t=0}.$$

The maximum error in Δ^* turns out to be independent of γ and is 23%. However, this error is present only at small t and, as a whole, the change in the current with time is described considerably more accurately with the aid of (5). Formula (5) introduces the error $\Delta < \Delta^*$ at times which are greater than a certain value dependent on Δ and γ: $t > t_0(\Delta, \gamma)$. Figure 1 shows two curves of t_0 values reduced to r_0^2/D as a function of $\log \gamma$. Curve 1 corresponds to the error $\Delta = 2\%$, while curve 2 corresponds to the error $\Delta = 5\%$. These curves are the solutions of the equation $I_0\Delta = I_1$ with corresponding Δ. (One can disregard the contribution of I_n when $n \geq 2$ in the γ interval given in Fig. 1.)

2. In the case of a cylindrical channel of radius r_0 with the help of (1c) and (2) we obtained

$$I = 16\pi v_0^H c_0 D \sum_{n=1}^{\infty} \mu_n^{-2} [D\mu_n^2/r_0^2 - 1/T]^{-1} [\exp(-t/T) - \exp(-D\mu_n^2 t/r_0^2)]. \tag{6}$$

for the limiting diffusion current of the electrode. For null μ_n Bessel functions J_0, when $n \geq 2$, one can use the asymptotic $\mu_n \simeq \pi(4n-1)/4$ from which it is apparent that series (6) converges rapidly, and the first term I_1 of series (6) which corresponds to $n = 1$ introduces a fundamental contribution to I. The characteristic time of the diffusion process is $\tau_D^c = r_0^2/D\mu_1^2 = r_0^2/5.8\,D$.

When $T \gg \tau_D^c$, using the results of [6], we obtain

$$I = I_c^c [\exp(-t/T) - 0{,}96 \exp(-t/\tau_D^c)], \tag{7}$$

where $I_c^c = \pi r_0^2 c_0 v_0^H/2$ is the steady current of complete absorption. According to the estimate in [6], one can assume that formula (7) is accurate with an error less than 1% when $t > 0.05\, r_0^2/D$. The diffusion current at any ratio between T and τ_D^c is approximately described by the first term I_1 of series (6)

$$I = 1{,}50 r_0^2 c_0 v_0^H (T/\tau_D^c)(e^{-t/T} - e^{-t/\tau_D^c})/(T/\tau_D^c - 1). \tag{8}$$

When $t = t^* = T \ln \alpha/(\alpha - 1)$ (where $\alpha = T/\tau_D^c$) the diffusion current reaches the maximum value

$$I_{max} = 1{,}50\, r_0^2 c_0 v_0^H \alpha^{-1/(\alpha-1)}. \tag{8'}$$

When $\alpha = 1$, expanding the indeterminacy in (8) we have

$$I|_{\alpha=1} = 1{,}50\, r_0^2 c_0 v_0^H (t/T) \exp(-t/T).$$

When $t = T$ the current $I|_{\alpha=1}$ reaches a maximum which, according to (8'), is equal to $I_{max}|_{\alpha=1} = 0.55\, r_0^2 c_0 v_0^H$.

The error in approximation (8) increases with decreasing t. When $t \to 0$ it converges to a maximum value Δ^*, which is found from the equality

$$\Delta^* = \left[\left(\sum_{n=2}^{\infty} dI_n/dt \right) \Big/ \, (dI_1/dt) \right]_{t=0},$$

where I_n is the term of series (6) corresponding to n. The error in Δ^* is independent of α and is 44%. If in addition to I_1, one also takes the second term of the series I_2 into account

$$I_2 = 1.65 v_0{}^n c_0 DT[\exp(-t/T) - \exp(-30.5Dt/r_0{}^2)]/(30.3DT/r_0{}^2 - 1),$$

the error in Δ^* decreases to 20%. Formula (8) introduces an error $\Delta < \Delta^*$ when $t > t_0(\Delta, \alpha)$. Figure 2 shows two curves of t_0 values reduced to $r_0{}^2/D$ as a function of log α. Curve 1 corresponds to the error Δ = 5%, while Curve 2 corresponds to the error Δ = 10%. These curves are the solution of the equation $I_1\Delta = I_2$ with corresponding Δ.

3. Having experimentally measured the dependence of the electrode current on the time I(t) during gradual external perturbation for a slotted system with an exponentially attenuating hydrodynamic flow and having used the previously obtained formula for the diffusion current, one can determine the values of both characteristic times (T and τ_D) of the slotted system.

Let us introduce into our examination the parameter β which is readily found from the experimental I(t) curve

$$\psi = \int_0^\infty I(t)\,dt; \quad \psi^* = \int_{t^*}^\infty I(t)\,dt;$$

where $\psi = \int_0^\infty I(t)\,dt$; $\psi^* = \int_{t^*}^\infty I(t)\,dt$; and t^* is the time corresponding to the maximum of the I(t) curve. Since expressions (5) and (8) have the same functional form, calculation of β both with the aid of (5) and with (8) leads to the same result, viz.,

$$\beta = (T - \tau_D)^{-1}(Te^{-t^*/T} - \tau_D e^{-t^*/\tau_D}). \tag{9}$$

An expression equally suitable for planar and cylindrical channels which reduces to the form

$$t^* = T\tau_D(T - \tau_D)^{-1}\ln(T/\tau_D). \tag{10}$$

was attained above for t^*.

Having solved the system of two transcendental equations (9) and (10) relative to T and τ_D, one can obtain the values of the characteristic times. Let us note, however, that system (9)-(10) is invariant with respect to the substitution $T \to \tau_D$ and $\tau_D \to T$ and it hence follows that it is impossible to show to which process corresponds each of the two times found on the basis of (9)-(10): one can only speak of longer (t^l) and shorter (t^s) characteristic times. The region of physically attainable β values lies between the minimum value β_{min} = 0.736 corresponding to the case $t^l = t^s$ ($T = \tau_D$) and the maximum value β_{max} = 1 corresponding to the case $t^l/t^s \to \infty$. When $\beta_{min} < \beta < \beta_{max}$ there is a solution of system (9)-(10) which is different from the trivial solution $T = \tau_D = t^*$. The values of the common logarithms (t^l/t^*) (curve 1) and log (t^s/t^*) (curve 2) obtained as a result of graphical solution of the system of equations (9)-(10) are presented in Fig. 3.

In order to determine which of the times t^l and t^s corresponds to τ_D and which to T, one can either theoretically estimate one of the times or find the characteristic times of attenutation of the hydrodynamic current from an independent experiment. Practically speaking this is easy to accumplish. Let us note that expressions (5') and (8') for maximum current are not invariant relative to the substitution $T \to \tau_D$ and $\tau_D \to T$, but the abundance of additional parameters complicates the practical use of (5')-(8') for determining T and τ_D.

LITERATURE CITED

1. L. Graetz, Ann. d. Physik, 25, 337 (1885).
2. W. Nusselt, Z. VDI, 54, 1157 (1910).
3. N. B. Mar'yamov, Proceedings of the Central Aero-Hydrodynamic Institute, No. 444 (1939).
4. B. S. Petukhov, Heat Exchange and Resistance during Laminar Flow of a Liquid in Tubes [in Russian], Énergiya, Moscow (1967).
5. G. M. Brown, A. I. Ch. E. Journal, 6, 179 (1960).
6. E. Ya. Klimenkov, B. M. Grafov, V. G. Levich, and I. V. Strizhevskii, Élektrokhimiya, 5, 202 (1969).
7. M. A. Lavrent'ev and B. V. Shabat, Methods in the Theory of Functions of a Complex Variable [in Russian], Nauka, Moscow (1965).