LIMITING CURRENT TO AN ELECTRODE ON THE INNER SURFACE OF A DUCT

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1. The electrical current to an electrode is related in a simple manner (by the Faraday law) to the diffusion current. In studying the electrical current one can limit the analysis to the diffusion process alone. Diffusion in a duct with a thin diffusion layer under conditions of Poiseuille flow was analyzed in [1, 2]. The solution presented in [1, 2], however, permits only an order-of-magnitude estimate of the total absorption length in the duct, L^0. We used the asymptotic solutions found for heat exchange in an aperture [3-5] and a cylinder [2, 3, 6-8] to get a more accurate value of L^0. For the diffusion current densities to plane (aperture) and cylindrical electrodes, respectively, we can write [4, 6]

$$j_p = (Dc_0 / r_0)\,[1.72 \exp(-2.83\, Dz / v_0 r_0^2) + 1.14 \exp(-32.1\, Dz / v_0 r_0^2) + \ldots], \tag{1p}$$

$$j_c = (Dc_0 / r_0)\,[1.50 \exp(-7.31\, Dz / v_0 r_0^2) + 1.09 \exp(-44.6\, Dz / v_0 r_0^2) + \ldots], \tag{1c}$$

where D is the diffusion coefficient; c_0 is the initial concentration of the electrically active substance; brought into the duct by the hydrodynamic flow at a velocity v_0; in the middle of the duct, r_0 is the half-width of the duct in the case of the plane and the canal radius in the case of the cylinder; the z axis is along the direction of the flow; the origin of coordinates is at the center of the duct in a plane passing through the beginning of the electrode; and the subscripts "p" and "c" indicate the electrode shape.

The first term in each of the sums (1p) and (1c) begins to dominate at a distance which can be evaluated from the relative magnitude of the first and second terms in each formula. The second term reaches 1% of the first term at $z_p^0 \approx 0.14\, v_0 r_0^2/D$ for the plane and $z_c^0 \approx 0.11\, v_0 r_0^2/D$ for the cylinder. For $z > z^0$, retention of the first term only introduces an error less than 1%. Then the diffusion current to an electrode of length L (with an error less than 1% if $L > z^0$) is equal to

$$I_p = Q_s - \Delta Q = 2\left(b r_0 c_0 \bar{v}_p - b \int_L^\infty j_p\, dz\right) = I_p^0\,[1 - 0.91 \exp(-2.83\, DL/v_0 r_0^2)], \tag{2p}$$

$$I_c = \pi r_0^2 c_0 \bar{v}_c - 2\pi r_0 \int_L^\infty j_c\, dz = I_c^0\,[1 - 0.82 \exp(-7.31\, DL/v_0 r_0^2)], \tag{2c}$$

where Q_s is the amount of electrically active substances brought into the duct by the hydrodynamic flow, ΔQ is the quantity of ions (which haven't yet reacted) brought across the electrode boundaries, b is the transverse dimension of the electrode plate (the factor of 2 in Eq. (2p) takes the two plates into account), $\bar{v}_p = 2v_0/3$; $\bar{v}_c = v_0/2$; $I_p^0 = 4\, r_0 c_0 v_0 b/3$ and $I_c^0 = 0.5\, \pi r_0^2 c_0 v_0$ are the diffusion currents for complete absorption.

Using (2p) and (2c) we can bring leakage factors into the discussion:

$$k_p = \Delta Q / Q_s = 0.91 \exp(-2.83 DL / v_0 r_0^2), \tag{3p}$$

$$k_c = \Delta Q / Q_s = 0.82 \exp(-7.31 DL / v_0 r_0^2). \tag{3c}$$

Using the z_p^0 and z_c^0 found earlier in (3p) and (3c), we find that the error in the calculated diffusion current does not exceed 1% if the condition $(\Delta Q/Q_s)_p < 0.62$ is satisfied for the plane and $(\Delta Q/Q_s)_c < 0.35$ for the cylinder. Using (3p) and (3c) we find the total absorption length L^0. Assuming, for example, that $k = 0.01$, we get

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$$L_p^0 = -\frac{v_0 r_0^2}{2.83D} \ln(k_p/0.91) = 1.61 v_0 r_0^2/D,$$

$$L_c^0 = -\frac{v_0 r_0^2}{7.31D} \ln(k_c/0.82) = 0.60 v_0 r_0^2/D.$$

An approximate expression for the diffusion current to an electrode with an aperture was found in [9, 10], under the assumption of a plane (rather than Poiseuille) velocity profile. It follows from [9, 10] that the leakage factor is

$$k^* = 0.81 \exp(-3.70DL / v_0 r_0^2),$$

significantly different from (3p). The ratio k_p/k^*, is shown as a function of $DL/v_0 r_0^2$ in Fig. 1.

2. Transient diffusion for a plane electrode was considered in [11], a study of heat exchange at an aperture (see also [3]). The result in [11] was in the form of double infinite series; to find the terms in the series one must solve the transcendental equation which itself contains an infinite series. The solution was accordingly not completely worked out in [11], and is of no use for applications. The transient process is treated in [9] under the assumption of a plane velocity profile. We present here an analytic solution for transient diffusion in a duct for both plane and cylindrical electrodes; this solution is suitable for applications.

One can get an order-of-magnitude transient diffusion time from $\tau_D \approx r_0^2/D$. We assume that the length of the electrode, L, is greater than the total absorption length, so that we can treat the electrode as being of infinite length (the leakage factor being much smaller than one). We can find the transient diffusion current for a gradual change in the external perturbation which causes the hydrodynamic flow. Since the transient time of the hydrodynamic process, $\tau_\nu \approx r_0^2/\nu$ is small compared with τ_D we assume that a Poiseuille velocity profile is established immediately for the hydrodynamic flow. We also assume that the concentration distribution does not change noticeable during the time τ_ν.

Let us consider the case of a plane duct. Since diffusion along the direction of the flow has no noticeable effect on the transport of the electrically active substance at high Peclet numbers (i.e., since the background current is assumed much smaller than the leakage current, which is set up during the relaxation period), we get the following boundary value problem for the limiting current regime:

$$\partial c / \partial t + v_0(1 - x^2 / r_0^2) \partial c / \partial z = D \partial^2 c / \partial x^2, \tag{4}$$

$$c \,|_{t=0} = 0; \quad c \,|_{z=0} = c_0; \quad c \,|_{x=\pm r_0} = 0, \tag{4'}$$

where c is the concentration of the electrically active substance, t is the time, and the x axis is directed perpendicular to the walls of the duct. Integrating (4) over z from zero to infinity, using the boundary conditions ($c\,|_{z=0} = c_0$; $c\,|_{z\to\infty} \to 0$) and the notation $Q = \int_0^\infty c\,dz$, we obtain for Q(x, t)

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

$$Q \,|_{t=0} = 0; \qquad Q \,|_{x=\pm r_0} = 0, \tag{5'}$$

where $\rho(x) = v_0 c_0 (1 - x^2/r_0^2)/4\pi D$. The solution to this problem can be written in the form [12]

$$Q(x, t) = \int_0^t dt' \int_{-r_0}^{r_0} \rho(x') G(x, t \,|\, x', t') \, dx'. \tag{6}$$

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

$$G(x, t \,|\, x' t') = (4\pi D/r_0) \sum_{n=0}^{\infty} \cos(k_n x) \cos(k_n x') \exp[-k_n^2 D (t - t')],$$

where $k_n = (n + {}^1/_2)\pi / r_0$, $(n = 0, 1, \ldots)$ are the eigenvalues of problems (5) and (5'). As a result, we find for Q, according to (6),

$$Q = (4 v_0 c_0 r_0^2/\pi^5 D) \sum_{n=0}^{\infty} (-1)^n (n + {}^1/_2)^{-5} \cos(k_n x) [1 - \exp(-k_n^2 D t)],$$

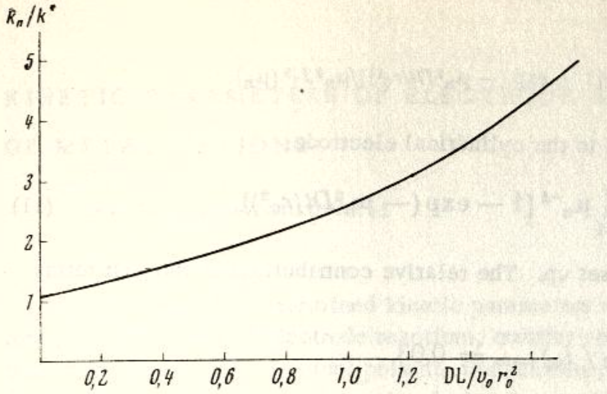

Fig. 1.

Using Q we can easily find the diffusion current to both electrode plates:

$$I = 2b\int_0^\infty j\,dz = -2bD\partial Q/\partial x\,|_{x=r_0},$$

where $j = -D\partial c/\partial x\,|_{x=r_0}$ is the diffusion current density to the electrode.

We finally find

$$I = (8v_0c_0r_0b/\pi^4)\sum_{n=0}^{\infty}(n+{}^1/_2)^{-4}\,[1-\exp(-k_n^2\,Dt)]\,. \quad (7)$$

As $t \to \infty$, a steady-state diffusion current, I_{ss}, is set up, equal to the amount of electrically active substance brought into the duct by the hydrodynamic current: $I_{ss} = 2c_0\bar{v}r_0b = 4c_0v_0r_0b/3$. Estimating the relative contributions of the first terms of the series (7), we find

$$(I_0\,/\,I_{ss})_{t\to\infty} = 0.987; \qquad (I_1\,/\,I_{ss})_{t\to\infty} = 0.012.$$

We can therefore rewrite (7) as

$$I = I_{ss}[1 - 0.987\exp(-2.46Dt\,/\,r_0^2) - 0.012\exp(-22.18Dt\,/\,r_0^2) - \ldots]. \quad (8)$$

The second term in formula (8) dominates over the third and succeeding terms for values of t exceeding some value t^0 which can be found from the relative contribution of the second and third terms. The third term is 1% of the second at $t^0 \approx 0.01r_0^2/D$. For $t > t^0$, the transient diffusion current to the plane electrode is given, with an error less than 1%, by

$$I = I_{ss}[1 - 0.99\exp(-2.46Dt\,/\,r_0^2)]. \quad (8')$$

An expression for the transient diffusion current to a plane electrode was found in [9] under the assumption of a plane velocity profile. It reduces to

$$I^* = I_{ss}[1 - 0.81\exp(-2.46Dt\,/\,r_0^2) - \ldots].$$

It is seen that the exponent is the same as in (8), but the preexponential factor is different.

A solution for the cylindrical duct can be found in the same manner. Using a cylindrical coordinate system with the z axis and origin located as before, we find the following boundary value problem for the limiting current regime:

$$\partial c\,/\,\partial t + v_0(1 - r^2\,/\,r_0^2)\,\partial c\,/\,\partial z = D[(\partial c\,/\,\partial r)\,/\,r + \partial^2 c\,/\,\partial r^2], \quad (9)$$

$$c\,|_{\,t=0} = 0;\; c\,|_{\,z=0} = c_0;\; c\,|_{\,r=r_0} = 0 \quad (9')$$

Using $Q\,(r,\,t) = \int_0^\infty c\,dz$, we find the boundary value problem

$$\partial^2 Q\,/\,\partial r^2 + (\partial Q\,/\,\partial r)\,/\,r - (\partial Q\,/\,\partial t)\,/\,D = -4\pi\rho(r), \quad (10)$$

$$Q\,|_{\,r=r_0} = 0;\; Q\,|_{\,t=0} = 0. \quad (10')$$

where $\rho(r) = v_0c_0(1 - r^2/r_0^2)/4\pi D$.

We can write the solution of (10) and (10') in the form [12]

$$Q\,(r,\,t) = \int_0^t dt'\int_0^{r_0}\rho\,(r')\,G\,(r,\,t\,|\,r',\,t')\,dr',$$

where G(r, t/r', t') is the appropriate Green's function:

$$G\,(r,\,t\,|\,r',\,t') = 8\pi Dr_0^2r'\sum_{n=1}^{\infty}J_0\,(\mu_n r/r_0)\,J_0\,(\mu_n r'/r_0)\exp\,[-\mu_n^2 D\,(t-t')/r_0^2]/J_1^2\,(\mu_n),$$

where J_ν is the Bessel function of order ν, and μ_n are the zeros of $J_0(\mu)$, $(n = 1, 2, \ldots)$. We find for Q(r, t):

$$Q(r, t) = 4\,(v_0 c_0 r_0^2/D) \sum_{n=1}^{\infty} J_2(\mu_n)\, J_0(\mu_n r/r_0)\, [1 - \exp(-\mu_n^2 Dt/r_0^2)]/\mu_n^4 J_1^2(\mu_n).$$

Using Q(r, t), we can find the transient diffusion current to the cylindrical electrode:

$$I = -2\pi r_0 D \partial Q/\partial r\,|_{r=r_0} = 16\pi v_0 c_0 r_0^2 \sum_{n=1}^{\infty} \mu_n^{-4}\, [1 - \exp(-\mu_n^2 Dt/r_0^2)]. \tag{11}$$

As $t \to \infty$, a steady-state current $I_{ss} = \pi r_0^2 c_0 \overline{v} = \pi c_0 \overline{v}_0 r_0^2/2$ is set up. The relative contributions of the first terms in the series (11), corresponding to n = 1 and n = 2, are

$$(I_1 / I_{ss})_{t\to\infty} = 0.96, \qquad (I_2 / I_{ss})_{t\to\infty} = 0.03.$$

Then (11) can be rewritten in the form

$$I = I_{ss}[1 - 0.96\exp(-5.76Dt/r_0^2) - 0.03\exp(-30.5Dt/r_0^2) - \ldots]. \tag{12}$$

We can estimate t^0 in the same way as we did for expression (8). The third term reaches 1% of the second at $t^0 \approx 0.05 r_0^2/D$. For $t > t^0$ the transient current to the cylindrical electrode is given, with an error less than 1%, by the formula

$$I = I_{ss}[1 - 0.96\exp(-5.76Dt/r_0^2)]. \tag{12'}$$

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