

## STEADY STATE DIFFUSION AND TIME-LAG IN MEMBRANES WITH MODEL HETEROGENEITIES

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Received April 30th, 1973

Exact expressions have been derived for the permeation coefficient and time-lag of a heterogeneous membrane consisting of two phases situated parallel to the direction of the net diffusion flow. The result was used to derive approximate expressions for the permeation coefficient and time-lag of a model heterogeneous membrane formed by a square lattice of rectangular parallelepipeds of one phase embedded in the continuum of the other phase. Applications of such model cases to various real heterogeneous systems are discussed.

The diffusion of liquids and gases through heterogeneous systems has a great importance, both theoretical and practical. In principle, three main types of the structural arrangement in a heterogeneous system can be distinguished: (a) dispersion of one phase in a continuum formed by the other phase (filled rubbers, foams, microcrystalline polymers *etc.*); (b) two (or more) mutually penetrating continuous phases (spongy polymers, ceramics, impregnated paper *etc.*); (c) laminated slabs of various types in which the individual layers are perpendicular to the direction of the diffusion flow (multilayer cable insulations, packaging materials). Although a certain success was recorded in solving the problems of steady-state diffusion for all types of heterogeneity mentioned above (see an excellent survey by Barrer<sup>1</sup>), calculation of even the simplest characteristics of the non-steady-state diffusion (such as *e.g.* time-lag or diffusion half-time) is hampered by considerable difficulties of mathematical nature and could be carried out successfully only for the type c heterogeneities, *i.e.* for laminates of various structure (*e.g.*<sup>2-5</sup>).

In this paper the permeation coefficient and time-lag have been derived for two simple geometries of heterogeneous membranes, the first of which is of the type *b* and the second of the type *a* according to the above classification. The permeation coefficient characterizes the steady-state diffusion rate; if we plot the time dependence of the amount of a diffusing compound which has passed through the membrane since the beginning of the experiment in an experimental arrangement when the membrane, initially free of solute, separates two compartments with a constant and mutually different concentration<sup>6</sup>, the intersection of the extrapolated straight part of this dependence with the time axis defines a quantity called time-lag.

### Parallel Two-Layer Membrane

The geometry of this model case of a two-phase heterogeneous membrane is shown schematically in Fig. 1, from which also follows the chosen orientation of the coordinate axes. The two layers are situated in the membrane parallel to the net diffusion flow. Both phases are distinguished by the indices 1 and 2; each of them is characterized by diffusion coefficient  $D$  and partition coefficient  $k$  which are assumed to be independent of the concentration of the diffusing component. The membrane thickness is  $l$  (cm); without loss of generality it can be assumed that the membrane dimension in the direction of the  $z$ -axis perpendicular to the drawing plane is 1 cm, so that the transverse dimensions of both layers  $m_1$  and  $m_2$  define both the surface and volume fractions of both phases according to the equations

$$\varphi_1 = m_1 / (m_1 + m_2), \quad \varphi_2 = m_2 / (m_1 + m_2). \quad (1)$$

It might seem that this model is too simplified and consequently of little practical importance. However, as will be shown below, the results thus derived remain valid even for a much more general arrangement of two phases situated parallel to the direction of the diffusion flow, where one or both may contain multiply connected subregions; thus, we obtain a case of diffusion in a parallel bunch of capillaries situated in a permeable continuum, which is very important from the practical viewpoint. By introducing adequate tortuosity factors, we have a model of a general spongy membrane.

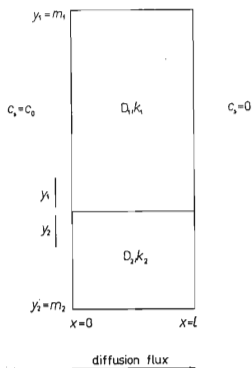


FIG. 1

Schematic Representation of a Parallel Two-Phase Membrane

Quantities related to the individual phases differ by indices 1 and 2.

The diffusion problem is described by a system of two partial differential equations

$$D_i \left[ \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y_i^2} \right] - \frac{\partial c_i}{\partial t} = 0, \quad i = 1, 2 \quad (2)$$

(in which  $c_1$  and  $c_2$  are concentrations of the diffusing compound in phase 1 or 2 respectively), which for the case of the experimental arrangement in the time-lag method (when the concentrations  $c_s$  of the diffusing compound on both sides of the membrane are constant,  $c_s = c_0$  or  $c_s = 0$ ) must be solved together with the initial and boundary conditions

$$t = 0, \quad 0 \leq x \leq l, \quad i = 1, 2, \\ c_i = 0, \quad 0 \leq y_i \leq m_i, \quad (3)$$

$$t > 0, \quad i = 1, 2 : \\ (\partial c_i / \partial y_i) = 0, \quad 0 \leq x \leq l, \quad y_i = m_i, \quad (4)$$

$$c_i = k_i c_0, \quad x = 0, \quad 0 \leq y_i \leq m_i, \quad (5)$$

$$c_i = 0, \quad x = l, \quad 0 \leq y_i \leq m_i, \quad (6)$$

$$D_1(\partial c_1 / \partial y_1) = -D_2(\partial c_2 / \partial y_2), \quad 0 \leq x \leq l, \quad y_1 = y_2 = 0. \quad (7)$$

Conditions (4) reflect the zero diffusion flux through the boundaries of the system; relationship (7) expresses the material balance on the boundary of the two phases — the sign minus is due to the chosen orientation of the coordinate axes  $y_1$  and  $y_2$ .

The problem can be reduced to a unidimensional case by introducing mean concentrations  $C_1$  and  $C_2$ , defined as follows:

$$C_i = (1/m_i) \int_0^{m_i} c_i(x, y_i, t) dy_i, \quad i = 1, 2. \quad (8)$$

Integrating Eqs (2) within the respective limits  $y_i = 0$  and  $y_i = m_i$  and dividing by  $m_i$  we get

$$(D_i/m_i) \int_0^{m_i} (\partial^2 c_i / \partial x^2) dy_i + (D_i/m_i) \int_0^{m_i} (\partial^2 c_i / \partial y_i^2) dy_i - \\ - (1/m_i) \int_0^{m_i} (\partial c_i / \partial t) dy_i = 0;$$

reversing the order of operations and evaluating the integral in the second term we have (with respect to condition (4)) the differential equations

$$D_i(\partial^2 C_i / \partial x^2) - (1/m_i) f_i(x, t) - (\partial C_i / \partial t) = 0, \quad (9)$$

where the functions  $f_i$  are defined by the expression

$$f_i(x, t) = D_i(\partial c_i / \partial y_i)_{y_i=0}. \quad (10)$$

According to (7) it holds

$$f_1(x, t) + f_2(x, t) = 0. \quad (11)$$

Let us now introduce the Laplace-Carson transforms of the functions  $C_1$  and  $C_2$

$$\mathcal{L}[C_i(x, t)] \equiv s_i(x, p) = p \int_0^\infty e^{-pt} C_i(x, t) dt, \quad i = 1, 2 \quad (12)$$

and define two new functions

$$g_i(x, p) = \mathcal{L}[f_i(x, t)], \quad i = 1, 2 \quad (13)$$

for which it again holds according to (7)

$$g_1 + g_2 = 0. \quad (14)$$

This gives us the subsidiary non-homogeneous differential equations

$$(d^2 s_i / dx^2) - (p/D_i) s_i = (1/m_i D_i) g_i(x, p), \quad i = 1, 2. \quad (15)$$

For instance, for  $i = 1$  the corresponding homogeneous differential equation has a general solution

$$s_{1,\text{hom}} = A_1 \sinh [x \sqrt{(p/D_1)}] + B_1 \cosh [x \sqrt{(p/D_1)}],$$

where  $A_1$  and  $B_1$  are integration constants; the method of variation of parameters<sup>7</sup> provides us with general solutions of Eqs (15)

$$s_i = A_i \sinh [x \sqrt{(p/D_i)}] + B_i \cosh [x \sqrt{(p/D_i)}] + [1/m_i \sqrt{(pD_i)}] \{ \sinh [x \sqrt{(p/D_i)}] I_{e,i}(x, p) - \cosh [x \sqrt{(p/D_i)}] I_{s,i}(x, p) \}, \quad i = 1, 2, \quad (16)$$

where

$$I_{c,i}(x, p) = \int g_i(x, p) \cosh [x \sqrt{(p/D_i)}] dx, \quad (17)$$

$$(i = 1, 2)$$

$$I_{s,i}(x, p) = \int g_i(x, p) \sinh [x \sqrt{p/(D_i)}] dx. \quad (18)$$

The four integration constants  $A_i$  and  $B_i$  ( $i = 1, 2$ ) can be found (by using conditions (5) and (6)) in the form

$$A_i = \operatorname{cotgh} [l \sqrt{(p/D_i)}] \left[ [1/m_i \sqrt{(pD_i)}] \int_0^l \sinh [x \sqrt{(p/D_i)}] g_i(x, p) dx - k_i c_0 \right] - I_{c,i}(l)/m_i \sqrt{(pD_i)}, \quad (19)$$

$$B_i = k_i c_0 + I_{s,i}(0)/m_i \sqrt{(pD_i)} \quad \text{for } i = 1, 2. \quad (20)$$

Relationships (16)–(20) represent the general solution of the subsidiary differential equations (15). To calculate the permeation coefficient and time-lag of the composite membrane, it is not necessary to perform the inverse Laplace–Carson transformation; it suffices to bear in mind that the amount  $Q(t)$  of the diffusing compound, which has passed through the membrane face at  $x = l$  since the beginning of the experiment, is given by

$$Q(t) = -D_1 \int_0^t d\tau \int_0^{m_1} \left( \frac{\partial c_1}{\partial x} \right)_{x=1} dy_1 - D_2 \int_0^t d\tau \int_0^{m_2} \left( \frac{\partial c_2}{\partial x} \right)_{x=1} dy_2$$

$$= -m_1 D_1 \int_0^t \left( \frac{dc_1}{dx} \right)_{x=1} d\tau - m_2 D_2 \int_0^t \left( \frac{dc_2}{dx} \right)_{x=1} d\tau \quad (21)$$

(cf. Eq. (8)).

If we designate by  $N(p)$  the Laplace–Carson transform of the function  $Q(t)$ , then

$$\mathcal{L}\{Q(t)\} = N(p) = (1/p) \left[ -m_1 D_1 \left( \frac{ds_1}{dx} \right)_{x=1} - m_2 D_2 \left( \frac{ds_2}{dx} \right)_{x=1} \right]. \quad (22)$$

If the operations indicated by (22) are carried out in Eqs (16) we obtain after re-arrangement

$$N(p) = \frac{1}{p} \frac{F(p)}{G(p)}, \quad (23)$$

$$F(p) = c_0 \sqrt{p} \left[ k_1 m_1 \sqrt{D_1} \sinh \left( l \sqrt{\frac{p}{D_2}} \right) + k_2 m_2 \sqrt{D_2} \sinh \left( l \sqrt{\frac{p}{D_1}} \right) \right] - \\ - \left[ \sinh \left( l \sqrt{\frac{p}{D_2}} \right) \int_0^l g(x, p) \sinh \left( x \sqrt{\frac{p}{D_1}} \right) dx - \right. \\ \left. - \sinh \left( l \sqrt{\frac{p}{D_1}} \right) \int_0^l g(x, p) \sinh \left( x \sqrt{\frac{p}{D_2}} \right) dx \right]. \quad (24)$$

$$G(p) = \sinh \left( l \sqrt{\frac{p}{D_1}} \right) \sinh \left( l \sqrt{\frac{p}{D_2}} \right), \quad (25)$$

where we write (cf. Eq. (14))

$$g(x, p) = g_1(x, p) = -g_2(x, p). \quad (26)$$

It can be shown<sup>8</sup> that, if the Laplace-Carson transform of some time function  $Q(t)$  has the form given by (23), the original function in the limit for long times is a straight line described by

$$Q(t) = \alpha(t - L), \quad (\text{for long } t), \quad (27)$$

where

$$\alpha = \lim_{p \rightarrow 0} (F/G) \quad (28)$$

and the time-lag  $L$  (intersection of the straight line with the time axis) is defined as

$$L = \lim_{p \rightarrow 0} \frac{F(dG/dp) - G(dF/dp)}{F \cdot G}. \quad (29)$$

By evaluating the corresponding derivatives and limits in Eqs (28) and (29) it can be derived by a straightforward, although rather time-consuming procedure that

$$\alpha = (c_0/l) (k_1 m_1 D_1 + k_2 m_2 D_2), \quad (30)$$

$$L = \frac{l^2}{6} \frac{k_1 m_1 + k_2 m_2 + R}{k_1 m_1 D_1 + k_2 m_2 D_2}, \quad (31)$$

where the quantity  $R$  is defined by

$$R = (1/c_0) \left( \frac{1}{D_1} - \frac{1}{D_2} \right) \left[ (1/l^2) \int_0^1 x^3 g_0(x) dx - \int_0^1 x g_0(x) dx \right], \quad (32)$$

where

$$g_0(x) = \lim_{p \rightarrow 0} g(x, p).$$

As proved in Appendix A,  $R = 0$ , so that the final expression for the time-lag reads

$$L = \frac{l^2}{6} \frac{k_1 m_1 + k_2 m_2}{k_1 m_1 D_1 + k_2 m_2 D_2}. \quad (33)$$

Since according to the First Fick Law the slope of the straight line (27) is given by

$$\alpha = \bar{P} c_0 F / l$$

and since the area  $F$  of the composite membrane equals in our notation the sum  $(m_1 + m_2)$ , we obtain from Eq. (30) for the net permeation coefficient of the parallel two-phase membrane the relationship

$$\bar{P} = (k_1 m_1 D_1 + k_2 m_2 D_2) / (m_1 + m_2). \quad (34)$$

With respect to the definition of the surface fractions (Eq. (1))  $\varphi_1$  and  $\varphi_2$ , this can be written as

$$\bar{P} = \varphi_1 P_1 + \varphi_2 P_2, \quad (35)$$

where  $P_i = k_i D_i$  are permeation coefficients in the individual phases. This relationship is very illustrative, especially in connection with the result derived in Appendix A, viz., that in the steady state (in the limit for large  $t$ ) there is no interaction of the diffusion fluxes in both parallel layers of the composite membrane, so that the resulting stationary flux is given simply by their sum and  $\bar{P}$  is the weighted average of individual permeation coefficients with the statistical weights represented by surface fractions of the two phases.

If we want to characterize the composite membrane also by its net diffusion coefficient  $\bar{D}$ , we can define the latter, by analogy with the expression for the time-lag of a simple membrane ( $L = l^2/6D$ ), on the basis of Eq. (33) as

$$\bar{D} = (k_1 m_1 D_1 + k_2 m_2 D_2) / (k_1 m_1 + k_2 m_2). \quad (36)$$

It is therefore again a weighted statistical average of individual diffusion coefficients; the statistical weights  $k_i m_i$  can be assigned a simple physical meaning if it is borne in mind that the product  $l m_i k_i$  defines the equilibrium sorption capacity of the  $i$ -th layer.

For a simple membrane it holds  $P = kD$ ; if the ratio  $\bar{P}/\bar{D}$  is calculated from Eqs (34) and (36), we obtain

$$\bar{P}/\bar{D} = (k_1 m_1 + k_2 m_2)/(m_1 + m_2) = \varphi_1 k_1 + \varphi_2 k_2 ; \quad (37)$$

it is easy to see that the right-hand side of expression (37) actually has the meaning of the net partition coefficient  $\bar{k}$  of the two-phase membrane investigated.

A question may arise whether the formal simplicity of Eqs (35) and (36) is not a consequence of the assumed geometrical simplicity of the model (two parallel layers in the form of a parallelepiped). This is not so, however: Appendix B shows that the derived relationships remain valid for any geometry of two parallel phases, as long as the cross-sections of all subregions are independent of the spatial coordinate parallel with the direction of the diffusion flow.

### Lattice of Rectangular Parallelepipeds in a Continuum

The geometrical arrangement of this simple model of dispersion of one phase in the other is shown schematically in Fig. 2 as two perpendicular cross-sections through

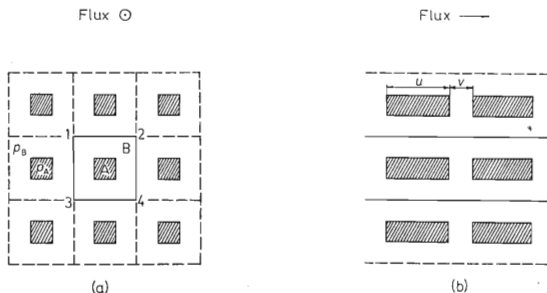


FIG. 2

Geometrical Arrangement of the Lattice of Rectangular Parallelepipeds of Phase A in a Continuum of Phase B

*a* View against the direction of the diffusion flow, *b* side view; cross-sections of both phases in one lattice element are  $\rho_A$  and  $\rho_B$ .



the membrane. We have here a simple square lattice formed by parallelepipeds of the phase A ( $u$  (cm) is the length of the edge parallel with the direction of the net diffusion flow,  $v$  is the distance between two neighbouring prisms in the same direction, and  $p_A$  is the area of the perpendicular cross-section (in  $\text{cm}^2$ ) in the continuum of phase B.

From symmetry considerations the diffusion flux through the boundary between the individual cells of the lattice (broken lines in Fig. 2) is zero, so that it is sufficient to consider diffusion down a single chain whose boundary is indicated by solid lines in Fig. 2. The area occupied in the cross-section of this single chain by phase B is designated by  $p_B$  ( $\text{cm}^2$ ), so that the area of the whole chain 1-2-3-4 is  $p_A + p_B$ .

This model was suggested and its behaviour in the steady state diffusion analyzed by Barrer and Petropoulos<sup>9</sup>. For the mean overall diffusion coefficient  $D$  they derived the expression

$$\bar{D} = \frac{u + v}{p_A + p_B} \left[ \frac{p_A \beta_A \kappa D_A}{u + (\beta_A / \beta_B \gamma) (\kappa D_A / D_B) v} + \frac{p_B \beta'_A D_B}{u + (\beta'_A / \beta'_B \gamma') v} \right], \quad (38)$$

where  $\kappa = k_A / k_B$ ;  $u$ ,  $v$ ,  $p_A$  and  $p_B$  are geometrical parameters of the model defined in Fig. 2, and the  $k$ 's and  $D$ 's are self-explanatory symbols. Relationship (38) has been derived on quite general assumptions and is therefore exact, but contains a number of undetermined parameters — the  $\beta$ 's and  $\gamma$ 's; they depend in an unknown way on geometrical and other characteristics of the model, which greatly reduces its practical importance. Therefore, the permeation coefficient and the net diffusion coefficient derived from the time-lag will be obtained below by employing a different procedure, which at the cost of a certain approximation leads to explicit expressions for the two characteristics as functions of relevant parameters of the model.

The total diffusion flux through the chain can be regarded as a sum of the flux through the internal part having the cross-section  $p_A$ , which consists of alternating layers of phases A and B, and of the flux through the surrounding tube of the phase B having the cross-section  $p_B$ . (The quantities related to the internal chain will be designated by index 1 and those related to the external tube by index 2.) Now we can apply the results derived in the first part of this paper for a parallel arrangement of two layers, if the internal chain is looked upon as a single "phase" characterized by appropriately selected mean quantities  $P_1$ ,  $D_1$  and  $k_1$ .

The permeation coefficient and time-lag for a laminated slab of the type  $(AB)_n$  have been derived by Ash and coworkers<sup>10</sup>. If we assume the height of the parallelepiped  $u$  to be very small compared with the total membrane thickness  $l$ , only results obtained for an infinite number of pairs  $(AB)$  in the laminated membrane ( $n \rightarrow \infty$ ) can be taken from the above paper. Then it holds

$$P_1 = \frac{k_A k_B D_A D_B}{k_B D_B v'_A + k_A D_A v'_B}$$

and from the expression for the time-lag it follows

$$D_1 = \frac{k_A k_B D_A D_B}{k_B D_B v'_A + k_A D_A v'_B} \frac{1}{v'_A k_A + v'_B k_B},$$

where the meaning of the  $k$ 's and  $D$ 's is evident;  $v'_A$  and  $v'_B$  respectively are volume fractions of both phases in the laminated membrane; according to Fig. 2 it holds  $v'_A = u/(u + v)$ ,  $v'_B = v/(u + v)$ .

By substituting these results into Eq. (34) and bearing in mind that  $D_2 \equiv D_B$ ,  $k_2 \equiv k_B$  and  $m_1 \equiv p_A$ ,  $m_2 \equiv p_B$ , we obtain for the net permeation coefficient of the heterogeneous membrane considered

$$\bar{P} = \frac{1}{(p_A + p_B)} \left[ p_B k_B D_B + p_A \frac{k_A k_B D_A D_B}{u k_B D_B + v k_A D_A} (u + v) \right]. \quad (39)$$

Similarly, Eq. (36) gives after rearrangement

$$\bar{D} = \frac{u + v}{p_A + p_B} \frac{1}{\bar{k}} \left[ \frac{p_A k_A k_B D_A D_B}{D_A k_A v + D_B k_B u} + \frac{p_B k_B D_B}{u + v} \right], \quad (40)$$

where

$$\bar{k} = [u(p_A k_A + p_B k_B) + (p_A + p_B) k_B v] / (p_A + p_B)(u + v). \quad (41)$$

Taking into account that the volume fractions of both phases in the heterogeneous membrane,  $v_A$  and  $v_B$ , are defined by

$$v_A = p_A u / (p_A + p_B)(u + v), \quad v_B = 1 - v_A$$

we can see that  $\bar{k}$  has again the meaning of an equilibrium partition coefficient of the diffusing component in the heterogeneous membrane under consideration, so that it follows also in this case from a comparison of relationships (39) and (40) that  $\bar{P}/\bar{D} = \bar{k}$ , by complete analogy with the case of a homogeneous membrane.

Of course, the calculation procedure outlined above, in which the internal region 1 of the membrane element is regarded as an independent "phase", is by no means equivalent to an exact solution of the Second Fick Law. However, such an approximation will be quite adequate to the real conditions if the respective partition and diffusion

coefficients of both phases do not differ too much, and/or if the area  $p_A$  which corresponds to the phase A is sufficiently small.

Within the present approximation, the following explicit expressions for the undetermined coefficients and their combinations occurring in the exact Eq. (38) are obtained by comparing (38) and (40):

$$\beta_A = \beta'_A = k_B/\bar{K}, \quad (\beta_A/\beta_B\gamma) = (\beta'_A/\beta'_B\gamma') = 1.$$

Some particular cases of Eqs (39) and (40) deserve a special comment: If the dispersed phase is impermeable ( $k_A = 0$ ), it holds

$$\bar{P} = k_B D_B p_B / (p_A + p_B) = P_B p_B / (p_A + p_B), \quad (42)$$

so that the net permeation coefficient is reduced by a factor equal to the ratio of the area  $p_B$  to the overall area of the membrane element; the diffusion coefficient (inversely proportional to the time-lag) then is

$$\bar{D} = D_B p_B / (p_A + p_B) [p_A v + p_B (u + v)] \quad (43)$$

and is reduced by an additional factor which reflects the fact that the time-lag is prolonged by a time needed for attaining a steady concentration of the diffusing component in spaces which are "in the shadow" of the impermeable parallelepipeds of the phase A.

For the second extreme case when the dispersed phase is much more permeable than the continuum ( $k_A D_A \gg k_B D_B$ ) it holds

$$P/P_B = [p_A (u + v) / v + p_B] / (p_A + p_B) > 1. \quad (44)$$

The main feature of the model under investigation, which enabled the above simple mathematical analysis to be carried out, but considerably restricted its general character, is the eclipsed arrangement of parallelepipeds into a simple square lattice. However, the model itself is very flexible: according to their dimensions, the parallelepipeds may approach plates, rods, or fibres, arranged in a parallel or transverse manner to the direction of the diffusion flow; in the limit for  $v \rightarrow 0$  we obtain the result for a parallel arrangement of two phases, while the limit for  $p_B \rightarrow 0$  gives the model of a laminated membrane of the ABAB... type, as can be easily proved. If we substitute  $p_A + p_B = A^2$ ,  $p_A = a \cdot b$ , then in the limit for  $a \rightarrow A$  (for simplicity's sake we can also choose  $u = b$ ) we obtain a model of heterogeneities formed by parallel "fibres" of the phase A situated perpendicularly to the net direction of the diffusion flow. All these special cases can be useful as approximations of various real systems.

## APPENDIX A

We have to prove that the quantity  $R$  defined by Eq. (32) equals zero. This will certainly be fulfilled if

$$g_0(x) = \lim_{p \rightarrow 0} g(x, p) \equiv 0. \quad (A-1)$$

According to Eqs (26), (13), (14) and (10) it holds

$$g(x, p) = \mathcal{L}\{D_1(\partial c_1/\partial y_1)_{y_1=0}\}; \quad (A-2)$$

the second Abel's theorem<sup>11</sup> ensures the fulfilment of requirement (A-1) if the relationship

$$D_1 \lim_{t \rightarrow \infty} (\partial c_1/\partial y_1)_{y_1=0} = 0, \quad (A-3)$$

is valid, *i.e.* if the diffusion flux through the boundary of both phases in the steady state is zero for each  $x$ . The validity of (A-3) will be demonstrated as follows: in the steady state, differential equations (2) with  $(\partial c_i/\partial t) = 0$  have to be solved along with the boundary conditions (4) to (7); in the steady state the boundary condition

$$k_1 c_1 = k_2 c_2, \quad 0 \leq x \leq l, \quad y_1 = y_2 = 0 \quad (A-4)$$

must be added. Let us apply to the variable  $x$  the operator of finite integral sine transform<sup>8</sup>:

$$v_i(n, y_i) = \mathcal{F}_s\{c_i(x, y_i)\} = \int_0^l c_i(x, y_i) \sin \frac{n\pi x}{l} dx, \quad (A-5)$$

$$i = 1, 2; \quad n = 1, 2, 3, \dots$$

In accordance with the basic property of this transform it holds

$$\begin{aligned} \mathcal{F}_s\{\partial^2 c_i/\partial x^2\} &= (n\pi/l) [c_i(0, y_i) - (-1)^n c_i(l, y_i)] - (n^2 \pi^2/l^2) v_i(n, y_i) = \\ &= (n\pi/l) k_i c_0 - (n^2 \pi^2/l^2) v_i(n, y_i), \end{aligned} \quad (A-6)$$

with respect to conditions (5) and (6).

By applying the operator (A-5) to Eq. (2) we obtain for the sine transforms  $v_1$  and  $v_2$  (with respect to (A-6)) the subsidiary differential equations

$$(d^2 v_i/dy_i^2) - (n^2 \pi^2/l^2) v_i = -(n\pi/l) k_i c_0, \quad i = 1, 2 \quad (A-7)$$

with a general solution

$$v_i(n, y_i) = G_i \sinh(n\pi y_i/l) + H_i \cosh(n\pi y_i/l) + lk_i c_0/n\pi, \quad i = 1, 2. \quad (A-8)$$

It follows from conditions (4) that

$$G_i \cosh(n\pi m_i/l) + H_i \sinh(n\pi m_i/l) = 0, \quad i = 1, 2 \quad (A-9)$$

and Eqs (7) and (A-4) yield the following relationships between the respective constants  $G_i$  and  $H_i$ :

$$G_1 = -G_2 D_2 / D_1, \quad k_1 H_1 = k_2 H_2. \quad (A-10)$$

By combining (A-9) and (A-10) we obtain

$$\begin{aligned} -(G_2 D_2 / D_1) \cosh(n\pi m_1 / l) + \kappa H_2 \sinh(n\pi m_1 / l) &= 0, \\ G_2 \cosh(n\pi m_2 / l) + H_2 \sinh(n\pi m_2 / l) &= 0 \end{aligned} \quad (A-11)$$

which for arbitrary  $l$ ,  $m_1$ ,  $m_2$ ,  $\kappa$  and for all integer  $n$  can be fulfilled only if it holds  $G_2 = H_2 = 0$ , and thus also (according to (A-10))  $G_1 = H_1 = 0$ . Consequently, the solution of Eq. (A-7) for the transforms  $v_1$  and  $v_2$  is given by the relations

$$v_i = lk_i c_0 / n\pi, \quad i = 1, 2 \quad (A-12)$$

which are completely independent of  $y_i$ . It can therefore be written for both concentrations in the steady state

$$c_1^+(x, y_1) = c_1^+(x), \quad c_2^+(x, y_2) = c_2^+(x), \quad (A-13)$$

where  $c_i^+ = \lim_{t \rightarrow \infty} c_i$ . In this way, not only the validity of the required Eq. (A-3) has been proved, but it has also been demonstrated that the concentrations  $c_i^+$  follow the equations

$$c_i^+ = k_i c_0 (1 - x/l), \quad i = 1, 2 \quad (A-14)$$

which ensue from the substitution of (A-13) into the differential equations (2) followed by double integration (taking into account conditions (5) and (6)). It is easy to prove by substitution that Eqs (A-14) actually fulfil (2) and the boundary conditions of the problem if  $(\partial c_i / \partial t) = 0$ .

## APPENDIX B

The problem of diffusion through a parallel arrangement of two phases can be considerably generalized. Fig. 3 shows the cross-section of a system in which phase 2 consists of several separated subregions, so that phase 1 is multiply connected. It must only be assumed that the surface forming the boundary of the whole system (in the cross-section in Fig. 3 this surface appears as curve  $\sigma'_1$ , if the boundary is formed by phase 1, or as  $\sigma'_2$ , if it is formed by phase 2), as well as the surfaces separating phases 1 and 2 (curves  $\sigma$  in the cross-section in Fig. 3) are always parallel with the  $x$ -axis (outward normals of all subregions are perpendicular to  $x$ ). Let us designate the direction cosines of outward normals in the phase  $i$  by  $\lambda_i, \mu_i, \nu_i$ , respectively (for the coordinates  $x, y, z$ ). Then the three-dimensional boundary-value problem is formulated as follows:

$$D_i \operatorname{div} \operatorname{grad} c_i - \partial c_i / \partial t = 0, \quad i = 1, 2 \quad (B-1)$$

$$i = 1, 2:$$

$$t = 0, \quad c_i = 0; \quad (B-2)$$

$$t > 0, \quad c_i = k_i c_0, \quad x = 0, \quad (B-3)$$

$$c_i = 0, \quad x = l \quad (B-4)$$

$$\int_{(\sigma_1')} [(\mu_i(\partial c_i/\partial y) + v_i(\partial c_i/\partial z))] d\sigma'_i = 0, \quad (B-5)$$

$$D_1 \int_{(\sigma)} [\mu_1(\partial c_1/\partial y) + v_1(\partial c_1/\partial z)] d\sigma = -D_2 \int_{(\sigma)} [\mu_2(\partial c_2/\partial y) + v_2(\partial c_2/\partial z)] d\sigma. \quad (B-6)$$

Eq. (B-5) describes the zero flow condition through the boundary of the system; Eq. (B-6) is the balance of the total mass exchange through the boundary between the two phases; the sign minus is a consequence of the opposite orientation of outward normals in both phases.

Let us introduce again (by analogy with Eqs (8) of the text) mean concentrations  $C_i$  in both phases by means of the relationships

$$C_i = (1/S_i) \iint_{(S_i)} c_i(x, y, z) dy dz, \quad (B-7)$$

where  $S_i$  is the total cross-sectional area of  $i$ -th phase, assumed to be independent of  $x$ . (For  $i = 2$  the integral in the right-hand side of (B-7) must be regarded as a sum of partial integrals over the individual connected subregions of phase 2). In the Cartesian coordinates it then follows from (B-1), by applying the operator according to (B-7) (it always holds  $i = 1, 2$ ):

$$D_i \partial/\partial x^2 \left[ (1/S_i) \iint_{(S_i)} c_i dy dz \right] + (D_i/S_i) \iint_{(S_i)} (\partial^2 c_i/\partial y^2 + \partial^2 c_i/\partial z^2) dy dz - (1/S_i) \iint_{(S_i)} (\partial c_i/\partial t) dy dz = 0,$$

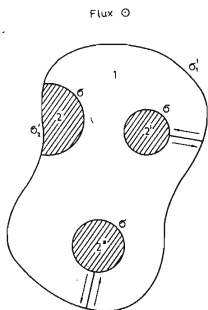


FIG. 3

Cross-Section through the General Parallel Two-Phase Membrane in Which Phase 1 is Multiply Connected

i.e.

$$D_1 \frac{\partial^2 C_i}{\partial x^2} + (1/S_1) f_i(x) - \partial C_i / \partial t = 0, \quad (B-8)$$

where we have defined

$$f_i(x) = D_1 \iint_{(S_1)} (\partial^2 c_i / \partial y^2 + \partial^2 c_i / \partial z^2) dy dz. \quad (B-9)$$

Let us apply to the integral in (B-9) the Gauss-Ostrogradski formula in two dimensions<sup>7</sup>. We have then

$$f_i(x) = D_1 \int_{(\sigma)} [(\partial c_i / \partial y) \mu_i + (\partial c_i / \partial z) \nu_i] d\sigma \quad (B-10)$$

and the condition (B-6) guarantees the validity of Eq. (11)

$$f_1(x) + f_2(x) = 0. \quad (11)$$

The problem has thus been reduced to the case solved in the main text, only the mean concentrations  $C_i$  and auxiliary functions  $f_i(x)$  are now defined by the more general expressions (B-7) and (B-9), respectively; the role of  $m_i$  is now played by the cross-sectional areas of both phases  $S_i$ . A further generalization for the case when both phases contain multiply connected subregions is now quite evident.

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Translated by L. Kopecká.