Transient Diffusion Through a Binary Laminate Separating Finite and Semiinfinite Volumes

INTRODUCTION

Equations for transient diffusion have been developed and tested for a system comprising a homogeneous membrane separating finite and semiinfinite baths.[1,2] Here the analysis is extended to cover a binary laminate slab as membrane under selected initial and boundary conditions; relatively simple expressions again obtain for the limiting condition of long times. A related system with a symmetrical ternary laminate slab as membrane has been analyzed for constant concentration gradient of penetrant in the outer layers.[3] These systems are representative of several of practical value, for example, loss of solute or vapor from binary laminate containers and homogeneous membranes with a boundary layer on one face.

DIFFUSION EQUATIONS

Consider a binary laminate slab AB of unit cross section with laminae A and B of thickness a and b, respectively. Lamina A is in contact with the semifinite bath at $x = -a$ and B with the finite volume V at $x = b$. The initial concentrations are uniform in each phase and are c^c and c^0 in the semiinfinite and finite volumes, respectively, and C_A^i and C_B^i in the respective laminae A and B. It is assumed that equilibrium is maintained at all interfaces and that the partition coefficients $K_A = C_A/c$, $K_B = C_B/c$, and $K = C_A/C_B = K_A/K_B$ are constant. It is also assumed that the diffusion constants D_A and D_B for the respective laminae are constant.

To simplify the presentation, the system is represented by AB), where the parenthesis closure denotes the finite volume V in contact with the lamina B. Permeation is initiated in a system previously at equilibrium by changing the concentration at an interface and is represented by a period; for example, AB.) represents permeation initiated by changing the concentration in volume V and hence at $x = b$ in lamina B. A bar above AB, as in $\overline{\text{AB}}$.), indicates that the concentration at the B interface is decreased to induce permeation. Conversely, $\underline{\text{AB}}$.) indicates that the concentration is increased. A constant gradient of concentration in a particular lamina is represented by a small letter, for example, aB.). The initial conditions examined here are represented by .AB.), .AB), AB.), A.B.), A.B), .aB.), aB.), and .aB).

The System .AB.)

The differential equations with the initial and boundary conditions are[4,5]

$$\frac{\partial^2 C_A}{\partial x^2} = \frac{1}{D_a}\frac{\partial C_A}{\partial t}; \qquad \frac{\partial^2 C_B}{\partial x^2} = \frac{1}{D_B}\frac{\partial C_B}{\partial t} \tag{1}$$

$$C_A(-a,t) = C_A^c, C_A(x,0) = C_A^i; \qquad C_B(b,0) = C_B^0, C_B(x,0) = C_B^i \tag{2}$$

$$\left(\frac{\partial C_B}{\partial x}\right)_{x=b} = \frac{-b}{D_B H_B}\left(\frac{\partial C_B}{\partial t}\right) \tag{3}$$

$$D_A\left(\frac{\partial C_A}{\partial x}\right)_{x=0} = D_B\left(\frac{\partial C_B}{\partial x}\right)_{x=0} \tag{4}$$

$$\frac{C_A(0,t)}{C_B(0,t)} = \frac{K_A}{K_B} = K \tag{5}$$

H_B is the ratio of the amount of diffusant in lamina B to that in volume V at equilibrium and is given by $H_B = K_B V_B/V$, where V_B is the volume of lamina B.

The concentrations in each lamina can be expressed as follows using the method of Laplace transformations[4]:

$$C_A(x,t) = C_A^c + \sum_{n=1}^{\infty} A_n(x)\exp(-D_B R_n^2 t/b^2) \tag{6}$$

where

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$$A_n(x) = 2\theta_n[(C_A^0 - C_A^i)R_n \cos(R_n\lambda/\delta) + (C_A^i - C_A^c)\Phi_n] \times [\cos(R_n\lambda/\delta)\sin(R_n\lambda x/\delta a) + \sin(R_n\lambda/\delta)\cos(R_n\lambda x/\delta a)]/L_n \quad (7)$$

and

$$C_B(x,t) = C_B^c + \sum_{n=1}^{\infty} B_n(x)\exp(-D_B R_n^2 t/b^2) \quad (8)$$

where

$$B_n(x) = 2\sin(R_n\lambda/\delta)[(C_B^0 - C_B^i)R_n\cos(R_n\lambda/\delta) + (C_B^i - C_B^c)\Phi_n] \times [\Phi_n \sin(R_n x/b) + \theta_n\cos(R_n x/b)]/L_n \quad (9)$$

and where

$$L_n = R_n\,[(H_B + H_B^2 + R_n^2)\sin(R_n\lambda/\delta)\cos(R_n\lambda/\delta) + (\lambda/\delta)\Phi_n\theta_n] \quad (10)$$

$$\Phi_n = H_B \sin R_n + R_n \cos R_n \quad (11)$$

$$\theta_n = H_B \cos R_n - R_n \sin R_n \quad (12)$$

and $\delta^2 = D_A/D_B$, $\lambda = a/b$, and R_n are the nonzero, positive roots of

$$\theta\delta K = \Phi\tan(R\lambda/\delta) \quad (13)$$

Normally the concentration or pressure of diffusant $c(t)$ in the volume V is measured. Using eq. (8) and $C_B(b,t) = K_B c(t)$, one obtains

$$c(t) = c^c + \sum_{n=1}^{\infty} B_n \exp(-D_B R_n^2 t/b^2) \quad (14)$$

with

$$B_n = 2H_B\sin(R_n\lambda/\delta)[(c^0 - c^i)R_n\cos(R_n\lambda/\delta) + (c^i - c^c)\Phi_n]/L_n \quad (15)$$

To illustrate the application of eq. (14), four experimentally accessible cases are considered and designated I, II, III, and IV, corresponding to the following initial conditions:

$$\begin{array}{ll} \text{(I) } \underline{\text{AB}}.);\ c^c = c^i = 0, & c^0 \neq 0 \\ \text{(II) } .\overline{\text{AB}});\ c^c = 0, & c^i = c^0 \neq 0 \\ \text{(III) } \overline{\text{AB}}.);\ c^c = c^i \neq 0, & c^0 = 0 \\ \text{(IV) } .\underline{\text{AB}});\ c^c \neq 0, & c^i = c^0 = 0 \end{array}$$

Equation (14) may be written as

$$F^i = \sum_{n=1}^{\infty} B_n^i \exp(-R_n^2\tau_B) \quad (16)$$

where $\tau_B = D_B t/b^2$ and F^i with $i = I, \ldots,$ IV are reduced concentrations such that $F^{I} = F^{II} = c(t)/c^0$ and $F^{III} = F^{IV} = 1 - c(t)/c^c$ and

$$B_n^{I} = B_n^{III} = 2H_B R_n \sin(R_n\lambda/\delta)\cos(R_n\lambda/\delta)/L_n \quad (17)$$

$$B_n^{II} = B_n^{IV} = 2H_B\Phi_n\sin(R_n\lambda/\delta)/L_n \quad (18)$$

As for the homogeneous slab .B.),[2] relatively simple expressions obtain for long times corresponding to the first term of the summation in eq. (16), namely,

$$F^i = B_1^i \exp(-R_1^2\tau_B) \quad (19)$$

A plot of ln F^i versus t in the limit of large t will be linear with slope $-D_B R_1^2/b^2$ and intercept ln B_1^i.

The System A.B.)

This corresponds to lamina A initially in equilibrium with the semiinfinite bath but not with lamina B; the differential equations and boundary conditions are identical with eqs. (1) to (5), except that in eq. (2)

$$C_A(-a,t) = C_A^c, \qquad C_A(x,0) = C_A^c \quad (20)$$

The solutions for the concentrations can be expressed as

$$C_A(x,t) = C_A^c + \sum_{n=1}^{\infty} G_n(x)\exp(-D_B R_n^2 t/b^2) \quad (21)$$

and

$$C_B(x,t) = C_B^c + \sum_{n=1}^{\infty} P_n(x) \exp(-D_B R_n^2 t/b^2) \quad (22)$$

where

$$G_n(x) = A_n(x) \cos(R_n \lambda/\delta) \quad \text{and} \quad P_n(x) = B_n(x) \cos(R_n \lambda/\delta) \quad (23)$$

In terms of the reduced variables F^i and τ_B, one obtains as before

$$F^i = \sum_{n=1}^{\infty} P_n^i \exp(-R_n^2 \tau_B) \quad (24)$$

where

$$P_n^i = B_n^i \cos(R_n \lambda/\delta) \quad (25)$$

It is likely that cases $\underline{A}.\overline{B})$ and $\overline{A}.\underline{B}.)$ corresponding to i = II and IV, respectively, are experimentally feasible.

The System .aB.)

Here $\partial C_A/\partial x$ is maintained constant; eq. (4) is now replaced by

$$\left(\frac{\partial C_B}{\partial x}\right)_{x=0} = \frac{\delta^2 K}{a}[C_B(0,t) - C_B^c] \quad (26)$$

Otherwise, eqs. (1) to (5) but for the first part of eq. (1) apply. The solution is

$$C_B(x,t) = C_B^c + \sum_{n=1}^{\infty} E_n(x) \exp(-D_B U_n^2 t/b^2) \quad (27)$$

with

$$E_n(x) = 2[(C_B^0 - C_B^i)R_n + (C_B^i - C_B^c)\Phi_n][\Phi_n \sin(R_n x/b) + \theta_n \cos(R_n x/b)]/M_n \quad (28)$$

where the U_n are the nonzero, positive roots of

$$\theta\delta K = \Phi U \lambda/\delta \quad (29)$$

and

$$M_n = U_n(H_B + H_B^2 + U_n^2) \quad (30)$$

In terms of the reduced variables, one obtains for the concentration in V

$$F^i = \sum_{n=1}^{\infty} E_n^i \exp(-U_n^2 \tau_B) \quad (31)$$

with

$$E_n^{\mathrm{I}} = E_n^{\mathrm{III}} = 2H_B U_n/M_n \quad (32)$$

and

$$E_n^{\mathrm{II}} = E_n^{\mathrm{IV}} = 2H_B \Phi_n/M_n \quad (33)$$

Comparing eqs. (29) and (13), it is clear that the rates of decay of F^i given by eq. (19) and by eq. (31) at long times will not be markedly different.

Comparison with System .B.)

In the limit $\lambda \to 0$, eqs. (16), (24), and (31) reduce to the corresponding equation for the homogeneous system .B.);

$$F^i = \sum_{n=1}^{\infty} A_n^i \exp(-D_B Q_n^2 t/l^2) \quad (34)$$

[eq. (13), ref. 2], where the F^i are the reduced concentrations; Q_n are the nonzero, positive roots of

$H_B = Q \tan Q$ [eq. (5), ref. 2]; and l is the thickness. Equation (16) also reduces to eq. (34) when $\delta = K = 1$, representing a homogeneous membrane with $l = (1 + \lambda)b$ where $Q_n = (1 + \lambda)R_n$.

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