# Transient Diffusion through Multilaminate Slabs Separating Finite and Semiinfinite Baths

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## Synopsis

Equations describing transient diffusion through multilaminate slabs with constant diffusion and partition coefficients for each lamina separating well-stirred finite and semiinfinite baths are presented. Application is illustrated using a representative slab with three laminae.

## INTRODUCTION

Equations have been reported describing transient diffusion through homogeneous slabs[1,2] and through binary laminate slabs[3] separating well-stirred finite and semiinfinite baths. This paper extends that work to provide equations describing such systems with the baths separated by slabs containing $N$ laminae, each with constant diffusion and partition coefficients. The equations are formulated in a manner suitable for computer evaluation using determinants and summations and are applicable in the range of modest to large time.[4] The procedure is illustrated by application to a system with $N = 3$.

## DIFFUSION EQUATIONS

Consider a laminate slab of unit cross section and $N$ laminae in contact with a well-stirred semiinfinite bath at $x = x_0$ and with a well-stirred finite bath of volume $V$ at $x = x_N$. The system is presented schematically and indexed in Figure 1. The diffusant concentration in the semiinfinite bath is constant, $c^c$, and its initial value in the finite bath is $c^0$. The concentration in each lamina prior to initiation of the diffusion is uniform, $C_j^i$ in lamina $j$, related to a bath concentration, $c^i$, at equilibrium by the partition coefficient $K_j = C_j^i/c^i$. Equilibrium is maintained at each phase interface described by $K_1 = C_1^c/c^c$ at $x = x_0$, $K_{j-1,j} = C_{j-1}/C_j$ at $x = x_{j-1}$ for $j = 2, \ldots, N$, and $K_N = C_N/c$, at $X = x_N$, where $c$ is in $V$. Each lamina is also characterized by a constant diffusion coefficient $D_j$ and a thickness $X_j = x_j - x_{j-1}$, $j = 1, \ldots, N$. The total thickness of the slab is $L = \Sigma_{j=1}^{N} X_j$.

The differential equations and boundary conditions for the determination of $C_j(x,t) \equiv C_j$ are

$$\frac{\partial^2 C_j}{\partial x^2} = \frac{1}{D_j} \cdot \frac{\partial C_j}{\partial t}, \qquad x_{j-1} < x < x_j, \quad j = 1, \ldots, N \tag{1}$$

$$c(t) = c^c, \qquad x \leqslant x_0, \quad t \geqslant 0; \qquad c(0) = c^0, \qquad x \geqslant x_N \tag{2}$$

$$C_1(x_0,t) = C_1^c, \qquad t \geqslant 0; \qquad C_N(x_N,0) = C_N^0 \tag{3}$$

$$\left(\frac{\partial C_N}{\partial x}\right)_{x=x_N} = \frac{X_N}{D_N H_N} \cdot \left(\frac{\partial C_N}{\partial t}\right)_{x=x_N}, \qquad t \geqslant 0 \tag{4}$$

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$$K_{j-1,j} = \frac{K_{j-1}}{K_j} = \frac{C_{j-1}}{C_j}, \qquad x = x_{j-1}, \quad t \geqslant 0, \quad j = 2, ..., N \tag{5}$$

$$C_j(x,0) = C_j^i, \qquad x_{j-1} \leqslant x \leqslant x_j \tag{6}$$

$$K_1 = \frac{C_1^c}{c^c}, \qquad x = x_0, \quad t \geqslant 0; \qquad K_N = \frac{C_N}{c}, \quad x = x_N, \quad t \geqslant 0 \tag{7}$$

$$D_{j-1}\frac{\partial C_{j-1}}{\partial x} = D_j\frac{\partial C_j}{\partial x}, \qquad x = x_{j-1}, \quad t \geqslant 0, \quad j = 2, ..., N \tag{8}$$

$H_N$ is the ratio of the amount of diffusant in lamina $N$ to that in volume $V$ at equilibrium and is given by

$$H_N = K_N V_N / V \tag{9}$$

where $V_N$ is the volume of lamina $N$.

Application of the Laplace transform method[5] using the inversion theorem gives solutions

$$C_j(x,t) = C_j^c + 2\sum_{n=1}^{\infty} e^{-D_N\alpha_{Nn}^2 t}\{[(C_1^c - C_1^i)A_n^{1,2j-1} + i\alpha_{Nn}X_N (C_N^0 - C_N^i)A_n^{2N,2j-1}]Y_{j,2j-1,n}(x) + [(C_1^c - C_1^i)A_n^{1,2j} + i\alpha_{Nn}X_N (C_N^0 - C_N^i)A_n^{2N,2j}]Y_{j,2j,n}(x)\} \Big/ \left[\alpha_N\left(\frac{\partial|A|}{\partial\alpha_N}\right)_n\right], \quad j = 1, ..., N \tag{10}$$

where $C_j^c$ is the concentration of diffusant in lamina $j$ in equilibrium with a bath of concentration $c^c$ and $|A|$ is the determinant of the elements $A_{lk}$ of order $2N$ generated by applying $j$ in sequence $1, ..., N$ with $l$ defined as indicated and $k = 1, ..., N$, as follows:

$j = 1,\quad l = 2j - 1:\quad A_{11} = i\sin\alpha_1 x_0, \quad A_{12} = \cos\alpha_1 x_0$

$j = 2, ..., N,\quad l = 2j - 2:\quad A_{l,l-1} = -i\sin\alpha_{j-1}x_{j-1}, \quad A_{l,l} = -\cos\alpha_{j-1}x_{j-1}$
$A_{l,l+1} = iK_{j-1,j}\sin\alpha_j x_{j-1}, \quad A_{l,l+2} = K_{j-1,j}\cos\alpha_j x_{j-1}$

$j = 2, ..., N,\quad l = 2j - 1:\quad A_{l,l-2} = \delta_{j-1,j}\cos\alpha_{j-1}x_{j-1},$
$A_{l,l-1} = i\delta_{j-1,j}\sin\alpha_{j-1}x_{j-1}, \quad A_{l,l} = -\cos\alpha_j x_{j-1},$
$A_{l,l+1} = -i\sin\alpha_j x_{j-1}$

$j = N,\quad l = 2N:\quad A_{2N,2N-1} = H_N\cos\alpha_N x_N - \alpha_N X_N \sin\alpha_N x_n$
$A_{2N,2N} = i(H_N\sin\alpha_N x_N + \alpha_N X_N\cos\alpha_N x_N) \quad (11)$

and all other $A_{lk} = 0$, with $\delta_{j-1,j} = (D_{j-1}/D_j)^{1/2}$. The $A^{lk}$ are the cofactors of the $A_{lk}$ and $Y_{j,2j-1,n}(x) = i\sin\alpha_{jn}x$ and $Y_{j,2j,n}(x) = \cos\alpha_{jn}x$ for $j = 1, ..., N$.

The $\alpha_N$ are the nonzero positive roots of

$$|A| = 0, \tag{12}$$

indexed as $\alpha_{Nn}$, where $\alpha_{jn} = \alpha_{Nn}/\delta_{j,N}$.

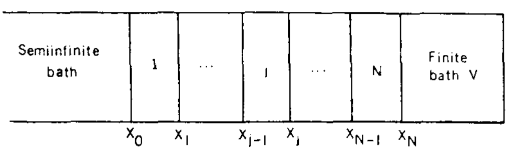


Fig. 1. Schematic representation of laminate slabs separating finite and semiinfinite baths.

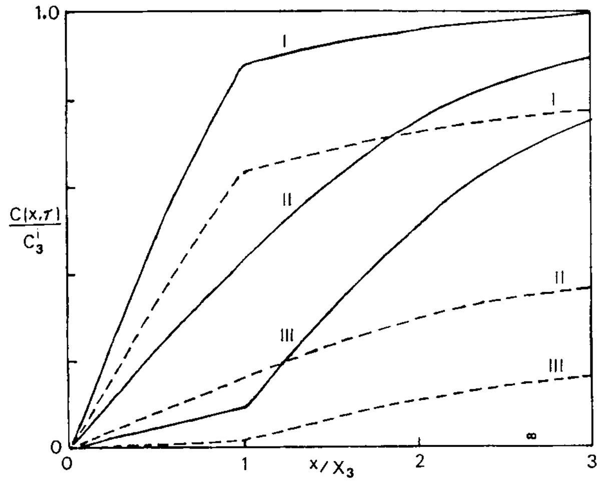


Fig. 2. Relative concentration profile, $C(x,\tau)/C_3^i$ vs. $x/X_3$, for systems with $H_3 = 2.0$, $\delta_{23} = 1.0$, and $K_{13} = K_{23} = K_3 = 1.0$: $I$, $\delta_{13} = 0.2$; II, $\delta_{13} = 1.0$; and III, $\delta_{13} = 5.0$. $\tau$: (—) 1.5; (- - -) 6.0.

In many experiments the concentration or pressure of the diffusant in the finite volume $c(t)$ is measured as a function of time. Using eq. (10) and setting $C_N(x_N,t) = K_N c(t)$, one obtains

$$c(t) = c^c + 2 \sum_{n=1}^{\infty} e^{-D_N \alpha_{Nn}^2 t} \{[(c^c - c^i)K_{1N}A_n^{1,2N-1} + i\alpha_{Nn}X_N (c^0 - c^i)A_n^{2N,2N-1}]Y_{N,2N-1,n}(x_N) + [(c^c - c^i)K_{1N}A_n^{1,2N} + i\alpha_{Nn}X_N (c^0 - c^i)A_n^{2N,2N}]Y_{N,2N,n}(x_N)\} \Big/ \left[\alpha_{Nn}\left(\frac{\partial |A|}{\partial \alpha_N}\right)_n\right] \quad (13)$$

where $K_{1N} = K_1/K_N$.

Adoption of eq. (13) to describe feasible experimental conditions is readily obtained by fixing the values of $c^c$, $c^i$, and $c^0$ appropriately. In addition, variations on the boundary conditions leading to different diffusion equations can

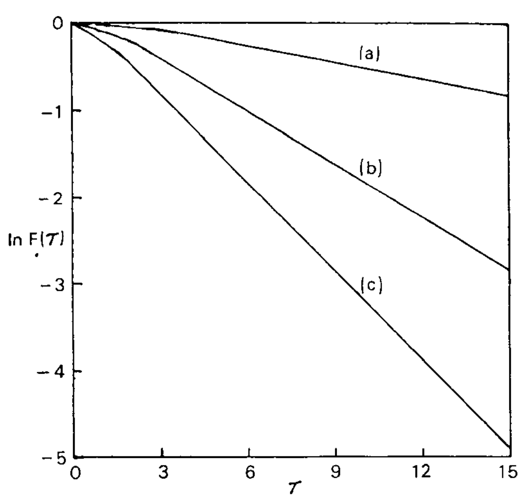


Fig. 3. ln $F(\tau)$ vs. $\tau$ for systems with $H = 2.0$, $\delta_{23} = 1.0$ and $K_{13} = K_{23} = K_3 = 1.0$: at (a) $\delta_{13} = 0.2$, (b) $\delta_{13} = 1.0$, and (c) $\delta_{13} = 5.0$.

be introduced. For example, assume lamina 1 is a film formed in the semiinfinite bath in which the slab with $j = 2, ..., N$ is placed to initiate the transport commencing at $x = x_1$. The differential equations and boundary conditions are provided in eqs. (1)–(8), with eq. (6) replaced by

$$\begin{aligned} C_1(x,0) &= C_1^c, \quad x_0 \leqslant x < x_1 \\ C_j(x,0) &= C_j^i \quad x_{j-1} \leqslant x \leqslant x_j, \quad j = 2, ..., N \end{aligned} \tag{14}$$

The solutions are

$$C_j(x,t) = C_j^c + 2 \sum_{n=1}^{\infty} e^{-D_N \alpha_{Nn}^2 t}$$

$$\vdots$$

$$\times \{[(C_1^c - C_1^0)A_n^{2,2j-1} + i\alpha_{Nn}X_N(C_N^0 - C_N^i)A_n^{2N,2j-1}]Y_{j,2j-1,n}(x)$$

$$+ [(C_1^c - C_1^0)A_n^{2,2j} + i\alpha_{Nn}X_N(C_N^0 - C_N^i)A^{2N,2j}]Y_{j,2j,n}(x)\} \Big/ \left[\alpha_{Nn}\left(\frac{\partial |A|}{\partial \alpha_N}\right)_n\right],$$

$$j = 1, ..., N \tag{15}$$

where $|A|$ is again defined and evaluated by eq. (11). The concentration in $V$ is given by

$$c(t) = c^c + 2 \sum_{n=1}^{\infty} e^{-D_N \alpha_{Nn}^2 t} \{[(c^c - c^0)K_{1N}A_N^{2,2N-1} + i\alpha_{Nn}X_N$$

$$(c^0 - c^i)A_n^{2N,2N-1}]Y_{N,2N-1,n}(x_N) + [(c^c - c^0)K_{1N}A_N^{2,2N} + i\alpha_{Nn}X_N$$

$$(c^0 - c^i)A_n^{2N,2N}]Y_{N,2N,n}(x_N)\} \Big/ \left[\alpha_{Nn}\left(\frac{\partial |A|}{\partial \alpha_N}\right)_n\right] \tag{16}$$

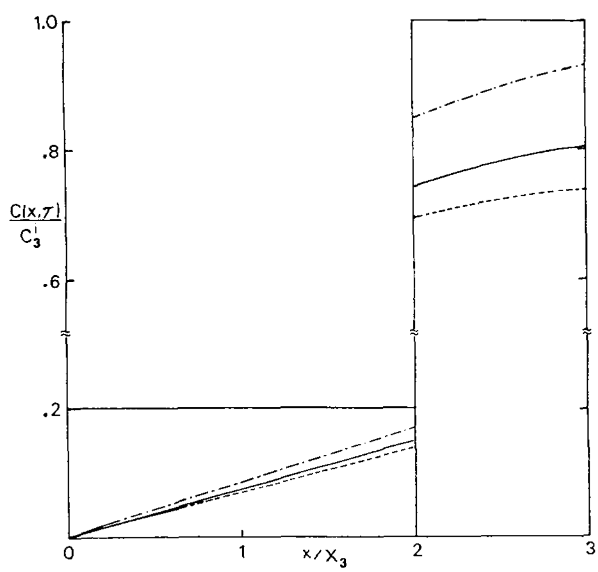


Fig. 4. Relative concentration profile, $C(x,\tau)/C_3^i$ vs. $x/X_3$, at $\tau = 6.0$ for systems with $\delta_{13} = \delta_{23} = 1.0$, $K_{13} = K_{23} = 0.2$, and $K_3 = 5.0$. $H_3$: (–·–) 0.2; (——) 1.0; (- - -) 2.0.

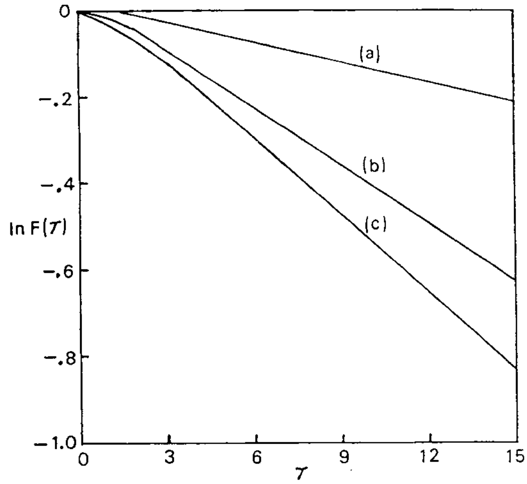


Fig. 5. $\ln F(\tau)$ vs. $\tau$ for systems with $\delta_{13} = 1.0, K_{13} = K_{23} = 0.2$, and $K_3 = 5.0$: at (a) $H_3 = 0.2$, (b) $H_3 = 1.0$, and (c) $H_3 = 2.0$.

## APPLICATION

Equations (10) and (13) were reduced to describe systems with $N = 3$, $c^i = c^0 \neq 0$, and $c^c = 0$, and recast in reduced dimensionless parameters: $D_3\alpha_{3n}^2 t = R_n^2\tau$, where $\alpha_{3n}X_3 = R_n$ and $\tau = D_3t/X_3^2$; $R_{13,n} = R_n\lambda_{13}/\delta_{13}$; $R_{23,n} = R_n\lambda_{23}/\delta_{23}$; $\delta_{13}^2 = D_1/D_3$; $\delta_{23}^2 = D_2/D_3$; $\lambda_{13} = X_1/X_3$; $\lambda_{23} = X_2/X_3$; and $K_{13} = C_1/C_3$ and $K_{23} = C_2/C_3$ at equilibrium.

The equations for each lamina and the concentration in $V$ are

$$\frac{C_1(x,\tau)}{C_1^i} = -2\sum_{n=1}^{\infty} e^{-R_n^2\tau}\left\{\left[\sin\left(\frac{R_{13,n}(x_1 - x)}{X_1}\right)\cos R_{23,n} + \delta_{12}K_{12}\cos\left(\frac{R_{13,n}(x_1 - x)}{X_1}\right)\sin R_{23,n}\right](H_3\sin R_n + R_n\cos R_n) + \left[\delta_{23}K_{23}\sin\left(\frac{R_{13,n}(x_1 - x)}{X_1}\right)\sin R_{23,n} - \delta_{13}K_{13}\cos\left(\frac{R_{13,n}(x_1 - x)}{X_1}\right)\cos R_{23,n}\right] \times (H_3\cos R_n - R_n\sin R_n)\right\}\Big/ R_n\left(\frac{\partial|A|}{\partial R}\right)_n \quad (17)$$

$$\frac{C_2(x_1\tau)}{C_2^i} = -2\delta_{12}K_{12}\sum_{n=1}^{\infty} e^{-R_n^2\tau}\left[\sin\left(\frac{R_{23,n}(x_2 - x)}{X_2}\right)(H_3\sin R_n + R_n\cos R_n) - \delta_{23}K_{23}\cos\left(\frac{R_{23,n}(x_2 - x)}{X_2}\right)(H_3\cos R_n - R_n\sin R_n)\right]\Big/ R_n\left(\frac{\partial|A|}{\partial R}\right)_n \quad (18)$$

$$\frac{c_3(x_1\tau)}{C_3^i} = 2\delta_{13}K_{13}\sum_{n=1}^{\infty} e^{-R_n^2\tau}\left[H_3\cos\left(\frac{R_n(x_3 - x)}{X_3}\right) - R_n\sin\left(\frac{R_n(x_3 - x)}{X_3}\right)\right]\Big/ R_n\left(\frac{\partial|A|}{\partial R}\right)_n \quad (19)$$

and

$$F(\tau) = \frac{c(\tau)}{c^i} = 2\delta_{13}K_{13}H_3\sum_{n=1}^{\infty}\frac{e^{-R_n^2\tau}}{R_n(\partial|A|/\partial R)_n} \quad (20)$$

Procedures for evaluating these types of equations have been described previously.[6] Relative concentrations were calculated as a function of $\tau$. Selected results obtained using three roots, $R_n$ with $n = 1, 2, 3$, for systems with $\lambda_{13} = \lambda_{23} = 1.0$, are shown in Figures 2–5. Figures 2 and 3 illustrate the effect of changing $D_1/D_3 = \delta_{13}^2$ on the time dependence of the relative concentration profile in the laminate and the relative concentration in $V$. Figures 4 and 5 illustrate the effect of $H_3$, the ratio of the equilibrium amounts of penetrant in lamina 3 and in $V$, on a relative concentration profile in the laminate and the time dependence of the relative concentration of the penetrant in $V$.

## NOMENCLATURE

| | |
|---|---|
| $\lvert A \rvert$ | determinant of order $2N$ used to evaluate $\alpha_{N,n}$ and the coefficients of the terms in the equation for $C(x,t)$. |
| $A_{lk}$ | elements of the determinant $\lvert A \rvert$ |
| $A^{lk}$ | cofactors of the elements $A_{l_k}$ in $\lvert A \rvert$ |
| $c(t)$ | diffusant concentration in the finite bath as a function of time. |
| $c^c$ | diffusant concentration in the semiinfinite bath; a constant |
| $c^0$ | initial diffusant concentration in the finite bath |
| $c^i$ | diffusant concentration in a bath in equilibrium with the diffusant in the laminae before the diffusion experiment is initiated |
| $C_j(x,t)$ | diffusant concentration in the slab at point $x$ and time $t$ |
| $C_j^0, C_j^i, C_j^c$ | concentrations in lamina $j$ in equilibrium with baths of concentrations $c^0$, $c^i$, and $c^c$ respectively |
| $D_j$ | diffusion coefficient in lamina $j$; a constant |
| $H_j$ | ratio of the amount of diffusant in lamina $j$ to that in the finite volume at equilibrium |
| $j$ | index that identifies laminae, $j = 1, 2, \ldots, N$ |
| $K_j$ | partition coefficient relating the concentration of diffusant in lamina $j$ to that in a bath, at equilibrium; $K_j = C_j/c$ |
| $K_{j-1,j}$ | partition coefficient relating the equilibrium concentration of the diffusant in lamina $j$ to that in lamina $j - 1$; $K_{j-i,j} = C_j/C_{j-1}$ |
| $L$ | total thickness of the slab |
| $N$ | number of laminae in the slab |
| $R_n$ | defined by $R_n = \alpha_{3n}X_3$, in example |
| $R_{jk,n}$ | defined by $R_{jk,n} = R_n\lambda_{jk}/\delta_{jk}$, in example |
| $t$ | time measured from the initiation of the diffusion experiment |
| $V$ | volume of the finite bath |
| $V_N$ | volume of lamina $N$ |
| $x_j$ | point along the direction of flow; the $x$-axis point at the plane separating lamina $j$ from lamina $j + 1$ |
| $X_j$ | thickness of lamina $j$; $X_j = x_j - x_{j-1}$ |
| $Y_{j,2j-1,n}(x)$ | terms in the $C(x,t)$ equation; $i \sin \alpha_{jn}x$ |
| $Y_{j,2j,n}(x)$ | terms in the $C(x,t)$ equation; $\cos \alpha_{jn}x$ |
| $\alpha_{Nn}$ | roots of the determinant $\lvert A \rvert$ |
| $\alpha_{jn}$ | defined by $\alpha_{jn} = \alpha_{Nn}/\delta_{j,N}$ |
| $\delta_{j-1,j}$ | defined by $\delta_{j-1,j} = (D_{j-1}/D_j)^{1/2}$ |
| $\lambda_{j,k}$ | defined by $\lambda_{jk} = X_j/X_k$ |
| $\tau$ | defined by $\tau = D_3t/X_3^2$, in example |

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