Transient Sorption in Multilaminate Slabs: Calculation of Diffusant Concentrations and Mass Fractions in Model Systems

INTRODUCTION

Equations have been reported describing transient sorption at intermediate to large time by symmetrical slabs composed of $2N$ laminae with constant diffusion and distribution coefficients.[1] In this note, applications of the equations are demonstrated using systems with arbitrarily selected diffusion and distribution coefficients and lamina thicknesses. Specifically, desorption characteristics of a diffusant from slabs with $N = 3$ into a well-stirred semi-infinite bath are determined. Diffusant concentration profiles and the fraction of the diffusant released by the slab are presented. These systems are representative models of possible laminated time-release devices in a well-stirred infinite sink.

EQUATIONS AND SYSTEM DESCRIPTION

The general system is a symmetrical laminate slab of $2N$ laminae in contact with a well-stirred semi-infinite bath, equivalent to an N-laminate slab with an impermeable exposed face of the Nth lamina. The diffusant concentration in the bath, c^0, is zero at $t \geq 0$. The concentration C_j^i in each lamina j prior to exposure of the slab to c^0 is uniform, and can be related at equilibrium to a bath concentration c^i by a partition coefficient $K_j = C_j^i/c^i$. Equilibrium is maintained at each phase interface during the sorption described by $K_1 = C_1^0/c^0$ at $x = x_0$ and $K_{j-1,j} = C_{j-1}/C_j$ at $x = x_{j-1}$, for $j = 2, \ldots, N$. For the symmetrical laminate, the interface at $x = x_N$ is impermeable. Each lamina is also described by a constant diffusion coefficient D_j and a thickness $X_j = x_j - x_{j-1}$, $j = 1, \ldots, N$. The total thickness for a free slab is $L = 2\,\Sigma_{j=1}^{N} X_j$.

The solution of the diffusion equation for the system is[1]

$$C_j(x,t) = C_j^0 + (C_1^0 - C_1^i) \sum_{n=1}^{\infty} \frac{2[A_n^{1,2j-1}\, Y_{n,j,2j-1}(x) + A_n^{1,2j}\, Y_{n,j,2j}(x)] \exp(-D_N \alpha_{Nn}^2 t)}{\alpha_{Nn}\, (\partial |A| / \partial\, \alpha_N)_n}, \qquad j = 1, \ldots, N \quad (1)$$

where C_j^0 is the final concentration in lamina j and $|A|$ is the determinant of the elements A_{lk} of order $2N$ as defined in eq. (7), Ref. 1. The α_N are the nonzero positive roots of

$$|A| = 0 \quad (2)$$

indexed as α_{Nn}, where $\alpha_j = \alpha_N/\delta_{jN}$ and $\delta_{jN} = (D_j/D_N)^{1/2}$. The $A^{1,2j-1}$ and $A^{1,2j}$ are the coefactors of $A_{1,2j-1}$ and $A_{1,2j}$, $Y_{j,2j-1}(x) = i \sin\alpha_j x$, and $Y_{j,2j}(x) = \cos\alpha_j x$, $j = 1, \ldots, N$.

The reduced change in the diffusant mass in the slab at time t, $F(t)$, is[1]

$$\begin{aligned} F(t) &= \frac{M(t) - M^0}{M^i - M^0} \\ &= \frac{C_1^i - C_1^0}{M^i - M^0} \sum_{n=1}^{\infty} \frac{2 \exp(-D_N \alpha_{Nn}^2 t)}{\alpha_{Nn}\, (\partial |A| / \partial \alpha_N)_n} \sum_{j=1}^{N} \frac{1}{\alpha_{jn}} \\ &\quad \times [iA_n^{1,2j+1}(\cos\alpha_{jn}x_j - \cos\alpha_{jn}x_{j-1}) - A_n^{1,2j}(\sin\alpha_{jn}x_j - \sin\alpha_{jn}x_{j-1})] \end{aligned} \quad (3)$$

where

$$M^0 = \sum_{j=1}^{N} C_j^0 X_j, \quad M^i = \sum_{j=1}^{N} C_j^i X_j, \quad M(t) = \sum_{j=1}^{N} \int_{x_{j-1}}^{x_j} C_j(x,t)\,dx$$

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EVALUATION PROCEDURES

The equations were evaluated for arbitrary sets of parameters D_j, C_j^i, C_j^0, X_j, and $K_{j-1,j}$ using FORTRAN IV language with an IBM 370/3033 computer. The program, including subroutines for plotting the resulting curves $C(x,t)$, $F(t)$, and 1-$F(t)$, is available from the authors upon request.

The first step in the calculation is the determination of the nonzero positive roots of eq. (2). The expansion of $|A| = 0$ is a transcendental equation with an infinite number of real roots. The roots were calculated by the method of interval halving.[2] The first root is sought by finding the smallest set of points xL and xR at the ends of an interval such that $f(xR)$ and $f(xL)$ are of opposite sign, where

TABLE I
Reduced Parameters of the Systems Studied

System	δ_{13}^2	δ_{23}^2	K_{13}	K_{23}
I	1.0	1.0	2.0	1.0
II	1.0	1.0	1.0	2.0
III	1.0	1.0	0.5	0.5
IV	0.3	1.0	1.0	1.0
V	1.0	0.3	1.0	1.0
VI	1.0	1.0	1.0	1.0

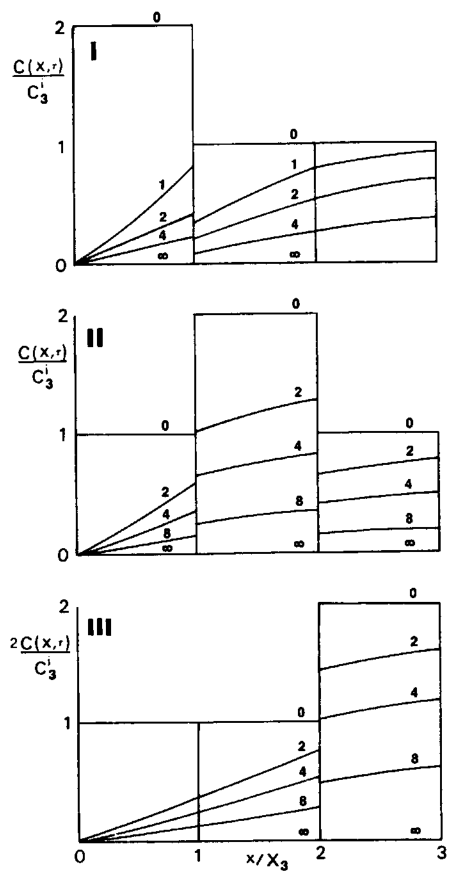

Fig. 1. Reduced concentration $C(x,\tau)/C_3^i$ vs reduced thickness x/X_3 at selected reduced times τ, indicated on the curves, for systems I–III.

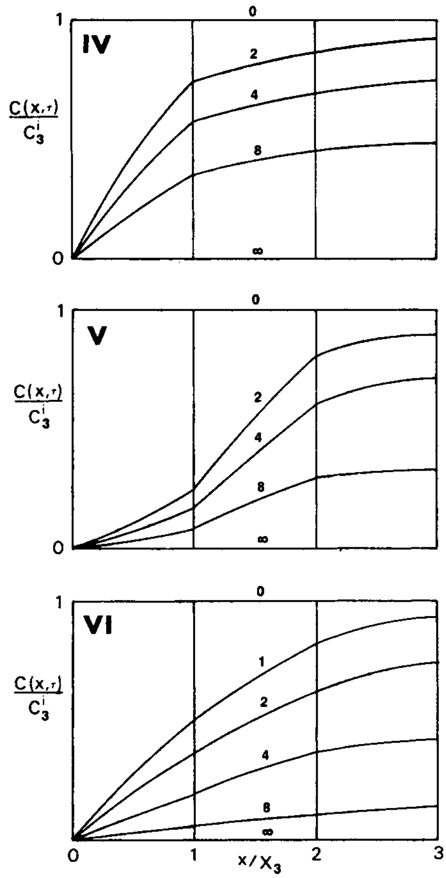

Fig. 2. Reduced concentration $C(x,\tau)/C_3^i$ vs reduced thickness x/X_3 at selected reduced times τ, indicated on the curves, for systems IV–VI.

$f = |A|$. The root is evaluated by the repetitive halving procedure. The value of xR is set as xL and the process is repeated to evaluate the next root. This process is repeated as many times as necessary to evaluate the desired number of roots.

The $(\partial|A|/\partial\alpha_N)_n$ are evaluated by applying the formula for partial differentiation of determinants.[3] The elements A_{lk} for each row are replaced by their partial derivatives one row at a time to generate $2N$ determinants. Their sum is equal to $(\partial|A|/\partial\alpha_N)_n$. The elements and their partial derivatives are determined for each set of roots α_{jn}, and the values of $A_n^{1,2j-1}$, $A_n^{1,2j}$, and $(\partial|A|/\partial\alpha_N)_n$ obtained by the efficient pivotal condensation method.[4] These quantities are then used to calculate $C(x,t)$ by eq. (1) and $F(t)$ by eq. (3).

APPLICATIONS

The systems used to illustrate the method are desorption of diffusant from $N = 3$ laminate slabs with arbitrary X_j, C_j^i, D_j^1, and $K_{j,l}$ in a semi-infinite bath with $c^0 = 0$. For generality the equations were recast in reduced dimensionless parameters: $D_3\alpha_{3n}^2 t = R_n^2$, where $\alpha_{3n}X_3 = R_n$ and $\tau = D_3t/X_3^2$; $\delta_{13}^2 = D_1/D_3$; $\delta_{23}^2 = D_2/D_3$; $\alpha_{1n}X_1 = \lambda_{13}R_n/d_{13}$; $\alpha_{2n}X_2 = \lambda_{23}R_n/d_{23}$; $\lambda_{13} = X_1/X_3$; $\lambda_{23} = X_2/X_3$; and $C_1 = K_{13}C_3$ and $C_2 = K_{23}C_3$ at equilibrium. The systems studied are described in Table I; $\lambda_{13} = \lambda_{23} = 1$ in all systems. Systems I–III demonstrate the effect of the diffusant solubility in one lamina being larger than in the others. Systems IV and V demonstrate the effects of one lamina with a lower diffusion coefficient than the others. System VI is a homogeneous slab used for comparison.

The profiles of the relative concentration $C(x,\tau)/C_3^i$ for the six systems at selected values of τ are

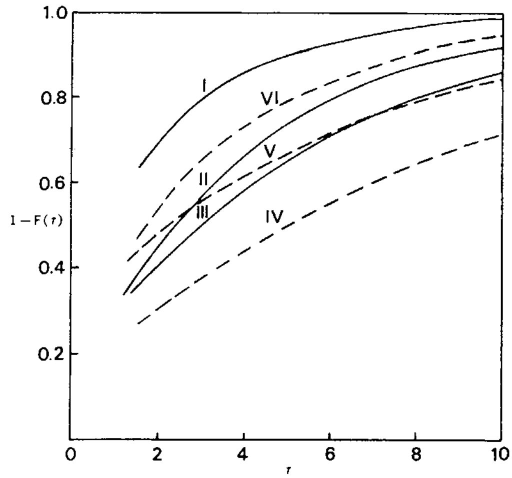

Fig. 3. Fraction of the diffusant released from the slabs, 1-$F(\tau)$, vs reduced time τ. Systems are identified in Table I.

presented in Figs. 1 and 2. The relative concentrations were calculated using three roots α_{jn}. Additional roots are significant only at $\tau < 2$ for any of these systems. Regions of increased slopes and curvature of relative concentration dependence on x/X_3 and the positions at which discontinuities occur are evident.

The fraction of the diffusant released from the slab, 1-$F(\tau)$, as a function of τ is provided for the six systems in Fig. 3. System I, which has $K_{13} > 1$, demonstrates a rapid initial release followed by a very slow release of the small remainder of the diffusant: 1-$F(\tau) \simeq 0.7$ at $\tau = 2$. System IV, which has $\delta_{13} < 1$, demonstrates a much more uniform release rate over an extended period. Intermediate characteristics are demonstrated in the other systems.

The procedures outlined here illustrate a practical analysis of transient diffusion in multilaminate slabs composed of laminae with constant diffusion and distribution coefficients.

References

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