

# Diffusion through a multilayered phase in electrochemical systems: an approach by numerical inversion of the Laplace transform

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Diffusion through a multilayered material is analysed by means of the Laplace transformation. An algorithm using a new method for numerical inversion of the Laplace transform is successfully developed for solving the diffusion equations. The procedure is applied to an analysis of hydrogen permeation through a simple multilayered material related to electrochemical testing. The problem appears simple, but the exact analytical solution is difficult; the present technique makes it possible to solve this problem while retaining a part of the advantage of the analytical method. The results are compared with results obtained by the conventional analytical method, which is based on diffusion through a single layer. The applicability and limit of use of the conventional analytical method is also investigated.

## List of symbols

$a$	approximation of parameter in the FILT	$h_i$	coefficient determined by boundary conditions
$a_i$	concentration gradient in the $i$ th layer at steady state	$j$	flux
$A_i$	dimensionless concentration gradient at steady state, $l_m a_i / c_s$	$j_0$	flux under the constant flux boundary condition
$b_i$	concentration at the left-hand end of the layer $i$ at steady state	$J$	dimensionless flux, $l_m j / D_m c_s$
$B_i$	dimensionless $b_i$ , $b_i / c_s$	$J_0$	dimensionless flux under the constant flux boundary condition, $l_m j_0 / D_m c_s$
$c_i$	concentration in the $i$ th layer	$k_i$	distribution coefficient at the $i$ th interface, $c_{i+1} _{x_{i+1}=0} / c_i _{x_i=\delta_i}$
$c_0$	initial concentration at the left-hand end of multilayer	$l_i$	thickness of the $i$ th layer
$c_s$	concentration at the left-hand end of multilayer	$l_m$	thickness of a reference layer $m$
$C_i$	dimensionless concentration, $c_i / c_s$	$n$	the number of layers
$\bar{C}_i$	the Laplace transformation of concentration $C_i$	$s$	variable for the Laplace transformation
$C_0$	dimensionless initial concentration, $c_0 / c_s$	$S_i$	parameter, $\sqrt{s / \alpha_i}$
$D_i$	diffusion coefficient in the $i$ th layer	$t$	time
$D_m$	diffusion coefficient in a reference layer $m$	$x_i$	distance from the left-hand end of the $i$ th layer
$E_i$	parameter, $e^{\sqrt{s / \alpha_i} \delta_i}$	$X_i$	dimensionless distance, $x_i / l_m$
$f(t)$	function	<i>Greek symbols</i>	
$F(t)$	the Laplace transform of function $f(t)$	$\alpha_i$	dimensionless diffusion coefficient, $D_i / D_m$
$g_i$	coefficient determined by boundary conditions	$\gamma$	large real number for the inversion of the Laplace transform
		$\delta_i$	dimensionless thickness, $l_i / l_m$
		$\tau$	dimensionless time, $D_m t / l_m^2$

## 1. Introduction

Diffusion problems are often encountered in electrochemical systems. Both analytical and numerical methods are employed for solving such problems. The advantages of the analytical method are that the solution is strictly correct, and that the physical significance of the solution is usually explicit and, hence, it is possible to obtain an approximate form which is easy to handle. The Laplace transformation is frequently utilized as an analytical method to solve partial differential equations. However, there are

sometimes difficulties in the mathematical analysis of diffusion equations for multilayered phases even if a one-dimensional problem is considered. The difficulties exist mainly in the inversion. It is often difficult to obtain solutions in complicated problems. Moreover, it may be difficult to discern the physical significance of the solution, even if the solution is available. For example, the solution of one-dimensional diffusion equations for a system consisting of only two layers contains a series of roots [1]. In consequence, a numerical method must be used to obtain the roots; this procedure may impair the

precision of the analytical solution. Thus, the analytical method is not always applicable to all systems, particularly to complicated ones. Alternatively, a technique using numerical inversion of the Laplace transform may extend the possibility of the Laplace transformation technique while retaining a part of the strictness of the analytical method. There seems to be no general technique for numerical inversion of the Laplace transform because of the ill-conditioned nature [2], although many efforts have been made, where functions such as Laguerre's polynomial and Fourier series were employed for the inversion [3–5]. Their applications are, however, restricted because there are problems of convergence, which cannot be attained depending on the type of image function to be treated, truncation errors, and so on. However, Hosono [6] has developed a new algorithm which is applicable to various types of Laplace transform numerical inversions although his applications were limited to simple problems. This inversion procedure is applied to the analysis of diffusion through a multilayer in the present study.

Electrochemical testing for hydrogen permeation using a bipolar cell developed by Devanathan and Stachurski [7] is one of the most popular techniques to evaluate the resistance of steel or other metallic materials against hydrogen induced cracking or embrittlement. The test specimen is normally plated with foreign metal which is resistant to corrosion. One surface of the specimen is polarized cathodically to generate hydrogen and the other surface is polarized anodically enough to oxidize hydrogen passing through the specimen so that the concentration at the surface is zero. Therefore, the specimen has a multilayered structure: test material and plated layers on the surface. Hydrogen permeation through it is a good example of diffusion through a multilayer if the diffusion process controls the permeation rate [8]. Since a thin test piece is employed, a one-dimensional diffusion equation may be used for the analysis. An analytical solution for diffusion through a single layer was given by McBreen *et al.* [8] and then Nanis *et al.* [9] presented a correct version;

verification and modifications have been also reported [10–12]. Approximate forms of the exact solution are often accommodated to systems consisting of multilayers on the assumption that the coating layer is thin and the coating material does not have a very small diffusion coefficient compared to that of the test specimen. This assumption is appropriate in many systems. However, it must be noted that there are some limits in applying the single layer approximation to multilayer systems. To know the limits or to obtain diffusion parameters of a thin coating layer itself, it is necessary to solve diffusion problems for multilayered systems. However, it is hard to find studies treating diffusion problems through a multilayer relating to hydrogen permeation, though Song and Pyun treated a system with a bilayer by the finite difference method [13]. In the present study, an analysis to solve diffusion problems through multilayered materials is presented using numerical inversion of the Laplace transform and the treatment is applied to verify the conditions of electrochemical testing for hydrogen permeation.

## 2. Analytical procedures

A multilayer system, which is simple but cannot be solved analytically, is treated: one-dimensional diffusion through a multilayered wall composed of  $n$  layers of different thickness,  $l_i$ , where  $i$  denotes the number of the layer from the left-hand side (Fig. 1). In the case of hydrogen permeation, hydrogen is electrochemically evolved at this side, and a part of the hydrogen adsorbed on the surface is dissolved into the material. In consequence, diffusion of hydrogen takes place from left to right. The system is at steady state at  $t < 0$  and each layer maintains a linear concentration distribution:  $a_i x_i + b_i$ , where  $x_i$  is distance from the left-hand end of  $i$ th layer. The concentration at the left-hand end of the sample is  $c_0 (= b_1)$  at time  $t < 0$ , and is then changed to  $c_s$  at  $t = 0$  (constant concentration boundary condition). The concentration at the right-hand end is zero during the experiment by applying an anodic potential sufficient to oxidize arriving hydrogen. The partial differential equations

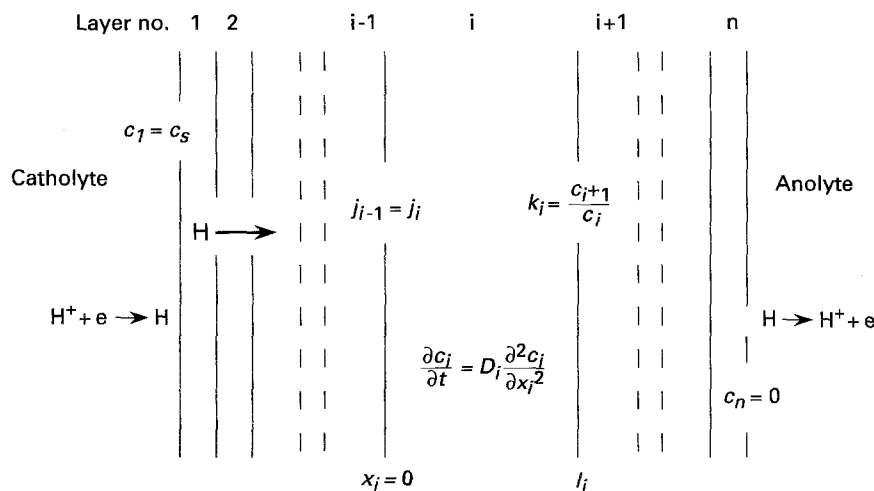


Fig. 1. Schematic diagram of diffusion through a multilayer and its parameters.

and the initial and boundary conditions are represented by Equations 1, 2 and 3, respectively, where dimensionless parameters are used:

$$\frac{\partial C_i}{\partial \tau} = \alpha_i \frac{\partial^2 C_i}{\partial X_i^2} \quad 0 \leq X_i \leq \delta_i \quad (i = 1, n) \quad (1)$$

Initial conditions:

$$C_i = A_i X_i + B_i \quad (i = 1, n) \quad C_n|_{X_n = \delta_n} = 0 \quad (2)$$

Boundary conditions:

$$C_1|_{X_1 = 0} = 1 \quad (3a)$$

$$C_n|_{X_n = \delta_n} = 0 \quad (3b)$$

$$C_i|_{X_i = 0} = k_{i-1} C_{i-1}|_{X_{i-1} = \delta_{i-1}} \quad (i = 2, n) \quad (3c)$$

$$\alpha_i \frac{\partial C_i}{\partial X_i} \Big|_{X_i = 0} = \alpha_{i-1} \frac{\partial C_{i-1}}{\partial X_{i-1}} \Big|_{X_{i-1} = \delta_{i-1}} \quad (i = 2, n) \quad (3d)$$

Parameters for the initial concentration distribution,  $A_i$  and  $B_i$  can be determined by solving the ordinary differential equation at steady state. Subscript  $m$  denotes a reference layer which is chosen in the  $n$  layers.

The Laplace transformation reduces Equation 1 to an ordinary differential equation:

$$\frac{d^2 \bar{C}_i}{dX_i^2} = \frac{1}{\alpha_i} (s \bar{C}_i - A_i X_i - B_i) \quad 0 \leq X_i \leq \delta_i \quad (i = 1, n) \quad (4)$$

The boundary conditions are

$$\bar{C}_1|_{X_1 = 0} = \frac{1}{s} \quad (5a)$$

$$\bar{C}_n|_{X_n = \delta_n} = 0 \quad (5b)$$

$$\bar{C}_i|_{X_i = 0} = k_{i-1} \bar{C}_{i-1}|_{X_{i-1} = \delta_{i-1}} \quad (i = 2, n) \quad (5c)$$

$$\alpha_i \frac{d\bar{C}_i}{dX_i} \Big|_{X_i = 0} = \alpha_{i-1} \frac{d\bar{C}_{i-1}}{dX_{i-1}} \Big|_{X_{i-1} = \delta_{i-1}} \quad (i = 2, n) \quad (5d)$$

The solution with boundary conditions Equation 5 gives as Equation 6 in the generalized form:

$$\bar{C}_i = g_i e^{\sqrt{s/\alpha_i} X_i} + h_i e^{-\sqrt{s/\alpha_i} X_i} + \frac{1}{s} (A_i X_i + B_i) \quad (6)$$

where  $s$  is a complex variable for the transformed function, and the coefficients  $g_i$  and  $h_i$  are given by the boundary conditions Equation 5. They produce the following equations.

$$g_1 + h_1 = \frac{1 - B_1}{s} \quad (7)$$

$$\begin{pmatrix} -k_{i-1} E_{i-1} & -k_{i-1} E_{i-1}^{-1} & 1 & 1 \\ -\alpha_{i-1} S_{i-1} E_{i-1} & \alpha_{i-1} S_{i-1} E_{i-1}^{-1} & \alpha_i S_i & -\alpha_i S_i \end{pmatrix}$$

$$\times \begin{pmatrix} g_{i-1} \\ h_{i-1} \\ g_i \\ h_i \end{pmatrix} = \frac{1}{s} \begin{pmatrix} k_{i-1}(A_{i-1}\delta_{i-1} + B_{i-1}) - B_i \\ \alpha_{i-1} A_{i-1} - \alpha_i A_i \end{pmatrix} \quad (i = 2, n) \quad (8)$$

$$E_n g_n + E_n^{-1} h_n = -\frac{A_n \delta_n + B_n}{s} \quad (9)$$

where  $E_i = e^{\sqrt{s/\alpha_i} \delta_i}$  and  $S_i = \sqrt{s/\alpha_i}$ . The solution of these simultaneous equations provides  $g_i$  and  $h_i$  and, hence, the concentration  $\bar{C}_i$  is obtained in its Laplace transformed form.

Another type of boundary condition which is often encountered in electrochemical systems is constant flux; substitution of Equation 10 for Equation 3(a) in a set of equations describing the diffusion problem at constant concentration, Equations 1–3, provides this situation:

$$-\alpha_1 \frac{\partial C_1}{\partial X_1} \Big|_{X_1 = 0} = J_0 \quad (10)$$

where  $J_0 = I_m j_0 / D_m c_s$  and  $j_0$  is the flux. On using this boundary condition, Equations 11 and 12 are employed instead of Equations 5(a) and 7; the other equations remain the same as those for the constant concentration boundary condition problem. That is,

$$-\alpha_1 \frac{d\bar{C}_1}{dX_1} \Big|_{X_1 = 0} = \frac{J_0}{s} \quad (11)$$

$$S_1 g_1 - S_1 h_1 = -\frac{J_0 + \alpha_1 A_1}{\alpha_1 s} \quad (12)$$

The inversion theorem of the Laplace transform (the Bromwich integral) is given by

$$f(t) = \frac{1}{2\pi j} \int_{\gamma-j\infty}^{\gamma+j\infty} F(s) e^{st} ds \quad (13)$$

According to Hosono's treatment [6], which he called FILT (fast inversion of Laplace transform), a function  $E(st, a)$  approximates  $e^{st}$  if the condition that an approximation parameter,  $a$ , is greater than the real part of  $s$  is fulfilled.

$$E(st, a) = \frac{e^a}{2 \cosh(a - st)} \quad (14)$$

The equation can be represented also as a series expansion (15(a)) or an expansion in partial fractions (15(b)):

$$E(st, a) = e^{st} - e^{-2a} e^{3st} + e^{-4a} e^{5st} - \dots \quad (15a)$$

$$= \frac{e^a}{2} \sum_{n=-\infty}^{\infty} \frac{(-1)^n j}{st - \{a + (n - 0.5)\pi j\}} \quad (15b)$$

The expression for  $E(st, a)$ , Equation 14, can be a good approximation when  $a \gg \text{Re}(st)$ , because Equation (15a) approximates  $e^{st}$  under the condition; we can choose an arbitrary value as the adjustable parameter,  $a$ . When  $E(st, a)$  as Equation 15(b) is employed in the Bromwich integral instead

of  $e^{st}$ , integration gives an approximate equation.

$$f(t, a) = \frac{e^a}{t} \sum_{n=1}^{\infty} (-1)^n \operatorname{Im} \left\{ F \left( \frac{a + (n-0.5)\pi j}{t} \right) \right\} \quad (16)$$

where  $\operatorname{Im}$  denotes the imaginary part of the complex. This approximation, originally proposed by Hosono, is used for inversion, instead of the Bromwich integral, in the present diffusion problems. The numerical inversion of  $\bar{C}_i$  (Equation 6) is accomplished using Equation 16:  $\bar{C}_i(s)$  is introduced into Equation 16 after the variable  $s$  is substituted by  $\{a + (n-0.5)\pi j\}/\tau$ ; then  $C_i(\tau)$ , at a given position  $X_i$  and time  $\tau$ , is calculated by summing each term for  $n = 1, \dots$ . This procedure is repeated at positions and times to be calculated. Furthermore, the permeation flux,  $J$ , which can be compared directly with experimental measurements, is also obtained by inversion of Equation 17.

$$\bar{J} = -\alpha_n \frac{d\bar{C}_n}{dX_n} \Big|_{X_n=\delta_n} \quad (17)$$

where  $J = l_m j / D_m c_s$ , and  $j$  is the dimensional flux.

### 3. Results and discussion

The numerical inversion, FILT, was tested using a simple diffusion problem: a single layer and constant concentration boundary condition. An analytical solution has been given [8, 9]; the Laplace transform and its inversion of concentration gradient at the right-hand end wall, which correspond to dimensionless flux in this case, are given as

$$-\frac{d\bar{C}}{dX} \Big|_{X=1} = \frac{1}{\sqrt{s} \sinh \sqrt{s}} \quad (18)$$

$$-\frac{dC}{dX} \Big|_{X=1} = \frac{2}{\sqrt{\pi\tau}} \sum_{n=0}^{\infty} e^{-(2n+1)^2/4\tau} \quad (19)$$

The dimensionless concentration gradient was calculated from Equation 18 where its numerical inversion was achieved using FILT; the results were compared with those calculated by the analytical solution Equation 19 and also by the first term approximation,  $(2/\sqrt{\pi\tau}) \exp(-1/4\tau)$ , as given by Nanis *et al.* [8, 9]. The comparison is presented in Table 1 in the dimensionless time range, 0.01 to 1. The calculations were performed with double precision; the approximation parameter  $a$  in Equation 16 was 10 and the summation was terminated by  $n = 20$  for the numerical inversion. The first six terms were summed for the analytical solution. The values by the numerical inversion agree up to four digits with those obtained by the analytical solution, whereas the results from the first term approximation deviate at large values of  $\tau$ . It is necessary, however, to calculate with high precision in order to obtain the values at small  $\tau$ . For example, overflow of calculation occurred at  $\tau$  smaller than 0.02 when an effective range,  $10^{-38}$  to  $10^{38}$ , single precision, was used,

Table 1. Comparison of the values  $-dC/dX|_{X=1}$  obtained by the FILT, and the analytical solution and the first term approximation

$\tau$	FILT	Analytical solution	First term approximation
0.01	0.0000	0.0000	0.0000
0.05	0.0340	0.0340	0.0340
0.10	0.2929	0.2929	0.2929
0.20	0.7229	0.7229	0.7229
0.30	0.8965	0.8965	0.8953
0.40	0.9614	0.9614	0.9550
0.50	0.9856	0.9856	0.9679
0.60	0.9946	0.9946	0.9603
0.70	0.9980	0.9980	0.9436
0.80	0.9993	0.9993	0.9230
0.90	0.9997	0.9997	0.9009
1.00	1.0000	1.0000	0.8788

whereas limit of the overflow was improved to 0.0003 when the range was extended to  $10^{-308}$  to  $10^{308}$ , double precision. The values at such small  $\tau$  would not be required for the analysis because the time region corresponds to the very beginning of temporal flux variation, as described later. Thus, FILT works well under the present conditions.

Permeation of hydrogen through a Fe/Ni bilayer system has been analysed numerically by Song and Pyun [13] who used the finite difference method. The present calculations under constant concentration boundary condition reproduced their results well under potentiostatic conditions. In such a bilayer system, parameters,  $g_i$  and  $h_i$ , in the solution of the Laplace transform are given explicitly as a function of  $s$ , where the inversion of  $\bar{C}_i$  can be accomplished directly by using Equation 16. On the other hand, the calculation becomes difficult when the number of layers exceeds two, because the explicit correlation of the parameters to  $s$  is no longer attained. As a result,  $\bar{C}_i$  cannot be explicitly expressed as a function of  $s$ . In consequence, the parameters,  $g_i$  and  $h_i$ , must be calculated numerically for each term of  $n$  in Equation 16 by solving the simultaneous equations consisting of Equations 7–9. Since the two parameters, as well as  $s$ , are complex numbers, they have to be separated by their real and imaginary parts; hence, the number of simultaneous equations to be solved increases to  $4 \times n$  from  $2 \times n$  shown in Equations 7–9. As an example, the concentration distribution of hydrogen in a five-layered system was calculated under simple conditions as shown in Fig. 2. The five layers had the same thickness, the diffusion coefficients of the second and fourth layers were five times greater than those of the other layers, and the distribution coefficient at each interface of two adjacent layers was five. Hydrogen dissolving at the left-hand surface of a multilayered material diffuses through the layers toward the right-hand end surface, where hydrogen is consumed by anodic reaction to hydrogen ions. The results describe the temporal variation of the concentration in each layer well. Concentration distributions approach linear as the time  $\tau$  advances, and finally linear distributions are

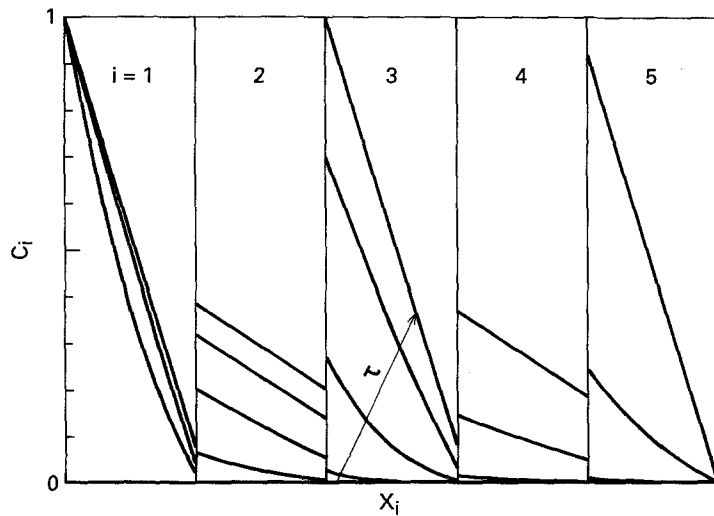


Fig. 2. An example of concentration distribution in a five-layered material.  $\tau = 0, 0.16, 0.41, 1.0,$  and  $6.5$ ;  $C_0 = 0$ ;  $k_i = 5$  ( $i = 1, 5$ );  $\delta_i = 1$  ( $i = 1, 5$ );  $\alpha_1, \alpha_3, \alpha_5 = 1$  and  $\alpha_2, \alpha_4 = 5$ .

achieved in all layers at steady state. Though the given conditions are simple, this procedure can be applied to more complex conditions: multilayers where each layer has a different thickness, distribution coefficient, and diffusion coefficient, or more multiple layers. However, it must be noted that such complicated conditions may cause overflow during computation, as mentioned above.

The use of the single layer approximation to determine diffusion coefficients for a multilayer is examined using a bilayer system. Figure 3 shows an example of calculated flux transient under the conditions of various diffusion coefficients,  $\alpha$ . A small diffusion coefficient for a layer causes a very slow change of flux for the bilayer. The change becomes fast as the diffusion coefficient increases. Finally, there is no change with the increase in the diffusion coefficient when  $\alpha$  exceeds unity, indicating that the layer no longer functions as an influential barrier for diffusion. The ultimate transient feature corresponds to that of a single layer; the transient is uniquely fixed in the dimensionless treatment.  $\tau_{1/2}$  is considered to be a characteristic parameter for diffusion and is defined as the dimensionless time at which  $J = J_\infty/2$  or  $-dC/dX|_{x_n=1} = 0.5$ . When a single layer is considered, the  $\tau_{1/2}$  is determined uniquely as 0.139 (the transient at  $\alpha = 1$  in Fig. 3). The definition for

$\tau$  gives a dimensional diffusion coefficient,  $D$ , for a single layer.

$$D = \frac{\tau_{1/2} l^2}{t_{1/2}} \tag{20}$$

The  $t_{1/2}$ , the dimensional time at which  $j = j_\infty/2$ , can be obtained experimentally, the thickness,  $l$ , is known, and the  $\tau_{1/2}$  is 0.139, and hence, the  $D$  can be determined.

An erroneous diffusion coefficient will be estimated if the single layer approximation is applied to a multilayer system, though the magnitude of error depends on the conditions treated. The variations of  $\tau_{1/2}$  are shown in Fig. 4 as a function of distribution coefficient,  $k$ , and diffusion coefficient,  $\alpha$ , where one of the parameters is fixed and the conditions of initial concentration  $C_0$  ( $= c_0/c_s$ ) and thickness  $\delta$  are assumed, 0 and 0.01, respectively; the latter means that the thickness of a protective coating is a hundredth of that of the test specimen. Of the two simplified conditions,  $k = 1$  means that there is no concentration difference at the interface of two layers and  $\alpha = 1$  is the condition that the two layers have an identical diffusion coefficient, which is equivalent to a single layer system. When  $\alpha < 1$  or  $k > 1$ ,  $\tau_{1/2}$  deviates from 0.139; the variation of  $\alpha$  gives the larger deviation than the  $k$  variation. This deviation causes an

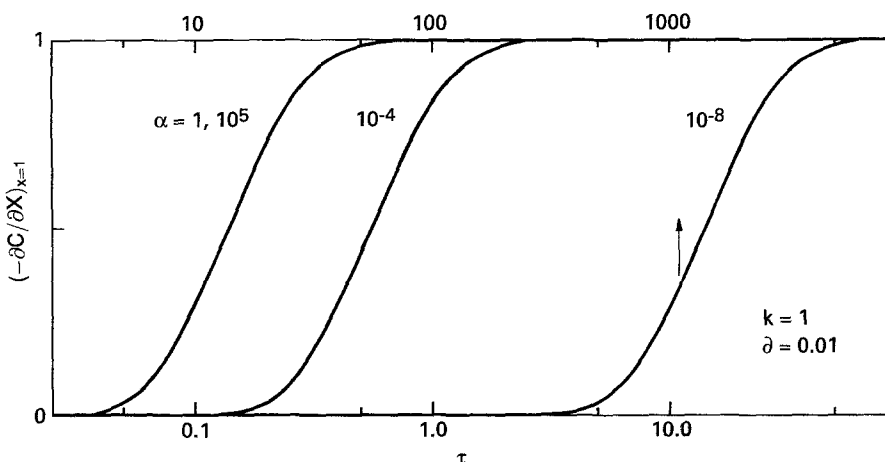


Fig. 3. Concentration gradient as a function of time at the end surface with variation of diffusion coefficient for a bilayer system:  $C_0 = 0$ ,  $k = 1$ , and  $\delta = 0.01$ . The negative concentration gradient is equivalent to normalized flux  $J/J_\infty$ .

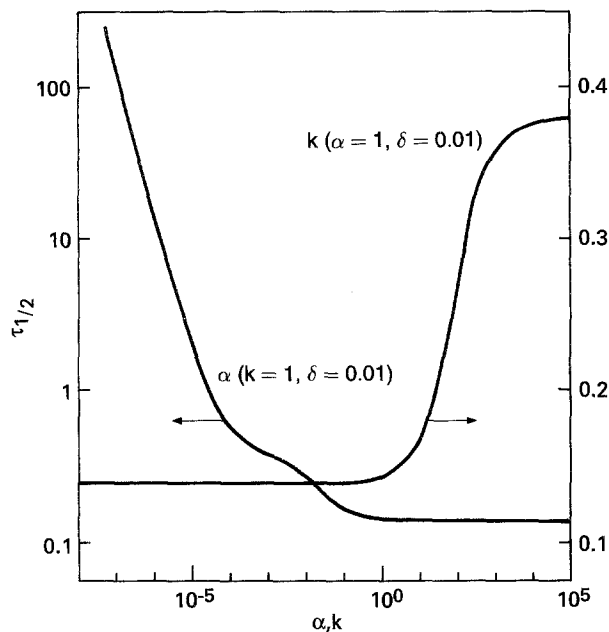


Fig. 4.  $\tau_{1/2}$  as a function of  $\alpha$  and  $k$  for a bilayer material.  $C_0 = 0$ ;  $\delta = 0.01$ .

erroneous estimation giving a smaller value than the actual diffusion coefficient, because the dimensional diffusion coefficient,  $D$ , is obtained from Equation 20 and 0.139 is used for  $\tau_{1/2}$  in the single layer approximation instead of the correct value greater than 0.139, which is shown in Fig. 4. Thus, under such conditions, the multilayer problem must be considered to obtain the correct diffusion coefficient when the diffusion coefficient of the thin surface film is smaller than that of the test specimen, or when the concentration at the film interface is lower than that of the test specimen. The deviation from the single layer approximation depends on the conditions to be treated, and, hence, the limitation should be tested for the respective cases.

Diffusion parameters, especially the diffusion coefficient,  $D$ , and the surface concentration,  $c_s$ , are derived from experimental results. Several methods have been proposed for their derivation [7, 11, 14]; time-lag methods, time constant methods, etc. For multilayered systems, the time-lag method has been utilized exclusively [13, 15–17], but the principle of the method is based on the use of the steady state condition though the transient is also utilized. On the other hand, the present procedure can be used for the determination of diffusion coefficients by the transient flux. Three kinds of parameter exist; diffusion coefficient,  $D_i$ , and thickness for each layer,  $l_i$ , and distribution coefficient for each interface,  $k_i$ . Of these,  $l_i$  is usually a known parameter. The diffusion coefficient for a single layer is readily determined, as already described. Now, a bilayer is considered as an example of how to obtain unknown parameters. When a second layer exists on a first layer with known diffusion parameters, the first layer is chosen as a reference layer. If the diffusion coefficient,  $D_2$ , of the second layer is known, an unknown parameter,  $k_1$ , at the interface can be determined as

follows.  $t_{1/2}$  is experimentally measured, then the corresponding dimensionless characteristic time,  $\tau_{1/2}$ , is calculated by the relation,  $\tau_{1/2} = D_m t_{1/2} / l_m^2$ , where  $m$  denotes a reference layer: the first layer in this case.  $k_1$  is determined by comparison of  $\tau_{1/2}$  thus obtained with the calculated  $\tau_{1/2}$  as a function of the unknown parameter  $k_1$  using the known parameters,  $D_1$  and  $D_2$  as can be seen in Fig. 4. On the other hand, if  $k_1$  is known, the unknown  $D_2$  can be obtained as follows. The experimentally measured  $t_{1/2}$  gives  $\tau_{1/2}$ , and  $\tau_{1/2}$  is compared with  $\tau_{1/2}$  as a function of the unknown parameter  $\alpha_1$ ; then the corresponding  $\alpha_1$  determines the  $D_2$  to be obtained:  $D_2 = \alpha_1 D_m$ . Repetition of this treatment can be extended to analysis of more than two multilayers. Other methods, like regression of the whole transient proposed by Kimble and White [11], would also be possible using the present method.

Compared to the usual finite difference analysis, the technique presented here is advantageous in some respects: it does not require small subintervals to obtain a precise value of flux, and the solution is explicitly given although it is in the form of the Laplace transform and, hence, some insight may be obtained in the transformed solution. There are also disadvantages, for instance, the determination of coefficients  $g_i$  and  $h_i$  in a complex matrix requires a wide range of numbers to be handled in the computation particularly when the number of layers is large. This may be overcome by using a multiple-precision routine for calculation as done by Shitara *et al.* [18] in their computation of heat conduction problems in multilayer systems where they employed Gaver's method [5]. This numerical inversion would be applicable, not only to diffusion problems such as those presented in this study but also to other problems in electrochemical systems, if they can be solved using the Laplace transforms. Of these, the analysis of the Laplace or the Poisson equation may be interesting in relation to potential or current distribution.

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