The calculations could have been pursued for curves are represented in Figure 5a for the CR-S-rev mechanism. represented in parts Aa and Ba of Figure 4 for tie CR-CR and CR-S-irr mechanisms, respectively, while the resulting of the additional charging of the polymer. The same is true except all A's were made equal to zero except XI. We first set all A's equal to zero except XI, XI, and complete irreversibility ([\alpha_0]_y=o \equiv 0, [a_j]_{j=1,...,n}=0). Thus, during the anodic potential step, the current varies between two limits corresponding to complete reversibility ([\alpha_0]_y=o \equiv 0, [a_j]_{j=1,...,n}=0).

Thus, during the anodic potential step, the current varies between two limits corresponding to complete reversibility ([\alpha_0]_y=o \equiv 0, [a_j]_{j=1,...,n}=0):

$$\frac{i(t)}{FC^0D^{1/2}} = \frac{1}{(\pi t)^{1/2}}$$

and complete irreversibility ([\alpha_0]_y=o \equiv 0, [a_j]_{j=1,...,n}=0):

$$\frac{i(t)}{FC^0D^{1/2}} = \frac{2n+1}{n+1} \frac{1}{(\pi t)^{1/2}}$$

In other words, the number of electrons per monomer passes from 1 to (2n+1)/(n+1), i.e., to 2 when n is large (not taking account of the additional charging of the polymer). The same is true in cyclic voltammetry.

Two types of calculations were performed for each mechanism. We first set all \lambda's equal to zero except \lambda_1, then all \lambda's were made equal to zero except \lambda_1 and \lambda_2, \lambda_3 was made equal to \lambda_1, finally all \lambda's were made equal to zero except \lambda_1, \lambda_2, and \lambda_3, and \lambda_2 and \lambda_1 were made equal to \lambda_1. The resulting R-kC0\theta curves are represented in parts Aa and Ba of Figure 4 for the CR-CR and CR-S-irr mechanisms, respectively, while the resulting R-kC0\theta curves are represented in Figure 5a for the CR-S-rev mechanism. The calculations could have been pursued for \lambda_1 = \lambda_2 = \lambda_3 = \lambda_4 and (\lambda_2)_p=0 and so forth, but we noticed that the R curves cease to vary appreciably in between the last two calculations (Figures 4Aa, Ba and 5a).

In the second series of calculations we apply the condition \lambda_1 \ll (\lambda_2)_p and considered the case where n \to \infty. That amounts to replacing the preceding sets of partial derivative equations, initial and boundary conditions, by the following ones.

**CR-CR**

$$\frac{\partial \alpha_0}{\partial t} = \frac{\partial^2 \alpha_0}{\partial y^2} + n \lambda_1 \alpha_1$$

$$\frac{\partial \alpha_1}{\partial t} = \frac{\partial^2 \alpha_1}{\partial y^2} - 2n \lambda_1 \alpha_1$$

**CR-S-irr**

$$\frac{\partial \alpha_0}{\partial t} = \frac{\partial^2 \alpha_0}{\partial y^2} + n \lambda_1 \alpha_0 \alpha_1$$

$$\frac{\partial \alpha_1}{\partial t} = \frac{\partial^2 \alpha_1}{\partial y^2} - 2n \lambda_1 \alpha_0 \alpha_1$$

**CR-S-rev**

$$\frac{\partial \alpha_0}{\partial t} = \frac{\partial^2 \alpha_0}{\partial y^2} + n \lambda_1 \alpha_0 \alpha_1$$

$$\frac{\partial \alpha_1}{\partial t} = \frac{\partial^2 \alpha_1}{\partial y^2} = 2n \lambda_1 \alpha_0 \alpha_1$$

Closed form solutions for the steady-state permeability P and the lag time L of a linear diffusion system with concurrent convection and reaction were obtained by two methods. In the first method, we identify the singularity at s = 0 of the Laplace transform of the total amount of diffusant, \Omega(t), released into the receiver as representation of the asymptotic diffusion behavior. P and L are then obtained from the time-independent coefficients of an expansion of \Omega(t) about s = 0. In the second method, we transform the convective–reactive diffusion equation into a form that contains only first and second derivatives of the concentration distribution function. By comparison of the resulting equation with that for a heterogeneous diffusion system, relationships of the convection velocity and rate constant with the position-dependent partition coefficient in heterogeneous diffusion is found. Taking advantage of the known solutions for permeability and lag time in heterogeneous diffusion, the corresponding expressions for P and L in convective–reactive diffusion are then obtained by transcription. These methods have the advantage over earlier approaches in that solutions in an infinite form are avoided.

**Introduction**

Diffusion plays an important role in numerous processes, such as chemical reactions in condensed phases,\textsuperscript{1} nucleation,\textsuperscript{2,3} nerve

**Calculation of Lag Time for Convective–Reactive Diffusion**

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(1) For a recent review, see: Hänggi, P.; Talkner, P.; Borkovec, M. Rev. Mod. Phys. 1990, 62, 251.
to transform the original convective–reactive diffusion equation into the form which contains only terms of first and second derivatives of the concentration distribution function. By comparison of the resulting diffusion equation with that for a heterogeneous diffusion system, relationships of the convection velocity and rate constant with the position-dependent partition coefficient in heterogeneous diffusion is found. Taking advantage of the known solutions for permeability and lag time in heterogeneous diffusion, the corresponding expressions for \( P \) and \( L \) in convective–reactive diffusion are then obtained by transcription.

**Laplace Transform Approach**

Consider a convective–reactive diffusion process taking place in a membrane extending from \( x = 0 \) to \( x = h \). The region \( x < 0 \) is designated as donor compartment, and the region \( x > h \) as receiver compartment. During an experiment, the concentration of diffusant in the donor is kept at a constant level, \( \rho_0 \), while that in the receiver is kept at zero. Thus, an "infinite constant supply and sink condition" is imposed. The membrane is void of diffusant at the onset of the experiment.

The mathematical description of the problem involves a diffusion equation of the form

\[
\frac{\partial}{\partial t} \rho(x,t) = D \frac{\partial^2 \rho(x,t)}{\partial x^2} - \alpha \frac{\partial \rho(x,t)}{\partial x} - \beta \rho(x,t)
\]

supplemented with the initial and boundary conditions

\[
\rho(x,0) = 0
\]

\[
\rho(0,t) = \rho_0
\]

\[
\rho(h,t) = 0
\]

Here, \( \rho(x,t) \) is the diffusant concentration at location \( x \) and time \( t \); \( D, \alpha, \) and \( \beta \) are the diffusivity, convective velocity, and rate constant of the first-order reaction, respectively. We assume that \( D, \alpha, \) and \( \beta \) are positive and constant. \( K(0) \) in eq 3 represents the partition coefficient characterizing the distribution of diffusant on both sides of the interface at \( x = 0 \) and accounts for the continuity of the diffusant's chemical potential at this interface. The foregoing linear differential equation with constant coefficients can effectively be solved by a Laplace transform technique. In the Laplace domain, eqs 1–4 take on the forms

\[
\tilde{\rho}(s) = \frac{D}{s} \tilde{\beta}(s,x,s) - \frac{\alpha}{s} \tilde{\beta}(s,x,s) - \beta \tilde{\beta}(s,x,s)
\]

\[
\tilde{\beta}(0,s) = \rho_0 K/s
\]

\[
\tilde{\beta}(h,s) = 0
\]

Here, \( \tilde{\beta}(s) \) is a Laplace transform of \( \beta(x,t) \) and its corresponding form is

\[
\tilde{\beta}(s) \equiv L[\beta(x,t)] \equiv \int_0^\infty \exp(-st)\beta(x,t) \, dt
\]

where \( s \) is a Laplace variable. Note that the initial condition (2) has been incorporated into eq 5, and the partial differential equation has been transformed into an ordinary differential equation. The solution to eqs 5–7 is found to be

\[
\tilde{\beta}(s) = \frac{\rho_0 K}{s} \exp \left( \frac{ux}{2D} \right) \frac{\sinh q(h-x)}{q \sinh qh}
\]

with

\[
q = \sqrt{(\alpha/2D)^2 + (s + \beta)/D}
\]

An experimentally measurable quantity, \( Q(t) \), the total amount of diffusant released into the receiver within time \( t \), is defined as

\[
Q(t) = \int_0^t J(h,r) \, dr = -\int_0^t \int \left[ D \frac{\partial \rho(x,t)}{\partial x} - \alpha \rho(x,t) \right] \, dx \, dr = -\int_0^t \int \left[ D \frac{\partial \rho(x,t)}{\partial x} \right] \, dx \, dr
\]

The lag time in simple homogeneous diffusion assumes a value of \( h^2/6D \), where \( D \) is the diffusivity, and \( h \) the length of the diffusive path (thickness of membrane, etc.). Expressions for lag times have also been derived for more complex systems. For instance, Jaeger, by employing a Laplace transform, gave a routine (instead of an explicit expression) for the calculation of the lag time for thermal conduction across a multilayer slab. His procedure was followed by Barrie et al. to calculate the lag time for mass diffusion in a three-layer slab. The pioneering work of Frisch and Rosenberger have recently extended the treatment to diffusion systems with serial and/or parallel paths and multiple and periodic laminates. Earlier, employing Frisch's concept, Petro- poulos and Roussis studied the lag time in diffusion systems with time- and position-dependent anomalies and the "directional diffusion lag time asymmetry."
where \( J(h,t) \) is the diffusion flux into the receiver, and the boundary condition (4) has been used. The Laplace transform of \( Q(t) \) in eq 11 acquires the form

\[
\hat{Q}(s) = -\frac{D}{s} \left[ \frac{\partial}{\partial \xi} \theta(x,s) \right]_{x=h}
\] (12)

On substituting eq 9 into eq 12, one obtains

\[
\hat{Q}(s) = \frac{\rho_0 DK}{s^2} \exp \left( \frac{v h}{2D} \right) \csc \text{h} \left( \frac{q h}{D} \right)
\] (13)

In general, the total release \( Q(t) \) in a linear diffusion system subject to an infinite constant supply and sink condition consists of two parts: (1) The transient part, which decays with time eventually to zero, is a linear combination of terms in the form of \( \exp(-\lambda_i t) \), where the \( \lambda_i \)'s are the eigenvalues of the Sturm-Liouville differential equation associated with the method of separation of variables.\(^9\) (2) The long-time asymptotic limit, which depends linearly on \( t \), defines the permeability \( P \) and lag time \( L \), respectively, as the slope of the asymptote and its intercept with the time axis. A combination of these two parts together gives \( Q(t) \) in terms \( P \) and \( L \) as

\[
Q(t) = \rho_0 P(t - L) + \sum_{i=1}^{\infty} c_i \exp(-\lambda_i t)
\] (14)

To obtain explicit expressions for \( P \) and \( L \), we take the Laplace transformation of \( Q(t) \) in eq 14:

\[
\hat{Q}(s) = \frac{\rho_0 P}{s} - \frac{\rho_0 PL}{s} + \sum_{i=1}^{\infty} \frac{c_i}{s + \lambda_i}
\] (15)

Equations 13 and 15 are different expressions for the same entity. Equation 13 contains the parameters \( D, v, \) and \( \kappa \) to characterize the convective-reactive diffusion, while eq 15 contains \( P \) and \( L \) to characterize its asymptotic behavior. Thus one can deduce relations of \( P \) and \( L \) with \( D, v, \) and \( \kappa \) from the following consideration. Note that \( \hat{Q}(s) \) possesses a pole at \( s = 0 \), and an infinite number of poles at \( s = -\lambda_i \). The pole at \( s = 0 \) is of second order and accounts for the asymptotic part. The rest of the poles, on the other hand, account for the transient part. To obtain expressions for \( P \) and \( L \), the singularity at \( s = 0 \) is removed by multiplying eq 18 by \( s^3 \) to obtain

\[
s^3 \hat{Q}(s) = \rho_0 P - \rho_0 PL s + \sum_{i=1}^{\infty} \frac{s^3 c_i}{s + \lambda_i}
\] (16)

In the infinitesimal neighborhood around \( s = 0 \), where the asymptotic part dominates, \( s^3 \hat{Q}(s) \) acquires the form of a Taylor series (instead of a Laurent expansion as in eq 15). Accordingly

\[
\rho_0 P = \lim_{s \to 0} s^3 \hat{Q}(s)
\] (17)

\[
\rho_0 PL = \frac{\partial}{\partial s} \left. s^3 \hat{Q}(s) \right|_{s=0}
\] (18)

On substituting eq 13 into eqs 17 and 18, one obtains

\[
P = \frac{DK}{h} \left[ \exp \left( \frac{v h}{2D} \right) \sqrt{\frac{v}{2D} + \frac{\kappa}{D}} \right] \text{csch} \left( \sqrt{\frac{v}{2D} + \frac{\kappa}{D}} \right)
\] (19)

\[
L = \frac{h^2}{6D} \left[ \frac{\text{coth} \left( \sqrt{\frac{v}{2D} + \frac{\kappa}{D}} \right)}{\sqrt{\frac{v}{2D} + \frac{\kappa}{D}}} - \frac{1}{\left[ \frac{v}{2D} + \frac{\kappa}{D} \right]^2} \right]
\] (20)

Thus, we have derived expressions for \( P \) and \( L \) in convective-reactive diffusion without resorting to any solutions in forms of infinite series. All manipulations were performed in closed form. The advantage of using a Laplace transform in the formulation of \( P \) and \( L \) results from the fact that the asymptotic part corre-
Lag Time for Convective-Reactive Diffusion

\[ g(x) = A \exp \left( \frac{v - \sqrt{v^2 + 4xh}}{2D} \right) \]

(31)

where \( A \) is a constant to be determined. Without loss of generality, we set \( A = 1 \), which, in turn, implies that the boundary conditions for \( g(x) \) in eq 23 are

\[ g(0) = 1 \]

(32)

\[ g(h) = \exp \left( \frac{v - \sqrt{v^2 + 4xh}}{2D} \right) \]

(33)

On substituting the boundary conditions (32) and (33) into eqs 2-4, one sees that \( f(x,t) \) in eq 24 possesses the same initial and boundary conditions as \( \rho(x,t) \). Specifically

\[ f(x,0) = 0 \]

(34)

\[ f(0,t) = K \rho_0 \]

(35)

\[ f(h,t) = 0 \]

(36)

Substitution of \( g(x) \) in eq 31 with \( A = 1 \) into eq 29 yields

\[ K(x) = B \exp \left( \frac{\sqrt{v^2 + 4xh}}{2D} \right) \]

(37)

At the interface \( x = 0 \), the partition coefficient \( K \) is given by eq 35 and, thus, from eq 37, \( B = K \). As a result, the partition coefficient for the \( f \) diffusant in heterogeneous diffusion takes on the position-dependent form

\[ K(x) = K \exp \left( \frac{\sqrt{v^2 + 4xh}}{2D} \right) \]

(38)

To obtain relations for the permeability and lag time in convective-reactive diffusion, we compare the time development of the total diffusant released into the receiver in the long-time limit for a \( \rho \) diffusant, \( Q^\rho(t) \), with that of an \( f \) diffusant, \( Q^f(t) \). This yields

\[ Q^\rho(t) = \int_0^t f^\rho(h,\tau) \, d\tau = \int_0^\tau \left[ -D \frac{\partial}{\partial x} \rho(x,\tau) + \right. \]

\[ v \rho(x,\tau) \bigg|_{x=h} \right. \, d\tau = \int_0^\tau \left[ -D \frac{\partial}{\partial x} \rho(x,\tau) \bigg|_{x=h} \right. \, d\tau \]

(39)

where the boundary condition (4) is used and \( f^\rho(x,t) \) denotes the diffusion flux (at location \( x \) and time \( t \)). Substitution of eq 21 into eq 39, with the help of eq 36, yields then

\[ Q^\rho(t) = \int_0^t g(x) \frac{\partial f(x,t)}{\partial x} \bigg|_{x=h} \, d\tau = \exp \left( \frac{v - \sqrt{v^2 + 4xh}}{2D} \right) \int_0^\tau - \left. \frac{\partial}{\partial x} \frac{f(x,\tau)}{2D} \bigg|_{x=h} \right. \, d\tau \]

\[ = \exp \left( \frac{v - \sqrt{v^2 + 4xh}}{2D} \right) Q^\rho(\tau) \]

(40)

This simple proportionality relationship between \( Q^\rho(t) \) and \( Q^\rho(t) \) holds for any \( t > 0 \). Specifically, in the long-time limit, we have

\[ \lim_{t \to \infty} Q^\rho(t) = \rho_0 \rho^\rho(t - L^\rho) = \]

\[ \exp \left( \frac{v - \sqrt{v^2 + 4xh}}{2D} \right) \lim_{t \to \infty} Q^\rho(t) = \]

\[ \rho_0 \exp \left( \frac{v - \sqrt{v^2 + 4xh}}{2D} \right) p^\rho(t - L^\rho) \]

(41)

which indicates that

\[ p^\rho(t) = \exp \left( \frac{v - \sqrt{v^2 + 4xh}}{2D} \right) \rho^\rho(t) \]

(42)

\[ L^\rho = L^\rho(t) \]

(43)

Expressions for the permeability and lag time in heterogeneous diffusion, in which both the diffusivity and partition coefficient are position dependent, have been derived previously. For constant diffusivity the expressions are

\[ P = \left\{ \int_0^h \frac{1}{DK(x)} \, dx \right\}^{-1} \]

(44)

\[ L = \left\{ \int_0^h \frac{1}{DK(x)} \, dx \right\}^{-1} K(x) \times \]

\[ \left\{ \int_0^x \frac{1}{DK(x')} \, dx' \int_0^h \frac{1}{DK(x')} \, dx \right\} \, dx \]

(45)

On substitution of eq 38 for \( K(x) \) into eqs 44 and 45 one obtains for the permeability for the \( f \) diffusant and lag time for the \( f \) and \( \rho \) diffusants

\[ P^f = K \sqrt{v^2 - 4Dh} \left\{ 1 - \exp \left( -\frac{\sqrt{v^2 - 4Dh}}{h} \right) \right\}^{-1} \]

(46)

\[ L^f = L^\rho = \]

\[ \frac{h^2}{6D} \left[ \frac{\coth \left( \sqrt{\frac{v^2}{2D} + \frac{k}{D}} h \right)}{\sqrt{\frac{v^2}{2D} + \frac{k}{D}} h} \right] \]

(47)

Substitution of eq 46 into eq 42 results then in

\[ p^f = \exp \left( \frac{v - \sqrt{v^2 - 4xh}}{2D} \right) K \sqrt{v^2 - 4Dh} \times \]

\[ \left\{ 1 - \exp \left( -\frac{\sqrt{v^2 - 4Dh}}{h} \right) \right\}^{-1} \]

\[ \frac{DK(x)}{h} \left\{ \exp \left( \frac{v - \sqrt{v^2 - 4xh}}{2D} \right) K \sqrt{v^2 - 4Dh} \right\} \left[ \frac{1}{\sqrt{\frac{v^2}{2D} + \frac{k}{D}} h} \right] \]

(48)

As expected, \( P \) and \( L \) obtained through the change of variables are identical to those resulting from Laplace transform, eq 20.

Discussion

The system dealt with above represents a prototype interplay between convection, reaction, and diffusion processes, of which convective diffusion, reactive diffusion, and simple diffusion systems are special cases. Hence, \( P \) and \( L \) for each subsystem should be derivable from our general expressions. For reactive diffusion, with \( \nu = 0 \) eqs 48 and 47 respectively give

\[ P = \frac{DK}{h} \sqrt{k/Db} \coth (\sqrt{k/Db}) \]

(49)

\[ L = \frac{h^2}{6D} \left[ \frac{\coth (\sqrt{k/Db})}{\sqrt{k/Db}} - \frac{1}{(\sqrt{k/Db})^2} \right] \]

(50)

Equation 50 was derived earlier by Leypoldt and Gough using a finite Fourier transform.

For convective diffusion, we chose, for comparison, an iontophoresis (electrodiffusion) system, in which an constant external
The convection velocity in this case is

\[ v = \frac{DZFE}{RT} \quad (51) \]

where \( Z \) is the valence of the ions, \( F \) the Faraday constant, \( R \) the universal gas constant, and \( T \) the absolute temperature. Substitution of eq 51 into eqs 48 and 47 with \( \kappa = 0 \) results in the solution obtained by Keister and Kasting:26

\[ P = \frac{DK}{h} \left( \sqrt{\frac{ZFE}{2RT}h} \cosh \left( \frac{ZFE}{2RT}h \right) \right) \] \[ (52) \]

\[ L = \frac{h^2}{6D} \left\{ \frac{\text{coth} \left( \frac{ZFE}{2RT}h \right)}{\left( \frac{ZFE}{2RT}h \right)^2} - \frac{1}{\left( \frac{ZFE}{2RT}h \right)^3} \right\} \] \[ (53) \]

With respect to simple diffusion, which corresponds to \( v = 0 \) and \( \kappa = 0 \), both eqs 47 and 48 yield indeterminate forms of \( 0/0 \). This difficulty, however, can be removed by applying the following series expansion:28

\[ x \cosh x = 1 - \frac{x}{6} + \frac{7x^3}{360} - ... \] \[ (54) \]

\[ x \coth x = 1 + \frac{x^2}{3} - \frac{x^4}{45} + ... \] \[ (55) \]

Substitution of eq 54 into eq 48 and eq 55 into eq 47, respectively, and taking the limit \( x \to 0 \), the well-known expressions \( P = KD/h \) and \( L = h^2/6D \) are recovered.

As revealed by eq 47, \( L \) is symmetric with respect to the direction (or the sign) of the convection velocity \( v \) and is independent of the partition coefficient \( K \). The reciprocity of the lag time in a general convective-reactive diffusion has been proved mathematically in terms of the symmetry of the related Green's function with respect to the exchange of coordinate variables.29 On the other hand, according to eq 48, \( P \) is proportional to \( K \) and asymmetric with respect to the direction of \( v \). Thus the permeabilities for forward and reverse direction, \( P^{+} \) and \( P^{-} \), can be related as

\[ \ln \left( \frac{P^{+}}{P^{-}} \right) = \frac{v h}{D} \] \[ (57) \]

which results from eq 48 on altering the sign of \( v \). In the iontophoresis experiment, eq 57 can be transformed with eq 51 to

\[ h = \frac{RT}{ZFE} \ln \left( \frac{P^{+}}{P^{-}} \right) \] \[ (58) \]

This relation can be used to determine the thickness of the membrane from the measurement of \( P^{+} \) and \( P^{-} \).

Siegel30 also used a Laplace transform, though in a different approach, to derive a lag time expression for a diffusion system governed by a linear equation with source terms. He obtained, written in our notation

\[ L = -\frac{d}{ds} \left[ \frac{sJ(s)}{J_r} \right]_{s=0} \] \[ (59) \]

where \( J \) is the steady-state diffusion flux. With \( J = \rho_0 P \) and \( J(s) = sQ(s) \), eq 59 is essentially identical to our eq 18.

The expression for lag time in eq 47 also reveals an interesting formal similarity between diffusion lag time and electric polarization. With eq 56, eq 47 can be rewritten to

\[ L(y) = \frac{h^2}{6D} \left( L(y) \right) \] \[ (60) \]

where \( L(y) \) is the Langevin function encountered in the theory of induced electric polarization. Though the connection between these two physical entities may be remote, eq 60 is still useful for mnemonic purposes.

In conclusion, we have obtained closed form solutions for the permeability and lag time of a diffusion system with convection and reaction. The Laplace transform and change-of-variables techniques have the advantage over earlier approaches that involve explicitly solving the relevant diffusion equation and manipulating the solution (usually in the form of infinite series) into a closed form. However, there is no guarantee that closed forms for lag time can be extracted from such infinite series solutions.29

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(30) Siegel, R. A. J. Membr. Sci. 1986, 26, 251. Note that eq 9 of this reference is dimensionally incorrect and should be read as eq 59 in this work.