An Analysis of Carrier-Facilitated Transport

The physical and mathematical characteristics of carrier-facilitated transport in a liquid film are examined for a reaction scheme of the form $A + B \rightleftarrows AB$, in which A is the permeating species and B and AB are diffusable species which are constrained not to leave the film. For thin films, a solution is developed as a perturbation from purely physical diffusion and is expressed as a second-order power series. For thick films, a solution is developed as a perturbation from a state in which the species concentrations at any one point within the film are related by an equilibrium constraint. This development utilizes the techniques of matched asymptotic analysis. Taken together, these solutions provide an excellent estimate of the facilitation for a film of any thickness, as shown by comparison with numerical results.

KENNETH A. SMITH
JERRY H. MELDON
and CLARK K. COLTON

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

SCOPE

Carrier-facilitated transport has attracted considerable recent attention from those who are interested in its role in life processes (Scholander, 1960; Hemmingsen, 1963; Wyman, 1966; Kotyk and Janacek, 1970; Kreuzer, 1970; Wittenberg, 1970) and from those who view it as an adjunct to commercial membrane separation processes (Ward and Robb, 1967; Ward, 1970). An attractive model system is provided by a stationary liquid film which contains a reactive carrier molecule, this molecule being mobile within the film but incapable of leaving it. The permeating species may move through the film in either the free state or in the complexed form, and the flux may be considerably in excess of that possible with purely physical diffusion of the free molecule. A notable example is the oxygen-hemoglobin system, in which some of the oxygen may be transported as oxyhemoglobin. The analytical problem is to predict the magnitude of this increase in flux.

For the situation described above, the governing differential equations are easily stated; but even simple reactions can present nonlinear kinetics, and general solutions therefore remain unavailable. Approximate analytical solutions are readily developed if the kinetic rate expression may be linearized in terms of small departures from a single state of chemical equilibrium in which the net reaction rate is zero. Such solutions are available both for the problem as stated here (Friedlander and Keller, 1965; Blumenthal and Katchalsky, 1969) and for the formally identical heat transfer analog (Brokaw, 1961; Brian and Reid, 1962). In either case, the forward reaction predominates in one-half of the film and the reverse reaction in the other half. Chemical equilibrium exists only at the mid-plane of the film, and concentration (or temperature) profiles are symmetric about this point. If the departures from any single equilibrium state are not particularly small, but the reaction rate is sufficiently fast, then one may obtain a simple solution in the manner of Olander (1960) by assuming that the reaction is at equilibrium at every point in the film. The works of Goddard et al. (1970) and Kreuzer and Hoofd (1972) are useful in defining the conditions of applicability for this assumption and for quantitatively assessing the magnitude of small departures from that solution. At the opposite extreme, the assumption that the carrier concentration is uniform throughout the film, as might be expected if the reaction is very slow, leads to the solution developed by Ward (1970).

Analytical solutions have thus been developed by various techniques and each has proved useful. However, no coherent framework has existed heretofore by which the applicability of each technique may be assessed for a given situation. Numerical analyses are free of these uncertainties, but they tend to be very specific in nature because the nondimensional flux is a function of four other nondimensional groups, and this makes it very difficult to extract general conclusions.

This paper develops approximate analytical solutions which are asymptotically exact and correspond to films which are either very thick or very thin. The ratio of reaction rate to diffusion rate increases with film thickness, and the terms thick and thin should be understood in that sense rather than as a measure of physical dimension. It is shown that, in the limit, the thick film case satisfies the assumption of reaction equilibrium at each point within the film, and the thin film case reduces to purely physical diffusion. Most important, the two cases are developed in enough detail to permit easy interpolation between them, thus permitting reasonably accurate flux predictions for films of any thickness. Each of the previously existing solutions is found to arise naturally within this framework, and the conditions for validity for each are readily established.

CONCLUSIONS AND SIGNIFICANCE

Analytical techniques are presented for the purpose of providing a simple quantitative estimate of the facilitation. The techniques are applied to the transport of a species A through a stationary liquid film, given that a reaction of the form

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB$$

Correspondence concerning this paper should be addressed to K. A. Smith.

occurs in the film and that the diffusible species B and AB are not free to leave the film. This example was chosen because it is both simple and of considerable interest in its own right; the techniques, however, could also have been applied to other specific kinetic schemes.

For thin films, a solution for the flux is obtained as a power series in the square of the film thickness. The leading term of that series corresponds to purely physical diffusion and the higher order terms describe the effect of chemical reaction. The first of these higher order terms is consistent with Ward's (1970) constant carrier concentration solution. For thick films, a very different procedure is used to describe deviations from a state in which the reaction is at equilibrium at each point in the film. In this case, however, the method of matched asymptotic analysis is found to be particularly well-suited to the nature of the problem. The result is obtained as a set of algebraic equations which satisfy the equilibrium assumption if the film is infinitely thick, but which also describe all effects causing deviations from that assumption and varying (for $L \to \infty$) as either the first or the second power of the reciprocal of the film thickness. Furthermore, it is shown that effects which vary as the reciprocal of the film thickness are physically identified with diffusion boundary layers which form at both faces of the film and which largely account for deviations from concentration profiles for which the reaction is at equilibrium at each point in the film.

The utility of these methods for a film of arbitrary thickness is shown in Figures 2 to 5, where comparison is made with the numerical results of Kutchai et al. (1970). The thin film and thick film analyses approach each other, and the analytical and numerical solutions are in essentially complete accord. The authors have also generated numerical solutions for the purpose of testing the analytical results over a wide range of parameter values. In all cases, the agreement is excellent and the results of one such test are shown in Figures 6 and 7. Thus, the thin film analysis and the thick film analysis together provide a comprehensive framework, both for the quantative prediction of flux facilitation and for a perspective as to the role of previously existing analyses.

The effect of chemical reaction upon heat or mass transfer rates has become a rather venerable topic, the quantitative understanding of which has been subject to active investigation since the pioneering work of Hatta (1928). The distinct topics of energy and mass transport augmentation in films seem to have developed largely independently and without the benefit of interaction with each other, despite the fact that the two are often formally identical, and independent approximate solutions to the present problem have been produced in both contexts (Brokaw, 1961; Brian and Reid, 1962; Friedlander and Keller, 1965; Blumenthal and Katchalsky, 1969).

With respect to either the energy transport problem or the mass transport problem, the following seems to have been unambiguously established:

1. If the driving force is sufficiently small, so as to permit linearization of the reaction rate expression in terms of small departures from a single equilibrium state (hereafter referred to as a single-point linearization), the above mentioned solutions are applicable.
2. If the reaction rate is in some sense fast, then one may assume reaction equilibrium to exist at each point in the film. This yields an equilibrium solution (Olander, 1960) which is valid if the film is sufficiently thick (Goddard et al., 1970).
3. The method of matched asymptotic expansions not only provides assurance that the equilibrium solution is a valid asymptotic limit, but it also provides the tools for expansions about that condition (Goddard et al., 1970; Kreuzer and Hoofd, 1970, 1972).

The remaining problem of real interest is the nonlinear, nonequilibrium, large driving force situation for which only numerical solutions are currently well-developed (Ward, 1970; Kutchai et al., 1970). For very thick films, the reaction may be regarded as fast and the method of matched asymptotic analysis is, in one form or another, the candidate of choice for an attack on the problem. For thin films, a more conventional perturbation procedure should suffice. By virtue of the authors' present motivations, the analysis which follows is cast in terms of mass transfer facilitation. Much of this work was reported earlier in a more preliminary fashion (Smith et al., 1971).

THEORY

Consider the reaction

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB \tag{1}$$

as occurring in a film of thickness L. The species B and AB are mobile within the film but constrained not to leave it. The primary task is to predict the flux of A, given the driving force ΔC_A. Following Ward (1970) and using his nomenclature, the governing relations are

$$D_A \frac{d^2C_A}{dx^2} = k_1\, C_A C_B - k_2\, C_{AB} \tag{2}$$

$$D_B \frac{d^2C_B}{dx^2} = k_1\, C_A C_B - k_2\, C_{AB} \tag{3}$$

$$D_{AB} \frac{d^2C_{AB}}{dx^2} = -\, k_1\, C_A C_B + k_2\, C_{AB} \tag{4}$$

subject to

$$x = 0 \;;\quad C_A = C_A{}^o \tag{5}$$

$$x = L \;;\quad C_A = C_A{}^L \tag{6}$$

$$x = 0, L; \quad \frac{dC_B}{dx} = 0 \tag{7}$$

$$x = 0, L; \quad \frac{dC_{AB}}{dx} = 0 \tag{8}$$

$$\int_0^L (C_B + C_{AB})dx = C_T L \tag{9}$$

As pointed out by Goddard et al. (1970), the last constraint does not imply overspecification because not all of the preceding boundary conditions may be regarded as independent.

It will further be assumed here that $D_B = D_{AB}$. This constraint is often not serious because the carrier molecule (B) is usually large compared to the molecule with which it reacts (A), for example, hemoglobin and oxygen, so that B and AB are of nearly equal size. If Equations (3) and (4) are summed and integrated twice, application of Equations (7), (8), and (9) yields

$$C_B + C_{AB} = C_T \qquad (10)$$

This permits Equations (2) and (3) to be rewritten as

$$D_A \frac{d^2C_A}{dx^2} = k_1\, C_AC_B + k_2\, C_B - k_2\, C_T \qquad (11)$$

$$D_B \frac{d^2C_B}{dx^2} = k_1\, C_AC_B + k_2\, C_B - k_2\, C_T \qquad (12)$$

Similarly, Equations (2) and (3) may be differenced and integrated to yield

$$D_A \frac{dC_A}{dx} - D_B \frac{dC_B}{dx} = a_1 \qquad (13)$$

so that the flux of A is given by $-a_1$. After a second integration, this becomes

$$D_A\, C_A - D_B\, C_B = a_1\, x + a_2 \qquad (14)$$

The following developments will utilize either Equations (11) and (14) or Equations (12) and (13). In either event, the boundary conditions are represented by Equations (5), (6), and (7). Within this framework, Equations (4), (8), and (9) are redundant.

An order of magnitude estimate for each of the terms appearing in either Equation (11) or (12) suggests that, for very thick films, the left-hand side will vary more or less inversely with L^2, at least within the core of the film, and thus as $L \to \infty$ it will eventually be small compared to two or more of the terms on the right, each of which is only weakly dependent on L (at a fixed x/L). In this sense, then, the diffusional term may be neglected for sufficiently thick films because it is small compared with both the forward and the reverse reaction rates, leading to the well-known equilibrium solution (Olander, 1960). Conversely, for sufficiently thin films, the value of the right-hand side is irrelevant because it is integrated over such a short interval (L) as to make no impact upon either dC_A/dx or C_A. For this reason, the reaction rate may ultimately be neglected and the process becomes one of purely physical diffusion.

THIN FILMS

Since purely physical diffusion is expected to predominate in the limit as $L \to 0$, it is reasonable to construct a power series expansion in L for C_A, C_B, and a_1 such that the leading term represents the solution for the usual nonreactive case. Further, if the foregoing equations and boundary conditions are rewritten in terms of ζ, where

$$\zeta = 2\frac{x}{L} - 1 \qquad (15)$$

it is found that L appears only as its square; and the expansion parameter should therefore contain L^2 rather than L. This, then, suggests expansions which are of the form:

$$C_A = \overline{C}_A - \frac{1}{2}\zeta\Delta C_A + \Delta C_A\, \{\epsilon\, f_1(\zeta) + \epsilon^2\, f_2(\zeta) + \epsilon^3\, f_3(\zeta) + \ldots\} \qquad (16)$$

$$C_B = \frac{k_2\, C_T}{k_1\, \overline{C}_A + k_2} + \frac{D_A}{D_B}\Delta C_A\, \{g_0(\zeta) + \epsilon g_1(\zeta) + \epsilon^2 g_2(\zeta) + \epsilon^3 g_3(\zeta) + \ldots .\} \qquad (17)$$

$$\frac{-a_1 L}{D_A\, \Delta C_A} = 1 + F = 1 + \epsilon\,\gamma_1 + \epsilon^2\gamma_2 + \epsilon^3\gamma_3 + \ldots . \qquad (18)$$

where

$$\overline{C}_A = \frac{C_A{}^o + C_A{}^L}{2} \qquad (19)$$

$$\Delta C_A = C_A{}^o - C_A{}^L \qquad (20)$$

and

$$\epsilon = \frac{1}{12}\, \frac{k_2 L^2}{D_A}\, \frac{k_1 C_T}{k_1\, \overline{C}_A + k_2} \qquad (21)$$

The leading term in the expansion for C_B corresponds to a state in which C_B is constant and in equilibrium with $\overline{C}_A$. That this should be a valid limit for $L \to 0$ is perhaps not immediately obvious, and for this reason $g_0(\zeta)$ is included in the expansion and subsequently shown to be zero. Apart from the L^2 dependency, the form of ϵ clearly benefits from hindsight.

If one now makes the appropriate substitutions, retains only first- and second-order terms, and equates powers of epsilon, then from Equation (12) one finds

$$g_1'' = -\frac{3}{2}\zeta + 3\frac{D_A}{D_B}\, \frac{k_1\overline{C}_A + k_2}{k_1k_2C_T}\left(k_1\overline{C}_A + k_2 - \frac{1}{2}\, k_1\, \zeta\Delta C_A\right)g_0 \qquad (22)$$

$$g_2'' = 3 f_1 + 3\frac{D_A}{D_B}\, \frac{k_1\overline{C}_A + k_2}{k_1k_2C_T}\left(k_1\overline{C}_A + k_2 - \frac{1}{2}\, k_1\, \zeta\Delta C_A\right)g_1 + 3\frac{D_A}{D_B}\, \frac{k_1\overline{C}_A + k_2}{k_2C_T}\,\Delta C_A g_0 f_1 \qquad (23)$$

and from Equation (13)

$$g_0' = 0 \qquad (24)$$

$$2 f_1' - 2 g_1' = -\gamma_1 \qquad (25)$$

$$2 f_2' - 2 g_2' = -\gamma_2 \qquad (26)$$

subject to

$$\zeta = \pm 1; \quad f_1 = f_2 = 0 \qquad (27)$$

$$\zeta = \pm 1; \quad g_0' = g_1' = g_2' = 0 \qquad (28)$$

where primes indicate differentiation with respect to ζ.

The solution is found to be

$$g_0(\zeta) = 0 \qquad (29)$$

$$g_1(\zeta) = -\frac{1}{4}\zeta^3 + \frac{3}{4}\zeta + \frac{1}{10}\, \frac{k_1\Delta C_A}{k_1 C_A + k_2} \qquad (30)$$

$$f_1(\zeta) = -\frac{1}{4}\zeta^3 + \frac{1}{4}\zeta \qquad (31)$$

$$\gamma_1 = 1 \qquad (32)$$

$$\gamma_2 = -\frac{1}{5}\left\{1 + 6\frac{D_A}{D_B}\, \frac{(k_1\overline{C}_A + k_2)^2}{k_1k_2C_T} - \frac{1}{2}\, \frac{D_A}{D_B}\, \frac{(k_1\Delta C_A)^2}{k_1k_2C_T}\right\} \qquad (33)$$

Solutions for $f_2(\zeta)$ and $g_2(\zeta)$ are not listed because, at this level of approximation, they are known only to within an unspecified additive constant.

This result may be compared with that obtained by Ward (1970) under the assumption that the reaction is "sufficiently slow that the concentrations of B and AB are essentially constant throughout the film." In terms of the present notation, Ward found

$$C_B = \frac{k_2 C_T}{k_1 \bar{C}_A + k_2} \tag{34}$$

and

$$-\frac{a_1 L}{D_A \Delta C_A} = \frac{\sqrt{3\epsilon}}{\sinh 2\sqrt{3\epsilon}} [1 + \cosh 2\sqrt{3\epsilon}] \tag{35}$$

or, for $\epsilon \rightarrow 0$,

$$-\frac{a_1 L}{D_A \Delta C_A} \cong 1 + \epsilon - \frac{1}{5}\epsilon^2 + \ldots . \tag{36}$$

Thus to zeroth order in epsilon, the present solution for C_B is the same as Ward's and the solution for the flux is the same to first order. Similarly if the result of a single-point linearization, such as that due to Friedlander and Keller (1965), is expressed in equivalent terms, it assumes the form

$$-\frac{a_1 L}{D_A \Delta C_A} = 1 + \epsilon - \frac{1}{5}\left[1 + 6\frac{D_A}{D_B}\frac{(k_1 C_A + k_2)^2}{k_1 k_2 C_T}\right]\epsilon^2 + \ldots . \tag{37}$$

in this limit, and is likewise correct to first order. Clearly, neither the single-point linearization nor the constant carrier concentration hypothesis produces a result which is correct to second-order. More importantly, the present solution incorporates a criterion for its own validity; that is, the first-order approximation to Equation (18) is valid if $\epsilon^2\gamma_2 << \epsilon\gamma_1$ where ϵ and γ_2 are given by Equations (21) and (33), and γ_1 is unity.

THICK FILMS

Whereas the thin film ($L \rightarrow 0$) problem treated above yielded quite readily to an ordinary power series analysis, very different techniques prove most useful for the thick film ($L \rightarrow \infty$) limit. In the latter case, the analysis is conveniently executed in terms of Equations (11) and (14), and, as discussed earlier, it is expected that the diffusion term on the left-hand side of Equation (11) will play a subordinate role. It is, therefore, the highest order derivative which is apparently small, and phenomena of a boundary layer character may be anticipated. If, for now, one ignores that possibility and neglects the diffusion term, Equations (11) and (14) become

$$\hat{C}_B = \frac{k_2 C_T}{k_1 \hat{C}_A + k_2} \tag{38}$$

and

$$D_A \hat{C}_A - D_B \frac{k_2 C_T}{k_1 \hat{C}_A + k_2} = a_1 x + a_2 \tag{39}$$

where the hat notation is used to denote solutions for C_A and C_B which are obtained by the use of Equations (38) and (39). It is useful to note that, as expected, Equation (38) requires $\hat{C}_A$ to be in equilibrium with $\hat{C}_B$ at each point in the film because the diffusion term in Equation (11) has been discarded, leaving only the forward and reverse reaction rate terms. However, $\hat{C}_A$ and $\hat{C}_B$ do not constitute a single equilibrium pair, but rather they each vary with position in the film, as is required by Equation (39). Unfortunately, this solution cannot, in general, satisfy all of the boundary conditions. If a_1 and a_2 are used to satisfy the boundary conditions on C_A, then the solution will ordinarily violate the boundary conditions on C_B. In fact, $d\hat{C}_B/dx$ will be found to vary as $1/L$ at any fixed x/L, including $x/L = 0$ and $x/L = 1$, and thus will not vanish for finite L. Near the film surfaces, a proper solution for C_B (and C_A) is therefore expected to differ from $\hat{C}_B$ (and $\hat{C}_A$) by a quantity which (in the limit $L \rightarrow \infty$) varies as $1/L$, so as to enforce the constraint that the gradient of C_B vanish there. It will also be recalled that neglected diffusional effects within the core of the film are expected to vary as $1/L^2$, and in this region a proper solution will be expected to differ from $\hat{C}_B$ (and $\hat{C}_A$) by a term which varies in that way.

As $\hat{C}_A$ and $\hat{C}_B$ are seen to differ from proper solutions by quantities which become ever smaller as the film becomes thicker, it is useful to set

$$C_A = \hat{C}_A + \delta c_a \tag{40}$$

$$C_B = \hat{C}_B + \delta c_b \tag{41}$$

so that δc_a and δc_b are perturbations from a solution which has an equilibrium character, rather than being perturbations from a single equilibrium state. Now, Equation (14) requires

$$\delta c_b = \frac{D_A}{D_B}\delta c_a \tag{42}$$

and Equation (11) becomes

$$\frac{d^2\hat{C}_A}{dx^2} + \frac{d^2}{dx^2}(\delta c_a) = \frac{1}{\lambda^2}(\delta c_a) + \frac{k_1}{D_B}(\delta c_a)^2 \tag{43}$$

where

$$\frac{1}{\lambda^2} = \frac{k_1 \hat{C}_A + k_2}{D_B} + \frac{k_1 k_2 C_T}{D_A (k_1 \hat{C}_A + k_2)} \tag{44}$$

Equation (43) contains a length scale λ such that the film may be regarded as thick if $\lambda/L << 1$, in which case the character of Equation (43) is quite different near $x = 0$ or $x = L$ (that is, within the boundary layers) than it is in the core. Consequently, it is well-suited to solution by the method of matched asymptotic expansions; and, in what follows, this technique will be used to develop separate approximate solutions for the region near $x = 0$, for the region near $x = L$, and for the core.

If one is content with a first approximation to δc_a, Equation (43) may be further simplified. In particular, it has already been noted that δc_a will at most vary as $1/L$ and that $d^2\hat{C}_A/dx^2$ varies as $1/L^2$. Clearly, as $L \rightarrow \infty$, terms which vary as $1/L$ will ultimately dominate over terms which vary as $1/L^2$, quite irrespective of the relevant proportionality factors. In this sense, we will henceforth speak of terms as being of order $1/L$ or of order $1/L^2$, without first rendering the terms nondimensional. Thus, near $x = 0$, and to order $1/L$, Equation (43) may be written as

$$\frac{d^2}{dx^2}[\delta c_a] = \frac{1}{\lambda_0^2}[\delta c_a] \tag{45}$$

where λ_0 is evaluated at $C_A = \hat{C}_A(0)$. Clearly, the solution is simply

$$\delta c_a = [C_A{}^o - \hat{C}_A(0)]\, e^{-x/\lambda_0}; \quad \frac{x}{L} \to 0 \tag{46}$$

Similarly, near $x = L$

$$\delta c_a = [C_A{}^L - \hat{C}_A(L)]\, e^{-(L-x)/\lambda_L}; \quad \frac{L-x}{L} \to 0 \tag{47}$$

Thus, as $\lambda/L \to 0$, two diffusion layers, of thicknesses λ_0 and λ_L, nonetheless persist and serve to enforce the boundary conditions on C_B. These boundary conditions are expressed by Equation (7) and now take the form

$$\frac{D_A[C_A{}^o - \hat{C}_A(0)]}{\lambda_0} + \frac{a_1}{\left[\dfrac{D_A}{D_B}\,\dfrac{(k_1\hat{C}_A(0) + k_2)^2}{k_1k_2C_T} + 1\right]} = 0 \tag{48}$$

and

$$\frac{D_A[C_A{}^L - \hat{C}_A(L)]}{\lambda_L} - \frac{a_1}{\left[\dfrac{D_A}{D_B}\,\dfrac{(k_1\hat{C}_A(L) + k_2)^2}{k_1k_2C_T} + 1\right]} = 0 \tag{49}$$

Further, from Equation (39), one finds

$$D_A[\hat{C}_A(0) - \hat{C}_A(L)] - D_B\frac{k_2C_T}{k_1\hat{C}_A(0) + k_2} + D_B\frac{k_2C_T}{k_1\hat{C}_A(L) + k_2} = -a_1L \tag{50}$$

Equations (48) to (50) may be solved for $\hat{C}_A(0)$, $\hat{C}_A(L)$, and the flux $-a_1$. This is necessarily a trial and error procedure. However, for sufficiently thick films, $\hat{C}_A(L) - C_A{}^L$ and $C_A{}^o - \hat{C}_A(0)$ each approach zero, and the equations may be algebraically linearized so as to yield

$$\frac{C_A{}^o - \hat{C}_A(0)}{C_A{}^o - C_A{}^L} \cong \frac{k_1k_2C_T\,\tilde{\lambda}_0{}^3}{D_A\,(k_1C_A{}^o + k_2)\,L}[1 + F_{eq}] \tag{51}$$

$$\frac{C_A{}^L - \hat{C}_A(L)}{C_A{}^o - C_A{}^L} \cong -\frac{k_1k_2C_T\,\tilde{\lambda}_L{}^3}{D_A\,(k_1C_A{}^L + k_2)\,L}[1 + F_{eq}] \tag{52}$$

$$a_1{}^* = \frac{-a_1L}{D_A\,[C_A{}^o - C_A{}^L]\,[1 + F_{eq}]} = \frac{1 + F}{1 + F_{eq}} \cong \frac{1}{1 + F_{eq}\left[Y\left(\dfrac{\tilde{\lambda}_0}{L}\right) + \dfrac{1}{Y}\left(\dfrac{\tilde{\lambda}_L}{L}\right)\right]} \tag{53}$$

where

$$F_{eq} = \frac{D_B}{D_A}\,\frac{k_1k_2C_T}{(k_1C_A{}^o + k_2)(k_1C_A{}^L + k_2)} \tag{54}$$

and

$$Y = \frac{k_1C_A{}^L + k_2}{k_1C_A{}^o + k_2} \tag{55}$$

As expected, $[C_A{}^o - \hat{C}_A(0)]$ and $[C_A{}^L - \hat{C}_A(L)]$ vary as $1/L$, and with increasing L the solution for the flux is seen to approach the well-known equilibrium solution, for which $F = F_{eq}$. In fact, Equation (53) serves largely to define the range of L for which that solution is acceptable. The physics therefore corresponds to chemical equilibrium in the core and diffusion layers at either face. These diffusion boundary layers specify the effective boundary values, $\hat{C}_A(0)$ and $\hat{C}_A(L)$, which are imposed upon the equilibrium core solution.

To this point, the above treatment of thick films is conceptually much like that of Kreuzer and Hoofd (1970). However, that treatment proceeds via an assumption which is equivalent to taking $\hat{C}_B + \delta c_b$ to be constant within the boundary layer region, and it then utilizes an analog to Equation (11) only, rather than both Equation (11) and (14). This assumption errs by a quantity of order $1/L$, an effect of the same order as the correction itself. More recently, and subsequent to the work of Smith et al. (1971), Kreuzer and Hoofd (1972) have provided an analysis which is nearly identical to the one above, except that they have also retained the term $k_1(\delta c_a)^2/D_B$ from Equation (43), while discarding all other terms of order $1/L^2$.

The present solution is readily improved. For instance, near $x = 0$, and to order $1/L^2$, Equation (43) is adequately represented by

$$\left[\frac{d^2\hat{C}_A}{dx^2}\right]_{x=0} + \frac{d^2}{dx^2}[\delta c_a] = \frac{1}{\lambda_0^2}[\delta c_a] + x\frac{d}{dx}\left[\frac{1}{\lambda^2}\right]_{x=0}[\delta c_a] + \frac{k_1}{D_B}[\delta c_a]^2 \tag{56}$$

in which one may use Equation (46) to provide acceptable estimates for those higher order terms which contain δc_a. Furthermore, as suggested by Equation (51), δc_a may be rendered appropriately nondimensional by setting:

$$C_A - \hat{C}_A = \delta c_a = \left\{\frac{k_1k_2C_T\,[C_A{}^o - C_A{}^L]\,\tilde{\lambda}_0{}^3}{D_A\,(k_1C_A{}^o + k_2)\,L}[1 + F_{eq}]\right\}\left\{G_0\,(x/\lambda_0)\right\}, \text{ for } \frac{x}{L} \to 0 \tag{57}$$

and

$$C_A - \hat{C}_A = \delta c_a = \left\{\frac{k_1k_2C_T\,[C_A{}^o - C_A{}^L]\,\tilde{\lambda}_L{}^3}{D_A\,(k_1C_A{}^L + k_2)\,L}[1 + F_{eq}]\right\}\left\{G_L\left(\frac{L-x}{\lambda_L}\right)\right\}, \text{ for } \frac{L-x}{L} \to 0 \tag{58}$$

so that Equation (56) becomes

$$G_0'' - G_0 = -2N_1\left(\frac{\lambda_0}{\lambda_0}\right)^8 a_1{}^{*2} + \mathrm{N}_1\left\{1 - \frac{N_2}{[1 - N_3G_0(0)]^2}\right\}[1 - N_3G_0(0)]\left(\frac{\lambda_0}{\lambda_0}\right)^5 \left\{a_1{}^*\,G_0(0)\,\frac{x}{\lambda_0}\,e^{-x/\lambda_0}\right\} + N_1N_2\left(\frac{\lambda_0}{\tilde{\lambda}_0}\right)^2 G_0{}^2(0)\,e^{-2x/\lambda_0} \tag{59}$$

The terms on the left are those which were present in the first-order model given above. For the region near $x = 0$, the quantity $2N_1(\lambda_0/\tilde{\lambda}_0)^8 a_1^{*2}$ provides a normalized measure of the error incurred by the first-order solution because $d^2\hat{C}_A/dx^2$ is not zero but varies as $1/L^2$. The other terms on the right are more complicated in form and result from the nonlinearity of the kinetic rate expression.

Integration and application of the boundary condition on C_B then leads to

$$G_0(0) - 2N_1\left(\frac{\lambda_0}{\tilde{\lambda}_0}\right)^8 (a_1^*)^2 + \frac{1}{3}N_1N_2\left(\frac{\lambda_0}{\lambda_0}\right)^2 G_0^2(0)$$

$$+\frac{1}{4}N_1\left\{1 - \frac{N_2}{[1-N_3G_0(0)]^2}\right\}$$

$$\left\{[1-N_3G_0(0)]\left(\frac{\lambda_0}{\tilde{\lambda}_0}\right)^5 a_1^*\, G_0(0)\right\}$$

$$= a_1^*\left(\frac{\lambda_0}{\tilde{\lambda}_0}\right)^3 \frac{1}{[1-N_3G_0(0)]} \qquad (60)$$

A similar procedure, applied near $x = L$, gives

$$G_L(0) + 2M_1\left(\frac{\lambda_L}{\tilde{\lambda}_L}\right)^8 (a_1^*)^2$$

$$-\frac{1}{3}M_1M_2\left(\frac{\lambda_L}{\tilde{\lambda}_L}\right)^2 G_L^2(0)$$

$$-\frac{1}{4}M_1\left\{1 - \frac{M_2}{[1+M_3G_L(0)]^2}\right\}$$

$$[1+M_3\,G_L(0)]\left[\left(\frac{\lambda_L}{\tilde{\lambda}_L}\right)^5 a_1^*\, G_L(0)\right]$$

$$= a_1^*\left(\frac{\lambda_L}{\tilde{\lambda}_L}\right)^3 \frac{1}{[1+M_3G_L(0)]} \qquad (61)$$

The complete solutions for $G_0(x/\lambda_0)$ and $G_L(L - x/\lambda_L)$ are given elsewhere (Meldon, 1973). For the region near $x = L$, the parameters M_1, M_2, and M_3 play the same role as do N_1, N_2, and N_3 for the region near $x = 0$. With this notation, the nondimensional analog Equation (50) is

$$a_1^* = \frac{1+F}{1+F_{eq}} = \left\{[1 - N_4G_0(0) - M_4G_L(0)]\right\}$$

$$\left\{\frac{1 + \dfrac{F_{eq}}{[1-N_3G_0(0)]\,[1+M_3G_L(0)]}}{1+F_{eq}}\right\} \qquad (62)$$

These three equations, together with the definition of λ_0 and λ_L, may be solved for the flux by a simple iterative process, just as with Equations (48) to (50).

With regard to the concentration profile prediction, all that remains is the development of a solution for the core. Indeed from Equation (59), it is apparent that G_0 does not vanish as $x/\lambda_0 \to \infty$, but rather

$$G_0(x/\lambda_0) \to 2\,N_1a_1^{*2}\,(\lambda_0/\tilde{\lambda}_0)^8 \qquad (63)$$

This results because, at this level of approximation, Equation (43) reduces to simply

$$[\delta c_a(x)]_{\text{core}} = \lambda^2\,\frac{d^2\hat{C}_A}{dx^2} \qquad (64)$$

within the core of the film. Use of the solution for $\hat{C}_A$ gives

$$[\delta c_a(x)]_{\text{core}} = 2\,\frac{k_1^2k_2\,C_T\,a_1^2\,\lambda^8}{D_A^3\,D_B^2} \qquad (65)$$

and, if this result is cast in terms of the boundary layer function $G_0(x/\lambda_0)$, the core solution becomes

$$G_0(x/\lambda_0) = 2\,N_1a_1^{*2}\,(\lambda/\tilde{\lambda}_0)^8 \qquad (66)$$

Clearly, the core solution for G_0 [Equation (66)] approaches the same value for $x \to 0$ as does the boundary layer solution for G_0 in the limit $x \to \infty$ [Equation (63)]. Asymptotically matched boundary and core solutions have thus been assured and the core solution has great simplicity. This situation is depicted schematically in Figure 1.

The method is philosophically very much like that employed by Goddard et al. (1970), although that analysis is applicable to generalized kinetics and does not require $D_B = D_{AB}$, whereas this one is more restricted. More importantly, that analysis proceeds via power series expansions in terms of $1/L$. For the present problem, the flux would be expressed as

$$a_1^* = \frac{1+F}{1+F_{eq}} = 1 + \beta_1/L + \beta_2/L^2 + \ldots. \qquad (67)$$

where Goddard et al. give

$$\beta_1 = -\,F_{eq}\,(\tilde{\lambda}_0Y + \tilde{\lambda}_L/Y) \qquad (68)$$

For sufficiently thick films, this result is indistinguishable from that given by Equation (53). An evaluation of β_2 may be achieved via methods presented by Goddard et al. or via an algebraic expansion of the relations presented above (Meldon, 1973).

DISCUSSION OF RESULTS

The foregoing results are intended to serve two purposes, one being purely qualitative and the other quantitative. For any particular case, they should permit a rapid and easy evaluation as to whether the situation corresponds to almost purely physical diffusion, or to very rapid

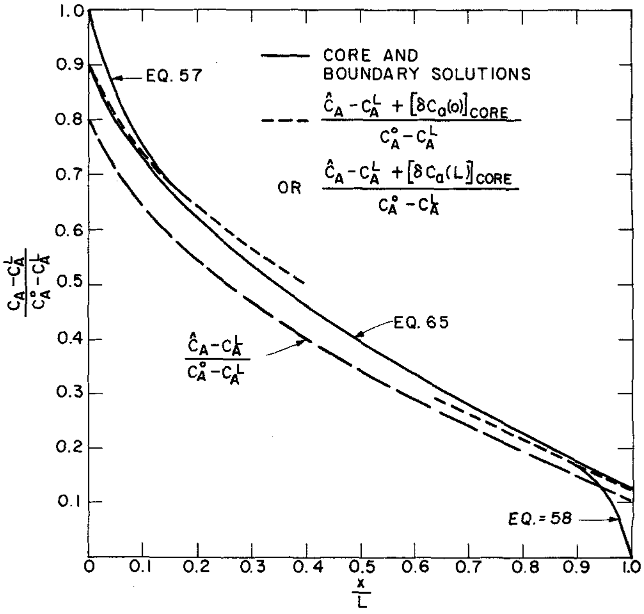

Fig. 1. Schematic representation of piece-wise approximations developed for thick film analysis. Cited equation numbers refer to the means for evaluating the difference between the indicated curve and the curve for C_A. $[\delta c_a\ (0)]$ core and $[\delta c_A\ (L)]$ core are evaluated from Equation (65) with λ equal to $\tilde{\lambda}_0$ and $\tilde{\lambda}_L$; respectively.

reaction with diffusion boundary layers at either face, or to an intermediate situation. The results should also permit a reasonably accurate quantitative prediction of the flux, perhaps at the expense of somewhat more labor than is required for the qualitative perspective.

The extent to which these objectives have been met is best assessed by comparison of the various analytical solutions with numerical analyses which are available for specific sets of parameters. For instance, Figure 2 presents numerical results obtained by Kutchai et al. (1970), for the facilitation of oxygen diffusion through a hemoglobin solution. Plotted in Figure 2a are the thin film results, Equation (18), and the algebraically linearized first-order thick film theory, Equation (53), of this paper and their asymptotes. These four lines are algebraically simple and serve to delimit both the qualitative and the quantitative behavior of the system. The first-order [Equations (48) to (50)] and second-order [Equations (60) to (62)] thick film theories are also included. These last curves are not easily produced by hand calculation but are readily obtained from a quite simple machine computation. Clearly, a composite solution based on the two second-order approximations would provide an evaluation of flux which would be adequate for nearly any purpose. It is noteworthy that the prediction of Kreuzer and Hoofd (1972) is less accurate than the first-order thick film prediction. This occurs because, in this example, one second-order term retained by those authors differs in sign from the totality of all second order effects.

The prediction of the single-point linearization technique is shown in Figure 2b for comparison. While the authors who applied this technique clearly recognized its inapplicability to cases for which the driving force is large, others appear not to have fully appreciated the significance of this limitation which is here clearly illustrated. The same figure presents a comparison with the power series formulations [Equation (67)]. As both the power series techniques and the methods of this paper retain all terms that (in the limit $L \to \infty$) vary as either $1/L$ or as $1/L^2$, it may be regarded as surprising that the latter provide substantially better predictions. This improvement is attributable to two factors: the present method permits a far more complicated functional dependence than does a simple power series, and, more importantly, the perturbation has been taken relative to a solution for $\hat{C}_A$ and $\hat{C}_B$ in which $\hat{C}_A(0)$ and $\hat{C}_A(L)$ are permitted to depend on the film thickness. By contrast, a power series approach to the problem proceeds most readily as a perturbation from a solution for $\hat{C}_A$ and $\hat{C}_B$ in which $\hat{C}_A(0)$ and $\hat{C}_A(L)$ are taken as C_A^o and C_A^L, respectively. Thus, by permitting $\hat{C}_A(0)$ and $\hat{C}_A(L)$ to vary with film thickness, the base state remains physically realistic down to far thinner films, and it is thought to be this difference which largely accounts for the improvement.

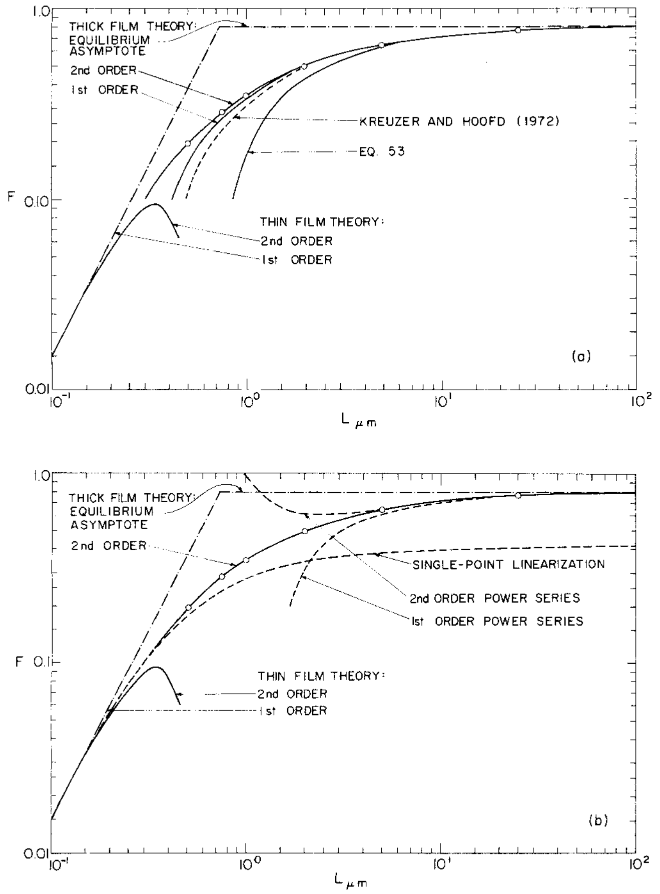

Fig. 2. Comparison of various solutions for facilitation of oxygen diffusion in a hemoglobin solution. ○ Numerical results of Kutchai, et al. (1970). Table VI.

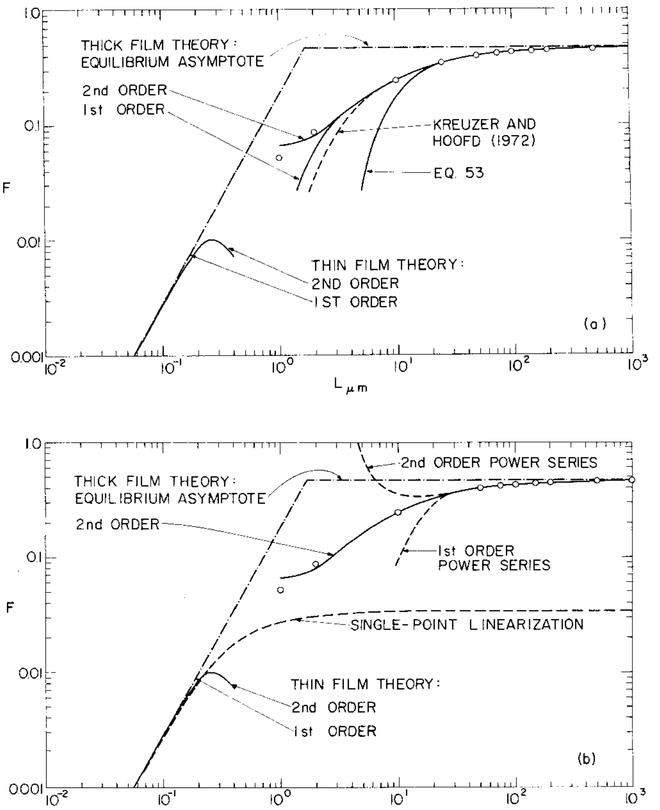

Fig. 3. Comparison of various solutions for facilitation of oxygen diffusion in a hemoglobin solution. ○ Numerical results of Kutchai, et al. (1970), Table I.

Figures 3 and 4 present similar comparisons for the oxygen-hemoglobin system and for the carbon monoxide-hemoglobin system. The results are qualitatively the same as in Figures 2a and 2b. Further comparisons, with similar results, have been made with other numerical results of Kutchai et al. (1970) and with the results of Ward (1970).

An examination of the concentration profile predictions is enlightening both as to the phenomenon and as to the mathematical techniques employed here. In particular,

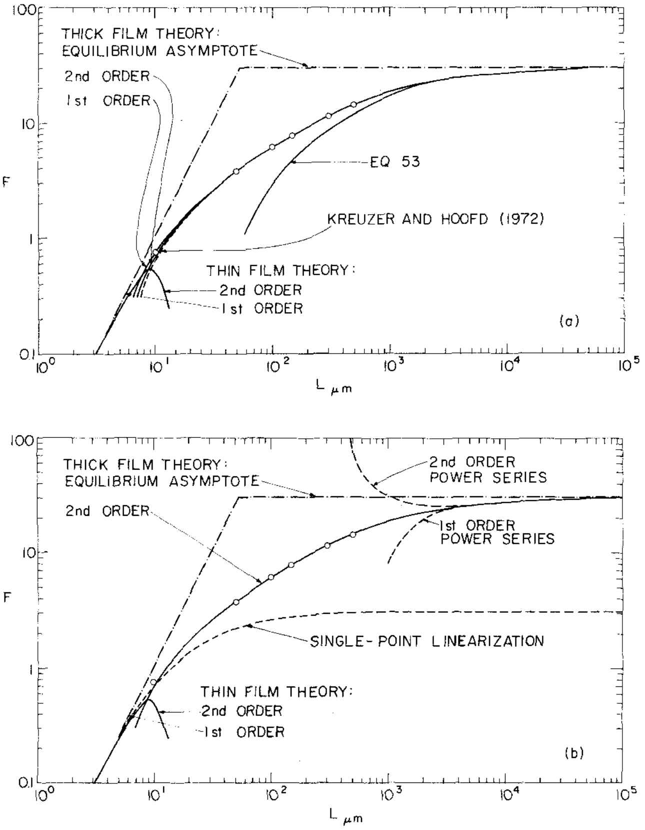

Fig. 4. Comparison of various solutions for facilitation of carbon monoxide diffusion in a hemoglobin solution. ○ Numerical results of Kutchai, et al. (1970), Table V.

Figures 5a to 5d illustrate the behavior of the same system as in Figures 4a and 4b. The concentration profiles appearing there are computed in accordance with Equations (10), (38), (39), (42), (57), and (58), for which all evaluations were made so as to include second-order effects. For simplicity, the solutions for $[\delta c_a]_{\text{core}}$ have been omitted. Figure 5d includes the profile predicted by thin film theory:

$$C_A = \overline{C}_A - \frac{1}{2}\zeta\,\Delta C_A + \epsilon\,\Delta C_A\, f_1(\zeta) \tag{69}$$

where $f_1(\zeta)$ is given by Equation (31).

For a thick film ($L = 500\mu$m, Figure 5a), diffusional effects are essentially absent, except for the apparent failure of C_A to vanish at $x = L$, as required by the boundary conditions for this example. The apparent value of C_A at $x = L$ is, of course, simply $\hat{C}_A(L)$, and the actual value of C_A does in fact fall to zero across an exceedingly thin boundary layer. For somewhat thinner films ($L = 100$ μm, Figure 5b and $L = 50$ μm, Figure 5c), the conclusions are much the same, except that diffusional effects are evident even within the core of the film. It should also be noted that the profiles for C_B and C_{AB} in this example are quite insensitive to C_A, that is, for the purpose of computing either C_B or C_{AB}, it matters but little whether C_A is evaluated from Equation (57) or Equation (58). Only in Figure 5d ($L = 10$ μm) is the effect even noticeable. Here, the thick film theory ceases to be realistic, but the thin film theory becomes applicable, thereby illustrating the near overlap of the two techniques.

The observed agreement between the numerical results of Kutchai et al. (1970) and the analytical methods developed here provide a valuable and unbiased demonstration of the utility which the new methods enjoy. The sample size is nonetheless so small that the agreement could conceivably be fortuitous, and for this reason the authors have generated many numerical solutions of their own by finite difference techniques (Meldon, 1973). Whereas the results of Kutchai et al. (1970) were best plotted in accordance with the available tabulated form, generality is best served by introducing a plotting technique which shows less parameter sensitivity. This is accomplished by following Friedlander and Keller (1965) and defining a new parameter ϕ which has a range of zero to one:

$$1 + F = \frac{1}{1 - \dfrac{F_{eq}}{1 + F_{eq}}\,\phi} \tag{70}$$

Clearly, ϕ is analogous to the function $F(\eta)$ as given by Friedlander and Keller. Comparison with Equation (53) shows that as $L \to \infty$

$$\phi \to 1 - \frac{1}{\left[\dfrac{L}{Y\bar{\lambda}_0 + \bar{\lambda}_L/Y}\right]} \tag{71}$$

irrespective of the value of any other parameter. Figure 6 depicts one of our numerical solutions plotted as suggested by Equation (71). Two parameters are necessarily held constant in such a plot, and these have been taken to be $D_BC_T/D_AC_A{}^o$ and $k_1C_A{}^o/k_2$. These do not arise naturally in the context of the theory, but they are natural physical choices if (for a given membrane-reaction system) upstream concentration and total carrier concentration are both fixed. The figure therefore explores the effect of membrane thickness and of downstream concentration. On such a plot the single-point linearization is exact for the limit $C_A{}^L/C_A{}^o = 1$ ($Y = 1$), and the methods developed here are therefore most interesting for the limit $C_A{}^L/C_A{}^o = 0$. In addition, the parameters have been chosen so as to illustrate behavior which is somewhat different from that seen in the earlier comparisons. For instance, the second-order solution provides only a modest improvement over the first-order thick film solution, whereas algebraic linearization of the first-order thick film solution involves a very considerable loss of accuracy. Nonetheless, a simple interpolation between the two second-order solutions provides excellent agreement with the numerical results, and in fact the authors found no parameter range for which this was not the case.

Figure 6 is particularly useful for thick films because it assures that, as $L \to \infty$, all proper solutions for ϕ will approach unity in the same way. Furthermore, the solution for $Y = 1$ is the very convenient one given by the single-point linearization solutions and is independent of all other parameters. A somewhat different plot is shown in Figure 7 and serves the same function for relatively thin films. It is based on the fact that as $L \to 0$, $F \to \epsilon$ which implies

$$\phi \to \frac{1 + F_{eq}}{F_{eq}}\,\epsilon \tag{72}$$

Thus, on the coordinates of Figure 7, all proper solutions for ϕ will approach zero in the same way. Furthermore, for $Y = 1$, the abscissa of Figure 7 reduces to L^2/λ^2 and thus the single-point linearizations are easily plotted, are exact for that case, and retain their parameter independence.

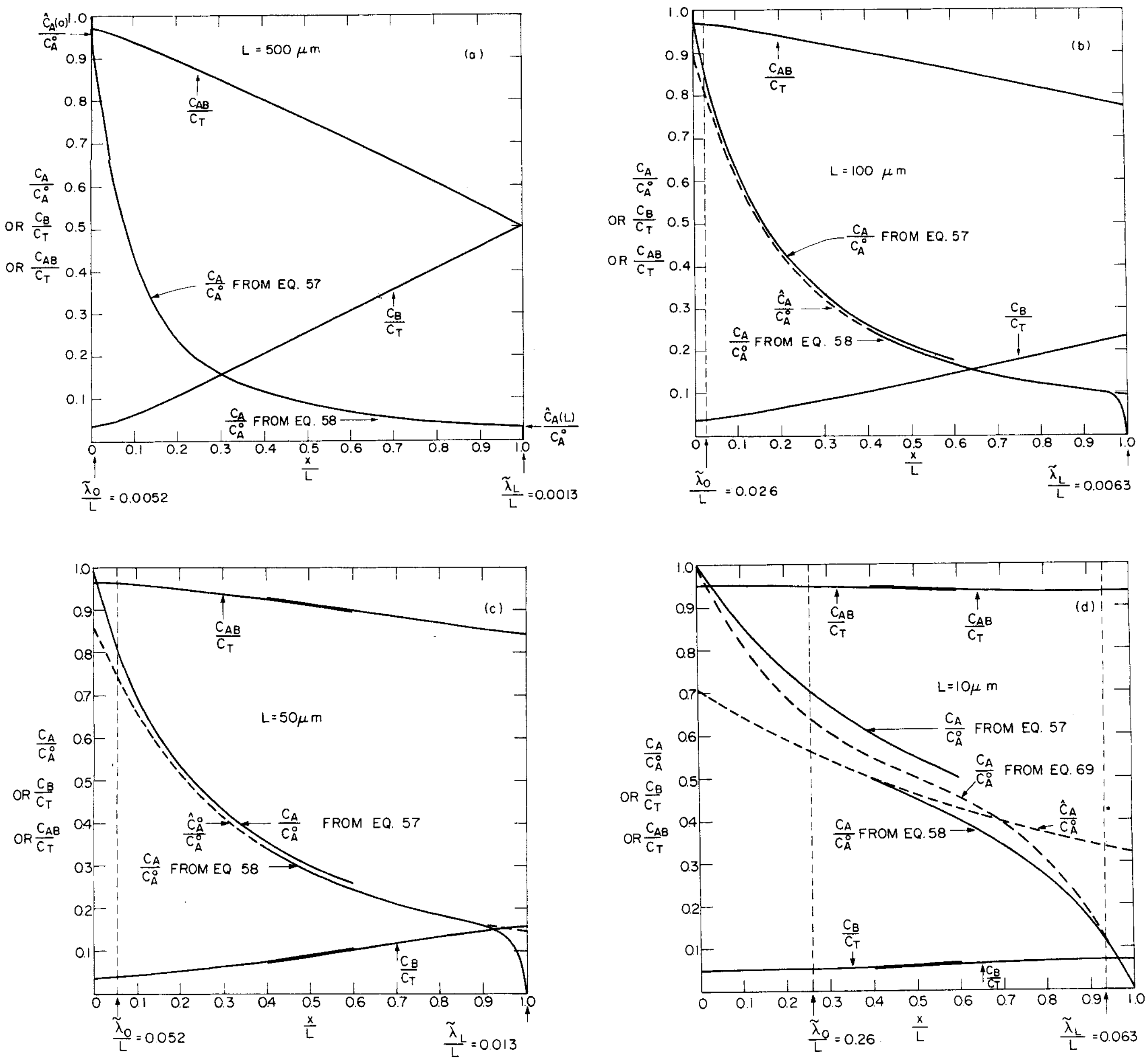

Fig. 5. Concentration profiles for carbon monoxide-hemoglobin system shown in Fig. 4. $C_A^L = 0$ for all cases.

CONCLUSIONS

Analytical techniques, corresponding to a perturbation from purely physical diffusion on the one hand and from reaction equilibrium at each point within the film on the other, have been developed and applied to facilitated transport for the reaction scheme $A + B \rightleftarrows AB$. For the systems examined, these methods are seen to provide satisfactory accuracy for essentially the entire range of parameter variation. Furthermore, if modest accuracy will suffice, then these methods are algebraically very simple.

The extension of these techniques to specific alternative reaction kinetics poses no intrinsic difficulties, and in fact the kinetics chosen here should merely be considered as illustrative.

ACKNOWLEDGMENT

J. H. Meldon was supported by an N.S.F. Predoctoral Fellowship and additional support was made available from funds supplied by E. I. DuPont deNemours Company by the

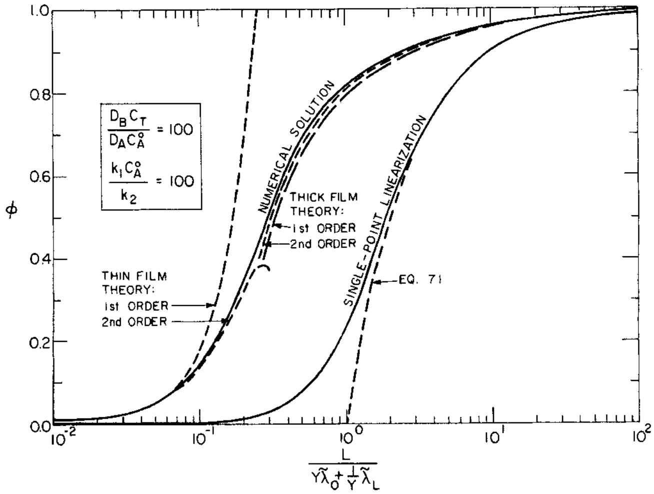

Fig. 6. Comparison of numerical and analytical results, plotted so as to be most useful for thick films. Single-point linearization shown for $C_A^L/C_A^o = 1$; for all other solutions, $C_A^L/C_A^o = 0$.

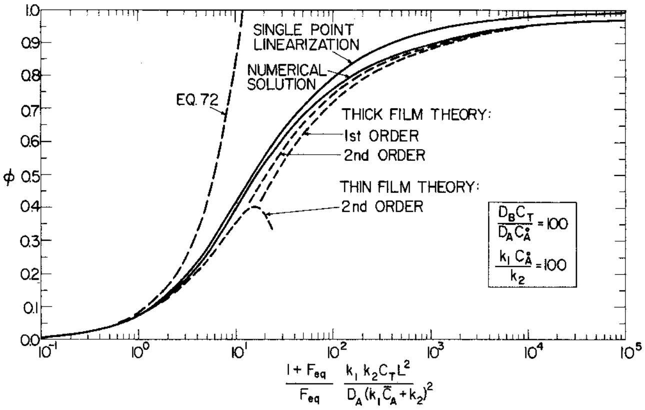

Fig. 7. Comparison of numerical and analytical results, plotted so as to be most useful for thin films. Single-point linearization shown for $C_A^L/C_A^o = 1$; for all other solutions, $C_A^L/C_A^o = 0$.

National Science Foundation. The authors deeply appreciate these awards.

Conversations with Professor P. L. T. Brian proved invaluable, and the authors are extremely grateful.

NOTATION

a_1 = constant, defined by Equation (13)
a_1^* = dimensionless flux, defined by Equation (53)
a_2 = constant, defined by Equation (14)
A, AB, B refer to chemical species
C = concentration
$\bar{C}_A$ = average concentration of A, defined by Equation (19)
$\hat{C}_A$, $\hat{C}_B$ = equilibrium solutions for C_A and C_B, defined by Equations (38) and (39)
C_T = total carrier concentration, defined by Equation (9)
D = diffusivity
F = facilitation factor, defined by Equation (53)
F_{eq} = facilitation factor for $L \to \infty$, defined by Equation (54)
f_1, f_2, f_3 = functions defined by Equation (16)
g_0, g_1, g_2, g_3 = functions defined by Equation (17)
G_0, G_L = functions defined by Equations (57) and (58)
k_1 = forward reaction rate constant
k_2 = reverse reaction rate constant
L = film thickness
$N_1 = k_1 \tilde{\lambda}_0^5 [C_A^o - C_A^L][1 + F_{eq}][k_1 C_A^o + k_2]/D_B^2 L$
$N_2 = D_B k_1 k_2 C_T / D_A (k_1 C_A^o + k_2)^2$
$N_3 = k_1^2 k_2 C_T \tilde{\lambda}_0^3 [C_A^o - C_A^L][1 + F_{eq}]/D_A(k_1 C_A^o + k_2)^2 L$
$N_4 = k_1 k_2 C_T \tilde{\lambda}_0^3 [1 + F_{eq}]/D_A(k_1 C_A^o + k_2) L$
$M_1 = k_1 \tilde{\lambda}_L^5 [C_A^o - C_A^L][1 + F_{eq}][k_1 C_A^L + k_2]/D_B^2 L$
$M_2 = D_B k_1 k_2 C_T / D_A (k_1 C_A^L + k_2)^2$
$M_3 = k_1^2 k_2 C_T \tilde{\lambda}_L^3 [C_A^o - C_A^L][1 + F_{eq}]/D_A(k_1 C_A^L + k_2)^2 L$
$M_4 = k_1 k_2 C_T \tilde{\lambda}_L^3 [1 + F_{eq}]/D_A(k_1 C_A^L + k_2) L$
x = distance, measured from upstream face of film
Y = defined by Equation (55)

Greek Letters

β_1, β_2 defined by Equation (67)
γ_1, γ_2, γ_3 defined by Equation (18)
δc_a, δc_b defined by Equations (40) and (41)
ΔC_A defined by Equation (20)
ϵ = perturbation parameter, defined by Equation (21)
ζ = dimensionless distance, defined by Equation (15)
λ = length scale, defined by Equation (44)
$\tilde{\lambda}_0$ = λ evaluated at $\hat{C}_A = C_A^o$
$\tilde{\lambda}_L$ = λ evaluated at $\hat{C}_A = C_A^L$
ϕ defined by Equation (70)

Superscripts

o refers to conditions at $x = 0$
L refers to conditions at $x = L$

Subscripts

A, AB, B refer to chemical species
core refers to "core" solution

LITERATURE CITED

Blumenthal, R., and A. Katchalsky, "The Effect of Carrier Association-Dissociation Rate on Membrane Permeation," *Biochim. Biophys. Acta.*, **173**, 357 (1969).
Brian, P. L. T., and R. C. Reid, "Heat Transfer with Simultaneous Chemical Reaction: Film Theory for a Finite Reaction Rate," *AIChE J.*, **8**, 322 (1962).
Brokaw, R. S., "Thermal Conductivity and Chemical Kinetics," *J. Chem. Phys.*, **35**, 1569 (1961).
Friedlander, S. K., and K. H. Keller, "Mass Transfer in Reacting Systems Near Equilibrium," *Chem. Eng. Sci.*, **20**, 121 (1965).
Goddard, J. D., J. S. Schultz, and R. J. Bassett, "On Membrane Diffusion with Near-Equilibrium Reaction," *ibid.*, **25**, 665 (1970).
Hatta, S., "On the Absorption Velocity of Gases by Liquids," *Tohoku Imp. Univ. Tech. Repts.*, **8**, 1 (1928).
Hemmingsen, E. A., "Enhancement of Oxygen Transport by Myoglobin," *Comp. Biochem. Physio.*, **10**, 239 (1963).
Kotyk, A., and K. Janacek, *Cell Membrane Transport*, Plenum Press, N. Y. (1970).
Kreuzer, F., "Facilitated Diffusion of Oxygen and its Possible Significance; a Review," *Respir. Physiol.*, **9**, 1 (1970).
———., and L. J. C. Hoofd, "Facilitated Diffusion of Oxygen in the Presence of Hemoglobin," *ibid.*, **8**, 280 (1970).
Kreuzer, F., and L. J. C. Hoofd, "Factors Influencing Facilitated Diffusion of Oxygen in the Presence of Hemoglobin and Myoglobin," *ibid.*, **15**, 104 (1972).
Kutchai, H., J. A. Jacquez, and F. J. Mather, "Nonequilibrium Facilitated Oxygen Transport in Hemoglobin Solution," *Biophys. J.*, **10**, 38 (1970).
Meldon, J. H., "Mass Transfer with Reversible Chemical Reaction Through Thin Liquid Films," Ph.D. thesis, Mass. Inst. Technol., Cambridge (1973).
Olander, D. R., "Simultaneous Mass Transfer and Equilibrium Chemical Reaction," *AIChE J.*, **6**, 233 (1960).
Scholander, P. F., "Oxygen Transport Through Hemoglobin Solutions," *Science*, **131**, 585 (1960).
Smith, K. A., J. H. Meldon, and C. K. Colton, "An Analysis of Carrier-Facilitated Transport," Preprint No. 48c at 64th Ann. Am. Inst. Chem. Engrs. Meeting, San Francisco, Calif. (1971).
Ward, W. J., "Analytical and Experimental Studies of Facilitated Transport," *AIChE J.*, **16**, 405 (1970).
———., and W. L. Robb, "Carbon Dioxide-Oxygen Separation: Facilitated Transport of Carbon Dioxide Across a Liquid Film," *Science*, **156**, 1481 (1967).
Wittenberg, J. B., "Myoglobin-Facilitated Oxygen Diffusion: Role of Myoglobin in Oxygen Entry into Muscle," *Physiol. Rev.*, **50**, 559 (1970).
Wyman, J., "Facilitated Diffusion and the Possible Role of Myoglobin as a Transport Mechanism," *J. Bio. Chem.*, **241**, 115 (1966).

Manuscript received August 5, 1971; revision received August 2, 1972; paper accepted August 7, 1972.