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Manuscript received February 9, 1966; revision received August 15, 1966; paper accepted August 15, 1966.

Penetration Theory for Diffusion Accompanied by a Reversible Chemical Reaction with Generalized Kinetics

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The penetration theory equations representing diffusion with a generalized, reversible chemical reaction of the form $\gamma_A A + \gamma_B B \rightleftharpoons \gamma_M M + \gamma_N N$ are solved by a finite-difference method. Many solutions are presented in graphical form. Approximate solutions to several limiting cases are obtained analytically by means of a steady state representation and are useful for estimating results of the solution to the penetration theory equations.

Since its inception, the penetration theory of Higbie (*14*) has been applied widely to unsteady state diffusional processes. The Higbie model has been particularly useful for solving many problems involving diffusion with chemical reaction. In most cases, interest has been directed toward diffusion of one reactant into a semi-infinite medium containing a second reactant that depletes the first according to some known kinetic mechanism. Obtaining an expression for the rate of diffusion of the first reactant through the boundary of the semi-infinite medium in general requires the solution of a set of simultaneous partial differential equations or in some cases a single such equation, with appropriate boundary conditions. Restrictions of various kinds have been placed on the physical problem in order to facilitate solution of these equations. Solutions to the penetration theory equations have been obtained for diffusion with:

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1. a first-order, irreversible reaction (*9, 11*);

2. an infinitely rapid, second-order, irreversible reaction, $A + B \rightarrow$ products (*9, 11, 38*);

3. a reversible reaction, $A \rightleftharpoons M$, first order in A and M (*11, 20, 39*);

4. an infinitely rapid, reversible reaction (thus requiring chemical equilibrium at all points in the medium), for several types of kinetic behavior (*28*);

5. a zero-order, irreversible reaction (*2, 42*);

6. a second-order, irreversible reaction (*6, 30*);

7. a reversible reaction, $A + B \rightleftharpoons 2M$, first order in each reactant and second order in the product (*31*);

8. an irreversible reaction, $A + \gamma_B B \rightarrow$ products, of general order (*4, 19*);

9. a two-step reaction comprising $A + B \rightarrow C$ followed by $C + B \rightarrow$ products, first order in each species (*5*);

10. simultaneous reaction of two species, A and B, both of which cross the interface, with a third species C by $\gamma_A A + C \rightarrow$ products, $\gamma_B B + C \rightarrow$ products, first order in each reactant (*17, 36*);

11. an irreversible reaction of two species, $A + \gamma_B B \rightarrow$ products, first order in A and B, which occurs after passage of both reactants through the interface (*36*).

Cases 1 to 4 were solved analytically and cases 5 to 10 were solved by finite-difference methods, although analytical solutions for some previously unsolved special cases have been obtained for cases 5 and 10. Machine computations were used to solve the finite-difference equations in cases 6 to 10. The method of moments was used in case 11.

The available solutions to the penetration theory equations have proven very useful in experimental investigations. These solutions have been used mainly for the study of reaction mechanisms (*1, 7, 13, 15, 21, 22, 24, 33, 40, 41, 43*) and the determination of reaction rate constants (*7, 8, 10, 12, 16, 24* to *27, 32, 35, 37, 40, 43*).

While the solutions that have been obtained will continue to be quite useful, many problems do not fit within any of the models for which the penetration theory equations have been solved. Accordingly, it is apparent that the general solution to a penetration theory model possessing a high degree of flexibility would be useful for solving many problems that are beyond the scope of existing models. It is the attainment of such a solution to which this study is directed. The present treatment is concerned with diffusion accompanied by a single, generalized, reversible, chemical reaction.

MATHEMATICAL DEVELOPMENT

The problem to be considered is the calculation of the rate of diffusion of a solute A, into a medium containing a species B with which A reacts according to the equation:

$$\gamma_A A + \gamma_B B \rightleftharpoons \gamma_M M + \gamma_N N$$

In the treatment that follows, the geometry of the medium must be such that the spatial variation in concentration of each diffusing species can be expressed in terms of a single distance variable. Consequently, the analysis applies to geometries such as a semi-infinite medium, an infinite plane sheet, a flat plate with impervious edges, an infinite cylinder, a cylinder with impervious ends, or a sphere.

It is assumed that:

1. The concentration of A at the surface of the medium is constant.
2. The concentration of B is initially uniform throughout the medium.
3. Species B, M, and N are nonvolatile.
4. Transport of all species is by molecular diffusion alone.
5. The diffusion coefficient of each species is constant.
6. Only a single reaction is kinetically significant.
7. Heat effects are negligible.

A differential material balance for each species yields the following equations:

$$D_A\left(\frac{\partial^2 A}{\partial x^2} + \frac{\lambda}{x}\frac{\partial A}{\partial x}\right) = \frac{\partial A}{\partial t} + \gamma_A\left(k_1 A^\alpha B^\beta - k_2 M^\mu N^\nu\right) \tag{1}$$

$$D_B\left(\frac{\partial^2 B}{\partial x^2} + \frac{\lambda}{x}\frac{\partial B}{\partial x}\right) = \frac{\partial B}{\partial t} + \gamma_B\left(k_1 A^\alpha B^\beta - k_2 M^\mu N^\nu\right) \tag{2}$$

$$D_M\left(\frac{\partial^2 M}{\partial x^2} + \frac{\lambda}{x}\frac{\partial M}{\partial x}\right) = \frac{\partial M}{\partial t} + \gamma_M\left(k_2 M^\mu N^\nu - k_1 A^\alpha B^\beta\right) \tag{3}$$

$$D_N\left(\frac{\partial^2 N}{\partial x^2} + \frac{\lambda}{x}\frac{\partial N}{\partial x}\right) = \frac{\partial N}{\partial t} + \gamma_N\left(k_2 M^\mu N^\nu - k_1 A^\alpha B^\beta\right) \tag{4}$$

where $\lambda = 0$ for a semi-infinite medium or an infinite plane sheet, $\lambda = 1$ for an infinite cylinder, and $\lambda = 2$ for a sphere.

The boundary conditions for a semi-infinite medium are

$$A = A_o, B = B_o, M = M_o, N = N_o, t = 0, x > 0 \tag{5}$$

$$A = A_i, \frac{\partial B}{\partial x} = 0, \frac{\partial M}{\partial x} = 0, \frac{\partial N}{\partial x} = 0, t > 0, x = 0 \tag{6}$$

$$A = A_o, B = B_o, M = M_o, N = N_o, t > 0, x = \infty \tag{7}$$

The boundary conditions for an infinite plane sheet, an infinite cylinder or a sphere are

$$A = A_o, B = B_o, M = M_o, N = N_o, t = 0, 0 \leq x \leq x_o \tag{8}$$

$$A = A_i, \frac{\partial B}{\partial x} = 0, \frac{\partial M}{\partial x} = 0, \frac{\partial N}{\partial x} = 0, t > 0, x = 0 \tag{9}$$

$$\frac{\partial A}{\partial x} = 0, \frac{\partial B}{\partial x} = 0, \frac{\partial M}{\partial x} = 0, \frac{\partial N}{\partial x} = 0, t > 0, x = x_o \tag{10}$$

The differential equations and boundary conditions may be put into the following convenient dimensionless form:

$$\left(\frac{\partial^2 a}{\partial y^2} + \frac{\lambda}{y}\frac{\partial a}{\partial y}\right) = \frac{\partial a}{\partial \theta} + \gamma_A\left(a^\alpha b^\beta - \frac{q m^\mu n^\nu}{p}\right) \tag{11}$$

$$r_B\left(\frac{\partial^2 b}{\partial y^2} + \frac{\lambda}{y}\frac{\partial b}{\partial y}\right) = \frac{\partial b}{\partial \theta} + \gamma_B\left(\frac{a^\alpha b^\beta}{q} - \frac{m^\mu n^\nu}{p}\right) \tag{12}$$

$$r_M\left(\frac{\partial^2 m}{\partial y^2} + \frac{\lambda}{y}\frac{\partial m}{\partial y}\right) = \frac{\partial m}{\partial \theta} + \gamma_M\left(\frac{m^\mu n^\nu}{p} - \frac{a^\alpha b^\beta}{q}\right) \tag{13}$$

$$r_N\left(\frac{\partial^2 n}{\partial y^2} + \frac{\lambda}{y}\frac{\partial n}{\partial y}\right) = \frac{\partial n}{\partial \theta} + \gamma_N\left(\frac{m^\mu n^\nu}{p} - \frac{a^\alpha b^\beta}{q}\right) \tag{14}$$

The dimensionless boundary conditions for a semi-infinite medium are

$$a = A_o/A_i, b = 1, m = M_o/B_o, n = N_o/B_o, \theta = 0, y > 0 \tag{15}$$

$$a = 1, \frac{\partial b}{\partial y} = 0, \frac{\partial m}{\partial y} = 0, \frac{\partial n}{\partial y} = 0, \theta > 0, y = 0 \quad (16)$$

$$a = A_o/A_i, b = 1, m = M_o/B_o, n = N_o/B_o, \theta > 0, y = \infty \quad (17)$$

The dimensionless boundary conditions for an infinite plane sheet, an infinite cylinder or a sphere are

$$a = A_o/A_i, b = 1, m = M_o/B_o, n = N_o/B_o, \theta = 0, \quad 0 \leq y \leq y_o \quad (18)$$

$$a = 1, \frac{\partial b}{\partial y} = 0, \frac{\partial m}{\partial y} = 0, \frac{\partial n}{\partial y} = 0, \theta > 0, y = 0 \quad (19)$$

$$\frac{\partial a}{\partial y} = 0, \frac{\partial b}{\partial y} = 0, \frac{\partial m}{\partial y} = 0, \frac{\partial n}{\partial y} = 0, \theta > 0, y = y_o \quad (20)$$

The average rate of diffusion of A through the interface over the interval from zero to t, is given by

$$R = -\frac{1}{t}\int_o^t D_A \left(\frac{\partial A}{\partial x}\right)_{x=o} dt$$

$$= -\frac{1}{\theta}\sqrt{k_1 B_o^{\beta} A_i^{\alpha+1} D_A}\int_o^{\theta}\left(\frac{\partial a}{\partial y}\right)_{y=o} d\theta \quad (21)$$

The ratio of the average rate of diffusion of A through the interface to that for physical diffusion over the same time interval, for a semi-infinite medium, is obtained from

$$R^o = 2(A_i - A_o)\sqrt{\frac{D_A}{\pi t}}$$

$$= 2(1 - a_o)\sqrt{\frac{k_1 B_o^{\beta} A_i^{\alpha+1} D_A}{\pi\theta}} \quad (22)$$

$$\Phi = \frac{R}{R^o} = \frac{k_L}{k_L^o} = \frac{1}{2(a_o - 1)}\sqrt{\frac{\pi}{\theta}} \int_o^{\theta}\left(\frac{\partial a}{\partial y}\right)_{y=o} d\theta \quad (23)$$

Another expression that can be used is

$$\Phi = \frac{1}{2(1-a_o)}\sqrt{\frac{\pi}{\theta}}\int_o^{\infty}\left[a - a_o + \frac{q(1-b)}{\gamma_B}\right] dy \quad (24)$$

There is no known method for solving the differential equations analytically. However, they can be solved by numerical procedures. An implicit, finite-difference method was used to obtain the solution.

NUMERICAL SOLUTION

The four partial differential equations, Equations (11) to (14), are nonlinear; therefore, analytical solutions are not expected, except for special cases, for example, $\alpha = \mu = 1$, $\beta = \nu = 0$. A variety of numerical techniques employing finite-difference methods are described in the literature. An implicit method was chosen for this problem, since these techniques are inherently numerically stable over the extreme variations in space and time increments and the extended time ranges required in the investigation of many physical parameters.

The method used for handling the nonlinear terms can be illustrated by considering Equation (11) as applied to a semi-infinite medium. The treatment for the other equations follows in an obvious fashion. Thus

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial y^2} - \gamma_A\left(a^{\alpha} b^{\beta} - \frac{q}{p} m^{\mu} n^{\nu}\right) \quad (25)$$

or

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial y^2} - \gamma_A q F\ (a, b, m, n) \quad (26)$$

Replacing the partial derivatives with the finite-difference approximations

$$\frac{\partial a}{\partial \theta} \simeq \frac{a_j^k - a_j^{k-1}}{\Delta\theta} \quad (27)$$

and

$$\frac{\partial^2 a}{\partial y^2} \simeq \frac{a_{j-1}^k - 2a_j^k + a_{j+1}^k}{\Delta y^2} \quad (28)$$

where the superscript k refers to the time increment $\Delta\theta$ and the subscript j refers to the space increment Δy, it is found that

$$a_j^k - a_j^{k-1} = S\left[a_{j-1}^k - 2a_j^k + a_{j+1}^k\right] - \Delta\theta\gamma_A q F_j^{k-1} \quad (29)$$

with $S = \Delta\theta/\Delta y^2$.

Collecting terms in k on the left-hand side, one obtains

$$Sa_{j-1}^k - (2S+1)a_j^k + Sa_{j+1}^k = -a_j^{k-1} + \Delta\theta\gamma_A q F_j^{k-1} \quad (30)$$

It is important to note that F has been evaluated at the $(k-1)^{th}$ time step instead of at the k^{th} step. In general, maximum accuracy is obtained in setting up finite-difference approximations by evaluating all factors at the pivot points, that is, at k and j. However, in the present case, if this general rule is followed and F_j^k is used, a trial and error iteration is required to evaluate F_j^k since it involves a_j^k.

By using F_j^{k-1} instead of F_j^k, equally accurate results [see Lees (23)] were obtained with a five- or sixfold reduction in computation compared with the best iterative methods. Taking advantage of this gain, we reduced $\Delta\theta$ to improve the accuracy of the calculations further. Lees also shows the applicability of this technique to an even wider range of nonlinearities.

This treatment of the reaction terms also makes it possible to solve sequentially for a, b, m, and n. In practice, the F_j^{k-1} are reevaluated in proceeding through the sequence, utilizing the latest values of a, b, m, and n. At a given time step, that is, k fixed, Equation (30) represents a set of j simultaneous algebraic equations, which are tridiagonal in form. Efficient solution is obtained by an elimination method suggested by Thomas and described in a paper by Peaceman and Rachford (29).

The remaining difficulty occurs in the treatment of the semi-infinite geometry where a finite number of mesh points must be distributed over an infinite range of y. Several approaches are possible. If a "practical infinity" is defined at a finite value of y, and the available mesh points distributed uniformly, a rather coarse grid in regions of interest with corresponding loss of accuracy may result. This difficulty can be offset either by using a very large number of mesh points, or by introducing a nonuniform grid, concentrating mesh points in regions of rapid change.

Since in this problem, practical infinity and regions of rapid change are difficult to predict in advance, a different approach was used. The independent variable y is transformed by means of the equation*

* Suggested to the authors by M. M. Wendel of the Repauno Development Laboratory, E. I. du Pont de Nemours and Company.

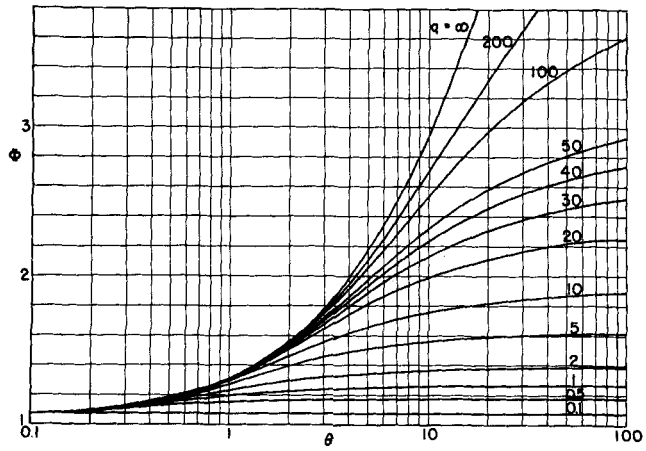

Fig. 1. Effect of chemical reaction $A + B \rightleftarrows M + N$ on the mass transfer rate in a semi-infinite medium for $p = 0.1$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_0 = M_0 = N_0 = 0$.

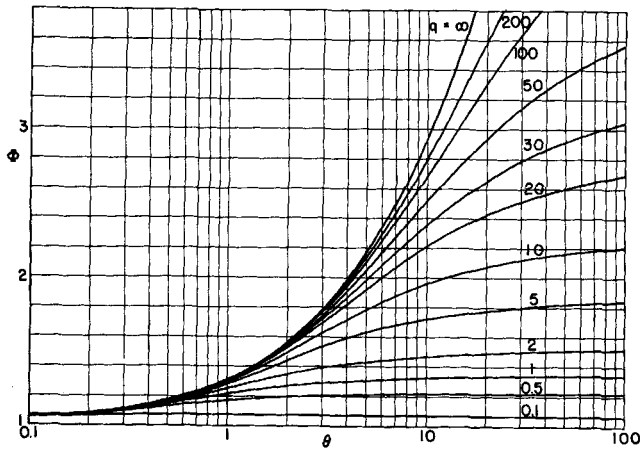

Fig. 2. Effect of chemical reaction $A + B \rightleftarrows M + N$ on the mass transfer rate in a semi-infinite medium for $p = 0.2$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_0 = M_0 = N_0 = 0$.

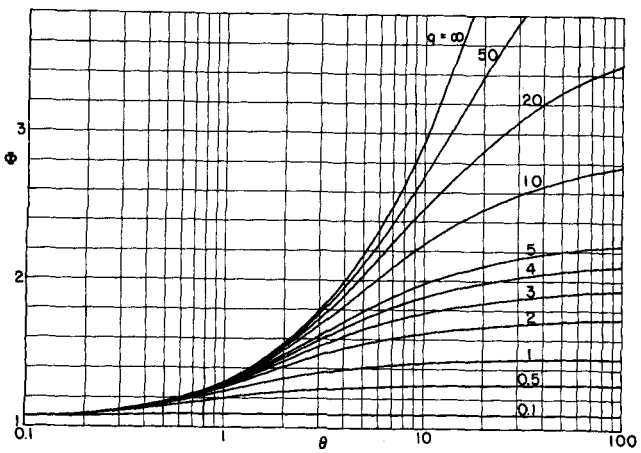

Fig. 3. Effect of chemical reaction $A + B \rightleftarrows M + N$ on the mass transfer rate in a semi-infinite medium for $p = 0.5$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_0 = M_0 = N_0 = 0$.

$$y = \frac{cz}{1-z} \tag{31}$$

This equation maps the infinite range of y into the finite strip from 0 to 1, that is, at $y = 0$, $z = 0$ and at $y \to \infty$, $z = 1$.

The arbitrary constant c controls the effective distribution of the grid with respect to the y variable. The actual value of c is determined experimentally, since it depends upon the effective reaction rate. The value of c used in the present work was 0.8. Because of this change in the independent variable, the following relations hold:

$$\frac{\partial a}{\partial y} = \frac{\partial a}{\partial z}\left[\frac{(1-z)^2}{c}\right] \tag{32}$$

and

$$\frac{\partial^2 a}{\partial y^2} = \frac{\partial^2 a}{\partial z^2}\left[\frac{(1-z)^4}{c^2}\right] - \frac{\partial a}{\partial z}\left[\frac{2(1-z)^3}{c^2}\right] \tag{33}$$

Although these transformations complicate the appearance of the original equations by incorporating variable coefficients, no particular difficulty is added to the numerical solution. With these modifications, Equation (11) becomes

$$\frac{\partial a}{\partial \theta} = \left[K_2 + (1-K_2)\frac{(1-z)^4}{c^2}\right]\frac{\partial^2 a}{\partial z^2} + \left[\frac{(K_2-1)2(1-z)^3}{c^2} + \frac{K_1}{z}\right]\frac{\partial a}{\partial z} - F \tag{34}$$

With $K_1 = K_2 = 0$, the semi-finite case is obtained. If $K_2 = 1$ and $K_1 = 0$, the plane sheet geometry is obtained. Retaining $K_2 = 1$ and setting $K_1 = 1$, the cylindrical coordinate solution is obtained and for $K_1 = 2$, the spherical system is obtained.

The preceding techniques have been incorporated into FORTRAN IV programs for the IBM 7070, IBM 7040, and Univac 1107.

RESULTS

The results of the computations can be expressed in many forms. The rate of diffusion of A through the interface can be calculated as a function of time if the various physical parameters are known. In addition, the concentration profiles of all species participating in the reaction can be calculated as a function of time. Mass transfer coefficients can also be calculated.

In real problems, the semi-infinite medium is a phase that is of sufficient extent in the direction of diffusion that the concentrations of all species remain unchanged far from the interface. Effectively semi-infinite media are encountered frequently in chemical engineering problems. The most convenient method of expressing the results of calculations for such media is by means of plots of $\Phi = k_L/k_L^o$ against the dimensionless time, $\theta = k_1 B_o^{\beta} A_i^{\alpha-1} t$. A series of such plots is shown in Figures 1 to 14 for various values of the controlling parameters.

In general, the curves for $q = \infty$ represent reactions that are pseudo first order in A, since B is negligibly depleted by the reaction. At small values of the dimensionless time, Φ is always close to unity, indicating an essentially physical diffusion process, with negligible influence of the reaction on the rate at which component A crosses the interface. Essentially physical diffusion of A occurs for every reaction when any one of the following is sufficiently small:

1. The real time t.
2. The forward reaction rate constant.
3. The initial uniform concentration of B in the medium (provided $\beta \neq 0$).

4. The concentration of A at the interface (provided $\alpha \neq 1$).

At sufficiently large times for any reaction, the value of Φ approaches a constant as θ increases. This asymptotic value of Φ corresponds to the existence of an infinitely rapid, reversible reaction. Under these conditions, chemical equilibrium exists throughout the semi-infinite medium.

The curves of Φ vs. θ show the gradual transformation with time from a purely diffusional process to one in which the reaction exerts its maximum relative effect on the rate at which A crosses the interface.

Figures 13 and 14 show the effects of the ratios D_B/D_A and D_N/D_A on the values of Φ. Despite a twenty-fivefold change in these ratios, the effect on Φ is small. Even at $\theta = 100$, where the curves are approaching their asymptotes and their divergence is greatest, the variation in Φ is less than $\pm$ 10%. It is evident that D_B/D_A has a greater effect on Φ than does D_N/D_A. This is attributable to the fact that the initial concentrations of M and N are zero and the effect of the reverse reaction is not as strongly felt as that of the forward reaction, especially at small values of θ.

It was observed that the Φ vs. θ curves were not very sensitive to p, q and the reaction orders when compared at the same asymptotic value of Φ. Similar results have been found by others (*4, 6*).

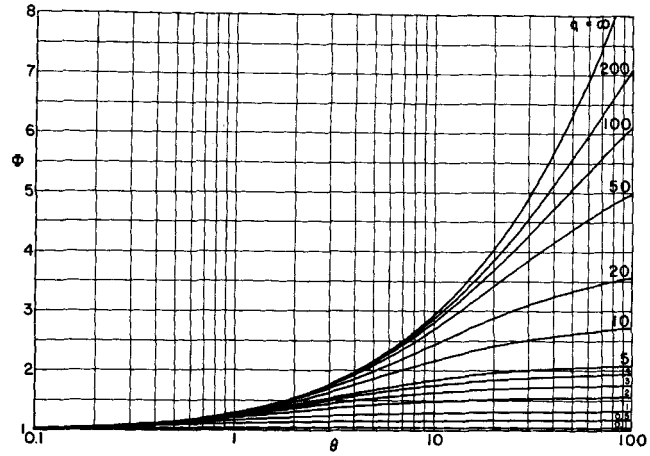

Fig. 4. Effect of chemical reaction $A + B \rightleftharpoons M + N$ on the mass transfer rate in a semi infinite medium for $p = 1$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

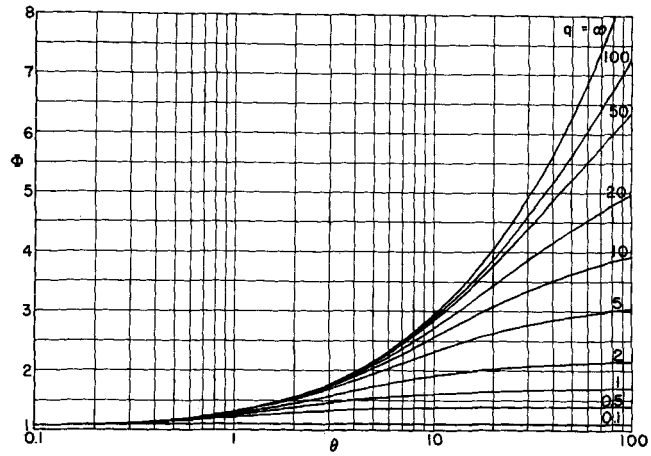

Fig. 5. Effect of chemical reaction $A + B \rightleftharpoons M + N$ on the mass transfer rate in a semi-infinite medium for $p = 2$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

SOME LIMITING CASES

It is well known that the numerical values obtained for $\Phi = k_L/k_L^o$ by means of the penetration theory are usually quite close to the values obtained by means of the film theory, particularly when the diffusivity ratios are near unity (*11*). It is apparent that analytical solutions based on film theory are quite valuable since they can be used as close approximations to the penetration theory values or as a check on the computer solutions.

One useful result would be a film theory solution for the asymptotic value of Φ at high values of θ. This limiting solution represents diffusion with an equilibrium chemical reaction. Under these conditions the forward and reverse reactions are infinitely rapid, chemical equilibrium prevails throughout the medium and Φ has its maximum possible value. Problems of this type can be treated by the method of Olander (*28*). The film theory equations representing total component material balances for diffusion with an equilibrium chemical reaction, $\gamma_A A + \gamma_B B \rightleftharpoons \gamma_M M + \gamma_N N$ are

$$\frac{D_A}{\gamma_A}\frac{d^2A}{dx^2} + \frac{D_M}{\gamma_M}\frac{d^2M}{dx^2} = 0 \qquad (35)$$

$$\frac{D_A}{\gamma_A}\frac{d^2A}{dx^2} + \frac{D_N}{\gamma_N}\frac{d^2N}{dx^2} = 0 \qquad (36)$$

$$\frac{D_B}{\gamma_B}\frac{d^2B}{dx^2} + \frac{D_M}{\gamma_M}\frac{d^2M}{dx^2} = 0 \qquad (37)$$

$$\frac{D_B}{\gamma_B}\frac{d^2B}{dx^2} + \frac{D_N}{\gamma_N}\frac{d^2N}{dx^2} = 0 \qquad (38)$$

The boundary conditions

$$x = 0, \quad A = A_i \qquad (39)$$

$$x = x_L, \quad A = A_o \qquad (40)$$

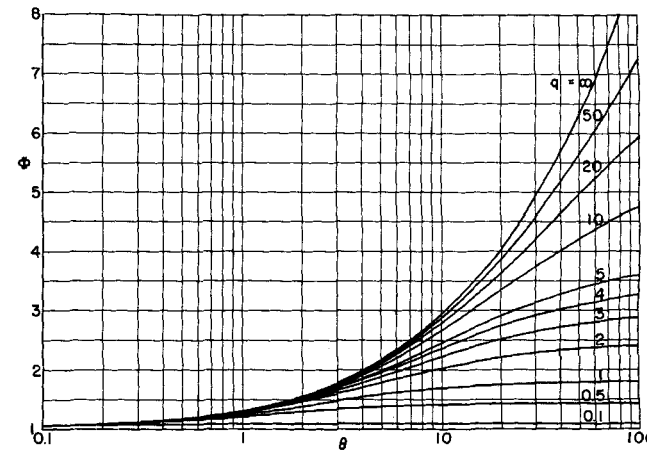

Fig. 6. Effect of chemical reaction $A + B \rightleftharpoons M + N$ on the mass transfer rate in a semi-infinite medium for $p = 5$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

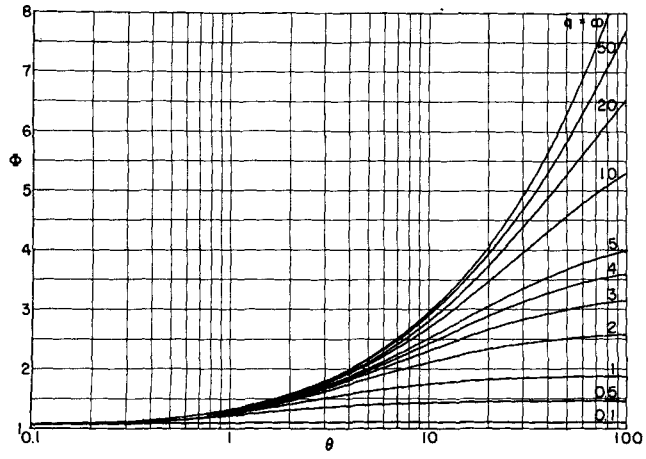

Fig. 7. Effect of chemical reaction $A + B \rightleftharpoons M + N$ on the mass transfer rate in a semi-infinite medium for $p = 10$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

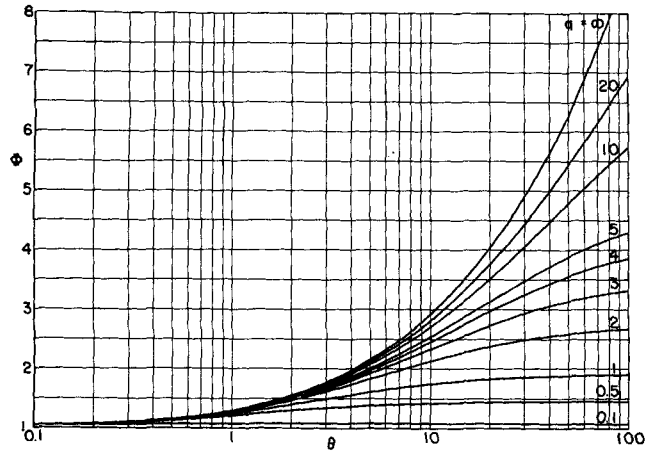

Fig. 8. Effect of chemical reaction $A + B \rightleftharpoons M + N$ on the mass transfer rate in a semi-infinite medium for $p = 20$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

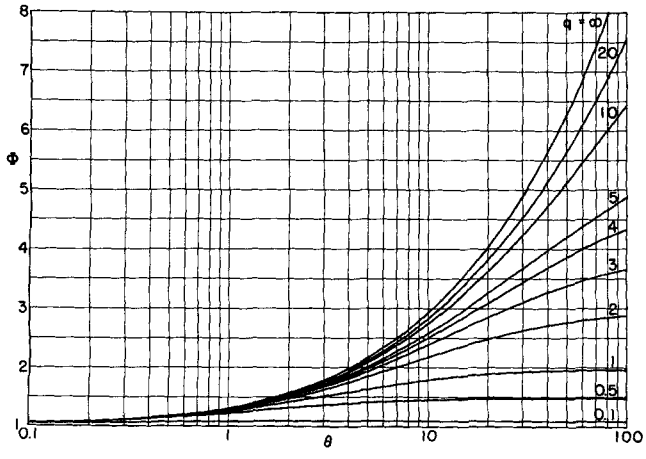

Fig. 9. Effect of chemical reaction $A + B \rightleftharpoons M + N$ on the mass transfer rate in a semi-infinite medium for $p = \infty$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

lead to the equation

$$\Phi = \frac{k_L}{k_L^o} = 1 + \frac{D_M \gamma_A}{D_A \gamma_M} \cdot \frac{\Psi}{(A_i - A_o)} \tag{41}$$

where $\Psi = (M_i - M_o)$. The additional boundary condition

$$x = 0, \frac{dB}{dx} = 0, \frac{dM}{dx} = 0, \frac{dN}{dx} = 0 \tag{42}$$

gives the following results:

$$B_i = B_o + \frac{D_M \gamma_B}{D_B \gamma_M} (M_o - M_i) \tag{43}$$

$$N_i = N_o + \frac{D_M \gamma_N}{D_N \gamma_M} (M_i - M_o) \tag{44}$$

Since chemical equilibrium prevails at the interface

$$K = \frac{M i^\mu N_i^\nu}{A_i^\alpha B_i^\beta} = \frac{M_i^\mu \left[N_o + \frac{D_M \gamma_N}{D_N \gamma_M} (M_i - M_o) \right]^\nu}{A_i^\alpha \left[B_o + \frac{D_M \gamma_B}{D_B \gamma_M} (M_o - M_i) \right]^\beta} \tag{45}$$

Various cases can now be treated by solving Equation (45) for M_i and substituting the result in Equation (41). It is evident that the solution for M_i does not require that α be known numerically. Accordingly, α will be carried through as a parameter, the value of which need not be specified until the final equation for Φ is applied to a particular problem.

Case 1.

α remains general and $\beta = 1$, $\mu = 1$, $\nu = 1$. The result is

$$\Psi = \frac{1}{2} \left\{ \left[\left(\frac{D_N \gamma_M}{D_M \gamma_N} - 1 \right) \sqrt{K A_o^\alpha B_o} + \frac{D_N \gamma_B}{D_B \gamma_N} K A_i^\alpha \right]^2 + 4 \left(\frac{D_N \gamma_B}{D_B \gamma_N} K A_i^\alpha \right) \left[\frac{D_B \gamma_M}{D_M \gamma_B} B_o + \sqrt{K A_o^\alpha B_o} \right] \right\}^{1/2} - \frac{1}{2} \left[\left(\frac{D_N \gamma_M}{D_M \gamma_N} + 1 \right) \sqrt{K A_o^\alpha B_o} \right.$$

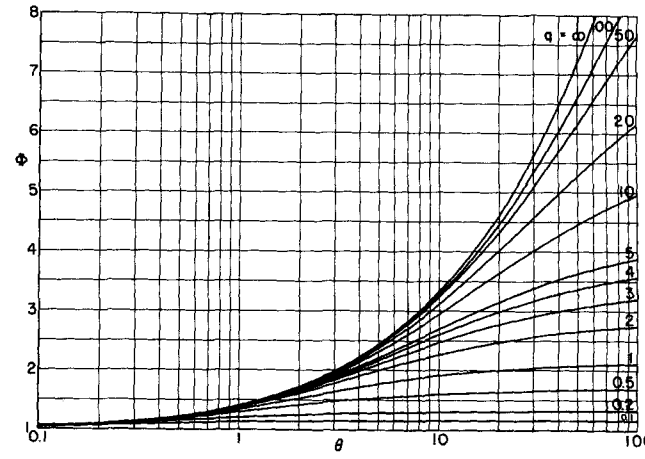

Fig. 10. Effect of chemical reaction $2A + B \rightleftharpoons M + N$ on the mass transfer rate in a semi-infinite medium for $p = 1$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

$$+\frac{D_N\gamma_B}{D_B\gamma_N}KA_i^{\alpha}\Bigg] \quad (46)$$

The same case with $\alpha = 1$ was solved by Olander (28), but his Equation (72), analogous to Equation (46), contains a misprint.

If one assumes $A_o = 0$, equal diffusivities and conformance of the reaction orders to the stoichiometry, the final result can be expressed in terms of the dimensionless parameters p and q (as employed in the penetration theory):

$$\Phi = 1 + \frac{\alpha q}{2}\left[\sqrt{\left(\frac{p}{q}\right)^2 + \frac{4p}{q}} - \frac{p}{q}\right] \quad (47)$$

Case 2.

α remains general and $\beta = 2$, $\mu = 1$, $\nu = 1$. The result is

$$\Psi = \frac{1}{2\left[\frac{D_M\gamma_N}{D_N\gamma_M} - KA_i^{\alpha}\left(\frac{D_M\gamma_B}{D_B\gamma_M}\right)^2\right]}$$

$$\Bigg\{\Bigg[\left(1-\frac{D_M\gamma_N}{D_N\gamma_M}\right)\sqrt{KA_o^{\alpha}B_o^2} + 2\,KA_i^{\alpha}\frac{D_M\gamma_B}{D_B\gamma_M}\left(B_o + \frac{D_M\gamma_B}{D_B\gamma_M}\sqrt{KA_i^{\alpha}B_o^2}\right)\Bigg]^2$$

$$+ 4\,KA_i^{\alpha}\left[B_o + \frac{D_M\gamma_B}{D_B\gamma_M}\sqrt{KA_o^{\alpha}B_o^2}\right]^2\left[\frac{D_M\gamma_N}{D_N\gamma_M} - KA_i^{\alpha}\left(\frac{D_M\gamma_B}{D_B\gamma_M}\right)^2\right]\Bigg\}^{1/2}$$

$$-\left[\left(1-\frac{D_M\gamma_N}{D_N\gamma_M}\right)\sqrt{KA_o^{\alpha}B_o^2} + 2\,KA_i^{\alpha}\frac{D_M\gamma_B}{D_B\gamma_M}\left(B_o + \frac{D_M\gamma_B}{D_B\gamma_M}\sqrt{KA_o^{\alpha}B_o^2}\right)\right]$$

$$2\left[\frac{D_M\gamma_N}{D_N\gamma_M} - KA_i^{\alpha}\left(\frac{D_M\gamma_B}{D_B\gamma_M}\right)^2\right]$$

$$-\sqrt{KA_o^{\alpha}B_o^2} \quad (48)$$

If one assumes $A_o = 0$, equal diffusivities and conformance of the reaction orders to the stoichiometry

$$\Phi = 1 + \frac{\alpha q\left(\sqrt{\frac{p}{q}} - \frac{2p}{q}\right)}{\left(1-\frac{4p}{q}\right)} \quad (49)$$

Case 3.

α remains general and $\beta = 1$, $\mu = 2$, $\nu = 1$. While the general solution is possible to obtain, it is extremely lengthy. Consequently, the result for the common case of $A_o = 0$ is given as

$$\Psi = \left\{\frac{1}{2}\left(\frac{D_N\gamma_M}{D_M\gamma_N}KA_i^{\alpha}B_o\right) + \left[\frac{1}{27}\left(\frac{D_N\gamma_B}{D_B\gamma_N}KA_i^{\alpha}\right)^3 + \frac{1}{4}\left(\frac{D_N\gamma_M}{D_M\gamma_N}KA_i^{\alpha}B_o\right)^2\right]^{1/2}\right\}^{1/3}$$

$$+\left\{\frac{1}{2}\left(\frac{D_N\gamma_M}{D_M\gamma_N}KA_i^{\alpha}B_o\right) - \left[\frac{1}{27}\left(\frac{D_N\gamma_B}{D_B\gamma_N}KA_i^{\alpha}\right)^3 + \frac{1}{4}\left(\frac{D_N\gamma_M}{D_M\gamma_N}KA_i^{\alpha}B_o\right)^2\right]^{1/2}\right\}^{1/3} \quad (50)$$

If, in addition to $A_o = 0$, one assumes equal diffusivities and conformance of the reaction orders to the stoichiometry

$$\Phi = 1 + \frac{\alpha}{2}\left[pq^2 + \sqrt{\frac{1}{27}(pq)^3 + (pq^2)^2}\right]^{1/3} + \frac{\alpha}{2}\left[pq^2 - \sqrt{\frac{1}{27}(pq)^3 + (pq^2)^2}\right]^{1/3} \quad (51)$$

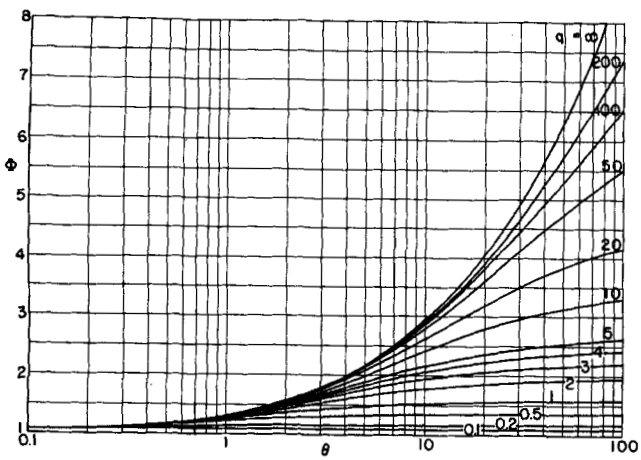

Fig. 11. Effect of chemical reaction $A + 2B \rightleftharpoons M + N$ on the mass transfer rate in a semi-infinite medium for $p = 1$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 2$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

Table 1 shows a comparison of the asymptotic penetration theory solutions obtained by computer with the film theory solutions obtained analytically. Of the twenty cases shown, fifteen agree within 5%. The largest deviation is 20%. It is apparent that useful estimates of the asymptotic penetration theory solutions usually can be obtained by using the analytical solutions based on film theory. As noted by others for simpler kinetics, it was found in this study that agreement between the film and penetration models was best when the diffusivity ratios were unity.

THERMODYNAMIC LIMITATIONS ON THE REACTION RATE EXPRESSION

In the mathematical formulation given by Equations (1) to (4), the stoichiometry of the reaction can be chosen independently of the reaction orders. This does not imply that the stoichiometric coefficient and reaction order of a given species are independent. In fact, they are not. Recognition of the nature of their relationship is important for the proper application of the differential equations.

It has been shown by Denbigh (*14*) that the following relationship is necessary to satisfy the thermodynamic requirements:

$$\frac{M^{\mu}N^{\nu}}{A^{\alpha}B^{\beta}} = f\left[M^{\gamma M}, N^{\gamma N}, A^{-\gamma A}, B^{-\gamma B}\right] \quad (52)$$

He states that the following power function is sufficient to satisfy these requirements:

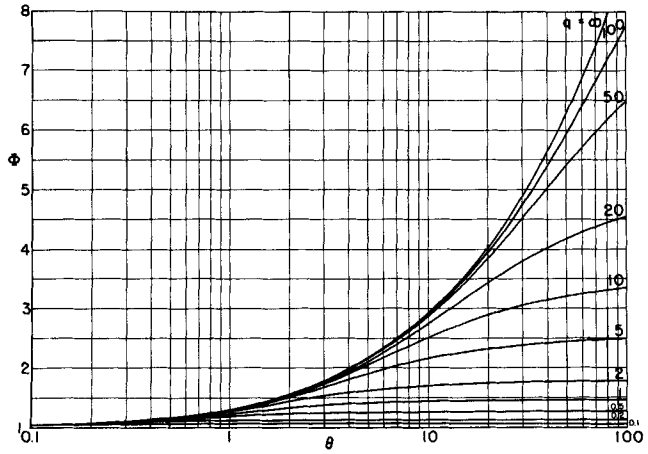

Fig. 12. Effect of chemical reaction $A + B \rightleftharpoons 2M + N$ on the mass transfer rate in a semi-infinite medium for $p = 1$, $r_B = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 2$, $\nu = 1$, $A_o = M_o = N_o = 0$.

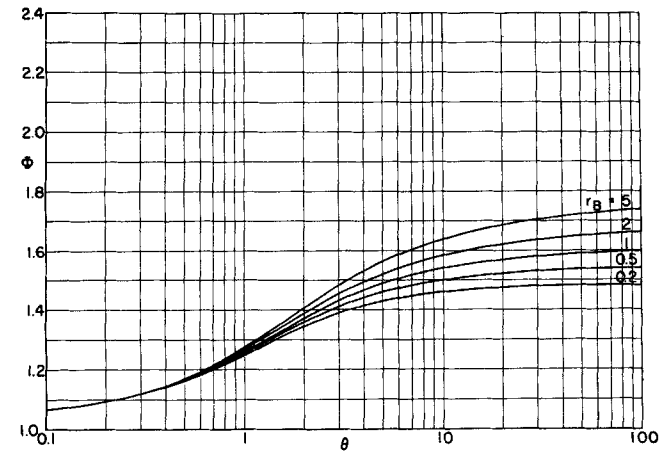

Fig. 13. Effect of the diffusivity ratio D_B/D_A on the mass transfer rate for the reaction $A + B \rightleftharpoons M + N$ in a semi-infinite medium for $p = 1$, $q = 1$, $r_M = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

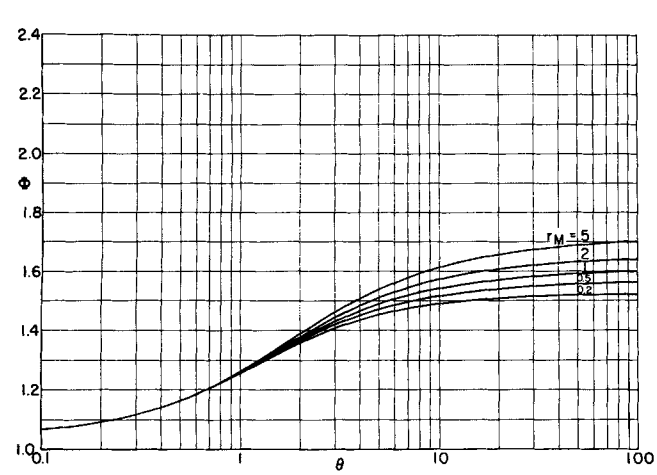

Fig. 14. Effect of the diffusivity ratio D_M/D_A on the mass transfer rate for the reaction $A + B \rightleftharpoons M + N$ in a semi-infinite medium for $p = 1$, $q = 1$, $r_B = 1$, $r_N = 1$, $\alpha = 1$, $\beta = 1$, $\mu = 1$, $\nu = 1$, $A_o = M_o = N_o = 0$.

TABLE 1. COMPARISON OF ASYMPTOTIC PENETRATION AND FILM THEORY SOLUTIONS

In all cases $A_o = 0$ and the reaction orders conform to the stoichiometry

Case No.	α	β	μ	ν	D_B/D_A	D_M/D_A	D_N/D_A	p	q	Φ Penetration	Φ Film
1	1	1	1	1	1	1	1	1	1	1.60	1.62
2	1	1	1	1	1	1	1	1	2	1.96	2.00
3	1	1	1	1	1	1	1	0.1	2	1.38	1.40
4	1	1	1	1	1	1	1	0.1	5	1.61	1.65
5	1	1	1	1	1	1	1	10	1	1.89	1.91
6	1	1	1	1	1	1	1	5	2	2.42	2.53
7	1	1	1	1	1	1	1	5	5	3.95	4.09
8	1	1	1	1	0.5	1	1	1	1	1.54	1.41
9	1	1	1	1	1	1	0.5	1	1	1.56	1.50
10	2	1	1	1	1	1	1	1	0.5	1.69	1.73
11	2	1	1	1	1	1	1	1	1	2.13	2.24
12	2	1	1	1	1	1	1	1	2	2.74	3.00
13	1	2	1	1	1	1	1	1	3	1.77	1.82
14	1	2	1	1	1	1	1	1	5	2.10	2.17
15	1	2	1	1	1	1	1	1	1	1.33	1.33
16	1	1	2	1	1	1	1	1	1	1.48	1.50
17	1	1	2	1	1	1	1	5	2	2.18	2.24
18	2	1	2	1	1	1	1	1	1	1.93	2.00
19	2	1	2	1	1	1	1	1	5	3.78	4.24
20	2	1	2	1	1	1	1	1	10	5.25	6.28

$$\frac{\alpha}{\gamma_A} = \frac{\beta}{\gamma_B} = \frac{\mu}{\gamma_M} = \frac{\nu}{\gamma_M} = \xi \qquad (53)$$

where ξ is a positive constant, which may be fractional.

More recently, it was shown by Blum and Luus (3) that Equation (53) is not only sufficient, but necessary to satisfy the thermodynamic consistency requirements. Thus, Equation (53) and no other defines the relationship that must be fulfilled between the stoichiometry and the reaction orders.

It is evident that the reaction order and stoichiometric coefficient of each species may be made equal without violating the requirements of Equation (53).

CONCLUSIONS

The penetration theory equations for diffusion with a generalized, reversible chemical reaction, $\gamma_A A + \gamma_B B \rightleftharpoons \gamma_M M + \gamma_N N$, have been solved. An implicit, finite-difference technique was employed for the calculations, resulting in stability of the computer solutions over wide ranges of the space and time increments.

Several special cases were solved analytically with the film theory. These show good agreement with the penetration theory solutions, provided the diffusivity ratios are not greatly different from unity.

The generalized model developed offers a high degree of flexibility for solving problems. The options provided for the kinetics and the geometry permit a large number of cases to be treated. As a result, many of the limitations imposed by previous solutions to the penetration theory equations for diffusion with a single chemical reaction have been removed.

ACKNOWLEDGMENT

Substantial assistance with the machine computations was given by Miss Phyllis M. G. Wong and is gratefully acknowledged.

NOTATION

A = concentration of the species entering the medium in which reaction occurs, moles/cc.
A_i = concentration of A at the interface, moles/cc.
A_o = initial concentration of A, moles/cc.
a = A/A_j
a_o = A_o/A_i
B = concentration of the species reacting with A, moles/cc.
B_i = concentration of B at the interface, moles/cc.
B_o = initial concentration of B, moles/cc.
b = B/B_o
c = arbitrary constant in Equation (31)
D = diffusion coefficient, subscript indicating the species, sq.cm./sec.
F = $F(a,b,m,n) = (a^\alpha b^\beta/q - (m^\mu n^\nu/p)$
K = k_1/k_2 = equilibrium constant, $(\text{moles/cc.})^{\mu+\nu-\alpha-\beta}$
k_1 = forward reaction rate constant, $(\text{moles/cc.})^{1-\alpha-\beta}$/sec.
k_2 = reverse reaction rate constant, $(\text{moles/cc.})^{1-\mu-\nu}$/sec.
K_1 = parameter in Equation (34)
K_2 = parameter in Equation (34)
k_L = average mass transfer coefficient, cm./sec.
k_L^o = average mass transfer coefficient in the absence of chemical reaction, cm./sec.
M = concentration of reaction product M, moles/cc.
M_i = concentration of M at the interface, moles/cc.
M_o = initial concentration of M, moles/cc.
m = M/B_o
N = concentration of reaction product N, moles/cc.
N_i = concentration of N at the interface, moles/cc.
N_o = initial concentration of N, moles/cc.
n = N/B_o
p = $KB_o^{1+\beta-\mu-\nu}/A_i^{1-\alpha}$
q = B_o/A_i
r_B = D_B/D_A
r_M = D_M/D_A
r_N = D_N/D_A
R = average rate of diffusion of A through the interface, moles/(sq.cm.)(sec.)
R^o = average rate of diffusion of A through the interface in the absence of chemical reaction, moles/(sq.cm.)(sec).
S = $\Delta\theta/\overline{\Delta y}^2$
t = time, sec.
x = distance in the direction of diffusion, cm.
x_L = film thickness, cm.
x_o = distance from the interface to the center, cm.
y = $x\sqrt{k_1 B_o^\beta A_i^{\alpha-1}/D_A}$, dimensionless distance
y_o = $x_o\sqrt{k_1 B_o^\beta A_i^{\alpha-1}/D_A}$
z = variable defined by Equation (31)

Greek Letters

α = kinetic order with respect to A
β = kinetic order with respect to B
γ = stoichiometric coefficient, subscript indicating the species
θ = $k_1 B_o^\beta A_i^{\alpha-1} t$, dimensionless time
λ = geometrical parameter (integer)
μ = kinetic order with respect to M
ν = kinetic order with respect to N
ξ = positive constant defined by Equation (53)
Φ = k_L/k_L
Ψ = $(M_i - M_o)$, moles/cc.

Subscript

j = space increment

Superscript

k = time increment

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Manuscript received January 17, 1966; revision received August 31, 1966; paper accepted August 31, 1966.