

Mathematical Models for Mass Transfer Accompanied by Reversible Chemical Reaction

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Based on the film-penetration theory, the film theory, and the surface renewal theory, theoretical equations are obtained for the rate of interphase mass transfer accompanied by a first-order reversible reaction. The film-penetration theory is again found to be the more general concept and the other two theories are merely the limiting cases of the film-penetration theory. The rate equation based on the film-penetration theory can also be reduced to those obtained by other investigators on the basis of simpler postulations.

Contrary to the previous findings in other chemical mass transfer systems, it is found that the predicted effects of chemical reaction on the overall mass transfer rate are indeed sensitive to the theory or the model adopted in postulating the mechanism. One exception to this is when the diffusivities of the reactant and the product are nearly equal. For this special case, the three theories predict practically the same effects of a reversible reaction.

An approximate rate equation is proposed for mass transfer with a high order reversible reaction. When the forward reaction is very rapid, the reaction rate constants become insignificant variables and the mass transfer rate is a simple function of the diffusivity ratio, the concentration ratio, and the order of reaction.

In a previous paper (14), the authors discussed the mechanism of mass transfer accompanied by a first-order irreversible chemical reaction. The mathematical model, which was based on the film-penetration concept (7, 26), was proposed to describe the physicochemical behavior at the interphase. The nature of mass transfer behavior and the transfer rate were analyzed and evaluated in terms of the dimensionless groups appearing in the proposed theoretical equations. It was shown that when the dimensionless groups approach the limiting values of zero or infinity, the general equations can be reduced to those based on simpler postulations, such as the film theory (9, 10), the penetration theory (2), and the surface renewal theory (1, 3). Thus, the conclusion that these simpler theories are merely the limiting cases of the more general film-penetration concept is also valid for mass transfer with a first-order irreversible reaction. The same conclusion was obtained earlier by Toor and Marchello (26) for mass transfer in the absence of chemical reaction.

Another interesting finding in the previous work was that the film-penetration concept, the film theory, and the surface renewal theory all predict practically the same effect of chemical reaction on the mass transfer rate. The theoretically predicted rate of mass transfer with a first-order irreversible reaction is insensitive to a model or theory, provided that the prediction begins at the same physical mass transfer rate.

Because of these encouraging and interesting findings on mass transfer with a first-order irreversible reaction, it was logical to then find out if similar conclusions could be reached for mass transfer accompanied by other more complicated and different reactions. Thus, the mechanism of mass transfer with a reversible reaction was chosen as the subject of the present study.

Despite its frequent occurrence in chemical engineering systems, a theoretical model for mass transfer with a reversible reaction has not been completely established.

Because of mathematical difficulties involved in establishing such a complete model, previous workers generally limited their studies to a much simpler system. Olander (20) and Toor and Chiang (25) studied the system with an equilibrium reversible reaction. Unless the molecular diffusion of the reactants and the products are extremely slow compared with the reaction rates, the assumption of an equilibrium reversible reaction is not always valid. Danckwerts (6) studied a special reversible reaction system where the diffusivities of both the reactant and the product are equal. This solution, thus, has only a limited application. Therefore, it is the first objective of the present study to establish a more complete theoretical model for the mechanism of mass transfer with a nonequilibrium reversible reaction.

The statement was made earlier that the film-penetration theory is a more general concept than the other two theories in postulating the interphase mass transfer mechanism. So far, this has been supported by two examples: one by Toor and Marchello for mass transfer in the absence of chemical reaction, and the other by the present authors for mass transfer with a first-order irreversible chemical reaction. However, more evidence is required to prove that the film-penetration theory is a more general theory. Thus, if the same can be proved for mass transfer with a reversible reaction, the usefulness of the film-penetration theory will be further broadened. This is the second objective of the current study. Therefore, three separate theoretical models for mass transfer with reversible reaction are developed independently based on three different concepts: the film theory, the surface renewal theory, and the film-penetration theory. The resulting equations are then analyzed and evaluated.

DIFFUSION WITH REVERSIBLE REACTION

A theoretical mechanism of interphase mass transfer is formulated by considering two aspects of physicochemical behavior at the interphase. One aspect deals with the

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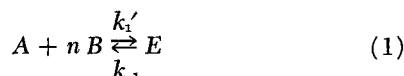
hydrodynamic activities of the phases near the phase boundary, and the other with the diffusional and reaction behavior of the transporting molecular species.

To postulate the hydrodynamic and the flow pattern of the liquid phase near the phase boundary, two distinctly different concepts were proposed in the past. One hypothesis is that a stationary film always exists at the interphase and that the turbulence does not reach the phase boundary. The other concept, instead, assumes that the interphase boundary is continuously renewed by the fresh liquid surface elements or eddies that are created by the turbulence.

Similarly, there are two schools of thought with regard to the manner by which the molecular species diffuse and react within the liquid film or surface element. One view is that the species are transported by steady state molecular diffusion, whereas the other assumes unsteady state diffusion.

In general, a theoretical model for interphase mass transfer mechanism is the result of a specific combination of the above postulations. For example, the film theory (19, 30) is a combination of the stationary film concept and the steady state diffusion concept.

Three theoretical models for the mechanism of mass transfer with a reversible reaction are developed in this study. Only the diffusional and reaction behavior will be discussed in this section; the hydrodynamic aspect of the models will be discussed in later sections. After dissolving into the liquid film or the liquid surface element from the opposite phase, the reactant A is assumed to penetrate through the element by one-dimensional unsteady state molecular diffusion. Convection transport is assumed to be insignificant. The diffusing stream of the reactant A is depleted along the path of diffusion by its reversible reaction with the reactant B, which is an existing component of the liquid film or element. If such a reversible reaction may be represented as



and if the order of reaction is $(n + 1)^{\text{th}}$ order, the material balances of each component within an infinitesimally small segment yield the following set of partial differential equations.

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_1' C_A C_B^n + k_{-1} C_E \quad (2)$$

$$\frac{1}{n} \frac{\partial C_B}{\partial t} = \frac{D_B}{n} \frac{\partial^2 C_B}{\partial x^2} - k_1' C_A C_B^n + k_{-1} C_E \quad (3)$$

$$\frac{\partial C_E}{\partial t} = D_E \frac{\partial^2 C_E}{\partial x^2} + k_1' C_A C_B^n - k_{-1} C_E \quad (4)$$

The exact analytical solution of this set of nonlinear partial differential equations has not been possible. However, in many actual operations, the amount of the reactant B in the liquid solvent is comparatively large and its concentration remains nearly constant during the diffusional and reaction process. Thus, the term $k_1' C_A C_B^n$ is approximately constant and the above system with a high order reaction may be treated as a pseudo first-order reaction.

The reaction of a simple first-order or pseudo first-order reversible reaction may be represented as



where E is the product. This is the reaction about which the present study is mostly concerned. When the diffusion

of the reactant A and the product E is accompanied by the above first-order reaction, the three material balance equations, that is Equations (2), (3), and (4), are replaced by the following set of two linear partial differential equations.

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_1 C_A + k_{-1} C_E \quad (6)$$

$$\frac{\partial C_E}{\partial t} = D_E \frac{\partial^2 C_E}{\partial x^2} + k_1 C_A - k_{-1} C_E \quad (7)$$

The concentration gradients of the reactant A and the product E can be established by simultaneously solving these equations. The boundary and initial conditions required for the solution vary, depending on the model adopted for the mass transfer mechanism. These will be discussed in the subsequent sections.

In the past, in order to minimize the mathematical difficulties, the above set of simultaneous equations could be reduced to a single equation with a simplifying assumption. For example, Danckwerts (5) treated the case where the diffusivities of both the reactant A and the product E are equal. In another case, Toor and Chiang (25) studied the situation where the reversible reaction is always at equilibrium.

Since the current study deals with the case where the diffusivities of both the reactant and the product are not necessarily equal, and where the reversible reaction is not always at equilibrium, Equations (6) and (7) should not be reduced to a single equation but must be solved simultaneously.

For the sake of brevity, hereafter in this paper mass transfer accompanied by reversible chemical reaction will be referred to as chemical mass transfer, and mass transfer in the absence of chemical reaction will be called physical mass transfer.

FILM THEORY

The film theory is based on the assumption that when two fluid phases are brought in contact with each other, there exists on each side of the phase boundary a thin layer of stagnant fluid. Mass transfer by convection within this thin layer is assumed to be insignificant, and accordingly the transport is achieved solely by steady state molecular diffusion. The review of the advantages and disadvantages of this model was given in previous papers (14, 15).

According to the film theory, the molecular species moves across the film by steady state molecular diffusion and there is no mass accumulation at any point within the film. Therefore

$$\frac{\partial C_A}{\partial t} = 0 \quad (8)$$

and

$$\frac{\partial C_E}{\partial t} = 0 \quad (9)$$

Thus, Equations (6) and (7), the material balance equations for the diffusing masses accompanied by a reversible reaction, may be reduced to the following set of simultaneous ordinary differential equations.

$$D_A \frac{d^2 C_A}{dx^2} - k_1 C_A + k_{-1} C_E = 0 \quad (10)$$

$$D_E \frac{d^2 C_E}{dx^2} + k_1 C_A - k_{-1} C_E = 0 \quad (11)$$

At the interphase boundary, the concentration of the reactant A is designated as \bar{C}_A , and may be assumed to

be in equilibrium with that of the opposite phase. If the product E is incapable of crossing the phase boundary to enter into the opposite phase, the concentration gradient of the product E at the interphase is zero. This situation occurs frequently, for example, when the product E is nonvolatile or insoluble into the opposite phase. Mathematically, these boundary conditions are written as

$$x = 0, \quad C_A = C_{A_i}, \quad \frac{dC_E}{dx} = 0 \quad (12)$$

The concentrations of the reactant A and the product E at the terminal of the film are equal to the concentrations in the bulk and are expressed as

$$x = L, \quad C_A = C_{A_L}, \quad C_E = C_{E_L} \quad (13)$$

Solving Equations (10) and (11) with the boundary conditions of (12) and (13), the concentration distributions of the reactant A and the product E are obtained.

$$C_A = - \left\{ \left[u \frac{K_1}{D_{EA}} (x - L) + \sinh ux + uL \frac{K_1}{D_{EA}} \cosh ux \right] \cdot \left\{ C_{A_i} - C_{A_L} + \frac{1 - \frac{1}{\cosh uL}}{1 + \frac{K_1}{D_{EA}}} (C_{A_L} - K_1 C_{E_L}) \right\} \right\} \left\{ \tanh uL + uL \frac{K_1}{D_{EA}} \right\} + \left\{ C_{A_i} - C_{A_L} + \frac{C_{A_L} - K_1 C_{E_L}}{1 + \frac{K_1}{D_{EA}}} \right\} \cosh ux - \frac{C_{A_L} - K_1 C_{E_L}}{1 + \frac{K_1}{D_{EA}}} + C_{A_L} \quad (14)$$

and

$$C_E = - \frac{1}{D_{EA}} \left\{ \left[u(x - L) - \sinh ux - uL \frac{K_1}{D_{EA}} \cosh ux \right] \cdot \left\{ C_{A_i} - C_{A_L} + \frac{(C_{A_L} - K_1 C_{E_L})(1 - \operatorname{sech} uL)}{1 + \frac{K_1}{D_{EA}}} \right\} \right\} \left\{ \tanh uL + uL \frac{K_1}{D_{EA}} \right\} - \frac{1}{D_{EA}} \left\{ C_{A_i} - C_{A_L} + \frac{C_{A_L} - K_1 C_{E_L}}{1 + \frac{K_1}{D_{EA}}} \right\} \cosh ux - \frac{1}{K_1} \frac{C_{A_L} - K_1 C_{E_L}}{1 + \frac{K_1}{D_{EA}}} + \frac{C_{A_L}}{K_1} \quad (15)$$

The rate of chemical mass transfer is then expressed as

$$\bar{N}_A = N_A = -D_A \left(\frac{dC_A}{dx} \right)_{x=0} = \frac{D_A}{L}$$

$$\frac{\left(1 + \frac{D_{EA}}{K_1} \right) (C_{A_i} - C_{A_L}) + \frac{D_{EA}}{K_1} (1 - \operatorname{sech} uL) (C_{A_L} - K_1 C_{E_L})}{1 + \frac{D_{EA}}{K_1} \frac{\tanh uL}{uL}} \quad (16)$$

where

$$K_1 = k_{-1}/k_1 \quad (17)$$

$$D_{EA} = D_E/D_A \quad (18)$$

and

$$u = \left[\frac{k_1}{D_A} \left(1 + \frac{K_1}{D_{EA}} \right) \right]^{1/2} \quad (19)$$

Equation (16) is the basic rate equation based on the film theory for mass transfer with a first-order reversible reaction. For the special case where a chemical equilibrium exists in the phase bulk, Equation (19) may be reduced to

$$\bar{N}_A = \frac{D_A}{L} \frac{\left(1 + \frac{D_{EA}}{K_1} \right) (C_{A_i} - C_{A_L})}{1 + \frac{D_{EA}}{K_1} \frac{\tanh uL}{uL}} \quad (20)$$

because

$$C_{A_L} = K_1 C_{E_L} \quad (21)$$

Equation (20) is identical to that proposed by Peaceman (22).

The liquid phase chemical mass transfer coefficient k_L may be defined in terms of concentration driving force as

$$\bar{N}_A = k_L (C_{A_i} - C_{A_L}) \quad (22)$$

Equation (20) may then be substituted into Equation (22) to yield the following expression for the chemical mass transfer coefficient.

$$k_L = \frac{D_A}{L} \frac{1 + \frac{D_{EA}}{K_1}}{1 + \frac{D_{EA}}{K_1} \frac{\tanh uL}{uL}} \quad (23)$$

SURFACE RENEWAL THEORY

Instead of assuming the existence of a stagnant film at the interphase, Danckwerts (3) and Kishinevskii (16, 17) thought that the liquid phase bulk is completely disturbed and that there is an infinite number of infinitesimally small surface elements or eddies in the liquid. These surface elements or eddies are continuously brought to the phase boundary where they are exposed to the other phase for a finite time before being replaced by other fresh eddies.

The Danckwerts surface renewal theory adopts this surface renewal concept to represent the hydrodynamic behavior and the unsteady state molecular diffusion for the diffusional activities through the eddies. Therefore, Equations (6) and (7) are proper differential equations that represent the material balances of the reactant A and the product E , which are transported across the surface elements by unsteady state molecular diffusion with a reversible reaction.

When the eddies are brought into contact with the phase boundary, the concentrations of A and E within the eddies are uniform and should be identical to those in the liquid phase bulk. This initial condition may be expressed as

$$x > 0, \quad t = 0, \quad C_A = C_{A_L}, \quad C_E = C_{E_L} \quad (24)$$

The boundary condition at the interphase, that is the concentration of the reactant A and the concentration gradient of the product E , should be the same as those used in the film theory. They are

$$x = 0, \quad t > 0, \quad C_A = C_{A1}, \quad \frac{\partial C_B}{\partial x} = 0 \quad (25)$$

Since the residence time of a surface element at the interphase is very short, it is quite possible that the diffusing reactant A has never penetrated to the outer edge of the surface element before the element is replaced. Therefore, mathematically, it is permissible to assume that the depth of the penetration is infinite and that there is no mass flux at the outer edge of a surface element. This boundary condition is expressed as

$$x = \infty, \quad t > 0, \quad \frac{\partial C_A}{\partial x} = 0, \quad \frac{\partial C_B}{\partial x} = 0 \quad (26)$$

Thus, the concentration gradients may be obtained by solving the set of partial differential equations, Equations (6) and (7), with the boundary and initial conditions, (24), (25), and (26). The method of integral transformation can be applied in the solution. The Laplace transform of the concentration $C_A(x, t)$ is obtained as

$$\bar{C}_A(x, s) = \frac{V(W - V^2)}{s(U - V)(U^2 + UV + V^2 - W)} \left[C_{A1} - \frac{(K_1 + \beta) C_{AL} + K_1 C_{BL}}{1 + \beta + K_1} \right] + \frac{U(W - U^2)}{V(W - V^2)} e^{-Vx} + \frac{(K_1 + \beta) C_{AL} + K_1 C_{BL}}{s(1 + \beta + K_1)} \quad (27)$$

where

$$\beta = s/k_1 \quad (28)$$

$$W = \frac{k_1}{D_A} (1 + \beta) \quad (29)$$

$$U = \left[\frac{k_1}{2D_A} \left\{ 1 + \beta + \frac{K_1 + \beta}{D_{EA}} + \sqrt{\left(1 + \beta + \frac{K_1 + \beta}{D_{EA}} \right)^2 - \frac{4\beta}{D_{EA}} (1 + \beta + K_1)} \right\} \right]^{1/2} \quad (30)$$

$$V = \left[\frac{k_1}{2D_A} \left\{ 1 + \beta + \frac{K_1 + \beta}{D_{EA}} - \sqrt{\left(1 + \beta + \frac{K_1 + \beta}{D_{EA}} \right)^2 - \frac{4\beta}{D_{EA}} (1 + \beta + K_1)} \right\} \right]^{1/2} \quad (31)$$

The mass transfer rate of an individual surface element is a function of its age and may be obtained by

$$N_A = -D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=0} \quad (32)$$

The average rate of mass transfer may be theoretically obtained by applying the appropriate surface age distribution function. For example, Higbie (12) assumed that the residence time of each eddy is the same regardless of its age. In other words, all the eddies are renewed at the same time. On the other hand, Danckwerts assumed the following surface age distribution function.

$$\phi(t) = se^{-st} \quad (33)$$

When the surface age distribution function and the mass transfer rate of an individual surface element are known, the average mass transfer rate may be obtained by the following equation.

$$\bar{N}_A = \int_0^\infty N_A \phi(t) dt \quad (34)$$

Therefore, if the Danckwerts surface age distribution function is adopted, Equation (34) may be rewritten, by substituting Equations (32) and (33) into Equation (34), as

$$\bar{N}_A = -D_A s \left(\frac{\partial \bar{C}_A}{\partial x} \right)_{x=0} \quad (35)$$

Finally, the theoretical expression, based on the surface renewal theory, for the average rate of chemical mass transfer may be obtained by substituting Equation (27) into Equation (35).

$$\bar{N}_A = \frac{D_A UV(U + V)}{U^2 + UV + V^2 - W} \left[C_{A1} - \frac{(K_1 + \beta) C_{AL} + K_1 C_{BL}}{1 + \beta + K_1} \right] \quad (36)$$

Again, for the special case where the chemical equilibrium between the reactant A and the product E exists in the liquid phase bulk, Equation (36), may be reduced to the following by applying Equation (21).

$$\bar{N}_A = \frac{D_A UV(U + V)}{U^2 + UV + V^2 - W} (C_{A1} - C_{AL}) \quad (37)$$

The chemical mass transfer coefficient defined by Equation (22) is then obtained by substituting Equation (37) into Equation (22).

$$k_L = \frac{D_A UV(U + V)}{U^2 + UV + V^2 - W} \quad (38)$$

For another special case where the diffusivities of the reactant A and the product E are the same, Equation (38) may be further reduced to

$$k_L = \frac{\sqrt{D_A s} (1 + K_1) \sqrt{1 + \frac{1 + K_1}{\beta}}}{K_1 + \sqrt{1 + \frac{1 + K_1}{\beta}}} \quad (39)$$

This is identical to the equation derived by Danckwerts (5).

FILM-PENETRATION THEORY

Similar to the surface renewal theory, the film-penetration theory adopts the unsteady state molecular diffusion mechanism as the means of mass transport through the film or the liquid element. Therefore, the unsteady state equations, Equations (6) and (7), are still applicable. However, a significant difference exists in postulating the penetration depth or the eventual distance of diffusion. The assumption of an infinite depth of penetration by the surface renewal theory is not in accord with the real physical picture. The film or the liquid element is very thin and its thickness must have a finite value. This is the assumption in the film-penetration theory and is expressed mathematically by the following boundary condition.

$$x = L, \quad t > 0, \quad C_A = C_{AL}, \quad C_B = C_{BL} \quad (40)$$

The thickness of a liquid eddy or the distance of the eventual penetration depends on the hydrodynamic turbulence. When the fluid turbulence is vigorous, the eddies are smaller and therefore the thickness is less.

The boundary conditions at the interphase boundary, and the initial conditions employed by the surface renewal theory, are also applicable to the film-penetration theory. Therefore, the concentration distribution of the reactant A that diffuses and reacts within the film or the liquid element may be obtained by solving simultaneously

Equations (6) and (7) with Equations (24), (25), and (40). The Laplace transformation may be used in the solution that yields the following Laplace transform of the concentration of the reactant A.

$$\bar{C}_A(x, s) = \frac{\frac{1}{s} [C_{A1} - f(C_{AL}, C_{EL})]}{\tanh UL - \frac{U(W - U^2)}{V(W - V^2)} \tanh VL} \left\{ -\sinh Ux + \tanh UL \cdot \cosh Ux + \frac{U(W - U^2)}{V(W - V^2)} [\sinh Vx - \tanh VL \cdot \cosh Vx] \right\} + \frac{1}{s(1 + \beta + K_1)} \left\{ \frac{C_{AL} - K_1 C_{EL}}{U^2 - V^2} \left[\frac{k_1}{D_A} (1 + \beta + K_1) \left(\frac{\cosh Ux}{\cosh UL} - \frac{\cosh Vx}{\cosh VL} \right) + \left(U^2 \frac{\cosh Vx}{\cosh VL} - V^2 \frac{\cosh Ux}{\cosh UL} \right) \right] + (K_1 + \beta) C_{AL} + K_1 C_{EL} \right\} \quad (41)$$

If the hydrodynamic aspect of the interphase behavior is now postulated by the Danckwerts surface renewal concept, the elements of all different ages are present at the interphase at any given time. The Danckwerts surface age distribution function is shown earlier as Equation (33). Thus, the combination of Equations (41) and (35) yields the following, based on the film-penetration theory, for the rate of mass transfer accompanied by a first-order reversible reaction.

$$\bar{N}_A = \frac{\frac{D_A}{L} (U^2 - V^2) [C_{A1} - f(C_{AL}, C_{EL})]}{(W - V^2) \frac{\tanh UL}{UL} - (W - U^2) \frac{\tanh VL}{VL}} \quad (42)$$

where

$$f(C_{AL}, C_{EL}) = \frac{1}{1 + \beta + K_1} \left\{ \frac{C_{AL} - K_1 C_{EL}}{U^2 - V^2} \left[\frac{k_1}{D_A} (1 + \beta + K_1) \cdot \left(\frac{1}{\cosh UL} - \frac{1}{\cosh VL} \right) + \left(\frac{U^2}{\cosh VL} - \frac{V^2}{\cosh UL} \right) \right] + (K_1 + \beta) C_{AL} + K_1 C_{EL} \right\} \quad (43)$$

For a special situation where the chemical equilibrium always exists at the liquid bulk, Equation (21) may be substituted in Equation (43) to yield

$$f(C_{AL}, C_{EL}) = C_{AL} \quad (44)$$

Equation (44) may then be used to simplify Equation (42) to yield the following rate equation for this special case.

$$\bar{N}_A = \frac{\frac{D_A}{L} (U^2 - V^2) (C_{A1} - C_{AL})}{(W - V^2) \frac{\tanh UL}{UL} - (W - U^2) \frac{\tanh VL}{VL}} \quad (45)$$

Thus, with the definition of Equation (22), the mathematical expression for the chemical mass transfer coefficient is obtained from Equation (45) as follows:

$$k_L = \frac{\frac{D_A}{L} (U^2 - V^2)}{(W - V^2) \frac{\tanh UL}{UL} - (W - U^2) \frac{\tanh VL}{VL}} \quad (46)$$

DISCUSSION

In the previous sections, the developed rate equations are based on the three different theories. As shown in Figure 1, the three models are not entirely independent but linked with each other. Equation (42), for mass transfer accompanied by a reversible reaction that is based on the film-penetration theory, is the key rate equation. It can be reduced to the other rate equations for mass transfer with a reversible reaction, with an irreversible reaction, or without reaction, and each based on the different mass transfer theories.

Recently, Harriott (8) proposed the subsurface renewal concept for interphase mass transfer in absence of reaction. The mathematical model based on this new concept was solved by a numerical method. It was concluded that at the limiting conditions, the subsurface renewal model can also be reduced to the film model and the penetration model. It remains to be shown whether this conclusion can be extended and applied to mass transfer with chemical reaction.

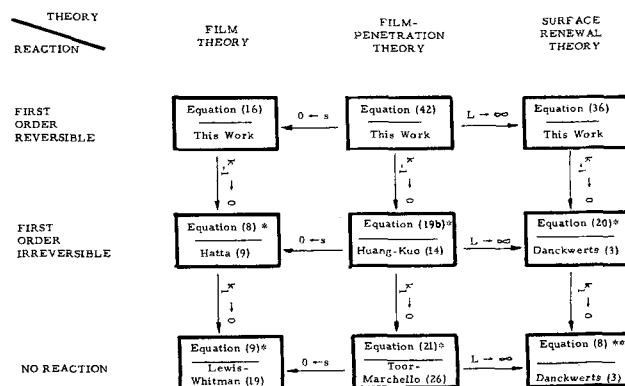
The effects of chemical reaction on the overall mass transfer rate may be discussed in terms of the ratio of chemical to physical mass transfer coefficients. For the sake of brevity hereafter in this paper, this ratio will be referred to as the transfer coefficient ratio. Theoretical expressions of the transfer coefficient ratio may be obtained by combining the appropriate equations shown in the previous sections. The following equations are obtained for the case where a chemical equilibrium between reactant A and product E is maintained in the liquid phase bulk.

Film Theory:

$$\frac{k_L}{k_L'} = \frac{\mu_1^2}{\frac{K_1}{D_{EA}} + \frac{\tanh \mu_1 \sqrt{M}}{\mu_1 \sqrt{M}}} \quad (47)$$

where

$$\mu_1 = [1 + (K_1/D_{EA})]^{1/2} \quad (48)$$



* Refers to Equation Number in Reference (14)
** Refers to Equation Number in Reference (3)

Fig. 1. Interrelationship of theories.

Surface Renewal Theory:

$$\frac{k_L}{k_L'} = \frac{\mu_2 \mu_{-2} (\mu_2 + \mu_{-2}) \sqrt{M}}{\mu_2^3 + \mu_2 \mu_{-2} + \mu_{-2}^3 - \left(1 + \frac{1}{M}\right)} \quad (49)$$

where

$$\mu_2 = \frac{1}{\sqrt{2}} \left\{ 1 + \frac{K_1}{D_{EA}} + \left(1 + \frac{1}{D_{EA}}\right) \frac{1}{M} + \sqrt{\left[1 - \frac{K_1}{D_{EA}} + \left(1 - \frac{1}{D_{EA}}\right) \frac{1}{M}\right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2} \quad (50)$$

$$\mu_{-2} = \frac{1}{\sqrt{2}} \left\{ 1 + \frac{K_1}{D_{EA}} + \left(1 + \frac{1}{D_{EA}}\right) \frac{1}{M} - \sqrt{\left[1 - \frac{K_1}{D_{EA}} + \left(1 - \frac{1}{D_{EA}}\right) \frac{1}{M}\right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2} \quad (51)$$

Film-Penetration Theory:

$$\frac{k_L}{k_L'} = \frac{\{\mu_2^3 - \mu_{-2}^3\}}{\left\{ \left[1 + \frac{1}{M} \left(\tanh \frac{1}{\sqrt{\gamma}} \right)^2 - \mu_2^2 \right] \frac{\tanh \left[\mu_2 \sqrt{\frac{M}{\gamma}} \coth \frac{1}{\sqrt{\gamma}} \right]}{\mu_2 \sqrt{M}} - \left[1 + \frac{1}{M} \left(\tanh \frac{1}{\sqrt{\gamma}} \right)^2 - \mu_{-2}^2 \right] \frac{\tanh \left[\mu_{-2} \sqrt{\frac{M}{\gamma}} \coth \frac{1}{\sqrt{\gamma}} \right]}{\mu_{-2} \sqrt{M}} \right\}} \quad (52)$$

where

$$\mu_2 = \frac{1}{\sqrt{2}} \left\{ 1 + \frac{K_1}{D_{EA}} + \left(1 + \frac{1}{D_{EA}}\right) \frac{1}{M} \left(\tanh \frac{1}{\sqrt{\gamma}} \right)^2 + \sqrt{\left[1 - \frac{K_1}{D_{EA}} + \left(1 - \frac{1}{D_{EA}}\right) \frac{1}{M} \left(\tanh \frac{1}{\sqrt{\gamma}} \right)^2\right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2} \quad (53)$$

$$\mu_{-2} = \frac{1}{\sqrt{2}} \left\{ 1 + \frac{K_1}{D_{EA}} + \left(1 + \frac{1}{D_{EA}}\right) \frac{1}{M} \left(\tanh \frac{1}{\sqrt{\gamma}} \right)^2 - \sqrt{\left[1 - \frac{K_1}{D_{EA}} + \left(1 - \frac{1}{D_{EA}}\right) \frac{1}{M} \left(\tanh \frac{1}{\sqrt{\gamma}} \right)^2\right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2} \quad (54)$$

As shown in our previous paper (14), the dimensionless group $\gamma (= D_A/sL^2)$ is the critical parameter in determining the applicability of a specific mathematical model. Equation (52) (the film-penetration theory) is applicable to any value of γ . However, when γ approaches infinity, since Equation (52) can be reduced to Equation (47), the film-penetration model may be approximated by the film theory. Similarly, Equation (49) can be obtained from Equation (52) by letting γ approach zero. The fact that Equation (52) may be reduced to Equations (47) and (49) is further evidence that the surface renewal theory and the film theory are limiting cases of the more general film-penetration theory.

As mentioned earlier, if the backward reaction is extremely slow compared with the forward reaction, the system is subjected to the utmost influence of chemical reaction. The line of $K_1 = 0$ in Figure 2 corresponds to this case and constitutes the upper limit of the family of curves illustrating the effects of a reversible reaction. This

line also shows that at very low M value, the transfer coefficient ratio is nearly equal to 1.0 and that its value increases as M is increased. Finally, when M is very large, the ratio can be approximated by \sqrt{M} .

Now, if the backward reaction rate is increased while the forward reaction rate is maintained constant, the transfer coefficient ratio is decreased as shown in the figure. The magnitude of the decrease depends on the

relative ratio of the backward to the forward reactions. When this ratio is very large, the overall chemical mass transfer coefficient is almost equal to the physical transfer coefficient, because all the three equations, Equations (47), (49) and (52), can be reduced to the following.

$$\lim_{K_1 \rightarrow \infty} k_L/k_L' = 1.0 \quad (55)$$

This can be explained by the following physical fact. When the backward reaction is strong, as soon as the product E is made it is almost instantaneously reconverted to the reactant A and there is almost no E in the phase element. Thus, the reactant A diffuses through the phase element as if there were no associated chemical reaction in the process. This discussion leads to the conclusion that the backward reaction tends to increase the resistance to the overall chemical mass transfer.

According to Equations (47) and (48), based on the film theory, the transfer coefficient ratio k_L/k_L' depends on the relative ratio of K_1 to D_{EA} but not on the absolute

value of D_{EA} . On the other hand, Equations (49) and (52), which are based on the surface renewal theory and the film-penetration theory, respectively, show that not

only the relative ratio of K_1 to D_{EA} , but also the absolute value of D_{EA} , are important in predicting the transfer coefficient ratio. As shown in Figure 3, D_{EA} indeed plays a very significant role in the prediction of the transfer coefficient ratio. First, the dotted line shows that the film theory is insensitive to the absolute value of D_{EA} , because all the lines for different values of D_{EA} fall on the same line as long as the relative ratios of K_1 to D_{EA} are the same. On the other hand, the surface renewal theory predicts different transfer coefficient ratios depending on the absolute value of D_{EA} , even though the K_1/D_{EA} ratios are identical. The slower the relative diffusion rate of the product E compared to A , the greater the effect of the reaction on the overall mass transfer rate. As also shown in Figure 3, the influence of the diffusivity ratio D_{EA} is more pronounced at high M values. At low M values, the transfer coefficient ratios are very close to unity, irrespective of the theories and of the diffusivity ratio.

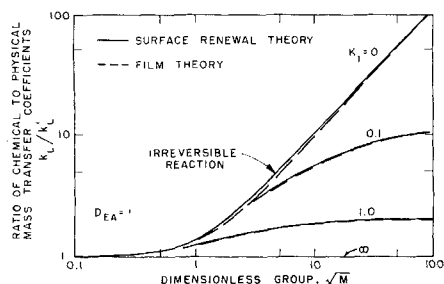


Fig. 2. Effect of first-order reversible reaction on chemical mass transfer (equal diffusivities of reactant and product).

Danckwerts and Kennedy (5) concluded in their studies of kinetics of liquid film process in gas absorption that the different models lead to closely similar predictions of the effect of physicochemical variables, such as solubility, diffusivity, and reaction rate. For the mass transfer with a first-order reversible reaction, their conclusion is true only when the diffusivities of the reactant A and the product E are equal. The proof was given in Table 1 of their paper, and is also evident in Figures 2 and 3 in that the dotted line (the film theory) and the solid line (the surface renewal theory) fall on each other for the cases where D_{EA} is equal to unity. However, it is important to note that this conclusion is not generally valid, because at any D_{EA} values other than 1.0, the surface renewal theory and the film theory predict entirely different effects of the reversible reaction on the overall mass transfer rate. This is illustrated in Figure 3.

Because of past studies (5, 14), chemical engineers are prone to accept, as a general rule, the previous conclusions that the three different theoretical models predict almost the same reaction effects on overall mass transfer rate. In view of the results shown in Figure 3, this conclusion should not be extended to other cases indiscriminately. The selection of a correct theoretical model is indeed very important in predicting the effects of reversible reaction on the transfer rate where the diffusivities of the reactant A and the product E are quite different. For example, as shown in Figure 4, when D_{EA} is other than 1.0, the three theoretical models predict fairly different transfer coefficient ratios, depending on the characteristic dimensionless group γ .

MASS TRANSFER WITH HIGH ORDER REVERSIBLE REACTION

When unsteady state diffusion is accompanied by a high order reversible reaction, the concentration distributions of the reactants A and B and the product E are obtained by solving simultaneously Equations (2), (3), and (4). As discussed earlier, the exact analytical solution has not been possible. In this section, an approximate solution based on the film theory will be attempted. According to the film theory, the steady state molecular diffusion and the reversible reaction takes place within a stagnant film. Thus, the set of these three partial differential equations can be reduced to the following ordinary equations by removing the terms of mass accumulation.

$$D_A \frac{d^2 C_A}{dx^2} - k_1' C_A C_B^n + k_{-1} C_E = 0 \quad (56)$$

$$\frac{D_B}{n} \frac{d^2 C_B}{dx^2} - k_1' C_A C_B^n + k_{-1} C_E = 0 \quad (57)$$

$$D_E \frac{d^2 C_E}{dx^2} + k_1' C_A C_B^n - k_{-1} C_E = 0 \quad (58)$$

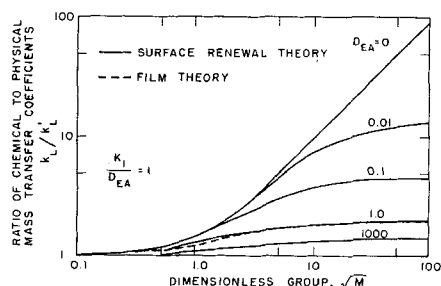


Fig. 3. Effect of diffusivity ratio on mass transfer accompanied by reversible chemical reaction.

The boundary condition at the interphase $x = 0$ may be written as

$$x = 0, \quad C_A = C_{Ai}, \quad C_B = C_{Bi}, \quad \frac{dC_B}{dx} = 0, \quad \frac{dC_E}{dx} = 0 \quad (59)$$

The above boundary condition implies that the reactant B and the product E do not move across the phase boundary to the other phase. The concentrations of the reactants A and B at interphase are assumed to be constant and represented by C_{Ai} and C_{Bi} , respectively. This assumption is valid with respect to the reactant A because its concentrations in the two phases at the boundary are usually in equilibrium and its concentration in the film is equal to the solubility. On the other hand, the assumption of a constant C_{Bi} may not always be true and its exact value may be difficult to ascertain independently.

The boundary condition at the terminal edge of the film may be represented by the following equations.

$$x = L, \quad C_A = C_{AL}, \quad C_B = C_{BL}, \quad C_E = C_{EL} \quad (60)$$

The average rate and the local rate of mass transfer across the interphase are the same if the mechanism is postulated by the film theory. They may be obtained by

$$\bar{N}_A = N_A = -D_A \left(\frac{dC_A}{dx} \right)_{x=0} \quad (61)$$

Equations (56), (57), (59), (60), and (61) are simultaneously solved to yield the following expression for the rate of mass transfer accompanied by a high order reversible reaction.

$$\bar{N}_A = \frac{D_A}{L} \left[(C_{Ai} - C_{AL}) - \frac{1}{n} \frac{D_B}{D_A} (C_{Bi} - C_{BL}) \right] \quad (62)$$

Again, if the mass transfer coefficient is defined in terms of the concentration driving force, the transfer coefficient ratio is obtained as

$$\frac{k_L}{k_L'} = 1 - \frac{1}{n} \frac{D_B}{D_A} \frac{C_{BL}}{C_{Ai}} \frac{\frac{C_{Bi}}{C_{BL}} - 1}{1 - \frac{C_{AL}}{C_{Ai}}} \quad (63)$$

This equation may be rearranged to give the following definition of λ .

$$\lambda = \frac{C_{Bi}}{C_{BL}} = 1 - n \frac{D_A}{D_B} \cdot \frac{C_{Ai}}{C_{BL}} \left(\frac{k_L}{k_L'} - 1 \right) \left(1 - \frac{C_{AL}}{C_{Ai}} \right) \quad (64)$$

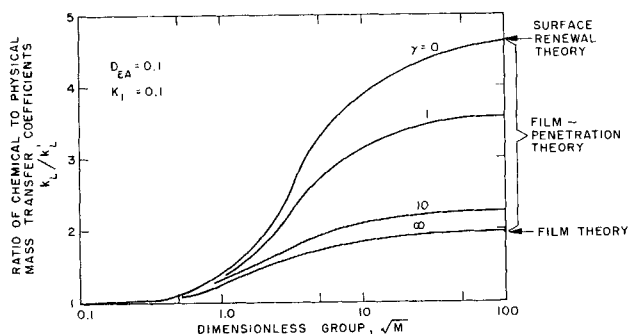


Fig. 4. Effect of chemical reaction on mass transfer with reversible reaction.

Equation (64) relates C_{Bi} , the interphase concentration of the reactant B , to k_L , the chemical mass transfer coefficient. The expression is exact, but since both C_{Bi} and k_L are unknown functions, one of them must be known before the other may be predicted. Or an additional independent relationship between C_{Bi} and k_L should be obtained so that the two equations can be solved simultaneously for the two unknowns. But, it is impossible to obtain such a relationship at this time. Thus, a compromise may be made to obtain an approximate solution based on a simplified assumption.

As an approximation, C_B , the concentration of the reactant within a film, is assumed to be uniform and may be equal to either C_{Bi} , the interphase concentration, or C_{BL} , the bulk concentration. If the former is chosen, it is visualized that the concentration profile of C_B is a step function, and at $x = L$, C_B is changed abruptly from C_{Bi} to C_{BL} . This approximation was found to be very satisfactory by Van Krevelen and Hoftijer (29) and Peaceman (22) for mass transfer accompanied by a second-order irreversible reaction. Therefore, it may be satisfactorily extended to the present problem. Mathematically, the assumption is written as

$$C_B = C_{Bi} \quad 0 < x < L \quad (65)$$

Therefore, the term $k_i' C_B^n$ in Equations (56) and (58) is a constant and may be designed as k_i . The constant k_i can be further related to C_{BL} as

$$k_i = k_i' C_{Bi}^n = k_i' C_{BL}^n (C_{Bi}/C_{BL})^n = k_i' C_{BL}^n \lambda^n \quad (66)$$

Substitution of Equation (66) into Equations (56) and (58) yields a set of two differential equations that have similar forms as Equations (10) and (11). Therefore, the solution can be easily obtained and the final transfer coefficient ratio k_L/k_L' should be in the form similar to Equation (47). Thus

$$\frac{k_L}{k_L'} = \frac{\mu_1^2}{\frac{K_1}{D_{EA}} + \frac{\tanh \mu_1 \sqrt{M'} \lambda^n}{\mu_1 \sqrt{M'} \lambda^n}} \quad (67)$$

where

$$M' = k_i' C_{BL}^n D_A / (k_L')^2 \quad (68)$$

and μ_1 is defined by Equation (48).

If no backward reaction is involved, the mass transfer system is reduced to that accompanied by the following irreversible reaction.



For this system, Equation (67) is then reduced to

$$\frac{k_L}{k_L'} = \frac{\sqrt{M'} \lambda^n}{\tanh \sqrt{M'} \lambda^n} \quad (70)$$

Van Krevelen and Hoftijer (27 to 29) proposed a rate equation for mass transfer accompanied by a second-order irreversible reaction. Their equation can also be obtained from Equation (70) by substituting $n = 1$.

Figure 5 shows the plots of the transfer coefficient ratio based on Equations (67) and (64) for $n = 1$. As shown in the figure, at the ultimate value of $\frac{D_B C_{BL}}{D_A C_{Ai}}$ approaching

infinity, the transfer coefficient ratio becomes equal to that of mass transfer accompanied by a first-order irreversible reaction. In the figure, this line is designated as *pseudo first-order reaction* and constitutes the upper limit of the transfer coefficient ratios. Then, for the same value of M' , the transfer coefficient ratio decreases as the value of $D_B C_{BL}/D_A C_{Ai}$ is decreased.

Another interesting observation may be made with respect to the effects of the dimensionless group M' . In order that the reactant B may diffuse from the terminal edge of the film toward the interphase, $\lambda = C_{Bi}/C_{BL}$ should be always larger than zero and smaller than 1.0, that is

$$1 \geq \lambda \geq 0 \quad (71)$$

If the concentration of the reactant A in the liquid bulk is negligibly small, Equation (64) may be substituted into Equation (71) to yield

$$1 + \frac{1}{n} \frac{D_B}{D_A} \frac{C_{BL}}{C_{Ai}} \geq \frac{k_L}{k_L'} \geq 1.0 \quad (72)$$

Therefore, for a given value of the parameter $D_B C_{BL}/D_A C_{Ai}$, the transfer coefficient ratio starts with 1.0 at a very low value of M' and increases as M' is increased. However, when M' is beyond a certain value, the transfer coefficient ratio approaches the maximum, which is equal to $1 + (1/n)(D_B C_{BL}/D_A C_{Ai})$. These are clearly illustrated in Figure 5.

Based on the film theory, Hatta (9 to 11) proposed a rate equation for mass transfer accompanied by instantaneous equimolar irreversible reaction. According to his theory, the transfer coefficient ratio for such mass transfer system is equal to $1 + (D_B C_{BL}/D_A C_{Ai})$. The same system may also be treated by the equation proposed here. The system is equivalent to the case where the forward reaction rate constant k_i' or the dimensionless group M' approaches infinity. Thus, according to Equation (72), the maximum transfer coefficient ratio of $1 + (D_B C_{BL}/D_A C_{Ai})$ must be obtained.

Peaceman (22) also investigated a theoretical mechanism of mass transfer accompanied by a second-order irreversible reaction. In solving the differential equations, he assumed that the concentration of the reactant B within the film is a linear function of the distance from the interphase. His results are very similar to those shown in

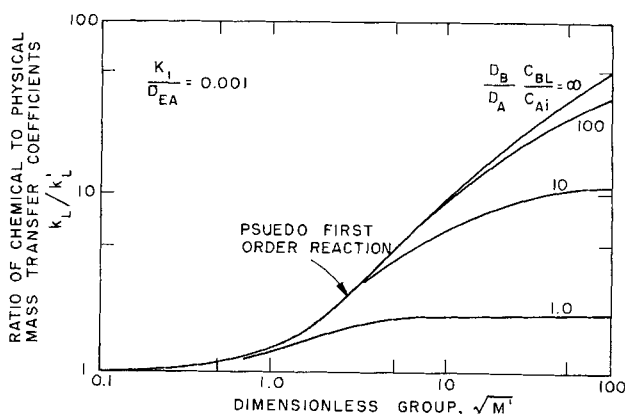


Fig. 5. Effect of second-order reversible reaction on mass transfer.

Figure 5, which are based on the assumption that the concentration C_B is constant and uniform within the film.

As mentioned earlier, another approximation, in contrast to Equation (65), is that the concentration of the reactant B at any point within a film is equal to its concentration in the liquid bulk. Mathematically, it means $C_B = C_{BL}$. The assumption is justified when the depletion of the reactant B within the film is relatively small. With this approximation, the transfer coefficient ratio may be expressed by Equation (67) with λ being equal to unity. As shown in Figure 5, this is also equivalent to the case of pseudo first-order reaction.

CONCLUSIONS

The following conclusions may be drawn from this study:

(1) Three theoretical rate equations are proposed for the interphase mass transfer accompanied by a first-order reversible chemical reaction. The mass transfer mechanism was formulated on the basis of the film theory, the surface renewal theory, and the film-penetration theory. For mass transfer with a reversible reaction, the film-penetration theory is again found to be the more general concept. The film theory and the surface renewal theory are limiting cases of the film-penetration theory. The transfer rate equation based on the film-penetration theory is versatile and can be reduced to other rate equations based on simple postulations. The latter includes Peaceman's equation and Danckwerts-Kennedy's equation for mass transfer with a reversible reaction.

The equation can also be reduced to those for mass transfer with a first-order irreversible reaction or to those for mass transfer without a reaction.

(2) The backward reaction tends to increase the resistance to the overall mass transfer. If the backward reaction rate is very small compared with the forward reaction rate, the transfer coefficient ratio is at its highest value. Then, as the backward reaction rate is increased, the transfer coefficient ratio begins to decline. Finally, where the backward reaction rate approaches infinity, the chemical reaction exerts no influence on the overall mass transfer and the system behaves as if no chemical reaction is involved.

(3) Contrary to the conclusions obtained for other types of mass transfer systems (5, 14), the theoretical rates of mass transfer with a reversible reaction are very sensitive to the theory or the model adopted to postulate the mechanism. Thus, the choice of mass transfer theory is very important when predicting an accurate mass transfer rate. One exception to this is when the diffusivities of the reactant and the product are nearly equal. Under this condition, all the three theories predict practically the same effects of a reversible reaction on the overall mass transfer.

(4) Based on the film theory, an approximate equation is proposed for the rate of mass transfer accompanied by a high order reversible reaction. Theoretically, the transfer coefficient ratio for the system with a high order reaction is always lower than that with a first-order reaction. The dimensionless groups $(D_B/D_A)(C_{BL}/C_{A1})$ and M' are important parameters in evaluating the mass transfer performance. At a constant M' value, as $(D_B/D_A)(C_{BL}/C_{A1})$ is decreased, the transfer coefficient is also decreased. On the other hand, at a constant value of $(D_B/D_A)(C_{BL}/C_{A1})$, the transfer coefficient ratio increases as M' is increased and finally it approaches $(1/n)(D_B/D_A)(C_{BL}/C_{A1})$ if M' becomes very large. Thus, for the mass transfer system with a rapid forward reaction, the reaction rate constant becomes an insignificant variable.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, which is administered by the American Chemical Society, and to the National Science Foundation for support of this research.

NOTATION

C_A	= concentration of component A, g.-mole/liter
C_{A1}	= concentration of component A at interphase, g.-mole/liter
C_{AL}	= concentration of component A at the outer edge of a surface element, or in the liquid bulk, g.-mole/liter
C_B	= concentration of component B, g.-mole/liter
C_{B1}	= concentration of component B at interphase, g.-mole/liter
C_{BL}	= concentration of component B at the outer edge of a surface element, or in the liquid bulk, g.-mole/liter
C_E	= concentration of component E, g.-mole/liter
C_{EL}	= concentration of component E at the outer edge of a surface element, or in the liquid bulk, g.-mole/liter
D_A	= molecular diffusivity of component A, sq. cm./sec.
D_B	= molecular diffusivity of component B, sq. cm./sec.
D_E	= molecular diffusivity of component E, sq. cm./sec.
D_{BA}	= diffusivity ratio, D_B/D_A
k_j	= first-order reaction rate constant, 1/sec., $j = 1$ for forward reaction, $j = -1$ for backward reaction
k_1'	= n th order forward reaction rate constant, (liter/g.-mole) $^{n-1}$ /sec.
k_L'	= liquid side mass transfer coefficient without chemical reaction, cm./sec.
k_L	= liquid side mass transfer coefficient with chemical reaction, cm./sec.
K_1	= ratio of reaction rate constants, k_{-1}/k_1
L	= average thickness of a surface element, or of a film, cm.
M	= dimensionless group, $k_1 D_A / (k_L')^2$
M'	= dimensionless group, defined by Equation (68)
N_A	= point rate of chemical mass transfer for component A, g.-mole/sq. cm./sec.
N_A'	= point rate of physical mass transfer for component A, g.-mole/sq. cm./sec.
\bar{N}_A	= average rate of chemical mass transfer for component A, g.-mole/sq. cm./sec.
\bar{N}_A'	= average rate of physical mass transfer for component A, g.-mole/sq. cm./sec.
s	= surface renewal rate, 1/sec.
t	= time, sec.
U	= dimensionless group, defined by Equation (30)
u	= dimensionless group, defined by Equation (19)
V	= dimensionless group, defined by Equation (31)
W	= dimensionless group, defined by Equation (29)
x	= distance, cm.

Greek Letters

α	= dimensionless group, $D_A / (k_1 L^2)$
β	= dimensionless group, s/k_1
γ	= dimensionless group, α/β or D_A/sL^2
λ	= dimensionless group, defined by Equation (64)
μ_1	= dimensionless group, defined by Equation (48)
μ_2	= dimensionless group, defined by Equation (50)
μ_3	= dimensionless group, defined by Equation (53)
μ_{-2}	= dimensionless group, defined by Equation (51)

μ_{-3} = dimensionless group, defined by Equation (54)
 $\phi(t)$ = surface age distribution function

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Manuscript received October 7, 1964; revision received May 14, 1965; paper accepted May 17, 1965. Paper presented at A.I.Ch.E. San Francisco meeting.

Falling Cylinder Viscometer for Non-Newtonian Fluids

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It is shown how previous analyses of the falling cylinder viscometer for Newtonian fluids can be extended to non-Newtonian fluids. Specific relations are given for the velocity of descent for several simple non-Newtonian viscosity functions. A differentiation procedure is presented whereby the non-Newtonian viscosity for a fluid can be deduced from velocity of fall measurements. In the course of the development, some useful approximate expressions for axial non-Newtonian flow in annuli are developed. Finally, a comparison of the Ellis and power law models is made by an analysis of the axial annular flow data of Frederickson and of McEachern.

The falling cylinder viscometer consists of a long cylindrical container filled with fluid in which a fairly tight-fitting cylindrical slug is allowed to fall under the influence of gravity (see Figure 1). As the cylinder falls, the fluid flows up through the narrow annular slit formed by the cylindrical tube and the falling cylinder. One can measure the rate of steady state descent of the cylinder, and thereby obtain viscometric information. Possible ap-

plications of such a device are in: (1) high-pressure measurements, where the sample must be contained in a tight, sturdy cylindrical tube; and (2) biological measurements, where the sample must have minimum contact with the atmosphere.

This system has already been studied for Newtonian fluids. Apparently the earliest analysis was that of Law-aceck (6), who assumed that the velocity profile in the