General Mathematical Model for Mass Transfer Accompanied by Chemical Reaction

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The present paper concerns the mechanism of mass transfer accompanied by a first-order irreversible chemical reaction between two phases. Based on the film-penetration concept a general mathematical model to describe the physico-chemical behavior at the interface has been formulated. Mass transfer mechanism may be analyzed and evaluated in terms of the dimensionless groups appearing in the derived equations.

For limiting conditions the derived general equations can be reduced to those based on the simple postulations such as the film theory, the penetration theory, and the surface renewal theory. For nonlimiting cases the film-penetration concept provides information which cannot be obtained by either the film theory or the surface renewal theory alone.

Experimental results appearing in literature show that the physical mass transfer coefficient is proportional to the molecular diffusivity to the ν-th power and that ν varies widely between 0.15 and 1.0. The film-penetration concept theoretically predicts this ν-variation, whereas, in accordance with the film theory or the surface renewal theory, ν has to be a certain fixed value.

It is shown that if an accurate physical mass transfer coefficient is available, 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. However if the chemical mass transfer coefficient is to be predicted without an accurate physical transfer coefficient, the choice of the theory or the mechanism may become important.

The true mechanism of mass transfer between phases accompanied by chemical reaction is only partially developed with little fundamental investigation. Even today the design of the systems involving mass transfer operation accompanied by chemical reaction is based almost entirely on empirical test data, either on laboratory or on pilot plant scales.

In the past three basic concepts of mass transfer at the interface were proposed. They are the film concept (*17, 27*), the penetration concept (*11*), and the surface renewal concept (*4*). The film concept was adopted by Hatta (*7, 8, 9, 10*) in developing the theory for mass transfer accompanied by a chemical reaction. The theory is based on the postulation that a stationary film exists at the interface. It is also assumed that mass is transported by steady state molecular diffusion through this film. Later Higbie (*11*) proposed the penetration concept which modifies the above postulation by assuming unsteady state molecular diffusion through a stagnant film. However the existence of a stagnant film is not always conceivable, particularly when the fluid motion is a disrupted one. Thus Danckwerts (*4*) proposed that for gas absorption in a packed column the turbulence creates numerous infinitesimal liquid elements which are constantly brought to the interface. While these elements are exposed to the opposite phase at the interface, diffusing molecules are transported by penetration or unsteady molecular diffusion into the elements. An objection to this model is that the depth of penetration or the thickness of the liquid element is assumed to be infinite. In reality the depth of penetration or the thickness of a liquid element should have a finite value, and it decreases as the turbulence is increased.

Recently Toor and Marchello (*23*) proposed the film-penetration model to describe the mass transfer mechanism in absence of chemical reaction. They showed that the film and the penetration theories are not separate concepts but merely limiting cases of their more general film-penetration model. However the application of the film-penetration model to the mechanism of simultaneous mass transfer and chemical reaction has not yet been attempted.

An investigation of mass transfer mechanism at the interface has been in progress by the authors. The first study (*12, 15*) dealt with the mass transfer mechanism where no chemical reaction was involved. It was an investigation of the rate of dissolution of cast organic acids from a flat surface into a turbulent liquid. The second phase of the project was the investigation of the transfer mechanism where an instantaneous chemical reaction was involved (*13, 14*). The present research continues the above studies to develop a general mathematical model for the mass transfer mechanism accompanied by a first-order irreversible chemical reaction. In particular the application of the film-penetration concept to the mechanism is pursued.

For the sake of brevity hereafter in this paper mass transfer accompanied by a first-order irreversible chemical reaction will be referred to as *chemical mass transfer* and likewise mass transfer in the absence of chemical reaction will be called *physical mass transfer.*

PROPOSED MASS TRANSFER EQUATIONS

Mass Transfer Mechanism

Similar to the surface renewal theory the interface is postulated as being replaced by infinitesimally small fresh liquid elements. Then the overall mass transfer mechanism across the interface consists of two steps, that is surface renewal by freshly formed liquid elements and simultaneous molecular diffusion and chemical reaction within the exposed liquid elements. When the surface renewal rate is slow, the surface elements remain at the interface for a long period before being replaced. At the extreme the elements are not replaced at all and become a part of the stationary liquid layer. However if the turbulence in the liquid bulk is vigorous, the residence time of the element at the interface will be short and the surface renewal theory prevails. When a fresh liquid element is brought to the interface to be exposed to the other phase, its concentration is assumed to be equal to that of the bulk of the liquid phase. The assumption is valid when the bulk of the liquid phase is well mixed and uniform.

Unlike the Danckwerts surface renewal theory the present authors assume that the average thickness of the surface element is equal to a certain finite value, which is denoted by L. This postulation was first proposed by Toor and Marchello (*23*).

Before a surface element is replaced and swept back into the bulk, the unsteady state mass transfer and chemi-

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cal reaction take place simultaneously throughout the distance L. At the instant of contact the reaction takes place at the interface. If the given reaction is instantaneous, the reaction zone is established first at the interface and then moves toward the inside of the liquid element as the residence time is prolonged. When the element remains in contact with the interface sufficiently long, the equilibrium position of the reaction zone may be established according to the Hatta film concept, and the reaction takes place instantaneously only at the reaction zone. On the other hand if the reaction is rather slow compared with the diffusion rate, the zone of reaction will not be concentrated in a thin plane but will be spread throughout a liquid element.

Now consider the action of the dissolving solute A within the liquid phase where it reacts slowly with the second reactant B. The present investigation is limited to a chemical reaction of the first order or the pseudo first order.

After dissolving into the liquid elements the reactant A is assumed to diffuse into the element in one direction only. The diffusing stream of reactant A is being depleted by the reaction along the path of diffusion. The interface concentration is assumed to be in equilibrium with that of dissolving solid, and the concentration at the other edge of the element is equal to that of the bulk liquid C_{AL}.

Then the expression of the concentration gradient within the liquid element may be obtained by solving the following partial differential equation

$$(\partial C_A/\partial t) = D_A\,(\partial^2 C_A/\partial x^2) - k_r C_A \qquad (1a)$$

$$0 < x < L$$

with the following initial and boundary conditions:

$$\begin{aligned} x &= 0, & t &> 0, & C_A &= C_{Ai} \\ x &= L, & t &> 0, & C_A &= C_{AL} \\ x &> 0, & t &= 0, & C_A &= C_{AL} \end{aligned} \qquad (1b)$$

The point mass transfer rate to a single surface element at time t is obtained by

$$N_A = -D_A\,(\partial C_A/\partial x)_{x=0} \qquad (2)$$

The average rate of the mass transfer across the entire interface shall be

$$\overline{N}_A = \int_0^\infty \phi(t)\,N_A\,dt = \int_0^\infty [s\,\exp(-st)]\,[-D_A(\partial C_A/\partial x)_{x=0}]dt = -D_A\,s\,(\partial \overline{C}_A/\partial x)_{x=0} \qquad (3)$$

Expression in Trigonometric Function Series

Expression of the concentration gradient within an element, in trigonometric function series, is convenient for analysis of the case involving long exposure of the element at the interface.

An approach to obtain the solution of Equation (1) is to represent the concentration gradient in terms of another pseudo concentration gradient. The details of the solution are shown in reference *16*.

The following expression is obtained for the concentration distribution within a liquid element:

$$C_A = C_{Ai} - \frac{C_{Ai} - C_{AL}}{L}\left[x + \frac{2L}{\pi}\sum_{n=1}^{\infty}\frac{1 + n^2\pi^2\alpha e^{-(1+n^2\pi^2\alpha)k_r t}}{n(1 + n^2\pi^2\alpha)}\sin\frac{n\pi x}{L}\right] \qquad (4)$$

Two important characteristics of the series appearing in the equation may be utilized advantageously. When α is large, the series in the equation converges rapidly. The point mass transfer rate is obtained by substituting Equation (4) into Equation (2):

$$N_A = \frac{D_A}{L}(C_{Ai} - C_{AL})\left[1 + 2\sum_{n=1}^{\infty}\frac{1 + n^2\pi^2\alpha e^{-(1+n^2\pi^2\alpha)k_r t}}{1 + n^2\pi^2\alpha}\right] \qquad (5)$$

At this point it is interesting to examine the above general equation for the limiting case where the time of contact at the interface approaches infinity. The mathematical expression $t \rightarrow \infty$ means physically that the surface element remains forever at the interface and becomes a stagnant film. Equation (5) is reduced to

$$N_A = \frac{D_A}{L}(C_{Ai} - C_{AL})\left[1 + 2\sum_{n=1}^{\infty}\frac{1}{1 + n^2\pi^2\alpha}\right] \qquad (6)$$

Equation (6) may be rearranged and expressed in hyperbolic function (16). Thus

$$N_A = \frac{D_A}{L}(C_{Ai} - C_{AL})\frac{1}{\sqrt{\alpha}}\coth\frac{1}{\sqrt{\alpha}} \qquad (7)$$

Equation (7) is exactly identical with that derived by Hatta for the case of low bulk concentration on the basis of the film concept. When the bulk concentration is not low in comparison with the interfacial concentration, Hatta obtained the following equation:

$$N_A = \frac{D_A}{L}\frac{1}{\sqrt{\alpha}}\left[C_{Ai}\coth\frac{1}{\sqrt{\alpha}} - C_{AL}\operatorname{csch}\frac{1}{\sqrt{\alpha}}\right] \qquad (8)$$

Thus for the numerical range where coth $(1/\sqrt{\alpha})$ is almost equal to csch $(1/\sqrt{\alpha})$ Equation (8) of Hatta is still reduced to Equation (7).

Furthermore if the reaction velocity constant approaches zero, that is diffusion in absence of chemical reaction, the value of α approaches infinity and Equation (6) is reduced to

$$N_A' = \frac{D_A}{L}(C_{Ai} - C_{AL}) \qquad (9)$$

which is the physical mass transfer rate equation obtained by Whitman and Lewis (*17*) based on the film concept.

Therefore it can be said that the film concept used by Hatta, and Whitman and Lewis is a limiting case of the film-penetration concept.

When the contact time of an individual surface element is not approaching the limiting value, the average mass transfer rate is obtained by substituting Equation (5) into Equation (3). Thus

$$\overline{N}_A = \frac{D_A}{L}\left[1 + 2\sum_{n=1}^{\infty}\frac{1 + \beta}{1 + \beta + n^2\pi^2\alpha}\right](C_{Ai} - C_{AL}) \qquad (10a)$$

or

$$\overline{N}_A = \frac{D_A}{L}\left[1 + 2\sum_{n=1}^{\infty}\frac{1 + 1/\beta}{1 + 1/\beta + n^2\pi^2\gamma}\right](C_{Ai} - C_{AL}) \qquad (10b)$$

Equation (10*a*) or (10*b*) is the general expression for the average mass transfer rate where a simultaneous chemical reaction is involved. The equation can be reduced to those proposed by previous workers (*7, 8, 9, 10, 23*) based on limited postulations.

For instance Equation (10*b*) can be reduced to the following, if the reaction velocity constant is equal to zero or β approaches infinity:

$$\overline{N}_A' = \frac{D_A}{L}\left[1 + 2\sum_{n=1}^{\infty}\frac{1}{1 + n^2\pi^2\gamma}\right](C_{Ai} - C_{AL}) \qquad (11)$$

This equation is identical with that derived by Toor and Marchello (*23*) for mass transfer in absence of chemical reaction.

If the surface renewal rate approaches zero, or β approaches zero, Equation (10*a*) can be reduced to the Hatta equation for mass transfer with slow chemical reaction based on the film concept, that is Equation (7).

Now if the mass transfer coefficient involving simultaneous chemical reaction is defined by

$$\overline{N}_A = k_L\,(C_{Ai} - C_{AL}) \qquad (12)$$

the mathematical expression for the coefficient can be obtained by combining Equations (10*a*) and (12). Thus

$$k_L = \frac{D_A}{L}\left[1 + 2\sum_{n=1}^{\infty}\frac{1+\beta}{1+\beta+n^2\pi^2\alpha}\right] \qquad (13)$$

Expression in Error Function Series

The basic differential equation, that is Equation (1), may be solved by Laplace transformation. The solution obtained by Laplace transformation is expressed in series of error function. The solution is suitable for analysis of transfer behavior when a surface element is exposed to the interface for a short period.

The Laplace transform of the concentration $\overline{C}_A(x, s)$ is obtained (*16*):

$$\overline{C}_A(x,s) = \int_0^{\infty} C_A(x,t)\cdot\exp(-st)\,dt = \Big\{\,[C_{Ai}\,(k_r+s) - sC_{AL}]\left[\exp\left(-\sqrt{\frac{k_r+s}{D_A}}\,x\right) - \exp\left(-\sqrt{\frac{k_r+s}{D_A}}\,\overline{2L-x}\right)\right]$$

$$+\,k_r\,C_{AL}\left[\exp\left(\sqrt{\frac{k_r+s}{D_A}}\,\overline{L-x}\right) - \exp\left(-\sqrt{\frac{k_r+s}{D_A}}\,\overline{L+x}\right)\right]\Big\}\Big/\left[s(k_r+s)\left(1-\exp\left\langle -2\sqrt{\frac{k_r+s}{D_A}}\,L\right\rangle\right)\right]$$

$$+\,C_{AL}/(k_r+s) \qquad (14)$$

The actual concentration $C_A(x, t)$ is then obtained by inversion of the above transform:

$$C_A(x,t) = \frac{C_{Ai}}{2}\sum_{n=0}^{\infty}\Big\{\,e^{-(2nL+x)\sqrt{\frac{k_r}{D_A}}}\,\text{erfc}\left(\frac{2nL+x}{2\sqrt{D_At}} - \sqrt{k_rt}\right) + e^{(2nL+x)\sqrt{\frac{k_r}{D_A}}}\,\text{erfc}\left(\frac{2nL+x}{2\sqrt{D_At}} + \sqrt{k_rt}\right)$$

$$-\,e^{-[2L(n+1)-x]\sqrt{\frac{k_r}{D_A}}}\,\text{erfc}\left[\frac{2L(n+1)-x}{2\sqrt{D_At}} - \sqrt{k_rt}\right] - \left\{e^{[2L(n+1)-x]\sqrt{\frac{k_r}{D_A}}}\right\}\text{erfc}\left[\frac{2L(n+1)-x}{2\sqrt{D_At}} + \sqrt{k_rt}\right]\Big\} +$$

$$\frac{C_{AL}}{2}\,\Big\{\,2e^{-k_rt}\left[1 - \text{erfc}\,\frac{x}{2\sqrt{D_At}} + \sum_{n=0}^{\infty}\left(\text{erfc}\,\frac{(n+1)L + (-1)^n x}{2\sqrt{D_At}} - \text{erfc}\,\frac{(n+1)\,L - (-1)^n x}{2\sqrt{D_At}}\right)\right] + \sum_{n=0}^{\infty}$$

$$\left(e^{-[(2n+1)L-x]\sqrt{\frac{k_r}{D_A}}}\,\text{erfc}\left(\frac{(2n+1)L-x}{2\sqrt{D_At}} - \sqrt{k_rt}\right) + \left[e^{[(2n+1)L-x]\sqrt{\frac{k_r}{D_A}}}\right]\text{erfc}\left(\frac{(2n+1)L-x}{2\sqrt{D_At}} + \sqrt{k_rt}\right) - \right.$$

$$\left.\left[e^{-[(2n+1)L+x]\sqrt{\frac{k_r}{D_A}}}\right]\text{erfc}\left(\frac{(2n+1)L+x}{2\sqrt{D_At}} - \sqrt{k_rt}\right) - e^{[(2n+1)L+x]\sqrt{\frac{k_r}{D_A}}}\,\text{erfc}\left(\frac{(2n+1)L+x}{2\sqrt{D_At}} + \sqrt{k_rt}\right)\right)\Big\} \qquad (15)$$

Now Equation (15) is substituted into Equation (2) to yield the expression for the point mass transfer rate:

$$N_A = \sqrt{\frac{D_A}{\pi t}}\,[C_{Ai}\,e^{-k_rt} + C_{AL}(e^{-1/4\alpha} + 2e^{-(1/4\alpha + k_rt)} - 1)] + C_{Ai}\sqrt{k_r D_A}\,\text{erf}\,\sqrt{k_rt} +$$

$$C_{Ai}\sum_{n=0}^{\infty}\left[2\sqrt{\frac{D_A}{\pi t}}\,e^{-(n^2/\alpha k_rt + k_rt)} + \sqrt{k_r D_A}\left\{e^{-2n/\sqrt{\alpha}}\,\text{erfc}\left(\frac{n}{\sqrt{\alpha k_rt}} - \sqrt{k_rt}\right) - e^{-2n/\sqrt{\alpha}}\,\text{erfc}\left(\frac{n}{\sqrt{\alpha k_rt}} + \right.\right.\right.$$

$$\left.\left.\left.\sqrt{k_rt}\right)\right\}\right] + C_{AL}\sum_{n=1}^{\infty}\left[\sqrt{\frac{D_A}{\pi t}}\left\{(-1)^n\,e^{\frac{-(n+1)^2}{4\alpha}} + 2e^{-\left[\frac{(2n+1)^2}{4\alpha} + k_rt\right]} - (-1)^n\,e^{\frac{-n^2}{4\alpha}}\right\}\right.$$

$$\left. + \sqrt{k_r D_A}\left\{e^{\frac{2n+1}{\sqrt{\alpha}}}\,\text{erfc}\left(\frac{2n+1}{2\sqrt{\alpha k_rt}} + \sqrt{k_rt}\right) - e^{-\frac{2n+1}{\sqrt{\alpha}}}\,\text{erfc}\left(\frac{2n+1}{2\sqrt{\alpha k_rt}} - - \sqrt{k_rt}\right)\right\}\right] \qquad (16)$$

At this point it is interesting to show that if the thickness of a surface element approaches infinity, or α approaches zero, and $C_{AL} = 0$, the above equation can be reduced to

$$N_A = C_{Ai}\left[\sqrt{\frac{D_A}{\pi t}}\exp(-k_rt) + \sqrt{k_r D_A}\,\text{erf}\,\sqrt{k_rt}\right] \qquad (17)$$

This equation is the same as that derived by Danckwerts (3) on the basis of the penetration concept of Higbie (*11*). If the mass transfer occurs in absence of reaction, Equation (17) is further reduced to

$$N_A = \sqrt{\frac{D_A}{\pi t}}\,(C_{Ai} - C_{AL}) \qquad (18)$$

which is identical with the equation derived by Higbie for physical mass transfer.

The average mass transfer rate is obtained by combining Equation (14) or (16) and Equation (3):

$$\overline{N}_A = \frac{\sqrt{D_A(k_r+s)}}{1 - \exp\left[-2L\sqrt{(k_r+s)/D_A}\right]}\,\Big\{[1 + \exp\left(-2L\sqrt{(k_r+s)/D_A}\right]\left[C_{Ai} - \frac{sC_{AL}}{k_r+s}\right] - \frac{k_r\,C_{AL}}{k_r+s}\exp\left[-L\right.$$

$$\left.\sqrt{(k_r+s)/D_A}\right]\Big\} \qquad (19a)$$

or

$$\overline{N}_A = \sqrt{k_r D_A(1+\beta)}\left[\left(C_{Ai} - \frac{\beta\,C_{AL}}{1+\beta}\right)\coth\sqrt{\frac{1+\beta}{\alpha}} - \frac{C_{AL}}{1+\beta}\,\text{csch}\sqrt{\frac{1+\beta}{\alpha}}\right] \qquad (19b)$$

These equations are other general expressions for the mass transfer rate with chemical reaction based on the film-penetration concept.

Again these general equations will be investigated through the light of limiting cases. When the dimensionless group α approaches zero, Equation (19b) is reduced to

$$\overline{N}_A = \sqrt{D_A(k_r + s)}\left(C_{Ai} - \frac{s\,C_{AL}}{k_r + s}\right) \tag{20}$$

which is exactly the same as the equation derived by Danckwerts based on his surface renewal concept. It is of interest to point out that when β approaches zero, Equation (19b) is reduced to Equation (8) which is the Hatta equation for chemical mass transfer.

When there is no chemical reaction in the process, the mass transfer rate equation is obtained by introducing $k_r = 0$ to Equation (19a). Thus

$$\overline{N}_A' = \sqrt{D_A\,s}\left[\frac{2}{1 - \exp\left(-2\sqrt{\frac{s}{D_A}L^2}\right)} - 1\right](C_{Ai} - C_{AL}) = \sqrt{D_A\,s}\left[1 + 2\sum_{n=1}^{\infty}\exp\left(-\frac{2n}{\sqrt{\gamma}}\right)\right](C_{Ai} - C_{AL}) \tag{21}$$

This is the same as the second general equation obtained by Toor and Marchello (23) for the physical mass transfer. It should also be mentioned that the physical mass transfer rate equation of Danckwerts based on the surface renewal concept can be obtained either by introducing $k_r = 0$ to Equation (20) or by introducing $\gamma = 0$ to Equation (21).

From the above illustrations for the case of mass transfer accompanied by a first-order chemical reaction it may also be concluded that the Higbie penetration concept, the Danckwerts surface renewal concept, or the Hatta film concept are limiting cases of the more general postulation, the film-penetration concept. Toor and Marchello (23) reached the same conclusion earlier for the case of mass transfer in absence of chemical reaction.

If the concentration of the reactant A in the liquid bulk is nearly equal to zero, the mass transfer coefficient with chemical reaction may be defined by

$$\overline{N}_A = k_L\,(C_{Ai} - 0) \tag{22}$$

Then the transfer coefficient can be expressed as

$$k_L = \sqrt{k_r\,D_A\,(1 + \beta)}\,\coth\sqrt{\frac{1 + \beta}{\alpha}} \tag{23}$$

DISCUSSION

Effect of Dimensionless Group γ on Physical Mass Transfer

One of the important characteristics of the proposed equations is that Equations (10a) and (19b) are not different equations but identical equations if the concentration of the dissolving solute in the liquid bulk is negligible. The left- and right-hand sides of the following equation are the expressions for the mass transfer coefficient k_L based on Equations (10a) and (19b), respectively. They are proven to be identical as shown in reference *16*:

$$\frac{D_A}{L}\left[1 + 2\sum_{n=1}^{\infty}\frac{1 + \beta}{1 + \beta + n^2\pi^2\alpha}\right] = \sqrt{k_r\,D_A\,(1 + \beta)}\,\coth\sqrt{\frac{1 + \beta}{\alpha}} \tag{24}$$

This relationship may be extended to the rate equations for physical mass transfer derived by Toor and Marchello (23). Equations (11) and (21) are identical equations because

$$k_L' = \frac{D_A}{L}\left[1 + 2\sum_{n=1}^{\infty}\frac{1}{1 + n^2\pi^2\gamma}\right] = \frac{D_A}{L}\,\frac{1}{\sqrt{\gamma}}\coth\frac{1}{\sqrt{\gamma}} = \sqrt{D_A\,s}\,\coth\frac{1}{\sqrt{\gamma}} = \sqrt{D_A\,s}\left[\frac{2}{1 - \exp(-2/\sqrt{\gamma})} - 1\right] \tag{25}$$

The significance of the above relationships is that the mass transfer rate equations obtained by the two different routes are in fact exactly identical.

The proposed equations contain three dimensionless groups: α, β, and γ. Two of them are independent groups, and the third can be obtained from the other two. It is pointed out that these three dimensionless groups contain unknown parameters s and L which cannot be directly measured. It is also noted that the constituent physico-chemical properties of these dimensionless groups may not always be changed independently. For instance both the diffusivity and the reaction velocity constant are functions of the same intensive variables such as temperature, chemical systems, and so on. Therefore if the diffusivity varies owing to changing temperature, the reaction velocity constant also varies accordingly.

Among the above three dimensionless groups, α and β do not appear in the mathematical expression for the physical mass transfer coefficient because both α and β contain the reaction rate constant k_r. On the other hand the dimensionless group γ plays an important role in the analysis of physical mass transfer mechanism. Figure 1 shows the plots of the physical mass transfer coefficient k_L' against γ. Both curves A and B represent the same equation, that is Equation (25) based on the film penetration concept, but they refer to the different ordinate notations. Line C, representing the surface renewal theory, is the plot of $k_L'/\sqrt{D_A\,s} = 1.0$, whereas Line D, representing the film theory, is the plot of $k_L'/(D_A/L) = 1.0$. For better discussion and illustration the entire area of Figure 1 is now divided into three regions according to the numerical values of γ:

Region I	$0 \leq \gamma \leq 0.46$
Region II	$0.46 \leq \gamma \leq 3.0$
Region III	$3.0 \leq \gamma \leq \infty$

In Region I, where γ is smaller than 0.46, the physical mass transfer coefficient k_L' calculated by the film-penetration concept may be approximated by $\sqrt{D_A\,s}$ with an error of less than 10%. On the other hand the k_L' calculated by the film theory deviates more than 10% from that based on the film-penetration concept. Thus in Region I as γ approaches zero, curve B becomes an asymptote to line C and the film-penetration concept converges to the surface renewal theory.

Now in Region III curve A becomes an asymptote to line D as γ approaches infinity. In this region the coefficient k_L' calculated by the film-penetration concept agrees closely with that based on the film theory. The deviation is less than 10%. As suspected k_L' calculated by the surface renewal theory does deviate greatly from k_L' calculated by the film-penetration concept. Thus the film theory may be considered to be a limiting case of the film-penetration concept where γ is large and approaches infinity.

Finally there is Region II where k_L' calculated by the film-penetration concept agrees neither with k_L' calculated by the film theory nor with k_L' calculated by the surface renewal theory. If the surface renewal theory is applied here, the deviation from the film-penetration concept may be as high as 90% and for the film theory it is as much as 65%. This is the region where the film-penetration concept provides valuable information which cannot be obtained by either the film theory or the penetration theory alone.

The above has shown that although near the extremes the film theory or the surface renewal theory might be substituted for the film-penetration concept, there remains a certain segment where such an approximation or substitution is invalid. Thus γ may be used as a criterion for selecting an appropriate or suitable mathematical model to represent a mass transfer mechanism.

The simple models for a mass transfer mechanism contain a single parameter in their respective mathematical description, for example fictitious film thickness for the film theory or the sur-

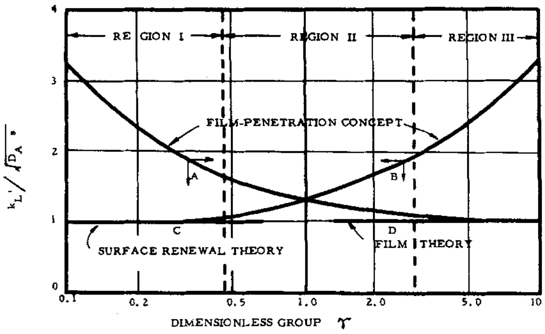

Fig. 1. Effect of dimensionless group γ on physical mass transfer.

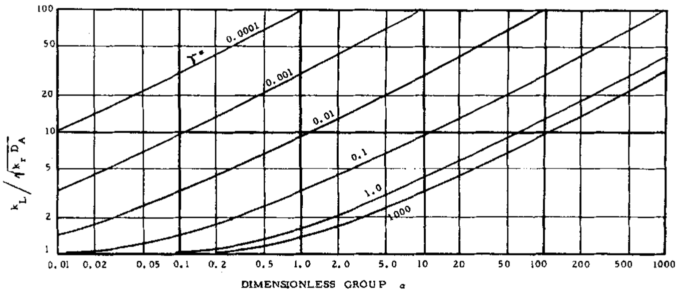

Fig. 3. Influence of dimensionless groups on mass transfer coefficient.

face renewal rate for the surface renewal theory. However because of the simplified postulations with a single parameter, the film theory or the surface renewal theory fails to explain some important experimental evidence. For example Gordon and Sherwood (6) showed that experimental values of the physical mass transfer coefficient may be related to the molecular diffusivity by

$$k_L' \propto D^\nu \tag{26}$$

In accordance with the film theory, the exponent ν should be equal to exactly 1.0, and it must be definitely 0.5 by the surface renewal theory or the penetration theory. However experimental values of ν reported in literature are somewhere between 0.15 and 1.0. This variation of experimental values cannot be explained by either the film theory or the penetration theory. In accordance with the film-penetration concept, which has two unknown parameters, the physical mass transfer coefficient is related to the molecular diffusivity by Equation (25), or by the following:

$$k_L' = \frac{D_A}{L}\left[f_1\left(\frac{D_A}{sL^2}\right)\right] = \frac{D_A}{L}\left[f_1(\gamma)\right] = \sqrt{D_A s}\left[f_2\left(\frac{D_A}{sL^2}\right)\right] = \sqrt{D_A s}\left[f_2(\gamma)\right] \tag{27}$$

Thus in accordance with the film-penetration concept the theoretical value of the exponent ν does not have to be a certain definite value but may vary depending on the hydrodynamic behavior, as represented by the dimensionless group γ. Particularly in Region II of Figure 1 the value of γ has a distinct effect on the mass transfer coefficient. In this region the exponent ν in Equation (26) may be any value, not necessarily a definite 0.5 or 1.0. The fact that the variation of exponent ν can be predicted by the film-penetration theory makes it a more general concept than the film theory or the surface renewal theory.

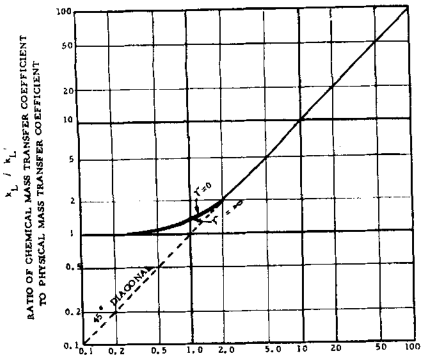

Fig. 2. Effect of chemical reaction on mass transfer rate.

Effect of Chemical Reaction on Mass Transfer Rate

The effect of a first-order irreversible chemical reaction on the mass transfer rate may be discussed in terms of the ratio of the chemical mass transfer coefficient to the physical mass transfer coefficient. In accordance with the film-penetration concept this ratio may be obtained by combining Equations (10*a*) and (11). The result is

$$\frac{k_L}{k_L'} = \frac{\sqrt{1+\dfrac{1}{\beta}}}{\coth\sqrt{\dfrac{1+\beta}{\alpha}}\;\tanh\sqrt{\dfrac{\beta}{\alpha}}} \tag{28a}$$

or

$$\frac{k_L}{k_L'} = \frac{\sqrt{1+\dfrac{\gamma}{\alpha}}}{\coth\sqrt{\dfrac{1}{\alpha}+\dfrac{1}{\gamma}}\;\tanh\sqrt{\dfrac{1}{\gamma}}} \tag{28b}$$

Equations (21) and (19*b*) may also be combined to yield the above equations, if one assumes the C_{AL} concentration is negligible. One drawback of Equation (28*a*) is that both the two dimensionless groups in the equation contain immeasurable quantities s and L. The same objection applies to Equation (28*b*). However Equations (28) may be rearranged to another form which includes the dimensionless group M. Thus

film-penetration concept $(0 \leq \gamma \leq \infty)$:

$$\frac{k_L}{k_L'} = \sqrt{1+M\left(\coth\frac{1}{\sqrt{\gamma}}\right)^2}$$

$$\frac{\left[\tanh\dfrac{1}{\sqrt{\gamma}}\right]}{\coth\sqrt{\dfrac{1}{\gamma}\left[1+M\left(\coth\dfrac{1}{\sqrt{\gamma}}\right)^2\right]}} \tag{29}$$

The dimensionless group M is defined as

$$M = \frac{k_r D_A}{(k_L')^2} \tag{30}$$

and all the quantities appearing in the definition can be measured experimentally.

As discussed in the previous section on physical mass transfer, as γ approaches zero the film-penetration concept may be represented by the surface renewal theory. On the other hand as γ approaches infinity, the film penetration concept converges to the film theory. For these two limiting cases Equation (29) may be reduced to the following:

surface renewal theory $(\gamma \to 0)$:

$$\frac{k_L}{k_L'} = \sqrt{1+M} \tag{31}$$

film theory $(\gamma \to \infty)$:

$$\frac{k_L}{k_L'} = \frac{\sqrt{M}}{\tanh\sqrt{M}} \tag{32}$$

The calculated values of the k_L/k_L' ratio based on the above three different equations are almost identical at different γ values as long as they are compared at the same M value. The deviation is very small when M is small. For instance if M is smaller than 0.01, the deviation is less than 0.5%. However as M increases, the difference increases, and the maximum deviation of about 8.8% occurs at $M \doteq 2.1$. Then as M increases further, the deviation now decreases and becomes less than 0.5% again if M is larger than 100. These facts are also shown in Figure 2, where the plots of k_L/k_L' vs. $\sqrt{M}$ at different values of parameter γ converge to a single line. This means that the three different theories predict practically the same effect of chemical reaction on the mass transfer rate, when the results are expressed in terms of physically measurable quantities. Thus if an accurate value of k_L' is available either by experiment or by theory, the chemical mass transfer coefficient predicted on the basis of the three different theories is practically the same.

However if the chemical mass transfer coefficient is to be predicted without an accurate physical mass transfer coefficient, the choice of the theory or the mechanism may become very critical. This can be illustrated by a numerical example. Consider a hypothetical system in which $k_r D_A$ is equal to 9.0×10^{-8} sq.cm./sec². For certain given operating conditions the physical mass transfer coefficient is predicted to be say 2.14×10^{-4} cm./sec. by the surface renewal theory and 4.06×10^{-4} cm./sec. (at $\gamma = 3.0$) by the film-penetration concept. Then the chemical mass transfer coefficient may be predicted as follows:

film-penetration concept:

$$\sqrt{M} = 0.74$$

$$\frac{k_L}{k_L'} = 1.22$$

$$k_L = 4.95 \times 10^{-4} \text{ cm./sec.}$$

surface renewal theory:

$$\sqrt{M} = 1.40$$

$$\frac{k_L}{k_L'} = 1.72$$

$$k_L = 3.68 \times 10^{-4} \text{ cm./sec.}$$

The above example shows that the chemical mass transfer coefficients differ appreciably because of the error in predicting the physical mass transfer coefficient on the basis of the different theories. This point can be elaborated further by Figure 3 which shows the plots of Equation (28*b*). In accordance with the plots the chemical mass transfer coefficient may differ greatly even at the same α value depending on the γ value. For instance at $\alpha = 1.0$ the predicted $k_L/\sqrt{k_r D_A}$ is only 1.35 based on the film theory (at $\gamma = 1{,}000$). On the other hand at the same α value the film-penetration theory may predict much higher k_L values depending on the γ values, for example at $\gamma = 0.0001$, $k_L/\sqrt{k_r D_A} = 100$.

When the chemical mass transfer coefficient k_L is to be predicted without knowledge of the physical mass transfer coefficient k_L', the numerical values of the surface renewal rate and the liquid element thickness L are required. But if the experimental values of both the chemical and physical mass transfer rates are available, L and s may be calculated by solving Equations (10*a*) and (11) simultaneously.

The dimensionless group M has other interesting influences on the chemical mass transfer rate. In accordance with Equation (31), when M is large, k_L/k_L' may be approximated by $\sqrt{M}$. Thus

$$\frac{k_L}{k_L'} \cong \sqrt{M} \quad (M \text{ is large})$$

or

$$k_L \cong k_L' \sqrt{M} = \sqrt{k_r D_A} \qquad (33)$$

This indicates that at higher M values the chemical mass transfer coefficient becomes independent of the hydrodynamic conditions. On the other hand when M is very small k_L/k_L' becomes equal to unity in accordance with Equation (32). Thus at low M values the chemical mass transfer coefficient is equal to the physical transfer coefficient.

The dimensionless groups α and β in Equation (28) may be related to M for the limiting cases. First they may be rearranged as follows:

$$\alpha = \frac{D_A}{k_r L^2} = \frac{1}{k_r D_A}\left(\frac{D_A}{L}\right)^2 \qquad (34)$$

$$\beta = \frac{s}{k_r} = \frac{(\sqrt{D_A s})^2}{k_r D_A} \qquad (35)$$

As the film-penetration concept approaches the film theory, $\left(\frac{D_A}{L}\right)$ is equal to k_L', and finally α becomes equal to $1/M$. Similarly as the film-penetration concept converges to the surface renewal theory, $\sqrt{D_A s}$ may be substituted by k_L' and finally β becomes equal to $1/M$.

Application of Proposed Equation to Mass Transfer Accompanied by Reversible Chemical Reaction

When the diffusion is accompanied by the first-order reversible chemical reaction, the concentration C_A in the path of diffusion can be obtained by solving

$$\partial C_A/\partial t = D_A(\partial^2 C_A/\partial x^2) - k_r C_A + k_r' C_{AB} \quad 0 < x < L \qquad (36)$$

Equation (1*b*) also represents the initial and boundary conditions for this case. It is assumed that a chemical equilibrium exists in the bulk of the liquid, or the outer edge of a liquid element is assumed to be in chemical equilibrium; that is

$$k_r C_{AL} = k_r' C_{AB} \quad \text{at } x = L \qquad (37)$$

Furthermore if the reaction product concentration in the path of diffusion does not vary greatly, the above equation is still valid for the entire path.

If the surface age distribution function of Danckwerts is applied, the average transfer rate is obtained (*16*) as follows:

$$\overline{N}_A = \sqrt{k_r D_A (1 + \beta)} \coth \sqrt{\frac{1 + \beta}{\alpha}}\,(C_{Ai} - C_{AL}) \qquad (38)$$

Mass Transfer Accompanied by High Order Chemical Reaction

The concentration gradient C_A for the case of the diffusion accompanied by the chemical reaction

$$aA + bB \rightarrow pP + qQ$$

may be expressed by

$$\partial C_A/\partial t = D_A(\partial^2 C_A/\partial x^2) - k_r' C_A C_B^{b/a} \quad 0 < x < L \qquad (39)$$

An approximate solution may be obtained if $k_r' C_A C_B^{b/a}$ can be taken as $k_r' C_A (C_{B\,\text{avg}})^{b/a}$. A similar approach was proposed by Van Krevelen and Hoftijer (*24*) for analysis of the gas absorption data of carbon dioxide into diethanolamine and ammonia solutions. If this simplification is permissible, Equation (39) is then reduced to Equation (1). Thus the proposed rate equations in this research may be applied to the situation by substituting $k_r'(C_{B\,\text{avg}})^{b/a}$ for k_r. Peaceman (*26*) showed this approximation is correct to within 8% at high value of C_B and becomes more correct as C_B decreases. When the chemical reaction is an instantaneous second-order reaction, the problem may be solved by a geometrical approximation (*14, 22*). Solutions by numerical approximation are also available (*1, 20, 25*).

Heat Conduction Accompanied by Heat Loss

Because of analogy between mass and heat transfer the proposed rate equations may be easily adopted for heat conduction problems. It may be pictured that heat is transferred by conduction along a thin rod of finite length. The rod is so thin that the temperature at any point of a given cross section may be taken to be uniform. If the amount of heat lost from the rod surface to a surrounding medium is directly proportional to the temperature of the rod, the heat balance around an infinitesimal segment of the rod gives the following basic differential equation:

$$\partial T/\partial t = \kappa(\partial^2 T/\partial x^2) - \eta T \quad 0 < x < L \qquad (40)$$

The initial temperature of the rod is uniform and represented by T_L. The temperatures at the terminals are kept constant, that is T_i and T_L, respectively. These initial and boundary conditions may be written as

$$\left.\begin{array}{lll} x = 0, & t > 0, & T = T_i \\ x = L, & t > 0, & T = T_L \\ x > 0, & t = 0, & T = T_L \end{array}\right\} \qquad (41)$$

Then the temperature distribution across the rod can be expressed by Equation (4) or Equation (15) by replacing C_A, D_A, and k_r by T, κ, and η, respectively.

CONCLUSIONS

The following conclusions were drawn from this study:

1. The formulation of a general mathematical model based on the film-penetration concept accompanied by a first-order irreversible chemical reaction has been successfully accomplished. When the dimensionless groups α or β in the equations approach the limiting values zero or infinity, the general equations can be reduced to those developed by previous workers based on simplified assumptions, that is the Whitman-Lewis equation, the Higbie equation, the Danckwerts equation, the Toor-Marchello equations for physical mass transfer, the Hatta equation, and the Danckwerts equations for chemical mass transfer.

2. The nature of mass transfer behavior and the transfer rate can be evaluated and analyzed in terms of the dimensionless groups. For mass transfer in absence of chemical reaction the film-penetration concept converges to the surface renewal theory as the dimensionless group γ approaches zero. On the other hand as γ becomes large, the film theory becomes a limiting case of the film-penetration concept. However when γ is neither small nor large the film-penetration concept provides valuable information which cannot be obtained by either the film theory or the surface renewal theory alone. For the region of $0.46 \leq \gamma \leq 3.0$ the mass transfer coefficient calculated by the film theory or by the surface renewal theory deviates from that by the film-penetration concept by more than 10% and as much as 90%.

3. Experimental results appearing in literature show that the physical mass transfer coefficient is proportional to the molecular diffusivity to the ν-th power and that ν varies widely between 0.15 and 1.0. The film-penetration concept theoretically predicts this ν-variation, whereas in accordance with the film theory or the surface renewal theory ν has to be a certain fixed value.

4. When an accurate value of the physical mass transfer coefficient is available, 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. However if the chemical mass transfer coefficient is to be predicted without an accurate physical transfer coefficient, the choice of the theory or the mechanism may become very important.

5. The proposed equations may be applied to mass transfer accompanied by a first-order reversible chemical reaction, if the concentration of the reaction product is almost constant. The proposed equations may also be directly applied to the problem of heat conduction accompanied by heat loss.

ACKNOWLEDGMENT

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

NOTATION

A = reactant A
B = reactant B
C_A = concentration of component A in solution, g.-mole/liter
$\overline{C_A}$ = Laplace transform of $C_A(x, t)$
C_{AB} = concentration of product AB in solution, g.-mole/liter
C_B = concentration of component B in solution, g.-mole/liter
C_{Ai} = concentration of component A at interface, g.-mole/liter
C_{AL} = concentration of component A at the outer edge of a surface element, g.-mole/liter
D = molecular diffusivity, sq.cm./sec.
D_A = molecular diffusivity of component A sq.cm./sec.
L = average thickness of a surface element, cm.
M = dimensionless group, $k_r D_A / k_L'^2$
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.
$\overline{N}_A$ = average rate of chemical mass transfer for component A, g.-mole/sq.cm.-sec.
$\overline{N}_A'$ = average rate of physical mass transfer for component A, g.-mole/sq.cm.-sec.
T = absolute temperature, °K.
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_r = reaction velocity constant, 1/sec.
n = integer
s = surface renewal rate, 1/sec.
t = time, sec.
x = distance, cm.
erf x = error function = $(2/\sqrt{\pi})\int_0^x \exp(-\lambda^2)\,d\lambda$
erfc x = complementary error function = $1 - \operatorname{erf} x = (2/\sqrt{\pi})\int_x^\infty \exp(-\lambda^2)\,d\lambda$

Greek Letters

α = dimensionless group, $D_A/(k_r L^2)$
β = dimensionless group, s/k_r
γ = dimensionless group, α/β or $D_A/(s\,L^2)$
π = 3.1416
$\phi(t)$ = surface age distribution function
κ = thermal diffusivity, sq.cm./sec.
ν = exponent
η = heat loss rate constant, 1/sec.

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Manuscript received December 1, 1961; revision received June 26, 1962; paper accepted June 29, 1962.