# Liquid Phase Mass Transfer with Complex Chemical Reaction

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Very little information has been available in the literature concerning mass transfer accompanied by complex chemical reaction (3). Thus, it has been a common practice in the past to approximate a combination of complex reactions by an overall single reaction in the prediction of the mass transfer rate. This approximation, however, is not always adequate. For example, Rehm et al. (9) measured the rate of carbon dioxide absorption by dilute sodium hydroxide solution. They reported that two consecutive reactions were involved in this system and that the rate equations based on the model of molecular diffusion with one reaction could not be used to predict accurately the experimental data. Therefore, a theoretical study on the subject of simultaneous mass transfer and complex chemical reaction is desirable. The present work was undertaken to fulfill this need.

Another objective of this study is to investigate the effect of the ratio of the intermediate product diffusivity to the reactant diffusivity on theoretical predictions of mass transfer rate for cases of simultaneous molecular diffusion and complex chemical reaction. This effect is very pronounced if the molecular diffusion is accompanied by a reversible chemical reaction (6); the theories deviate significantly in predictions of mass transfer rate when the diffusivities are different. On the other hand, the theories agree well for cases of mass transfer accompanied by irreversible chemical reaction (5, 10).

On the basis of the film-penetration model, the theoretical rate equation has been derived for mass transfer accompanied by first-order complex chemical reactions. As will be discussed in the following sections, the rate equations for the film theory and for the surface renewal theory can also be obtained from this general equation. The effects of complex reaction on mass transfer rate will also be discussed in this paper.

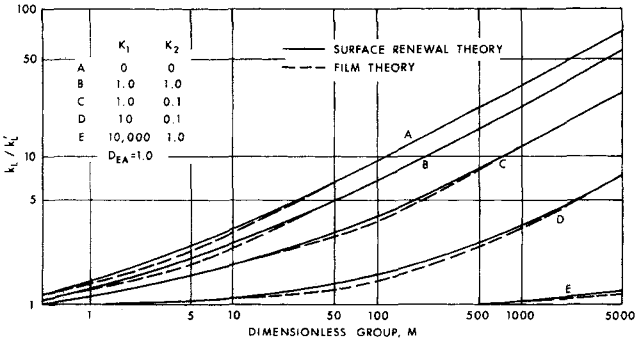


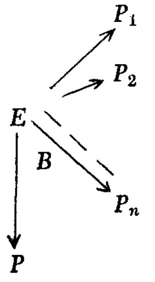
**Fig. 1. Comparison of theories.**

## THEORY

The problem to be considered is a transport process between gas and liquid phases. As the reactant $A$ diffuses from the gas phase into the interface, it is assumed that a complex reaction takes place along the path of diffusion in liquid phase. A typical complex reaction to be treated in this study includes consecutive, reversible, and parallel reactions. As a liquid element is exposed in the interface, the reactant $B$ from the liquid phase reacts reversibly with the diffusing solute $A$ to form an intermediate product $E$:

$$A + B \rightleftharpoons E$$

Consecutively, this intermediate product $E$ may react further or may be decomposed to yield the final products. The kinetics of this decomposition follows the following simultaneous reaction:



The reactant $A$ may also be capable of reacting with some other components from the liquid phase:

$$A + B_1 \rightarrow Q_1$$

$$A + B_2 \rightarrow Q_2$$

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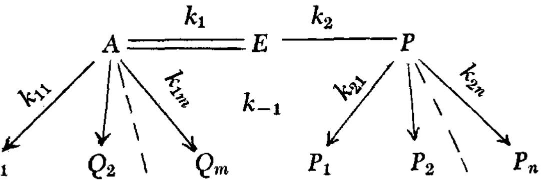
$$A + B_m \rightarrow Q_m$$

For many systems, the concentrations of the components $B$, $B_1$, $B_2$, . . ., $B_m$ in the solution are significantly greater than that of the solute reactant. Thus, the kinetics of these reactions may be approximated by a first-order or pseudo first-order complex reaction with respect to the solute concentration. With this simplification, these reactions may be summarized in the following manner:



The molecular diffusion is considered to be one dimensional only, and the convective transfer is unimportant. The equations of continuity for components $A$ and $E$ are

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial \chi^2} - \left[ k_1 + \sum_{i=1}^{m} k_{1i} \right] C_A + k_{-1}\, C_E \tag{1}$$

$$\frac{\partial C_E}{\partial t} = D_E \frac{\partial^2 C_E}{\partial \chi^2} + k_1\, C_A - \left[ k_{-1} + k_2 + \sum_{j=1}^{n} k_{2j} \right] C_E \tag{2}$$

The diffusivities and the first-order reaction rate constants are considered constants for a given system. It is assumed that the intermediate $E$ is not volatile, so it does not move across the interphase boundary.

The concentration distributions of the reactant $A$ and the intermediate $E$ can be obtained by solving simultaneously the above set of partial differential equations. Different sets of initial and boundary conditions may be used depending upon the postulation of the interphase hydrodynamic behavior. In accordance with the film-penetration model (*2*, *11*), the initial and boundary conditions can be stated mathematically as

$$\left.\begin{aligned} &\chi = 0, \quad t > 0, \quad C_A = C_{Ai}, \quad \frac{\partial C_E}{\partial \chi} = 0 \\ &\chi = L, \quad t > 0, \quad C_A = C_{AL}, \quad C_E = C_{EL} \\ &\chi > 0, \quad t = 0, \quad C_A = C_{AL}, \quad C_E = C_{EL} \end{aligned}\right\} \qquad (3)$$

The method of the Laplace transformation can be employed to obtain the concentration distributions.

By applying the surface age distribution of Danckwerts (*1*), the average chemical mass transfer rate can be obtained from

$$\overline{N}_A = - D_A \int_0^\infty \left[ \frac{\partial C_A}{\partial \chi} \right]_{\chi=0} s\, e^{-st}\, dt \qquad (4)$$

The ratio of chemical to physical mass transfer coefficients can be derived from

$$\frac{k_L}{k_L'} = \frac{\overline{N}_A}{k_L' \, (C_{Ai} - C_{AL})} \qquad (5)$$

where the expressions for the physical mass transfer coefficient are available in the literature (*1*, *8*, *11*).

The details of the mathematical derivation are given elsewhere (*7*). The final expression for the ratio of chemical to physical mass transfer coefficients is found to be

$$\frac{k_L}{k_L'} = \frac{\mu^2{}_3 - \mu^2{}_{-3}}{\left[ 1 + K_3 + \frac{1}{M}\left(\tanh\frac{1}{\sqrt{\gamma}}\right)^2 - \mu^2{}_{-3} \right] \frac{\tanh\left[ \mu_3 \sqrt{\frac{M}{\gamma}} \coth\frac{1}{\sqrt{\gamma}} \right]}{\mu_3\sqrt{M}} - \left[ 1 + K_3 + \frac{1}{M}\left(\tanh\frac{1}{\sqrt{\gamma}}\right)^2 - \mu_3{}^2 \right] \frac{\tanh\left[ \mu_{-3} \sqrt{\frac{M}{\gamma}} \coth\frac{1}{\sqrt{\gamma}} \right]}{\mu_{-3}\sqrt{M}}} \qquad (6)$$

where

$$\mu_3 = \frac{1}{\sqrt{2}} \left\{ 1 + K_3 + \frac{K_1 + K_2 + K_4}{D_{EA}} + \left( 1 + \frac{1}{D_{EA}} \right) \frac{1}{M} \left( \tanh \frac{1}{\sqrt{\gamma}} \right)^2 + \sqrt{\left[ 1 + K_3 - \frac{K_1 + K_2 + K_4}{D_{EA}} + \left( 1 - \frac{1}{D_{EA}} \right) \frac{1}{M} \left( \tanh \frac{1}{\sqrt{\gamma}} \right)^2 \right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2}$$

$$\mu_{-3} = \frac{1}{\sqrt{2}} \left\{ 1 + K_3 + \frac{K_1 + K_2 + K_4}{D_{EA}} + \left( 1 + \frac{1}{D_{EA}} \right) \frac{1}{M} \left( \tanh \frac{1}{\sqrt{\gamma}} \right)^2 - \sqrt{\left[ 1 + K_3 - \frac{K_1 + K_2 + K_4}{D_{EA}} + \left( 1 - \frac{1}{D_{EA}} \right) \frac{1}{M} \left( \tanh \frac{1}{\sqrt{\gamma}} \right)^2 \right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2}$$

and

$$M = \frac{k_1 D_A}{k_L'^2}$$

## LIMITING CASES

As mentioned in the previous section, Equation (6) is developed on the basis of the film-penetration concept. In accordance with this mechanism, the liquid elements of different ages, from old to young, are exposed to the interphase at the same time in the transport process (*11*). When the surface renewal rate approaches zero, the phase elements at the interphase remain there for an infinite period, and a layer of stagnant phase element is eventually formed at the phase boundary. For this case, the steady state molecular diffusion and reaction are the controlling transfer mechanisms, and the film theory is valid. The ratio of chemical to physical mass transfer coefficients for this case can be obtained by substituting $\gamma = \infty$ in Equation (6):

$$\frac{k_L}{k_L'} = \frac{\mu^2{}_1 - \mu^2{}_{-1}}{[1 + K_3 - \mu^2{}_{-1}] \frac{\tanh \mu_1 \sqrt{M}}{\mu_1 \sqrt{M}} - [1 + K_3 - \mu^2{}_1] \frac{\tanh \mu_{-1} \sqrt{M}}{\mu_{-1} \sqrt{M}}} \qquad (7)$$

where

$$\mu_1 = \frac{1}{\sqrt{2}} \left\{ 1 + K_3 + \frac{K_1 + K_2 + K_4}{D_{EA}} + \sqrt{\left[ 1 + K_3 - \frac{K_1 + K_2 + K_4}{D_{EA}} \right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2}$$

and

$$\mu_{-1} = \frac{1}{\sqrt{2}} \left\{ 1 + K_3 + \frac{K_1 + K_2 + K_4}{D_{EA}} - \sqrt{\left[ 1 + K_3 - \frac{K_1 + K_2 + K_4}{D_{EA}} \right]^2 + \frac{4K_1}{D_{EA}}} \right\}^{1/2}$$

On the other hand, when the phase element is renewed at a very rapid rate, the penetration of the diffusing reactant A never reaches the terminal edge of the phase element. Thus, the phase element may be considered to have infinite thickness from the diffusion point of view. For this limiting case, the surface renewal model prevails. The ratio of chemical to physical mass transfer coefficients on the basis of the model can be obtained by letting the film thickness $L$ approach infinity ($\gamma = 0$) in Equation (6):

$$\frac{k_L}{k_L'} = \frac{\mu_2\mu_{-2}\left[\mu^2_2 - \mu^2_{-2}\right]\sqrt{M}}{\mu_{-2}\left[1 + K_3 + \frac{1}{M} - \mu^2_{-2}\right] - \mu_2\left[1 + K_3 + \frac{1}{M} - \mu^2_2\right]} \qquad (8)$$

where

$$\mu_2 = \frac{1}{\sqrt{2}}\left\{1 + K_3 + \frac{K_1 + K_2 + K_4}{D_{EA}} + \left(1 + \frac{1}{D_{EA}}\right)\frac{1}{M} + \sqrt{\left[1 + K_3 - \frac{K_1 + K_2 + K_4}{D_{EA}} + \left(1 - \frac{1}{D_{EA}}\right)\frac{1}{M}\right]^2 + \frac{4K_1}{D_{EA}}}\right\}^{1/2}$$

and

$$\mu_{-2} = \frac{1}{\sqrt{2}}\left\{1 + K_3 + \frac{K_1 + K_2 + K_4}{D_{EA}} + \left(1 + \frac{1}{D_{EA}}\right)\frac{1}{M} - \sqrt{\left[1 + K_3 - \frac{K_1 + K_2 + K_4}{D_{EA}} + \left(1 - \frac{1}{D_{EA}}\right)\frac{1}{M}\right]^2 + \frac{4K_1}{D_{EA}}}\right\}^{1/2}$$

## DISCUSSION

Equations (7) and (8) are the mathematical expressions of the ratio of chemical to physical mass transfer coefficients based on the film theory and the surface renewal theory, respectively. These equations can also be obtained directly by solving the original partial-differential equations with the appropriate initial and boundary conditions (7). Computations were made to see the effects of the dimensionless groups $K_1$, $K_2$, $D_{EA}$, and $M$ on the ratio of chemical to physical mass transfer coefficients. The results are illustrated in Figure 1 for cases where mass transfer is accompanied by reversible and consecutive reactions but without parallel reactions. It is observed that when the dimensionless parameter $M$ is either very large or very small, the three different theories predict the same effect of chemical reactions on mass transfer. As shown in Figure 1, when $M$ approaches zero, the ratio of chemical mass transfer to physical mass transfer coefficients is equal to unity regardless of which theory is used to postulate the mass transfer mechanism. Furthermore, it is also found that if $M$ is less than 0.1, the effect of chemical reaction on mass transfer is very small, that is, less than 5%. Within this range of small $M$ values, the mass transfer rate is controlled by diffusion. However, once $M$ goes beyond 0.1, the influence of chemical reaction on mass transfer rate becomes appreciable, and the degree of such influence depends on the theory adopted.

Finally, as shown in Figure 1, when $M$ becomes very large, the ratio of chemical to physical mass transfer coefficients again converges to the same value irrespective of the theories. This observation can be verified mathematically. When $M$ is large, Equations (6), (7), and (8) based on three different theories can be approximated by the same equation as follows:

$$\frac{k_L}{k_L'} = \eta\,(\mu_1, \mu_{-1}) \cdot \sqrt{M} \qquad (9)$$

where

$$\eta(\mu_1, \mu_{-1}) = \frac{\mu_1\mu_{-1}\,(\mu_1 + \mu_{-1})}{\mu_1{}^2 + \mu_1\mu_{-1} + \mu_{-1}{}^2 - 1}$$

According to the above equation, the $k_L/k_L'$ ratio increases linearly with $\sqrt{M}$. The proportionality constant $\eta(\mu_1, \mu_{-1})$ is a function of the reaction rate constants and the diffusivities, and the hydrodynamic effects on the mass transfer are insignificant. Similar to the previous finding for mass transfer accompanied by irreversible first-order reaction (*5, 10*), the effects of complex chemical reactions on the mass transfer rates are almost the same regardless of which theory is adopted to represent the mass transfer mechanism. The proportionality constant increases as $K_1/D_{EA}$ and $K_1/K_2$ decrease, and the rate of change of $\eta$ depends more on $K_1/K_2$ than on $K_1/D_{EA}$. If both $K_1/D_{EA}$ and $K_1/K_2$ approach zero, the constant $\eta$ may be approximated by 1.0, and the transfer coefficient ratio is equal to $\sqrt{M}$.

The above conclusion is not valid, however, if the reaction rate constant $k_2$ of the consecutive reaction is comparatively very small or nearly equal to zero. The predicted effects of chemical reaction on mass transfer rate are sensitive to the theory or the model adopted in postulating the mechanism. The deviations between calculated transfer coefficients based on the different theories increase as $M$ is increased and as $k_2$ is decreased. In particular, when the diffusivity of $E$ is less than that of $A$ by a factor of 10 or more, the theoretical effect of chemical reaction on mass transfer rate is strongly dependent on the theory. The same conclusion was also obtained in a previous study (*6*) for mass transfer and reversible reaction.

Approximation of mass transfer with reversible and consecutive reactions by that with a first-order irreversible reaction is permissible for cases where the square root of the physical mass transfer coefficient is very large compared with the chemical reaction rate constant. Under these conditions, the overall mass transfer rate is almost identical to the rate of physical mass transfer, and chemical reaction has little influence.

However, if the first forward reaction rate and the physical mass transfer rate are comparable in magnitude, both the reaction rate and the physical transfer rate exert their respective influences. On the other hand, if the physical mass transfer rate is very small compared with the chemical reaction rate, the chemical reaction rate has a dominating influence in determining the overall mass transfer rates. For these two latter cases, the above approximation or simplified treatment may yield a great error. The magnitude of such errors depends on the relative values of $K_1$, $K_2$, $D_{EA}$, and $M$.

## CONCLUSION

The following conclusions can be drawn from the present research:

1. Theoretical rate equations have been derived for liquid phase mass transfer accompanied by first-order complex chemical reactions. The kinetics considered is a combination of consecutive, reversible, and parallel chemical reactions.
2. The film-penetration model has been shown to be a general model among the theories considered. It takes the film theory and the surface renewal theory as the lower and upper limits, respectively, in the theoretical predictions.
3. The ratio of chemical to physical mass transfer coefficients is smaller than that for mass transfer with a first-order irreversible reaction. The theories deviate significantly for cases where the reversible reaction is strong, and the diffusivities of the intermediate product and the reactant are quite different.

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## NOTATION

$C_A$ = concentration of component $A$, g.-mole/liter
$C_{Ai}$ = 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
$C_E$ = 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.
$D_E$ = molecular diffusivity of component $E$, sq.cm./sec.
$D_{EA}$ = diffusivity ratio, $D_E/D_A$
$K_1$ = ratio of reaction rate constants $k_{-1}/k_1$
$K_2$ = ratio of reaction rate constants, $k_2/k_1$
$K_3$ = ratio of reaction rate constants, $\sum_{i=1}^{m} k_{1i}/k_1$
$K_4$ = ratio of reaction rate constants, $\sum_{j=1}^{n} k_{2j}/k_1$
$L$ = average thickness of a surface element, or of a film, cm.
$M$ = dimensionless group, $k_1 D_A/(k_L')^2$
$\overline{N}_A$ = average rate of chemical mass transfer for component $A$, g.-mole/(sq.cm.)(sec.)
$k_r$ = first-order reaction rate constant, sec.$^{-1}$, $r = 1, 11, 12, \ldots. 1m, 2, 21, 22, \ldots 2n$, for forward reactions, $r = -1$ for backward reaction
$k_L'$ = liquid side mass transfer coefficient without chemical reaction, cm./sec.
$k_L$ = liquid side mass transfer coefficient with chemical reaction, cm./sec.
$s$ = surface renewal rate, sec.$^{-1}$
$t$ = time, sec.
$\chi$ = distance, cm.
$\gamma$ = dimensionless group, $D_A/sL^2$

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# Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State

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It was shown by us in a previous paper (*1*) that a modified Redlich-Kwong equation may be used to calculate both liquid-phase and vapor-phase fugacity coefficients of components in mixtures, provided that the dimensionless R-K parameters $\Omega_a$ and $\Omega_b$ of each pure component are first established from the P-V-T properties of the saturated liquid. The values of $\Omega_a$ and $\Omega_b$ were obtained at each of a series of temperatures by solving simultaneously the R-K equation

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}V(V + b)} \qquad (1)$$

and

$$\ln \phi_L^s = \ln RT/P(V_l - b) + (PV_l/RT) - 1 - (a/RT^{3/2}b)\ln (V_l + b)/V_l \qquad (2)$$

The values of the fugacity coefficient $\phi_L^s$ were obtained from the generalized correlation of Lyckman, Eckert, and Prausnitz (*2*). The R-K constants $a$ and $b$ are related to the dimensionless $\Omega_a$ and $\Omega_b$ parameters as follows:

$$a = \Omega_a R^2 T_c^{2.5}/P_c \qquad (3)$$

$$b = \Omega_b R T_c/P_c \qquad (4)$$