Unsteady State Diffusion and Selectivity in Gas-Liquid Systems

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The aim of the present investigation was to study the effect of unsteady state mass transfer on selectivity in heterogeneous systems involving consecutive chemical reactions. In many chemical and petroleum processes of commercial interest, such as the liquid phase oxidation of hydrocarbon by absorbed oxygen reported by Spielman (1964), the desired product may be an intermediate in a sequence of reactions. On the other hand, Veselov and Sipeeva (1965) showed that an intermediate product may be undesirable and have to be converted into final products via the consecutive reaction steps. In both cases, it is important to determine the selectivity or the yield of a reaction system for the design of such a reactor.

This paper concerns unsteady state gas absorption and first-order consecutive reactions in a liquid phase with formation of an intermediate product which is volatile. The problem of steady state mass transfer and selectivity was discussed earlier by Bridgwater (1967). Szekely and Bridgwater (1967) also investigated a special case of unsteady state systems utilizing the penetration model. In this study, rate and yield equations are derived on the basis of the film-penetration and surface renewal models. Factors affecting the selectivity are discussed and a comparison is made of results predicted by the steady state and unsteady state mechanisms.

THEORETICAL DEVELOPMENT

The problem to be considered is a transport process between gas and liquid phases. As a solute A diffuses from the gas phase into a liquid element or film at the surface adjacent to the gas, it is assumed that the following isothermal first-order consecutive chemical reaction takes place along the path of diffusion.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} P$$

The intermediate product B is considered volatile, and so it may diffuse back into the gas phase or be converted into the final product P. The unsteady state molecular diffusion is considered to be one-dimensional and mass transfer by convection is unimportant. Thus, the equations of continuity for the species A and B are

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_1 C_A \tag{1}$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} + k_1 C_A - k_2 C_B \tag{2}$$

where the reaction rate constants k_1 and k_2 and the diffusivities D_A and D_B are assumed constants. In accordance with the postulation of the film-penetration theory discussed by Huang and Kuo (1963) for example, the film or the liquid element has a finite thickness and the initial and boundary conditions can be stated mathematically, as,

$$x > 0, \quad t = 0, \quad C_A = C_{AL}, \quad C_B = C_{BL} \tag{3a}$$

$$x = 0, \quad t > 0, \quad C_A = C_{Ai}, \quad k_{GB} H_B (C_B{}^* - C_B|_{x=0}) = -D_B \left. \frac{\partial C_B}{\partial x} \right|_{x=0} \tag{3b}$$

$$x = L, \quad t > 0, \quad C_A = C_{AL}, \quad C_B = C_{BL} \tag{3c}$$

By applying the surface age distribution of Danckwerts (1970), the average rate of absorption of species i can be derived from

$$\overline{N_i} = -D_i\, s \int_0^\infty \left. \frac{\partial C_i}{\partial x} \right|_{x=0} \exp(-st)\, dt \tag{4}$$

Thus, the expression for the rate of absorption of A is found to be

$$\overline{N_A} = k_L\, (C_{Ai} - C_{AL})\, [1 + M \coth^2 a]^{1/2} \tanh a / \tanh [a(1 + M \coth^2 a)^{1/2}] \tag{5}$$

where the liquid phase mass transfer coefficient without chemical reaction is

$$k_L = \sqrt{D_A s} \coth a \tag{6}$$

Finally, the yield of the intermediate product B is derived to be

$$\begin{aligned} Y &= -\overline{N}_B / \overline{N}_A \\ &= \frac{MD}{m_1 D - m_2} \Bigg\{ 1 - \frac{\sqrt{m_2}}{\sqrt{m_1} D \left[b \sqrt{\dfrac{m_2}{D}} + \tanh \beta \right]} \\ &\quad \cdot \Bigg[b\sqrt{m_1} - \frac{\tanh \alpha}{1 - (M \operatorname{sech} \alpha + m_1 - M) C_{AL} / (m_1 C_{Ai})} \\ &\quad \Bigg(-1 + \left\langle \operatorname{sech} \beta + \frac{m_1 - M}{m_2} (1 - \operatorname{sech} \beta) \right\rangle \\ &\quad \left\langle \frac{C_{AL}}{C_{Ai}} + \frac{m_1 D - m_2}{M} \frac{C_{BL}}{C_{Ai}} \right\rangle - \frac{m_1 D - m_2}{M} \frac{C_B{}^*}{C_{Ai}} \Bigg) \Bigg] \Bigg\} \end{aligned} \tag{7}$$

where

$$m_1 = M + \tanh^2 a \tag{8}$$

$$m_2 = KM + \tanh^2 a \tag{9}$$

$$\alpha = \sqrt{m_1} \cdot a \coth a \tag{10}$$

$$\beta = \sqrt{\frac{m_2}{D}} \cdot a \coth a \tag{11}$$

LIMITING CASES

Equations (5) and (7) are developed on the basis of the film-penetration concept. When the surface renewal

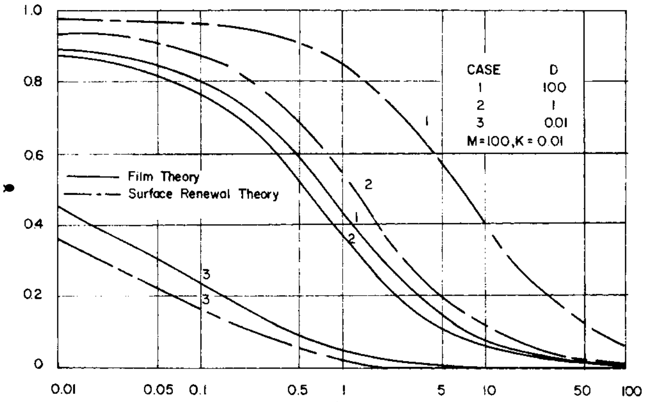

Fig. 1. Factors controlling the yield.

rate approaches zero, the film theory prevails, and the yield can be obtained by substituting $s = 0$ in Equation (7):

$$Y = \frac{D}{D-K}\left\{1 - \frac{\sqrt{K/D}}{b\sqrt{KM/D} + \tanh\sqrt{KM/D}}\left[b\sqrt{M} - \frac{\tanh\sqrt{M}}{1 - C_{AL}\operatorname{sech}\sqrt{M}/C_{Ai}}\left(-1 + \left\langle\frac{C_{AL}}{C_{Ai}} + (D-K)\frac{C_{BL}}{C_{Ai}}\right\rangle \operatorname{sech}\sqrt{KM/D} - (D-K)\,C_B{}^*/C_{Ai}\right)\right]\right\} \quad (12)$$

Equation (12) is the same as that derived by Bridgwater (1967) and Szekely and Bridgwater (1967) based on steady state molecular diffusion and consecutive reaction.

On the other hand, if the phase element is renewed at a very rapid rate, the surface renewal model is valid, and the expression for the yield can be obtained by substituting $L = \infty$ in Equation (7)

$$Y = \frac{MD}{(1+M)D - (1+KM)}\left\{1 - \frac{\sqrt{(1+KM)/[(1+M)D]}}{b\sqrt{(1+KM)/D} + 1}\left[b\sqrt{1+M} - \frac{1}{1 - C_{AL}(1+M)/C_{Ai}}\left(-1 + \frac{C_{AL}}{C_{Ai}}\,\frac{1}{1+KM} + <(1+M)D - (1+KM)> \left\langle\frac{C_{BL}}{C_{Ai}}\,\frac{1}{1+KM} - \frac{C_B{}^*}{C_{Ai}}\right\rangle /M\right)\right]\right\} \quad (13)$$

YIELD OF THE INTERMEDIATE

The theoretical equations developed in the previous section can be applied to investigate effects of various parameters on the yield of the intermediate. These physical and chemical properties can be grouped into four dimensionless quantities b, D, K, and M and three concentration ratios C_{AL}/C_{Ai}, C_{BL}/C_{Ai}, and $C_B{}^*/C_{Ai}$. For most cases, the interfacial concentration of A is much larger than the concentrations of A and B in the liquid bulk and the concentration of B in the gas bulk. Therefore, influences of these concentration ratios are ignored in calculating theoretical yields. Calculated results indicate that the intermediate product is transported back into the gas phase (values of the yield are positive).

In Figure 1, the yield is plotted against the dimensionless quantity b which is a measure of relative importance of resistances in the gas and liquid phases; the gas phase resistance of component B is negligible when b approaches zero. The yield decreases with the increase of b as expected, since a higher resistance in the gas phase (smaller gas phase mass transfer coefficient) would have adverse effects on the desorption of the intermediate. The influence of the diffusivity ratio $D = D_B/D_A$ can also be examined from results shown in Figure 1. By comparing the values predicted by a theory at a fixed value of b, we found that the yield is enhanced by the diffusivity ratio. This is reasonable since the mass transfer rate of a species increases with its diffusivity and a high diffusivity ratio ($D_B > D_A$) provides a favorable condition for the transport of the intermediate. It should be mentioned that if b is fixed and D is increased, then k_{GB}/k_L must increase approximately in proportion to D. Hence, an increase in yield at constant b is not due exclusively to an increase in D.

The effects of K and M on the yield are shown in Figures 2, 3, and 4 for cases of different diffusivity ratios. In these figures, Y is plotted against $\sqrt{M}$ to illustrate asymptotic behaviors of the yield at very large and very small values of $\sqrt{M}$. For a given set of K and D, the yield increases as $\sqrt{M}$ increases because of strong influences of chemical reactions. A further examination of the theoretical equations shows that in a heterogeneous system the maximum yield of the intermediate product can be achieved by choosing conditions such that $b < M^{-1/2}$ and $K > M^{-1}$ at a fixed value of M. If the intermediate is the desired product, then, complete conversion to B is attainable at large M values when K/D is much smaller than unity. The results observed here are in general accord with the conclusions of Bridgwater (1967). The rates of conversion and selectivity were also discussed by Carberry (1962), Harriott (1970), Van de Vusse (1966), and others for cases where the intermediate product is considered nonvolatile.

COMPARISON OF THEORIES

A fair appraisal of an unsteady state model is not possible in the work of Szekely and Bridgwater (1967) because their solution for the penetration theory was derived by neglecting the effects of the diffusivity ratio, the resistance to mass transfer in the gas phase and other factors. Nevertheless, they found that the yields predicted by the film

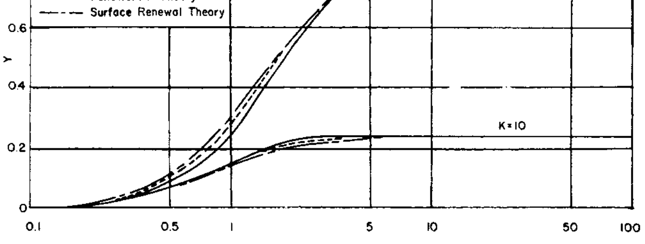

Fig. 2. Comparison of theories for cases of equal diffusivities.

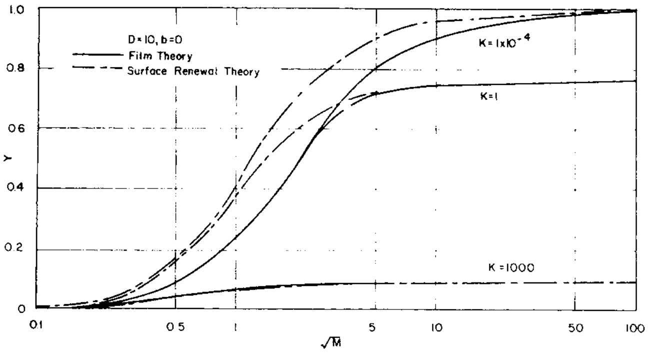

Fig. 3. Comparison of theories for diffusivity ratio greater than unity.

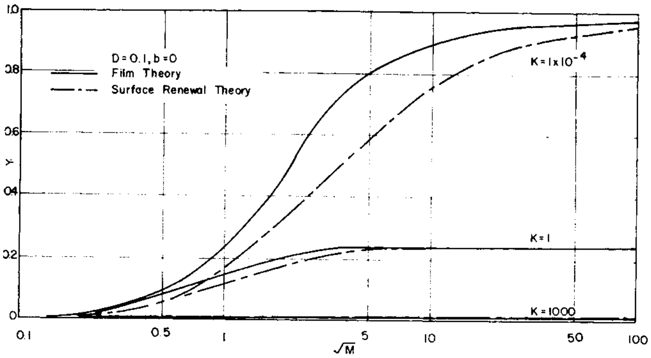

Fig. 4. Comparison of theories for diffusivity ratio less than unity.

and penetration models may differ by as much as 23% in the particular case considered. This result suggests that the theoretical yield of the intermediate may be sensitive to a model or theory applied to postulate the mechanism of mass transfer. Therefore, an extensive comparison of the steady state and unsteady state models is needed. One of the advantages of the film-penetration model is that the equation derived on the basis of this concept can be reduced to those based on simplified assumptions as demonstrated in an earlier section. Since this model takes the film and surface renewal theories as the limiting cases, it is only necessary to present results calculated by Equations (12) and (13) in order to investigate the upper and lower limits of the steady state and unsteady state solutions.

In a previous study for mass transfer and simple reactions, Huang and Kuo (1963) concluded that the maximum deviation among the models is 9% in the predictions of the absorption rate of *A*. The yield of *B*, however, is very sensitive to the theory as can be seen in Figure 1. Considering Case 1 given in this figure, a value predicted by the surface renewal theory can be several times larger than that calculated by the film theory for a given set of the physical and chemical parameters. For example, the surface renewal and the film theories predict the yield of 0.404 and 0.082, respectively, at $b = 10$ for this case. Therefore, the choice of a diffusion model is critical in the prediction of the desorption rate of the intermediate. Figure 1 also illustrates that the maximum deviation among the theories occurs at a moderate value of *b*. Results predicted by the various models may not be distinguishable if $KM >> 1$ and $b\,[KM/D]^{1/2} << 1$.

For special conditions of $D = 1$ and $b = 0$, the solution of the penetration theory was derived by Szekely and Bridgwater (1967), and the predicted results are compared with that calculated by the equations developed in this study as shown in Figure 2. As expected, the values predicted by the penetration mechanism fall between the values calculated by the film theory and the surface renewal theory. The deviations among the theories are rather small for these special cases of equal diffusivities compared with other cases shown in Figures 3 and 4. Again, this finding suggests that it is of significance to select a proper model to compute the theoretical yield if the diffusivities of the reactant and the intermediate are different. These figures also indicate that the deviation among the theories is insignificant when the rate of first step reaction is much slower than the rate of physical absorption of *A*. Under this circumstance ($M \rightarrow 0$), the yield approaches zero as predicted by all models. Another interesting observation is that depending upon combined values of the dimensionless quantities, the unsteady state model may predict a yield either larger or smaller than that calculated by the steady state model. This phenomenon also was observed in the report of Szekely and Bridgwater (1967).

The enhancement of mass transfer by simple chemical reactions is well known in the literature. When the molecular diffusion is accompanied by a first-order simple reaction, the absorption rate of the reactant is directly proportional to $\sqrt{M}$ at large values of *M* as discussed by Danckwerts (1970) and others. This is a reason that the yield is plotted against $\sqrt{M}$ in Figures 2, 3, and 4 for the convenience of studying the influence of consecutive reactions on the desorption rate of the intermediate. As can be seen in these figures, the theories converge to a constant asymptotic value for a given set of the physico-chemical parameters at large *M* values. This result confirms that if *M* is large, the desorption rate of the intermediate as well as the absorption rate of the reactant is directly proportional to $\sqrt{M}$.

CONCLUSION

The film-penetration model has been applied to predict the yield of intermediate product for systems of gas absorption accompanied by first order consecutive reactions. The equation developed on the basis of this mechanism can be simplified to give solutions of the film and the surface renewal theories.

It is found that the maximum yield of the intermediate can be achieved at large *M* values if $KM > 1$ and $b\sqrt{M} < 1$. Furthermore, complete conversion to the intermediate is possible when K/D is much less than unity. Results of this study also indicate that the desorption rate of the intermediate is directly proportional to $\sqrt{M}$ if the rate of the first step reaction is much faster than the physical absorption rate of the reactant.

Comparisons of the steady state and unsteady state models show that the theoretical yield is very sensitive to a mechanism adopted to postulate the diffusion process. In some cases, the theories predict values of different order of magnitude for a given set of the physical and chemical properties. The deviation among the models, however, is insignificant if $KM >> 1$ and $b\,[KM/D]^{1/2} << 1$ or if *M* is very small.

NOTATION

a = $[sL^2/D_A]^{1/2}$, dimensionless group
b = $k_L D_B/(k_{GB} H_B D_A)$, ratio of liquid side mass transfer coefficient to gas side mass transfer coefficient for physical absorption of *B*
C_A = concentration of the reactant *A*
C_{Ai} = interfacial concentration of *A*

C_{AL} = concentration of A in liquid bulk
C_B = concentration of the intermediate B
C_B^* = concentration of B in liquid for it to be in equilibrium with the gas phase
C_{BL} = concentration of B in liquid bulk
D = D_B/D_A, diffusivity ratio
D_A = diffusivity of A in liquid phase
D_B = diffusivity of B in liquid phase
H_B = Henry's Law constant for B
K = k_2/k_1, rate constant ratio
k_1 = first-order rate constant in the first step reaction
k_2 = first-order rate constant in the second step reaction
k_{GB} = gas side mass transfer coefficient of B for physical absorption
k_L = liquid side mass transfer coefficient of A for physical absorption
L = average thickness of a liquid element or film
M = $k_1 D_A/k_L^2$, dimensionless group
m_1 = dimensionless group defined by Equation (8)
m_2 = dimensionless group defined by Equation (9)
$\overline{N_A}$ = average chemical absorption rate of A
$\overline{N_B}$ = average chemical absorption rate of B
s = surface renewal rate
t = time
x = distance
Y = $-\overline{N_B}/\overline{N_A}$, yield of the intermediate B in a heterogeneous system
α = dimensionless group defined by Equation (10)
β = dimensionless group defined by Equation (11)

LITERATURE CITED

Bridgwater, J., "Mass Transfer and Selectivity in Fluid-Fluid Systems," *Chem. Eng. Sci.*, **22**, 185 (1967).

Carberry, J. J., "Mass Diffusion and Isothermal Catalytic Selectivity," *ibid.*, **17**, 675 (1962).

Danckwerts, P. V., Gas-Liquid Reactions, McGraw-Hill, New York (1970).

Harriott, P., "The Effect of Mass Transfer on Selectivity for Heterogeneous Reactions," *Can. J. Chem. Eng.*, **48**, 109 (1970).

Huang, C. J., and C. H. Kuo, "General Mathematical Model for Mass Transfer Accompanied by Chemical Reaction," *AIChE J.*, **9**, 161 (1963).

Spielman, M., "Selectivity in Hydrocarbon Oxidation," *AIChE J.*, **10**, 496 (1964).

Szekely, J., and J. Bridgwater, "Some Further Considerations on Mass Transfer and Selectivity in Fluid-Fluid Systems," *Chem. Eng. Sci.*, **22**, 711 (1967).

Van de Vusse, J. G., "Consecutive Reactions in Heterogeneous Systems," *ibid.*, **21**, 645 (1966).

Veselov, V. V., and Z. V. Sipeeva, "Effect of Diffusion Complications on the Direction of Liquid-Phase Oxidation of Hydrocarbons," *Intern. Chem. Eng.*, **5**, 12 (1965).

Measurement of Interfacial Tension During the Absorption of Carbon Dioxide into Monoethanolamine-Water Mixtures Using an Oscillating Jet

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The origin of interfacial turbulence and spontaneous agitation of the interface between two unequilibrated liquids has been explained by Sternling and Scriven (1959) in terms of the Marangoni effect, wherein movement in an interface is caused by longitudinal variations of interfacial tension. They proposed that interfacial turbulence was a manifestation of hydrodynamic instability caused by small random fluctuations about the interface. By desorbing an inert tracer propylene simultaneously with the absorption of carbon dioxide into monoethanolamine (MEA) in a short wetted-wall column, Brian et al. (1967) showed that the physical mass transfer coefficient was increased substantially over that predicted by the Penetration theory and attributed this increase to interfacial turbulence driven by surface tension gradients. Thomas (1966) studied the absorption of carbon dioxide into aqueous MEA in a laminar jet and showed that the reaction of importance for short exposure times was that in which the carbamate is formed:

$$CO_2 + R \cdot NH_2 \rightleftharpoons R \cdot NH \cdot COOH$$
$$\rightleftharpoons R \cdot NH \cdot CO\bar{O} + H^+$$

Later, with Mck. Nicholl (1969), the interfacial turbulence produced by this reaction was examined using an optical method, with a wavefront shearing interferometer, where it was shown in a stagnant pool of 2.5 M. MEA that a minimum time of 4.5 seconds elapsed before turbulence occurred. Danckwerts and Silva (1967) have investigated the surface instability produced during the absorption of carbon dioxide by MEA solutions by measuring the surface tension of the reacting amine solution using an oscillating jet. No increase in surface tension was observed, although an increase was recorded using static measurements and this increase was attributed to the ionic nature of the reaction products. Ruckenstein (1970) has qualitatively shown, using a roll-cell model, that a small-scale turbulence of small intensity due to Marangoni instability leads to a large increase in the rate of mass transfer of the same order of magnitude as that reported by Brian et al. (1967). In a subsequent

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