y	= particle size	[mm]
Z	= number of collisions of balls	[—]
θ	= angle of nip	[deg.]
μ	= coefficient of dynamical friction	[—]
σ	= strength of particle	[kg/cm ²]
σ_0	= constant	

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MASS TRANSFER EFFECT ON THE SELECTIVITY OF GAS-LIQUID REACTIONS*

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1. Introduction

Consider a consecutive gas-liquid reaction between gas component A and liquid component B :

where R is the desired intermediate product, and S the undesired final product. The effect of mass transfer on the selectivity of the desired intermediate product R for the above reaction was quantitatively studied by van de Vusse⁵⁾ and Teramoto *et al.*^{1,3,4)}. As pointed out by them, the mass transfer through the interface will affect the selectivity of the reaction only when there is a concentration difference of the liquid components B and R between the gas-liquid interface and the liquid bulk. If the concentrations of components B and R are constant throughout the liquid, the selectivity of R will be the same as that obtained in the case of a homogeneous reaction.

Assume now that the rate of reaction r_1 and r_2 in liquid phase for each stoichiometric Eqs.(1) and (2), respectively, can be expressed as follows:

$$r_1 = k_1 C_A C_B \quad (3)$$

$$r_2 = k_2 C_A C_R \quad (4)$$

In practical cases, when the desired product is the intermediate R in Eqs.(1) and (2), one can usually say the value of k_1 is larger than or about the same as that of k_2 . Therefore, it will be useful to consider the reaction regimes for the reaction of Eq.(1) which give the knowledge of concentration distributions of components A and B near the gas-liquid interface. On the basis of the film model, there will be two cases where the concentrations of liquid components are not uniform. These are shown in Fig. 1.

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2. Graphical Representation of the Reaction Regimes

To exhibit the reaction regimes for the reaction of Eq.(1) graphically, η defined by Eq.(5) is plotted against q defined by Eq.(6) with parameters γ and δ by Eqs.(7) and (8), respectively.

$$\eta = r_{1e} / k_{lA} a_s C_{Ai} \quad (5)$$

$$q = D_B C_{Bo} / D_A C_{Ai} \quad (6)$$

$$\gamma = \sqrt{k_1 C_{Bo} D_A} / k_{lA} \quad (7)$$

$$\delta = \varphi_l k_{lA} / a_s D_A \quad (8)$$

Such a diagram presented by previous investigators is limited to the region of $\eta > 1$, where only the fast reaction regime and the instantaneous reaction regime as well as the transition region between them are included. In this work, an attempt is made to display the slow reaction regime in the same figure. For this purpose an approximate method has been proposed by van Krevelen and Hoftijzer⁶⁾ on the basis of the film model as follows:

$$\eta = \frac{Y}{\tanh Y} \left[1 - \frac{Y / \sinh Y \cosh Y}{\gamma^2 \delta + Y / \tanh Y} \right] \quad (9)$$

where

$$Y = \gamma \sqrt{1 + (1 - \eta) / q} \quad (10)$$

It has been shown by them that the combination of

(a) Region between fast and instantaneous reaction regime (b) Region between slow and instantaneous reaction regime

Fig. 1 Film model concentration profiles for a consecutive reaction

- Note: (1) In this region η depends only on γ , and not on δ .
 (2) In this region η depends on γ and δ . The curves show illustratively the case where $\delta=100$.
 (3) In this region η is expressed as a function of $\gamma^2\delta$. But chained curves are calculated from Eq.(9) with Eq.(10) where $\delta=100$.

Fig. 2 The details of reaction regimes

Eqs.(9) and (10) gives adequate results as an approximate method to predict the values of η at $\eta > 1$, where the second term of the parenthesis of Eq.(9) is negligible. However, the present authors' calculation indicates that this approximate equation does not give the correct representation for small values of q in the slow reaction regime. As shown by chained curves in Fig. 2, at small values of q the calculated values from Eq.(9) approach unity. Even when the rate is highly controlled by chemical resistance, η should be independent of q . The reason is that, in order to derive the above equations, the concentration of A in the liquid bulk is assumed to be negligibly small compared with C_{Ai} . This corresponds to the case indicated in Fig. 1(a). Therefore, their equations must be modified when C_{A0} is not so different from C_{Ai} , that is the case in Fig. 1(b). It is quite reasonable to consider that their assumptions are applicable to this case again. In the same way used by van Krevelen and Hoftijzer⁶, the location of the apparent reaction plane, distance from the gas-liquid interface, will be determined by the following equation.

$$\frac{D_A}{l_0} \frac{YC_{Ai}}{\tanh Y} \left[1 - \frac{C_{A0}}{C_{Ai}} \frac{1}{\cosh Y} \right] = \frac{D_A C_{Ai}}{l} \left[1 - \frac{C_{A0}}{C_{Ai}} \right] \quad (11)$$

where

$$Y = \sqrt{k_1 D_A C_{Bf}} / k_{lA} \quad (12)$$

C_{Bf} is the assumed concentration of B in the liquid film (see Fig. 1(b)), and l_0 is the film thickness. Since the component A will react stoichiometrically with B , the following relation must hold.

$$\frac{D_A C_{Ai}}{l} \left[1 - \frac{C_{A0}}{C_{Ai}} \right] = \frac{D_B C_{B0}}{l_0 - l} \left[1 - \frac{C_{Bf}}{C_{B0}} \right] \quad (13)$$

Combination of Eqs.(11), (12) and (13) gives:

$$Y = \gamma \sqrt{1 - \frac{(\eta - 1 + K \cosh Y)}{q}} \quad (14)$$

where

$$K = \frac{Y / \tanh Y}{(\gamma^2 \delta + Y / \tanh Y) \cosh^2 Y} \quad (15)$$

The same relation of Eq.(14) is first derived by Yamaguchi *et al.*^{7,8}.

The value of η is obtained by the trial iterative method by applying Eqs.(9) and (14) even in the region of small values of q , as shown in Fig. 2. As discussed above, the effect of mass transfer on selectivity will exist in the transition region to the instantaneous reaction regime, which is clearly indicated in Fig. 2. While, at $\gamma > 3$, η is independent of δ as is well known, at $\gamma < 0.2$, η is conveniently plotted for constant values of the parameter $\gamma^2\delta$, where δ will have practically reasonable values of $10 \leq \delta \leq 1000$. van de Vusse⁵ postulated that there will be no effect of mass transfer on selectivity in the following cases:

- (i) $q \gg \gamma$ for $\gamma > 2$
- (ii) all values of q for $\gamma < 0.5$

But one can easily observe in Fig. 2 that these conditions are not adequate for all regions.

3. Change in Operating Conditions and Selectivity

To determine the effect of mass transfer on selectivity van de Vusse⁵ and Teramoto *et al.*³ proposed approximate methods. A comparison of their approximate methods is shown in Fig. 3, which is reproduced from Teramoto *et al.*'s paper. The results of their calcu-

Fig. 3 Calculated results reproduced from Teramoto *et al.*'s paper³⁾

lations are based on the condition that all the conditions are fixed except the concentration of B in liquid bulk. The operating conditions corresponding to such calculations will be expressed by dotted curves in Fig. 2. For a given value of $\gamma_0 (= \gamma/\sqrt{q} = \sqrt{k_1 D_A^2 C_{Ai}} / D_B k_{LA}^2)$, the decrease in q shifts the reaction regime from the fast reaction regime to the transition region to the instantaneous reaction regime, and then to the slow reaction regime, or sometimes directly from the fast reaction to the slow reaction regime. The slope of the operating curves is half in the fast reaction regime, and unity in the slow reaction regime. It is interesting to compare the results of Teramoto *et al.*'s calculation given in Fig. 3 with the operating curve in Fig. 2 for the corresponding same value of γ_0 . If γ_0 is smaller than 0.1, no such operating curves will exist in the transition region to the instantaneous reaction regime, that is, there will be no effect of mass transfer on selectivity. It is also obvious in Fig. 2 that the experimental work on the consecutive chlorination of p -cresol by Teramoto *et al.*^{3,4)} is carried out in the transition region. Therefore, the maximum yields of monochloride are considerably lower than those in homogeneous reactions. In the study of oxidation of cumene by one of the authors and his coworkers²⁾, on the other hand, the experimental conditions are far beyond the instantaneous reaction regime, that is $\gamma_0 \simeq 0.01$, so that there will be no effect of mass transfer on selectivity in that reaction. This great difference between these two examples is considered to be caused by the different

saturated solubilities of gas components C_{Ai} in the two cases.

Nomenclature

a_s	= interfacial area per unit volume of liquid phase	[1/cm]
C_{Ai}	= concentration of component A in gas-liquid interface	[g-mole/cm ³]
C_{A0}, C_{B0}, C_{R0}	= concentrations of components A, B and C , respectively, in liquid bulk	[g-mole/cm ³]
C_{Bf}	= assumed constant concentration of B in the liquid film, see Fig. 1(b)	[g-mole/cm ³]
D_A, D_B	= diffusivities of A and B , respectively, in liquid phase	[cm ² /sec]
k_1, k_2	= reaction rate constants of reaction of stoichiometric equations (1) and (2), respectively	[cm ³ /g-mole-sec]
k_{LA}	= liquid-film mass transfer coefficient	[cm/sec]
l_0	= liquid-film thickness	[cm]
l	= location of apparent reaction plane, distance from gas-liquid interface	[cm]
q	= $D_B C_{B0} / D_A C_{Ai}$	[—]
r_1, r_2	= rates of reactions (1) and (2), respectively, number of times proceeded from left to right of the stoichiometric equation expressed in moles-change per unit time and unit volume of liquid phase	[g-mole/cm ³ -sec]
r_{1e}	= effective rate of reaction (1), which includes mass transfer effect	[g-mole/cm ³ -sec]
Y	= defined by Eq. (10) or (14)	[—]
γ	= $\sqrt{k_1 C_{B0} D_A} / k_{LA}$	[—]
γ_0	= $\gamma / \sqrt{q} = \sqrt{k_1 D_A^2 C_{Ai}} / D_B k_{LA}^2$	[—]
δ	= $\varphi_l k_{LA} / a_s D_A$	[—]
η	= $r_1 / k_{LA} a_s C_{Ai}$	[—]

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