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ISOTHERMAL INTERPHASE DIFFUSION WITH CONSECUTIVE REACTIONS

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Abstract — For multi-step heterogeneous consecutive reactions affected entirely by interphase diffusion under isothermal condition, the equations for the effectiveness factors, the surface concentrations and the point yields were derived in terms of the Damkoehler numbers or the measurables from the mass balances set up on the assumption that the mass-transfer rate balances the surface-reaction rate at steady state.

From the analyses of the equations derived, the effectiveness factors for the intermediate steps and the surface concentrations of intermediates were understood to be enhanced by the measurables inclusive of the concentrations and the mass-transfer coefficients. Then the effect of the concentrations was concluded to be most significant. The effects of these measurables to the effectiveness factors and the surface concentrations were qualitatively discussed for simple consecutive reactions and also for additive consecutive reactions. Especially, as for two-step additive consecutive reactions, the effects of measurables η Da and the concentrations to the effectiveness factors were examined with graphical presentations.

Finally, the brief discussion of the dependency of the Damkoehler number upon reaction time and the effect of the Renolds number and diffusivity to the extent of the mass-transfer resistance were presented.

INTRODUCTION

In the treatment of the kinetic data of the reactions on heterogeneous catalyst, mass transfer sometimes complicates the analyses of the kinetics even if simple power principle is applied to the rate equations.

Many works treated diffusional effect to the reaction rates on heterogeneous catalyst, and thus some of them were introduced [1-7]. Also some examples of the reactions affected by mass transfer appears in the literatures: the oxidation of ammonia [8, 9], the oxidation of naphthalene [10] and the disproportionation of olefin [11]

In common single reaction affected by only external mass transfer, since the surface concentration of a reactant is always thinner than that in the bulk under isothermal condition due to diffusional resistance, the measured reaction rate is less than expected in the bulk condition. Also, since the reaction rate is usually measured by the bulk concentration, it is required to obtain the rate by the surface reaction. Then the Damkoehler number Da becomes a measure of the extent of the diffusional resistance. But, on account of its unmeasurablity directly from experiment, the effectiveness factor η defined by the ratio of the surface-reaction rate to the bulk-reaction rate is usually measured from the measurabls, so-called η Da. Then the following division of η Da by η indirectly produces the calculated value of the Da.

What is of interest in this study is to relate the desired variables with the measurables from the experiment on the ground that the mass-transfer rate within film around the catalyst particle balances the surface reaction rate. Of course, the Stefan-Maxwell equations may be applicable to multi-component system, but the introduction of the mass-transfer coefficients were attempted because of the convenience to obtain the desired equations.

SIMPLE CONSECUTIVE REACTIONS

Surface Concentrations and Effectiveness Factors

Multi-step consecutive reactions schemized as the following were considered.

$$A \xrightarrow[k_1]{} B \xrightarrow[k_2]{} \dashrightarrow I \xrightarrow[k_j]{} \dashrightarrow N \xrightarrow[k_n]{} P \qquad (1)$$

where each step is regarded to be elementary.

At steady state, a mass balance for the reactant A is set up as

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$$(k_ga)_A(C_A-C_{AS}) = k_1C_{AS} = R_1 \tag{2}$$

For the intermediate I,

$$(k_ga)_I(C_{IS}-C_I) = k_{j-1}C_{(I-1)S}-k_jC_{IS} = R_{j-1}-R_j \tag{3}$$

$$(I = B,C,\cdots,N, \text{ and } j = 2,3,\cdots,n)$$

where the subscript I means the intermediate corresponding to the j-th step, and I-1 indicates the intermediate corresponding to the (j-1)-th step.

And for the product P,

$$(k_ga)_P(C_{PS}-C_P) = k_nC_{NS} = R_n \tag{4}$$

If Z_I is defined as the ratio of the surface concentration of a species I to the bulk concentration, C_{IS}/C_I, and the effectiveness factor η_j as the ratio of the surface-reaction rate to the bulk-reaction one, η_j for isothermal reaction becomes

$$\eta_j = Z_I \tag{5}$$

Thus, from the relations (2)-(4), η_js and Z_Is are written as the followings in terms of the Damkoehler number Da_j defined by the ratio of the reaction rate to the mass-transfer rate, $k_j/(k_ga)_I$.

That is,

$$\eta_1 = Z_A = \frac{1}{1+Da_1} \tag{6}$$

$$\eta_j = Z_I = \frac{1+\nu_I\gamma_I Z_{I-1} Da_{j-1}}{1+Da_j} \tag{7}$$

where ν_I and γ_I are defined by

$$\nu_I = \frac{(k_ga)_{I-1}}{(k_ga)_I} \text{ and } \gamma_I = \frac{C_{I-1}}{C_I}$$

$$(I = B,C,\text{—},N)$$

$$\text{and } Z_P = 1 + \nu_P\gamma_P Z_N Da_n \tag{8}$$

In case of two-step consecutive reactions, the eq. (7) virtually becomes same as the Carberry's result [1] while the eq. (6) is essentially for the first-order reaction.

Now it is required to obtain the equations for η_j and Z_I in terms of the measurables $\eta_j Da_j$ because Da_j is not determined directly from experiment, but $\eta_j Da_j$ determined directly since $\eta_j Da_j = R_j/(k_ga)_I C_I$. The reusing of the relations (2)-(4) and the introduction of $\eta_j Da_j$ let us reach the following results.

$$\eta_1 = Z_A = 1 - \eta_1 Da_1 \tag{9}$$

$$\eta_j = Z_I = 1 + \nu_I\gamma_I\eta_{j-1}Da_{j-1} - \eta_j Da_j \tag{10}$$

and

$$Z_P = 1 + \nu_P\gamma_P\eta_n Da_n \tag{11}$$

Point Yields

If Y_{IS}, the point yield by the surface reaction, are defined as

$$Y_{IS} = \frac{dC_{IS}}{dC_{AS}} \tag{12}$$

Y_{IS} is written as the followings. That is,

$$Y_{IS} = K_{j-1}\frac{Z_{I-1}}{Z_A}\frac{C_{I-1}}{C_A} - K_j\frac{Z_I}{Z_A}\frac{C_I}{C_A} \tag{13}$$

In terms of Da_j,

$$Y_{IS} = K_{j-1}\frac{1+Da_1}{1+Da_j}(1+\nu_{I-1}\gamma_{I-1}Z_{I-2}Da_{j-2})\prod_{I=B}^{I-1}(1/\gamma_I)$$

$$-K_j\frac{1+Da_1}{1+Da_j}(1+\nu_I\gamma_I Z_{I-1}Da_{j-1})\prod_{I=B}^{I}(1/\gamma_I) \tag{14}$$

In terms of $\eta_j Da_j$,

$$Y_{IS} = K_{j-1}\frac{1+\nu_{I-1}\gamma_{I-1}\eta_{j-2}Da_{j-2}}{1-\eta_1 Da_1}\prod_{I=B}^{I-1}(1/\gamma_I)$$

$$-K_j\frac{1+\nu_I\gamma_I\eta_{j-1}Da_{j-1}}{1-\eta_1 Da_1}\prod_{I=B}^{I}(1/\gamma_I) \tag{15}$$

where

$$K_j = k_j/k_1$$

Then $\eta_j Da_j = 0$ in case that the number of the step does not match the corresponding species. For example, $\eta_2 Da_3 = 0$ since $\eta_2 Da_3$ has no physical meaning.

If Y_I, the point yields by the bulk reactions, are defined as

$$Y_I = \frac{dC_I}{-dC_A}$$

Y_I is written as

$$Y_I = K_{j-1}\prod_{I=B}^{I-1}(1/\gamma_I) - K_j\prod_{I=B}^{I}(1/\gamma_I) \tag{16}$$

Thus the comparison can be made between Y_{IS} and Y_I.

ADDITIVE CONSECUTIVE REACTIONS

Surface Concentrations and Effectiveness Factors

Multi-step consecutive reactions schemized as the following were considered as well

$$A \xrightarrow[k_1]{+M} B \xrightarrow[k_2]{+M} \dashrightarrow I \xrightarrow[k_j]{+M} \dashrightarrow N \xrightarrow[k_n]{+M} P \tag{17}$$

Where each step is also elementary.

The mass balances are set up for each species as the followings. That is,

$$(k_ga)_M(C_M - C_{MS}) = \sum_{j=1}^{n} k_jC_{MS}C_{IS} = \sum_{j=1}^{n} R_j \tag{18}$$

$$(k_ga)_A(C_A - C_{AS}) = k_1C_{MS}C_{AS} \tag{19}$$

$$(k_ga)_I(C_{IS} - C_I) = k_{j-1}C_{MS}C_{(I-1)S} - k_jC_{MS}C_{IS}$$

$$= R_{j-1} - R_j \tag{20}$$

and

$$(k_ga)_P(C_{PS} - C_P) = k_nC_{MS}C_{NS} = R_n \tag{21}$$

If new definitions for ν_I, γ_I and Da_j are given as

$$\nu_I = \frac{(k_S a)_M}{(k_g a)_I},\ \gamma_I = \frac{C_M}{C_I} \quad \text{and} \quad Da_j = \frac{k_j C_I}{(k_g a)_M}$$

from the above mass balances, Z_M, which is C_{MS}/C_M, and Z_Is are written as the followings. That is,

$$Z_M = 1 - \sum_{j=1}^{n} Z_M Z_I Da_j \tag{22}$$

where the usage of the subscripts are same as before.

$$Z_A = 1 - \nu_A \gamma_A Z_M Z_A Da_1 \tag{23}$$

$$Z_I = 1 + \nu_I \gamma_I (Z_M Z_{I-1} Da_{j-1} - Z_M Z_I Da_j) \tag{24}$$

· and

$$Z_P = 1 + \nu_P \gamma_P Z_M Z_N Da_n \tag{25}$$

Meanwhile,

$$\eta_j = Z_M Z_I, \quad \text{and} \quad \eta_j Da_j = \frac{R_j}{(k_g a)_M C_M}$$

Thus Z_Is are written in terms of $\eta_j Da_j$ as the followings. That is,

$$Z_M = 1 - \sum_{j=1}^{n} \eta_j Da_j \tag{26}$$

$$Z_A = 1 - \nu_A \gamma_A \eta_1 Da_1 \tag{27}$$

$$Z_I = 1 + \nu_I \gamma_I (\eta_{j-1} Da_{j-1} - \eta_j Da_j) \tag{28}$$

and

$$Z_P = 1 + \nu_P \gamma_P \eta_n Da_n \tag{29}$$

According to the definition, η_js are written in terms of Da_j as the followings. That is,

$$\eta_1 = \left(1 - \sum_{j=1}^{n} Z_M Z_I Da_j\right) \left(1 - \nu_A \gamma_A Z_M Z_A Da_1\right) \tag{30}$$

and

$$\eta_j = \left(1 - \sum_{j=1}^{n} Z_M Z_I Da_j\right) \left[1 + \nu_I \gamma_I (Z_M Z_{I-1} Da_{j-1} - Z_M Z_I Da_j)\right] \tag{31}$$

In terms of $\eta_j Da_j$,

$$\eta_1 = \left(1 - \sum_{j=1}^{n} \eta_1 Da_j\right) \left(1 - \nu_A \gamma_A \eta_1 Da_1\right) \tag{32}$$

and

$$\eta_j = \left(1 - \sum_{j=1}^{n} \eta_j Da_j\right) \left[1 + \nu_I \gamma_I (\eta_{j-1} Da_{j-1} - \eta_j Da_j)\right] \tag{33}$$

Although the different reactants denoted by M_j are added to each step in this type of reaction, the results are obtained by the identical method to the previous development. Thus Z_{Mj}, which is C_{MjS}/C_{Mj}, is written as

$$Z_{Mj} = 1 - \eta_j Da_j \tag{34}$$

where Da_j is defined as

$$Da_j = \frac{k_j C_I}{(k_g a)_{Mj}}$$

But the eqs. (26)-(28) can be used without modification in the forms on the definition (34) and the following definitions.

$$\nu_I = \frac{(k_g a)_{Mj}}{(k_g a)_I} \quad \text{and} \quad \gamma_I = \frac{C_{Mj}}{C_I}$$

Also, since $\eta_j Da_j = R_j / (k_g a)_{Mj} C_{Mj}$, η_js are written as the followings. That is,

$$\eta_1 = (1 - \eta_1 Da_1)\ (1 - \nu_A \gamma_A \eta_1 Da_j) \tag{35}$$

$$\eta_j = (1 - \eta_j Da_j)\ \left[1 + \nu_I \gamma_I (\eta_{j-1} Da_{j-1} - \eta_j Da_j)\right] \tag{36}$$

Point Yields

By the definition, Y_{IS} is written in terms of Z_I, Da_j or $\eta_j Da_j$ as the followings. That is,

$$Y_{IS} = K_{j-1} \left(\frac{Z_{I-1}}{Z_A}\right) \frac{\gamma_A}{\gamma_{I-1}} - K_j \left(\frac{Z_I}{Z_A}\right) \frac{\gamma_A}{\gamma_I} \tag{37}$$

$$Y_{IS} = \frac{Z_{I-1} Da_{j-1} - Z_I Da_j}{Z_A Da_1} \tag{38}$$

Or

$$Y_{IS} = \frac{\eta_{j-1} Da_{j-1} - \eta_j Da_j}{\eta_1 Da_1} \tag{39}$$

Since Y_I is written as

$$Y_I = K_{j-1} \frac{\gamma_A}{\gamma_{I-1}} - K_j \frac{\gamma_A}{\gamma_I} \tag{40}$$

the comparison can be made between Y_{IS} and Y_I.

DETERMINATION OF VARIABLES

The following algorithm is available in determining the effectiveveness factors, the surface concentrations and the rate constants from the experimental data.

(1) Determine $\eta_j Da_j$s from R_js, $(k_g a)_I$s and C_Is and C_M Here a R_j is the slope of the curve in the plots of C_I vs. time, and $(k_g a)_I$ is obtained from the mass-transfer data.

(2) Determine η_j and Z_I from the equations derived or the graphs as shown in Figs. (1)-(16). In case of simple consecutive reactions, η_j and Z_I are calculated directly from the eqs. (9)-(11) at the same time. In case of additive consecutive reactions, Z_I is obtained from the eqs. (26)-(29), and η_j from the eqs. (32) or (33), or from the graphs.

(3) Once η_j is known, Da_j is calculated from the division of $\eta_j Da_j$ by η_j, and then k_j from the definition for Da_j because $(k_g a)_I$ was already known from the mass-transfer data.

(4) Y_{IS}s are easily calculated from one of the eqs. (13)-(15) for simple consecutive reactions and the eqs. (37)-(39) for additive consecutive reactions because K_js are determined by the definition.

Further calculations can be done for the comparison of Y_{IS} with Y_I. Meanwhile, the surface concentration C_{IS}

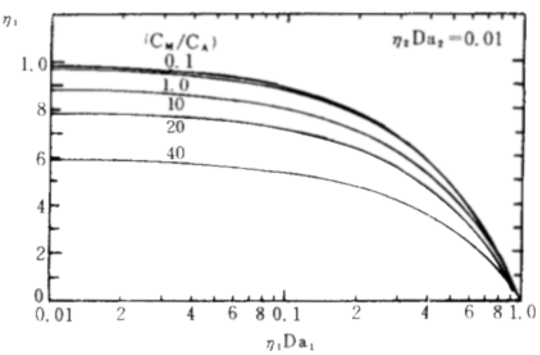

Fig. 1. The effects of C_M/C_A to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant $\eta_2 Da_2$ · ($\eta_2 Da_2=0.01$).

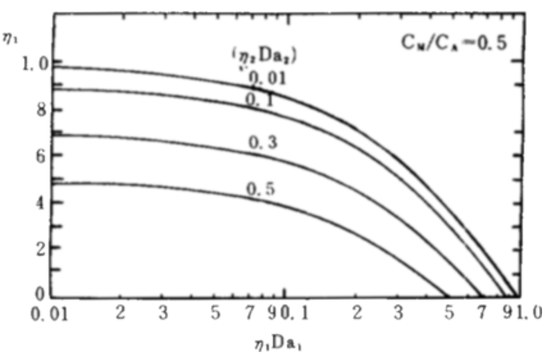

Fig. 3. The effects of C_M/C_A to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant $\eta_2 Da_2$ · ($\eta_2 Da_2=0.5$).

is determined by the multiplication of Z_I by the bulk concentration of I.

RESULTS AND DISCUSSION

From the equations obtained by the mass balances, the effectiveness factors, the surface concentrations and the dependency of the Damkoehler numbers upon reaction time were discussed. The emphases were given especially on the effectiveness factors for the intermediate steps and on the surface concentrations of the intermediates because they vary greatly with the variations of the measurables.

The First Steps

In general, for single-path reactions on non-porous catalyst, affected by external mass transfer through isothermal process, the effectiveness factors are expected to be less than unity. Also the surface concentrations of the reactants are usually thinner than the bulk ones, but those of the products are reverse to those of the reactants. These concepts are applied to the first steps in consecutive reactions as well.

In simple consecutive reactions, η_1 is linearly dependent upon $\eta_1 Da_1$, decreasing with the increase of $\eta_1 Da_1$. The reason is due to diffusional resistance. Also Z_A has the same trend as η_1. These are supported by the eq. (9). Meanwhile, Z_p is linearly dependent upon $\eta_n Da_n$, increasing with the increase of $\eta_n Da_n$. The reason is that the escaping of the product from the surface to the bulk is retarded by the film resistance. It is supported by the eq. (11). In fact, the above mentioned are phenomenologically natural.

In additive consecutive reactions, Z_A and Z_M are less than the unity. According to the eq. (27), Z_A is explained similarly to that in simple consecutive reactions. Then, according to the eq. (26), Z_M is the unity minus the summation of all the $\eta_j Da_j$s, and thus presumed to be very small compared with Z_A in the magnitudes. As for Z_p, similar interpretation to that in simple consecutive reac-

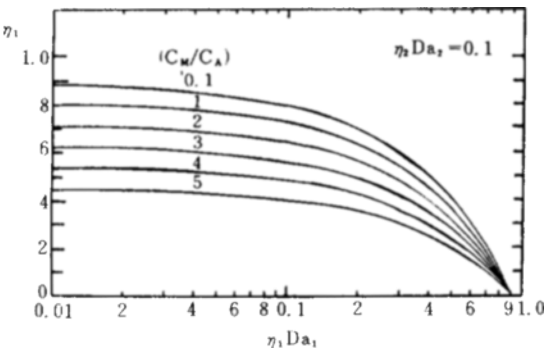

Fig. 2. The effects of C_M/C_A to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant $\eta_2 Da_2$ · ($\eta_2 Da_2=0.1$).

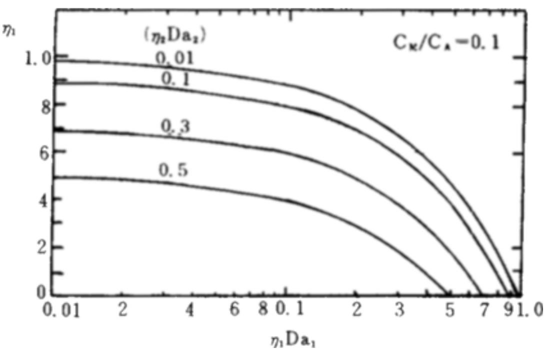

Fig. 4. The effects of $\eta_2 Da_2$ to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_A · ($C_M/C_A=0.1$).

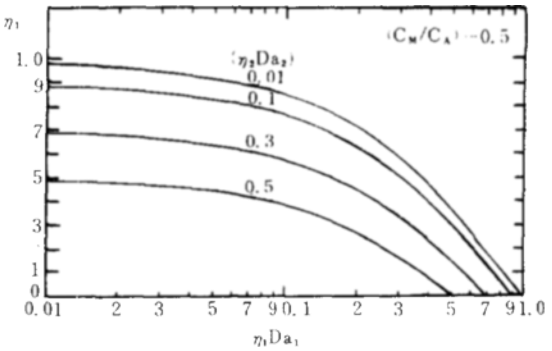

Fig. 5. The effects of η_2Da_2 to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_A · $(C_M/C_A=0.5)$.

tions can be made by the eq. (29). The η_I is always less than the unity as before by the eq. (32), but greatly affected by the measurables. From the relation that $\eta_I = Z_AZ_M$, the molecularity of the reaction is assumed to be apparently significantly involved in the first step unlike the case of simple consecutive reactions because the additive reaction of single path in this study is bimolecular. But, from the view point that M is added to each step, and resultantly Z_M is extremely small, the significance of the molecularity is reduced rather than that in single-path addition. In fact, Z_A and Z_M are greatly affected by the bulk concentrations themselves, the mass-transfer coefficients and η_jDa_js. The eqs. (26) and (27) support these.

Intermediate Steps & Intermediates of Simple Consecutive Reactions

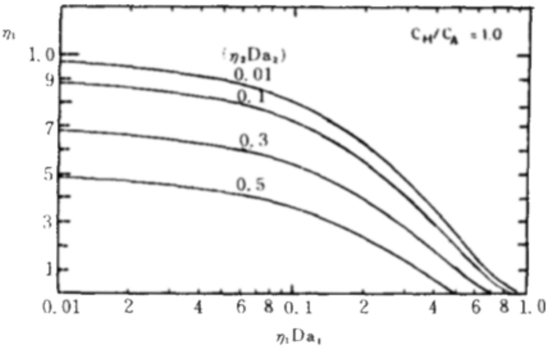

Fig. 6. The effects of η_2Da_2 to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_A · $(C_M/C_A=1.0)$.

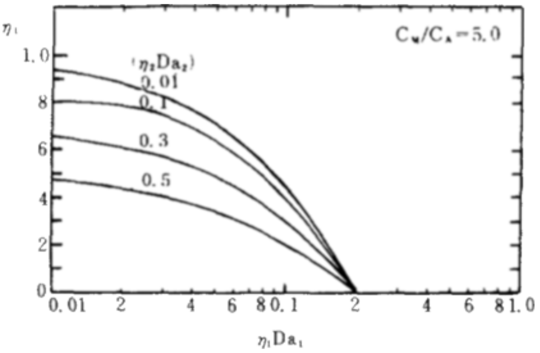

Fig. 7. The effects of η_2Da_2 to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_A · $(C_M/C_A=5)$.

In simple consecutive reactions, from the eq. (10), Z_I and η_j are dependent upon ν_I and γ_I as well as η_jDa_j. If $(k_ga)_I$s are assumed not to be considerably different in their magnitudes, ν_I can be set approximately to the unity. Then Z_I and η_j are expected to be mainly affected by γ_I and η_jDa_j. The above assumption is rationalized by the fact that the diffusion rate of gas is inversely proportional to the square root of the molecular weight (in case that the molecular weight of A doubles that of B, ν_B becomes 0.71). Of course, the precise estimations of Z_I and η_j must be carried out on the consideration of ν_I.

The comparison of the eq. (10) with the eq. (9) enables us to regard the term $\phi_I\,(=\phi_J=\nu_I\gamma_I\eta_{J-1}Da_J)$ as an enhancement for the increase of η_j or Z_I because two equations are identical in the form if this term is eliminated from the eq. (10). Here ϕ_I is for an intermediate, and ϕ_j for the effectiveness factor. This enhancement is presumed to be due to temporary abundance within the film of the intermediate to the next step. This abundance is also presumed to be resulted

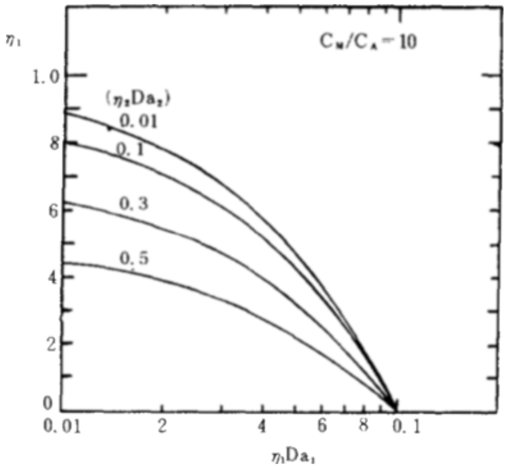

Fig. 8. The effects of η_2Da_2 to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_A · $(C_M/C_A=10)$.

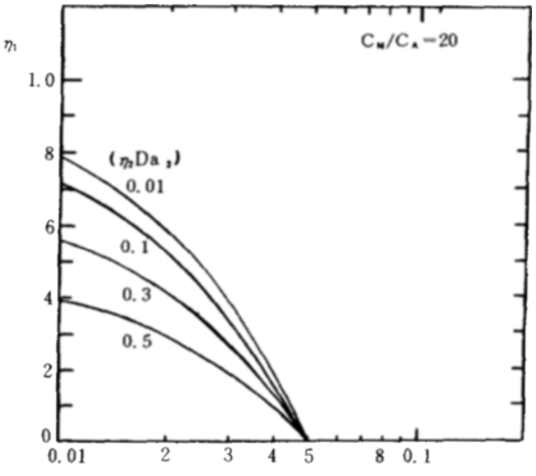

Fig. 9. The effects of η_2Da_2 to η_1 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_A · ($C_M/C_A=20$).

from the retardation of the diffusing of the intermediates produced from the earlier steps from the surface to the bulk.

If γ_I is small, the influence of γ_I to ϕ_I or ϕ_j and resultantly to Z_I or η_j is not significant. But, instead, if γ_I is large, the contribution of γ_I to Z_I or η_j is expected to be considerable. Thus there may be the case that Z_I or η_j exceed the unity even if consecutive reactions occur under isothermal condition. If fact, the former case is frequently encountered when exothermic reactions occur under non-isothermal condition. From this point of view, the effect of γ_I to Z_I or η_j is regarded to be important. But the effect of η_jDa_j is not great because $\eta_jDa_j<1$.

Intermediate Steps & Intermediates of Additive Consecutive Reactions

From the comparison of the eq. (28) with the eq. (27), ϕ_I becomes $\nu_I\gamma_I\eta_{J-1}Da_{J-1}$ identical to that in simple consecutive reactions. Therefore, as for ϕ_I, similar explanation to that of simple consecutive reactions can be made. But, as for ϕ_j or η_j, careful considerations are required rather than in simple consecutive reactions. From the comparison of the eq. (33) with the eq. (32), ϕ_j becomes

$$\phi_J = \nu_I\gamma_I\eta_{J-1}Da_{J-1}\,(1-\sum_{I=A}^{N}\eta_JDa_J) \qquad (41)$$

According to the eq. (28), Z_I is greater than the unity if $\eta_{J-1}Da_{J-1} > \eta_JDa_J$, but less than the unity in case of the reverse. On the other hand, η_j can be less than the unity, even if $Z_I>1$.Because $\eta_j = Z_IZ_M$, where $Z_M<1$,the multiplication of Z_I by Z_M can be less than the unity. But, on the assumption that ν_I can be set approximately to the unity as before, if γ_I has the large value, Z_I can become far greater than the unity, and its magnitude depends upon the value of γ_I.

In this study, two-step reactions were taken as an example in order to investigate the influence of γ_I and η_jDa_j to η_j. Here ν_B was taken as the unity. the results were plotted from the Figs. (1) to (16). Then the plots of η_2 vs. η_2Da_2 with the variation of η_1Da_1 where $\gamma_B = 1$ were omitted because η_2 becomes simply

$$\eta_2 = (1-\eta_2Da_2)^{'} - (\eta_1Da_1)^{'} \qquad (42)$$

from the eq. (33). These graphs can be used for the determination of η_js from the experimental data, but, if the slopes of the curves are steep, the use of the equations derived before is recommended rather than the graphs.

As shown in the Figs. (1)-(3) and (10)-(12), the in-

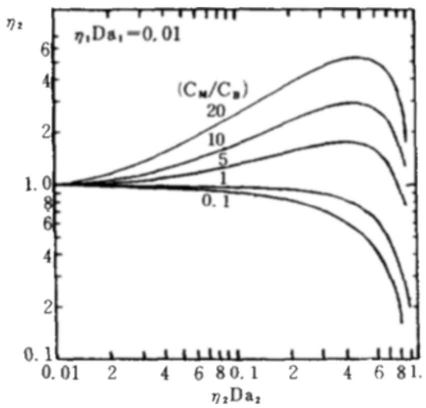

Fig. 10. The effects of C_M/C_B to η_2 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant η_1Da_1 · ($\eta_1Da_1=0.01$).

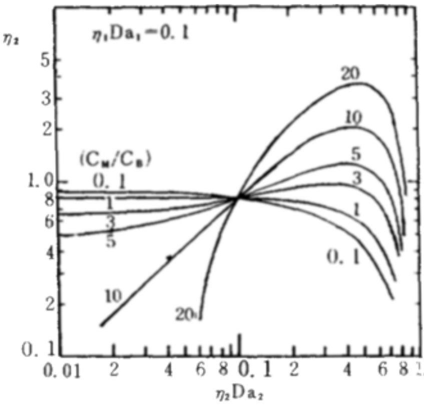

Fig. 11. The effects of C_M/C_B to η_2 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant η_1Da_1 · ($\eta_1Da_1=0.1$).

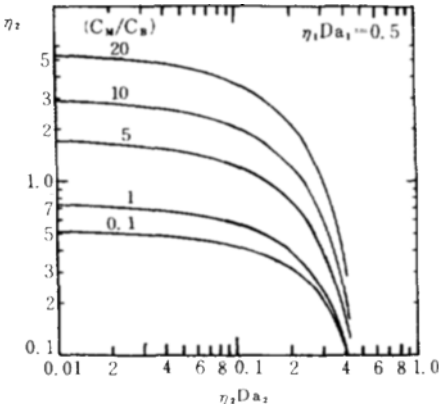

Fig. 12. The effects of C_M/C_B to η_2 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant $\eta_1 Da_1$ · ($\eta_1 Da_1 = 0.5$).

fluences of γ_is to η_js, when investigated at the condition that another $\eta_j Da_j$ was fixed as a constant, are greater at the large value of $\eta_j Da_j$ than at the small value of $\eta_j Da_j$. According to the Figs. (1)-(3), at constant $\eta_2 Da_2$, η_1 decreases with the increase of γ_A. Then, in the Fig. (11) plotted for $\eta_1 Da_1$ fixed as 0.1, η_2 decreases with the increase of γ_B where $\eta_1 Da_1 > \eta_2 Da_2$, but increases where $\eta_1 Da_1 < \eta_2 Da_2$. In the Fig. (10), the above tendency was not shown explicitly because the curves were cut where $\eta_2 Da_2 < 0.01$, and also, in the Fig. (12), only the increasing tendency of η_2 with the increase of γ_B was shown. But, if plotted over the whole range of $\eta_2 Da_2$, the Fig. (10) will show the same fashion as the Fig. (11).

According to the Fig. (4-9) and (13-16), the influence of $\eta_2 Da_2$ to η_1 at fixed γ_A is not severer than those of $\eta_1 Da_1$ to η_2 at fixed γ_B. The influence of $\eta_1 Da_1$ to η_2 is great especially at the large value of γ_B.

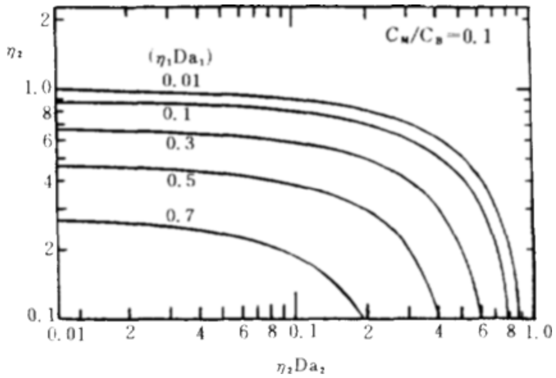

Fig. 13. The effects of $\eta_1 Da_1$ to η_2 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_B · ($C_M/C_B = 0.1$).

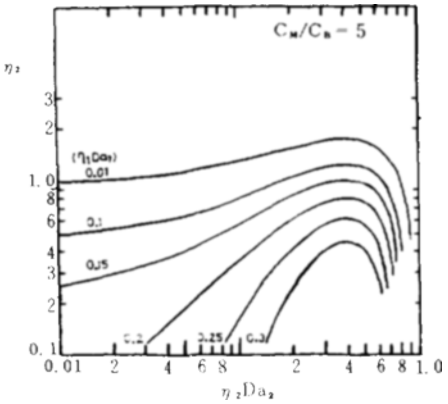

Fig. 14. The effects of $\eta_1 Da_1$ to η_2 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_B · ($C_M/C_B = 5$).

Therefore the conspicuous effects of γ_is to η_js are obvious from the figures plotted for two-step reactions.

Dependency of Da upon Reaction Time

For a single first-order reaction, Da is constant regardless of reaction time or the bulk concentration of the reactant if the variation of the concentration during the reaction does not affect the mass-transfer coefficient. Da_js for simple consecutive reactions are also independent of reaction time or the concentrations of the species because the Da_js are expressed by the same from as that for the first-order reaction.

But Da_js vary with reaction time or the concentrations in case of multi-component reactions or the reac-

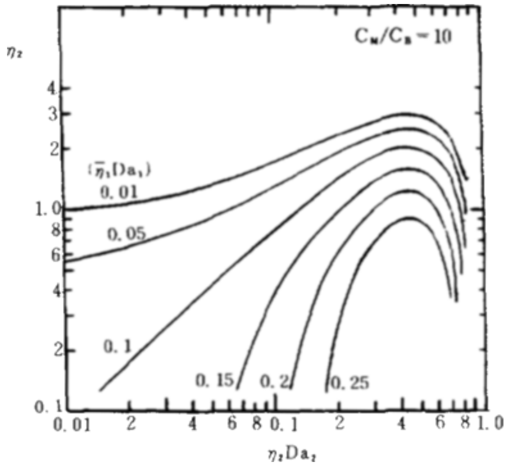

Fig. 15. The effects of $\eta_1 Da_1$ to η_2 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_B · ($C_M/C_B = 10$).

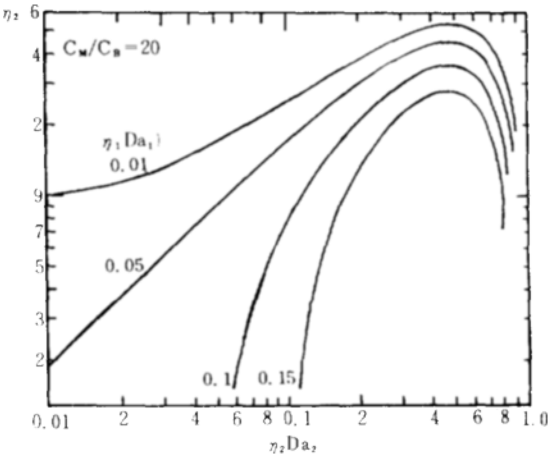

Fig. 16. The effects of $\eta_1 Da_1$ to η_2 in consecutive reactions, $A+M \xrightarrow[k_1]{} B+M \xrightarrow[k_2]{} P$, at constant C_M/C_B · ($C_M/C_B=20$).

tions of non-linear kinetics. In additive consecutive reactions under consideration, Da_1 decreases as the reactions proceed. Then Da_js for the intermediate steps vary with reaction time depending upon the magnitudes of k_js.

In general, the dependency of Da upon reaction time is expected to be conspicuous in the batch reactors or PFRs, but to be nil in CSTRs after the reactions reach steady state throughout the reactors.

Effect of Diffusivity and Reynolds Number

In general, the mass-transfer coefficient is measured by the Sherwood number or the Stanton number correlated by

$$St=\frac{Sh}{ReSc}$$

As for forced convection around a sphere, generalized relation is

$$Sh\left(\propto\frac{k_g}{D}\right)=2.0+f(Re, Sc) \tag{43}$$

where the first term 2.0 is for only molecular diffusion in case of no fluid motion, and the last term for convective diffusion. If hydraulic boundary layer thickness is approximately equal to concentration boundary layer thickness, Sc ≅ 1. In this case, Sh or K_g is the function of Re only. Even in case that Sc is not too large, the same statement can be made. Therefore, at low Re, the dependence of the mass-transfer coefficient upon Re is negligible. In this case, the resistance by mass transfer is presumed to be considerable. In the extreme case that Re = O (no fluid motion), Sh = 2.0, and thus the mass-transfer coefficient is directly proportional to the diffusivity.

At high Re, Sh is dependent mainly upon Re because the effect of molecular diffusion is neglected and convective diffusion increases the mass-transfer rate by increasing the concentration gradient within the film. Therefore, in this case, the resistance by mass transfer is presumed to be greatly reduced.

CONCLUSIONS

From this study of consecutive reactions affected by isothermal interphase diffusion, the following conclusions are made.

The surface concentration of the reactant is always thinner than the bulk one, but that of the final product thicker than the bulk one. Then Z_I for the intermediate is increased by the enhancements ϕ_I, and ϕ_I is affected especially by the concentrations.

η_1 is linearly dependent upon $\eta_1 Da_1$, decreasing with the increase of $\eta_1 Da_1$ in simple consecutive reactions, but greatly affected by the measurables in additive consecutive reactions. Also η_j for the intermediate steps is increased by the enhancement ϕ_j, and ϕ_j is affected especially by the concentrations, too.

The Da_j is invariant with reaction time in simple consecutive reactions, but variant in additive consecutive reactions.

The diffusional resistance is affected greatly by the diffusivity at low Re, but by Re itself at high Re.

NOMENCLATURE

A,B,I,M,N,P	: species
a	: effective interfacial area for mass transfer
C	: concentration
D	: Diffusivity
Da	: Damkoehler number
K	: ratio of the rate constant to that for the first step
k	: rate constant
k_g	: mass transfer coefficient
R	: reaction rate
Re	: Reynolds number
Sc	: Schmidt number
Sh	: Sherwood number
St	: Stanton number
Y	: Point yield
Z	: ratio of surface concentration to bulk concentration.
γ	: ratio defined by C_{I-1}/C_I, C_M/C_I or C_{Mj}/C_I for species I
η	: interphase effectiveness factor
ν	: ratio defined by $(k_g a)_{I-1}/(k_g a)_I$ or $(k_g a)_M/(k_g a)_I$ for species I
ϕ	: enhancement for Z or η

Subscripts

A,B,I,M,N,P : for species A,B,I,M,N,P
j,n : for the j-th or n-th step
S : for surface condition

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