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# Kinetics of Heterogeneous Liquid Phase Reaction : Simultaneous Mass Transfer and Chemical Reaction

By

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The solution of the over-all rate of reaction for a steady state mass transfer accompanied by a  $(1+n)$ -th order irreversible reaction was derived by applying an approximate concentration distribution model for the heterogeneous liquid phase reaction which might proceed in a diffusion film and homogeneous mixed bulk liquid of finite volume.

The numerically calculated diagrams showing the functional relation between the over-all rate of reaction and the reaction conditions such as the resistances to diffusion and chemical reaction, liquid volume and the interfacial contact area, etc. were presented.

The authors made clear the conditions for the five states of over-all reaction rate which were different in comparative magnitude in the resistances to diffusion and chemical reaction, and interpreted the various types of rate controlling step by comparing the reaction conditions and the concentration distribution of reactants both in diffusion film and bulk liquid.

## Introductions

The over-all rate of heterogeneous liquid phase reaction such as solid-liquid, liquid-liquid or gas-liquid reaction is controlled by a series of resistances to diffusion and chemical reaction. The present report refers to a reaction in a heterogeneous liquid phase comprising a phase "a" which may be solid, liquid or gas containing a reactant "A" and of a phase "b" which is liquid containing a reactant "B". A diffuses into the liquid phase b and reacts with the reactant B.

The analysis of chemical absorption of gas into liquid was the first step in this field. In the early stage of the studies, S. Hatta, et al.<sup>2)</sup> obtained the solution for the following four cases of mass transfer in a steady state molecular diffusion followed by a chemical reaction.

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[1] Mass transfer followed by an irreversible chemical reaction of first or pseudo-first order where the concentration of reactant  $A$  in the bulk of phase  $b$  is nearly equal to zero, i.e. the reaction resistance is smaller than the mass transfer resistance or the volume of the bulk liquid of phase  $b$  is large compared with the interfacial area.

[2] Mass transfer followed by an irreversible chemical reaction of first or pseudo-first order where the volume of the bulk of phase  $b$  is small compared with the interfacial area and the unreacted reactant  $A$  accumulates in the bulk liquid of the phase  $b$ .

[3] Mass transfer followed by a reversible chemical reaction of first or pseudo-first order where the volume of the bulk of phase  $b$  is small compared with the interfacial area.

[4] Chemical absorption with fast irreversible second order reaction, which is a limiting case of the heterogeneous liquid phase reaction of second order.

A reaction of more than first order is generally encountered in industrial operation. D. W. van Krevelen, et al<sup>5)</sup> tried to obtain a general solution for chemical absorption with second order irreversible reaction by applying an approximate concentration distribution. They derived a solution for the case where the concentration of the reactant  $A$  in the bulk of the phase  $b$  was substantially zero. (Hence the solution is not applicable for the case where the concentration of  $A$  in  $b$  is not zero). The classification of heterogeneous reactions by the rate controlling factor is still incomplete and the definition of the individual rate controlling steps is not given.

R. B. Bird, et al.<sup>1)</sup> reported that the differential form of the rate equation for a steady state molecular diffusion accompanied by an irreversible, unimolecular and  $n$ -th order reaction might be transformed into an indefinite integral form, yet impossible to solve analytically. Olander, et al.<sup>4)</sup> studies gas absorption by steady state molecular diffusion followed by (1) a reversible reaction of first order:  $A \rightleftharpoons 2E$ , and (2) a reversible reaction of second order:  $A+B \rightleftharpoons B$  and (3)  $A+B \rightleftharpoons E+F$ .

Though many other solutions have been presented for unsteady state diffusion with a chemical reaction of second order, all of them are derived in the case of semi-infinite stagnant liquid.

Practically, the system which consists of a diffusion film of finite thickness and homogeneously mixed bulk liquid of finite volume is important. For a system where the steady state molecular diffusion accompanied by an irreversible  $(1+n)$ -th order (i.e., 1st order in  $A$  and  $n$ -th order in  $B$ ) reaction occurs in the diffusion film, the authors derive an analytical solution for the over-all

rate of reaction modifying the method of approximate concentration distribution suggested by D. W. van Krevelen, et al.<sup>5)</sup> They also interpret the relation between the over-all reaction rate, resistances to diffusion and chemical reaction, interfacial contact area of the two phases and the other various reaction conditions, and present several numerically calculated diagrams showing the results of the analysis.

The following five classes of the controlling steps are assigned in general by applying the concentration distribution of a reactant to the heterogeneous reaction system where diffusion is followed by a second order reaction. The controlling steps are (1) chemical reaction between the reactants *A* and *B* in the diffusion film and bulk of the phase *b*, (2) both the reaction of the reactants (*A* and *B*) and the diffusion of the reactant *A* in the diffusion film and bulk of the phase *b*, (3) diffusion of the reactant *A* in the diffusion film of the phase *b*, (4) diffusion of the reactant *A* and reaction of *A* and *B* in the diffusion film of the phase *b* and (5) diffusion of *B* in the diffusion film of the phase *b*. These five steps were suggested by I. Yamaguchi<sup>6)</sup> who also pointed out that all of the five steps stated above were not always realized by merely changing the ratio of the resistances to chemical reaction versus diffusion by adding catalysers, changing the reaction temperature and physical properties of the system and intensifying agitation.

Accordingly, in the contact process in an agitation vessel, it is very important to know in what reaction conditions the mass transfer accompanied by chemical reaction is perfectly controlled by diffusion and in what conditions this is not the case, and it is also important to know the state where the step (2) shifts to the step (4) without passing through the step (3).

In this paper the authors would like to solve the problems and also to clarify the physical meaning of the solutions derived by mathematical analysis.

#### Basic Rate Equations and the Boundary Conditions

When the reactant *A* dissolves into the liquid phase *b* and the following chemical reaction takes place with the reactant *B*,



The concentration distribution of both reactants is shown by curves (1) and (1') in Figure 1 assuming a steady state of molecular diffusion.

Taking a material balance in *A* in the reaction zone which is bounded by two surfaces of unit area at the distance of *x* and *x+dx* from the interface, we have the following relation;

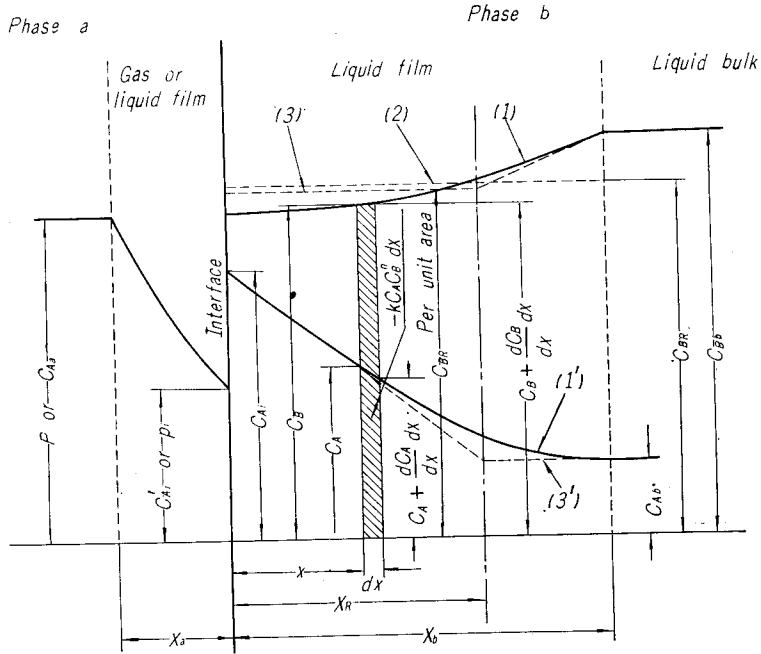


Fig. 1. Diagram Showing Concentration Distribution of Reactants in the Vicinity of Interface.

$$D_A \frac{d^2 C_A}{dx^2} = k C_A C_B^n \quad (2)$$

similarly for the reactant B;

$$\frac{1}{\nu} D_B \frac{d^2 C_B}{dx^2} = k C_A C_B^n \quad (3)$$

From Equations (2) and (3), we have

$$\frac{d^2 C_A}{dx^2} = \frac{1}{\nu} \frac{D_B}{D_A} \frac{d^2 C_B}{dx^2} = \frac{k C_A C_B^n}{D_A} \quad (4)$$

The boundary conditions are generally given by the equations,

$$\left. \begin{aligned} C_A &= C_{Ai}, & \frac{dC_B}{dx} &= 0 & \text{at } x &= 0 \\ C_B &= C_{Bb}, & -D_A \left( \frac{dC_A}{dx} \right) &= k C_{Ab} C_{Bb}^n \nu & \text{at } x &= X_b \end{aligned} \right\} \quad (5)$$

Since Equation (4) is non-linear, analytical solution is not obtained.

The concentration of the reactant A in the bulk of the phase b is given by

$$C_{Ab} = (C_A)_{x=X_b} \quad (5')$$

The rate of mass transfer is given by

$$N = -D_A \left( \frac{dC_A}{dx} \right)_{x=0} \quad (6)$$

### Solution by Approximate Concentration Distribution

The following equation is derived by integrating Equation (4) within the diffusion film,

$$\frac{1}{\nu} \frac{D_B}{D_A} C_B - C_A = mx + n \quad (7)$$

where  $m$  and  $n$  are arbitrary constants to be determined by the boundary conditions. To solve Equation (2), let the approximation be made that the concentration of the reactant  $B$  in the diffusion film is constant which is smaller than the concentration in the bulk of the phase  $b$  as shown by curve (2) in Figure 1, that is,  $C_B = C_{BR} = \text{Const.} \leq C_{Bb}$ , and that the values of  $(dC_A/dx)_{x=0}$  and  $(dC_A/dx)_{x=X_b}$  do not change so much by taking  $C_B \doteq (C_B)_{x=0} = \text{Const.}$

Hence, Equation (4) is approximated as follows;

$$\frac{d^2 C_A}{dx^2} = \frac{C_{BR}^n C_A}{D_A} \quad (8)$$

The boundary conditions are the same as shown in Equation (5).

The solution of Equation (8) is obtained as follows;

$$\begin{aligned} N &= -D_A \left( \frac{dC_A}{dx} \right)_{x=0} \\ &= \frac{Y}{\tanh Y} k_b C_{Ai} \left\{ 1 - \frac{C_{Ab}}{C_{Ai}} \frac{1}{\cosh Y} \right\} \end{aligned} \quad (9)$$

$$\frac{C_{Ab}}{C_{Ai}} = \frac{1}{\cosh Y + (\alpha \nu) \left( \frac{\tau}{Y} \right) \sinh Y} = \Phi \quad (10)$$

where,

$$\begin{aligned} k_b &= D_A / X_b \\ \alpha &= \sqrt{k C_{Bb}^n / D_A} \\ \tau &= \sqrt{k C_{Bb}^n D_A} / k_b \\ Y &= \sqrt{k C_{BR}^n D_A} / k_b \end{aligned} \quad (11)$$

The ratio  $(C_{Ab}/C_{Ai})$  is denoted by  $\Phi$  and the authors suggested that it should be called "the degree of transitional saturation" (3). When the value  $\Phi$  tends to unity, it is useless to increase the intensity of agitation further [refer to Figure 11].

In order to determine the value of  $C_{BR}$  with an approximate concentration distribution, a reaction zone of thickness  $X_R$  is assumed in the diffusion film of thickness  $X_b$  as shown by curve (3) in Figure 1. The assumption that

$-D_A(dC_A/dx)_{x=0} \gg -D_A(dC_A/dx)_{x=X_b}$  or  $-D_A(dC_A/dx)_{x=X_b} \neq 0$  is made and Equation (7) is applied to this concentration distribution, then we have

$$\frac{C_{Ai}-C_{Ab}}{X_R} = \frac{1}{\nu} \frac{D_B}{D_A} \frac{(C_{Bb}-C_{BR})}{X_b-X_R} \quad (12)$$

From this equation,

$$C_{BR} = C_{Bb} \left\{ 1 - \left( \frac{1-\kappa}{\kappa} \right) \left( \nu \frac{D_A}{D_B} \frac{C_{Ai}}{C_{Bb}} \right) \left( 1 - \frac{C_{Ab}}{C_{Ai}} \right) \right\} \quad (13)$$

where

$$\kappa = X_R/X_b \leq 1$$

By combining Equations (11) and (13),

$$Y = \gamma \left\{ 1 - \left( \frac{1-\kappa}{\kappa} \right) \left( \nu \frac{D_A}{D_B} \frac{C_{Ai}}{C_{Bb}} \right) \left( 1 - \frac{C_{Ab}}{C_{Ai}} \right) \right\}^{n/2} \quad (14)$$

The rate of diffusion in the reaction zone of thickness  $X_R$  is,

$$N = \frac{D_A}{X_R} (C_{Ai} - C_{Ab}) = k_b C_{Ai} \frac{1}{\kappa} \left( 1 - \frac{C_{Ab}}{C_{Ai}} \right) \quad (15)$$

Accordingly, the following equations are obtained from Equations (9), (10), (11), (14) and (15).

$$\frac{N}{k_b C_{Ai}} = \frac{Y}{\tanh Y} \left\{ 1 - \frac{C_{Ab}}{C_{Ai}} \frac{1}{\cosh Y} \right\} \quad (16)$$

$$= \frac{1}{\kappa} \left( 1 - \frac{C_{Ab}}{C_{Ai}} \right) \quad (17)$$

$$Y = \gamma \left\{ 1 - \left( \frac{1-\kappa}{\kappa} \right) \left( \nu \frac{D_A}{D_B} \frac{C_{Ai}}{C_{Bb}} \right) \left( 1 - \frac{C_{Ab}}{C_{Ai}} \right) \right\}^{n/2} \quad (18)$$

$$\frac{C_{Ab}}{C_{Ai}} = \frac{1}{\cosh Y + (av) \left( \frac{\gamma}{Y} \right) \sinh Y} \quad (19)$$

In the special case of constant concentration of the reactant  $B$  in the phase  $b$  ( $C_B = C_{Bb} = \text{const.}$ ), Equation (8) becomes,

$$\frac{d^2 C_A}{dx^2} = \left( \frac{k C_{Bb}^n}{D_A} \right) C_A \quad (20)$$

As  $\kappa=1$  for this case, Equations (16) to (19) are simplified into the following ones which agree with the solution by S. Hatta<sup>2)</sup>.

$$\begin{aligned} N &= -D_A \left( \frac{dC_A}{dx} \right)_{x=0} \\ &= \beta k_b C_{Ai} \left\{ 1 - \frac{C_{Ab}}{C_{Ai}} \frac{1}{\cosh \gamma} \right\} \end{aligned} \quad (21)$$

$$\frac{C_{Ab}}{C_{Ai}} = \frac{1}{\cosh \gamma + (av) \sinh \gamma} \quad (22)$$

In the case where the approximation of  $C_{Ab}/C_{Ai} \neq 0$  is made, Equation (15) is reduced to

$$N = k_b C_{Ai} \frac{1}{\kappa} \quad (23)$$

Combining this Equation (23) and Equation (13) with the condition,  $C_{Ab}/C_{Ai} \neq 0$ , we have the following equations, which were presented by van Krevelen, et al.<sup>5)</sup>

$$\frac{N}{k_b C_{Ai}} = \frac{Y}{\tanh Y} \left\{ 1 - \frac{C_{Ab}}{C_{Ai}} \frac{1}{\cosh Y} \right\} \quad (24)$$

$$= 1/\kappa \quad (25)$$

$$Y = \gamma \left\{ 1 - \left( \frac{1-\kappa}{\kappa} \right) \left( \nu \frac{D_A}{D_B} \frac{C_{Ai}}{C_{Bb}} \right) \right\}^{n/2} \quad (26)$$

$$\frac{C_{Ab}}{C_{Ai}} = \frac{1}{\cosh Y + (\alpha\nu) \left( \frac{\gamma}{Y} \right) \sinh Y} \quad (27)$$

Since  $Y$  is always smaller than  $\gamma$  as is evident from the assumption and Equation (26), and  $\gamma$  is possibly very small,  $C_{Ab}/C_{Ai}$  is approximately equal to 1, when  $(\alpha\nu)$  is finite, hence this is inconsistent with the assumption:  $(C_{Ab}/C_{Ai} \neq 0)$ . As  $\kappa$  is equal to or less than 1 in the range of  $0 \leq \gamma < \infty$ , and this is satisfied only when  $\alpha\nu = \infty$ , Equations (24), (25) and (26) are reduced to;

$$\frac{N}{k_b C_{Ai}} = \frac{Y}{\tanh Y} \quad (24')$$

$$= 1/\kappa \quad (25')$$

$$Y = \gamma \left\{ 1 - \left( \frac{1-\kappa}{\kappa} \right) \left( \nu \frac{D_A}{D_B} \frac{C_{Ai}}{C_{Bb}} \right) \right\}^{n/2} \quad (26')$$

### Numerical Calculation Diagram

Equations (16) to (19) are the solutions where  $Y$  and  $\kappa$  are taken as parameters and  $\{(1/\nu)(D_B/D_A)(C_{Bb}/C_{Ai})\} \equiv \lambda$ ,  $\gamma$  and  $(\alpha\nu)$  are independent variables.  $\kappa$  and  $Y$  are difficult to eliminate from these equations. Hence, the authors intend to proceed with numerical calculation by trial and to obtain the relation between  $N/k_b C_{Ai}$  and  $\gamma$  for various values of  $\lambda$  by taking  $(\alpha\nu)$  as a parameter. At first a combination is selected for the value of  $\gamma$  and  $\alpha\nu$  at a certain value of  $\lambda$ . A value of  $Y$  is assumed to be close to the value of  $\gamma$  as the first trial. The value of  $(C_{Ab}/C_{Ai})$  is calculated from Equation (19). Accordingly, the value of  $\kappa$  is given by Equations (16) and (17). The second trial value of  $Y$  is obtained from Equation (18) by introducing predetermined values. If the second value of  $Y$  does not agree with the first, the same procedure of calculation is repeated until these two check. Figures 2 to 7 are the diagrams showing the results of the numerical calculation for  $n=1$  within the ranges:



$10^{-3} < \gamma < 10^3$ ,  $0 \sim \infty$  for  $av$  and 0, 0.1, 0.5, 1, 10, 100 and  $\infty$  for the value of  $\lambda$ . In the case where the volume of the bulk liquid per unit interfacial area ( $v$ ) is small as in an agitation vessel, we should discuss it under the condition of constant total volume of the phase  $b$ , because the magnitude of  $X_b$  is not negligible compared with  $v$ .

Denoting the total liquid volume per unit interfacial area by  $v'$ , we have

$$v' = v + X_b \tag{28}$$

Hence,

$$av' = av + aX_b = av + \gamma \tag{29}$$

From this relation, curves for constant  $av'$  are easily obtained and the calculated results are shown by the dotted lines in Figures 2 to 7.

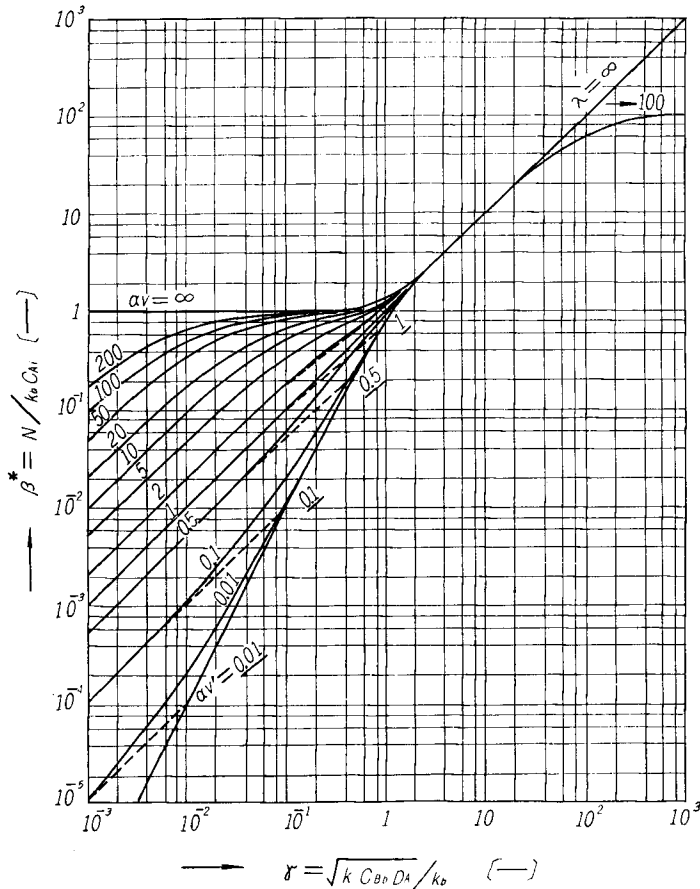


Fig. 2. Numerical Calculation of Functional Relation between  $\beta^*$  vs.  $\gamma$  for  $\lambda = \infty$  and 100,

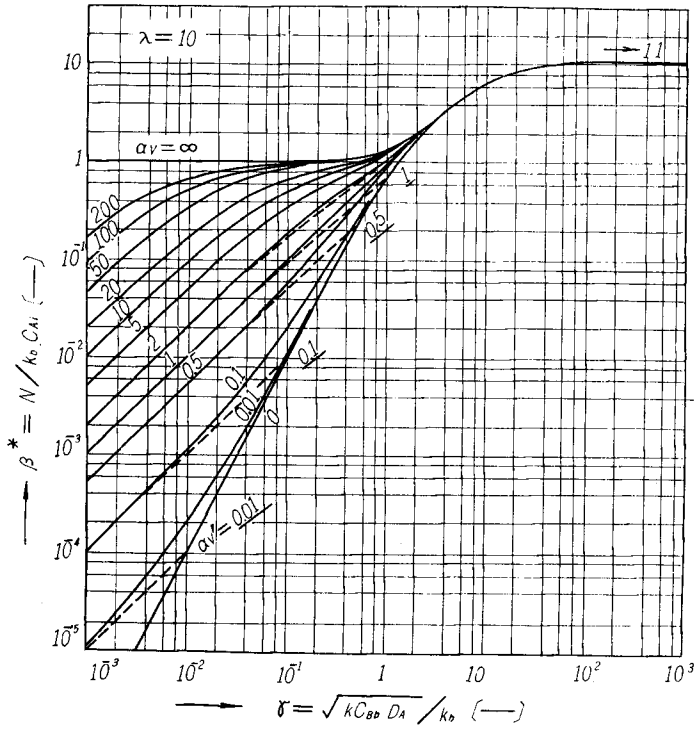


Fig. 3.  $\beta^*$  vs.  $\gamma$  for  $\lambda=10$ .

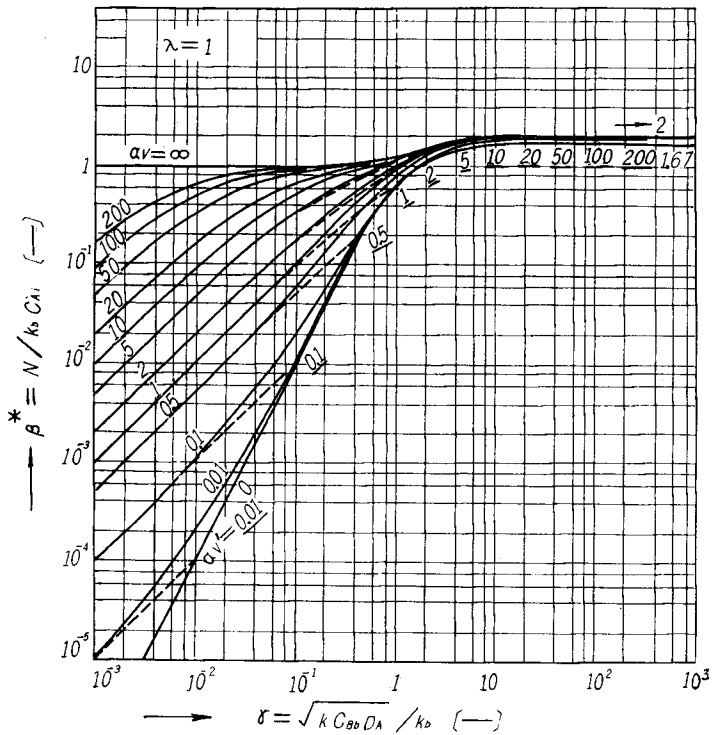


Fig. 4.  $\beta^*$  vs.  $\gamma$  for  $\lambda=1$ .

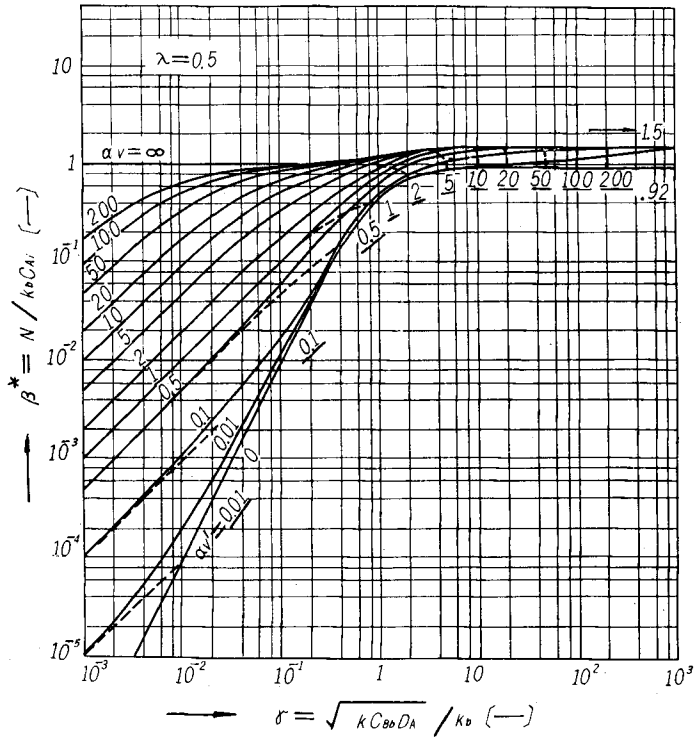


Fig. 5.  $\beta^*$  vs.  $\gamma$  for  $\lambda=0.5$ .

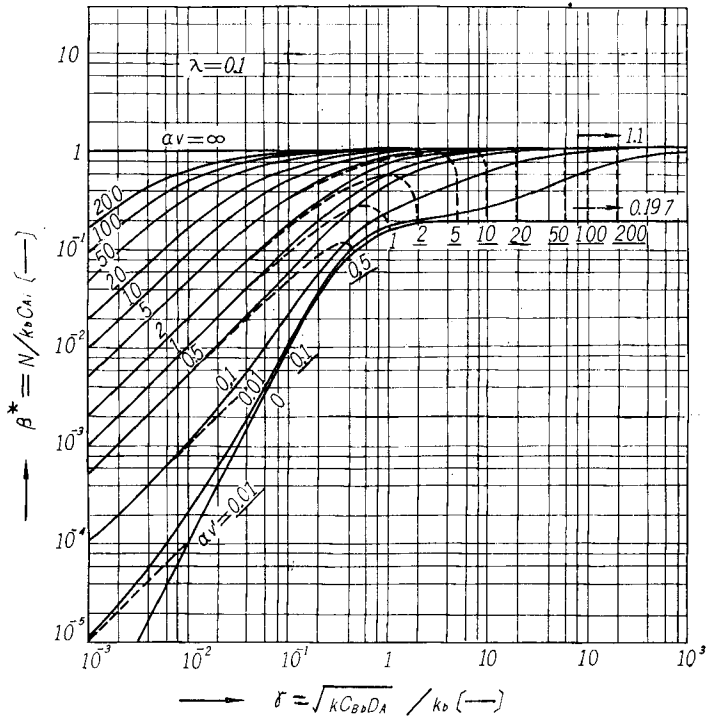
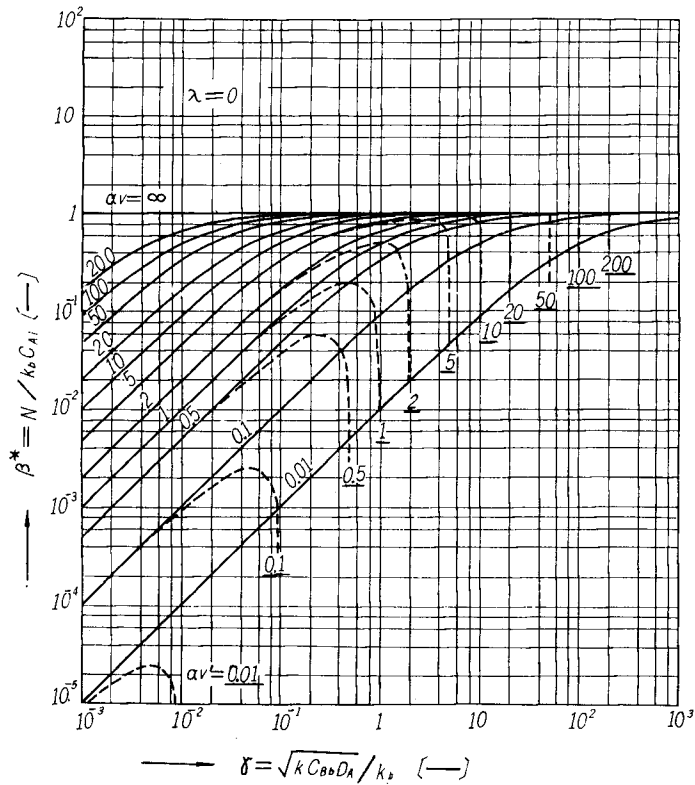


Fig. 6.  $\beta^*$  vs.  $\gamma$  for  $\lambda=0.1$ .

Fig. 7.  $\beta^*$  vs.  $\gamma$  for  $\lambda=0$ .

### Analysis and Discussion of the Results of Calculation

In Figures 2 to 7 the value of  $(N/k_b C_{A_i})$  is taken on the ordinate. This value is called the reaction coefficient for mass transfer and denoted by  $\beta^*$ . The abscissa shows the value which relates to the value of the ratio of resistances to reaction and diffusion, and is denoted by  $\gamma$ .  $\lambda$  shows the value which relates to the ratio of the diffusion coefficient of the reactant  $B$  to that of  $A$  in the phase  $b$  and to the ratio  $(C_{B_b}/\nu)$  to  $C_{A_i}$ .  $(av)$  shows the value which relates to the ratio of the reaction rate constant to the diffusion coefficient and the volume of the bulk per unit interfacial area  $(V/A)$ .

As the number of parameters is two, the functional relations between  $\beta^*$  and  $\gamma$  are shown by the diagrams in which the parameter may be either  $\lambda$  or  $(av)$ . In the diagrams of this paper,  $(av)$  is taken as the parameter for several constant values of  $\lambda$ . The value of  $\beta^*$  is the function of  $(av)$  only in the range of small value of  $\gamma$  and is the function of  $\lambda$  only in the range of large value of  $\gamma$  provided that  $av \neq 0$ .

In the following pages, all the possible cases which are different in reaction conditions will be interpreted and discussion will be presented on the  $\beta^*$  vs.  $\gamma$  relations as well as several concentration distributions.

**I. A class where  $(\alpha v)$  is large**

This is a typical case where all the five steps of reaction rate appear as predicted by the concentration distribution diagrams. As shown in Figure 8, the over-all rate of reaction is controlled by the resistance to chemical reaction

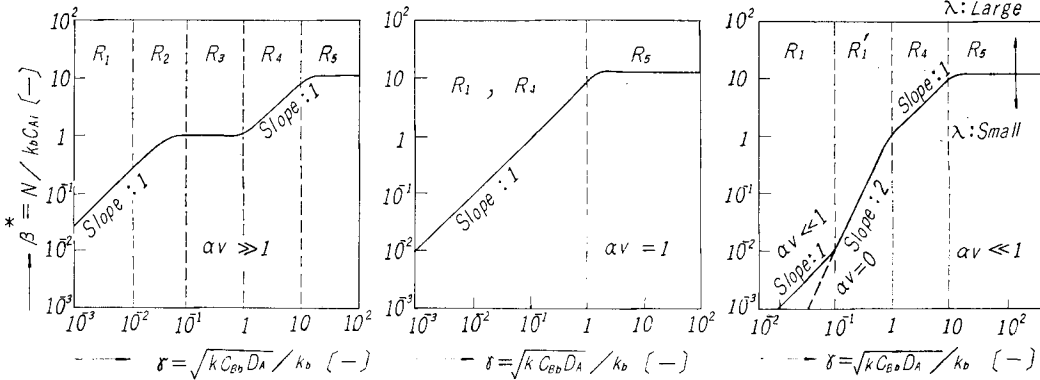


Fig. 8. Typical Curve of  $\beta^*$  vs.  $\gamma$  in the Range of  $\alpha v \gg 1$ . Fig. 9.  $\beta^*$  vs.  $\gamma$  in the Range of  $\alpha v \leq 1$ . Fig. 10.  $\beta^*$  vs.  $\gamma$  in the Range of  $\alpha v \ll 1$ .

in the region  $R_1$ , by the resistances to reaction and diffusion in the phase  $b$  in the region  $R_2$ , by the resistance to diffusion of the reactant  $A$  in  $R_3$ , by the resistance to diffusion and reaction within the diffusion film of the phase  $b$  in  $R_4$  and by the resistance to diffusion of the reactant  $B$  in the phase  $b$  in  $R_5$ .

Case (a) A case where  $\gamma$  is very small and the value of  $\gamma$  ( $\alpha v$ ) is also small.

Since  $Y \leq \gamma$  from Equation (18), for small value of  $\gamma$ ,

$$1 \leq \frac{Y}{\tanh Y} \approx 1 + \frac{Y^2}{3} \leq 1 + \frac{\gamma^2}{3}$$

$$1 \geq \frac{1}{\cosh Y} \approx 1 - \frac{Y^2}{2} \geq 1 - \frac{\gamma^2}{2}$$

the value of  $\gamma^2$  is regarded very small compared with 1 and is negligible, then  $\kappa \approx 1$  from Equations (16) and (17), and  $Y \approx \gamma$  from Equation (18). Accordingly the following equations are obtained from Equations (16) and (19).

$$\frac{N}{k_b C_{A_i}} \approx 1 - \frac{1}{1 + \gamma(\alpha v)} = \frac{\gamma(\alpha v)}{1 + \gamma(\alpha v)} \tag{30}$$

$$N = \frac{C_{Ai}}{\frac{1}{k_b} + \frac{1}{kC_{Bb}^n v}} \quad (30')$$

In addition, in the case where  $1 \gg \gamma(av)$ ,

$$N = kC_{Bb}^n C_{Ai} v \quad (31)$$

The over-all rate of reaction becomes equal to the rate of reaction in the phase *b* and the concentration distribution in the diffusion film is shown by Figure 11. This corresponds to the stage  $R_1$  in Figure 8.

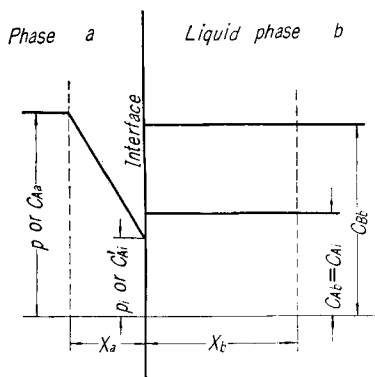


Fig. 11. Concentration Distribution in Case Chemical Reaction Controls.

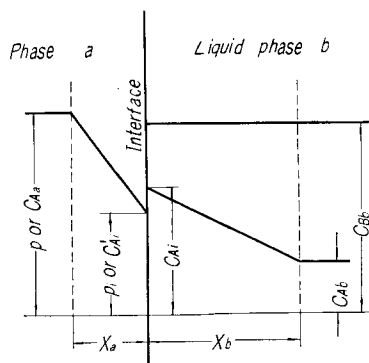


Fig. 12. Concentration Distribution in Case Diffusion of A and Chemical Reaction Control.

Case (b) A case where  $\gamma$  is very small and  $\gamma(av)$  closes to 1.

This stage corresponds to  $R_2$  in Figure 8 and Equations (30) and (30') are applicable. The resistances to diffusion and reaction are comparable in magnitude and the concentration distribution in the diffusion film is shown in Figure 12.

Case (c) A case where  $\gamma$  is small and  $\gamma(av)$  is large

In the case where  $1 \leq \gamma(av)$  in Eq. (30),  $N/k_b C_{Ai} = 1$ ,

$$N = k_b C_{Ai} \quad (32)$$

Where  $N$  is equal to the rate of diffusion of the reactant  $A$  in the diffusion film. This is the case where the effect of agitation is most marked as in a gas-liquid reaction, so it is very important to make the physical meaning clear.

Arranging the above conditions,

$$\gamma \ll 1 \ll \gamma(av) \ll (av) \quad (33)$$

From this equation,

$$\gamma \ll (av) \quad (33')$$

$$X_b \ll v \quad (34)$$

The condition for the existence of diffusion step controlling is that the volume of the bulk liquid per unit interfacial area is very large compared with the thickness of the diffusion film and that the value of  $\gamma$  is in the following range regardless of the values of  $k$ ,  $C_{Bb}$  and  $D_A$ .

From Equation (33),

$$1/(av) \ll \gamma \ll 1 \quad (35)$$

and,

$$D_A/kC_{Bb}^n v \ll X_b \ll \sqrt{D_A/kC_{Bb}^n} \quad (36)$$

It is seen from Equation (36) that in an agitation system the state of diffusion rate controlling appears in a wide range of the intensity of agitation when the value of  $kC_{Bb}^n$  is large. In Figure 8 the range  $R_3$  corresponds to this condition and the concentration distribution in diffusion film is shown in Figure 13.

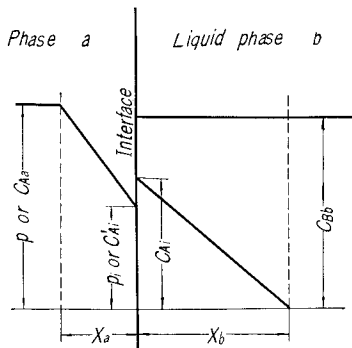


Fig. 13. Concentration Distribution in Case Resistance to Diffusion of A Controls.

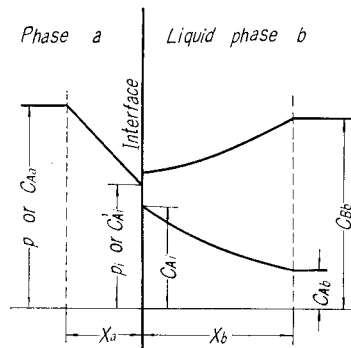


Fig. 14. Concentration Distribution in Case Diffusion of Both Components (A, B) and Chemical Reaction Control.

Case (d) A case where  $\gamma^2$  is not negligible for 1

Since the condition that  $\kappa=1$  or  $C_{BR} \approx C_{Bb}$  is not satisfied, Equation (30) is not applicable, and the concentration distribution in the diffusion film becomes such that is shown in Figure 14 and the rate of absorption may not be predicted except by the method of numerical calculation. The ranges of small value in  $av$  in the stages of  $R_2$ ,  $R_3$  and a part of  $R_4$  in Figure 3 correspond to this case.

Case (e) A case where  $\gamma$  and  $\lambda$  are large

When the value of  $\lambda$  is large and also  $\gamma$  is large,  $Y$  may possibly be

large, that is,  $\tanh Y \doteq 1$  and  $1/\cosh Y \doteq 0$ . Hence, Equations (16) and (18) are reduced to

$$N/k_b C_{Ai} = Y \tag{37}$$

$$\left(\frac{Y}{\gamma}\right)^2 = \left\{1 - (Y-1)\left(\frac{1}{\lambda}\right)\right\}^n \tag{38}$$

When  $\lambda$  in Equation (38) is large, i.e. the reaction is of pseudo first order,  $Y = \gamma$ . Hence,

$$\begin{aligned} N &= k_b C_{Ai} \gamma \\ &= \sqrt{k C_{Bb}^n D_A} \cdot C_{Ai} \end{aligned} \tag{39}$$

This is the case where the over-all rate is controlled both by the resistances to diffusion and by reaction within the diffusion film, and the concentration distribution in the diffusion film becomes such that is shown in Figure 15. The central part of the range  $R_4$  in Figure 8 corresponds to this case.

It is obvious from Figures 2 and 3 that the range where this approximation is applicable becomes wider as the value of  $\lambda$  is larger.

Case (f) A case where  $\gamma$  is large

Since  $(1 - C_{Ab}/C_{Ai})$  is equal to or less than  $\{1 - (C_{Ab}/C_{Ai})(1/\cosh Y)\}$ ,  $Y/\tanh Y$  is also equal to or less than  $1/\kappa$  from Equations (16) and (17).

Because  $1/\kappa$  have the limiting value except for the case where  $\lambda \rightarrow \infty$  as can be seen from Equation (18),  $Y$  also has the limiting value. The inner term of the root in Equation (18) becomes zero when  $\gamma \rightarrow \infty$ .

Furthermore, as  $C_{Ab}/C_{Ai} = 0$  from Equation (19), for the cases where  $av \neq 0$  and  $\gamma \rightarrow \infty$ ,

$$\frac{N}{k_b C_{Ai}} = 1 + \lambda \tag{40}$$

$$N = k_b C_{Ai} + k_b \left(\frac{1}{\nu}\right) \left(\frac{D_B}{D_A}\right) C_{Bb} \tag{41}$$

This is the case of diffusion resistance controlling for the reactant  $B$  in the diffusion film of the phase  $b$  and is the state shown in the range  $R_5$  in Figure 8, that is, the case of mass transfer followed by fast irreversible reaction. This was already solved by S. Hatta. The concentration distribution in the diffusion film becomes that

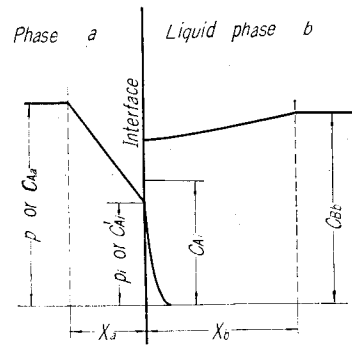


Fig. 15. Concentration Distribution in Case Diffusion of Both Components and Chemical Reaction Control within Diffusion Film.

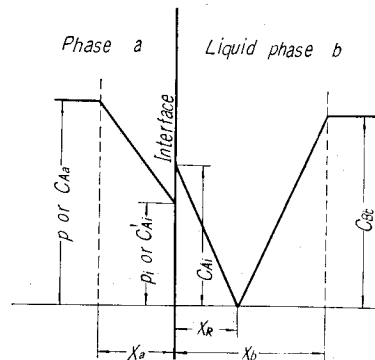


Fig. 16. Concentration Distribution in Case Diffusion of  $B$  Controls.



which is shown in Figure 16.

**II. A class where  $av=1$**

Some of the five states do not appear as in the case of Class I. The stages of  $R_1$  and  $R_4$  in Figure 8 overlap each other as shown in Figure 9. Only two stages of rate controlling appear; that is, (1) reaction resistance controlling ( $R_1, R_4$  in Figure 9) and (2) diffusion resistance controlling of the reactant  $B$  in the phase  $b$  ( $R_5$  in Figure 9).

Case (a) A case where  $\gamma$  is small

In this case,  $Y \approx \gamma$  as in the Case I, (a).

In the case where  $\lambda$  is large as shown in the Case I. (e),  $\gamma \approx Y$  as long as the value of  $\gamma$  is considerably large. Since  $av=1$ , Equations (24) and (27) are written as follows for the case where  $\gamma=Y$ .

$$\frac{N}{k_b C_{Ai}} = \frac{\gamma}{\tanh \gamma} \left\{ 1 - \frac{1}{\cosh \gamma + \sinh \gamma} \frac{1}{\cosh \gamma} \right\} = \gamma \tag{42}$$

Therefore,

$$N = k_b C_{Ai} \gamma = \sqrt{k C_{Bb}^n D_A} \cdot C_{Ai} \tag{43}$$

$$= \sqrt{k C_{Bb}^n D_A} \cdot C_{Ai} (av) = k C_{Bb}^n C_{Ai} v \tag{31}$$

This refers to the cases; [1] chemical reaction resistance controlling and [2] both the resistances to diffusion and chemical reaction controlling. The concentration distribution in the diffusion film is expressed by the relation:  $C_A = C_{Ai} e^{-\alpha X}$ . Since  $C_{Ab} = e^{-\alpha X_b} C_{Ai} = e^{-\gamma} C_{Ai}$ , the concentration distribution in the diffusion film dose not change with change in the value  $X_b$ . The concentration distribution is shown in Figure 17.

**III. A class where  $av$  is small**

As shown in Figure 10, four stages appear, that is (1) reaction resistance cotrolling ( $R_1$  in Figure 10), (2) reaction resistance in the diffusion film controlling ( $R_1'$  in Figure 10), (3) diffusion and reaction resistances in diffusion film controlling ( $R_4$  in Figure 10) and (4) resistance to diffusion of the reactant  $B$  in the phase  $b$  controlling. A state different from the cases in the classes I and II appears especially in the case where  $\gamma$  is small.

In addition, as stated in the previous sections, the curves drawn by the dotted lines in the numerically calculated diagrams become important, because

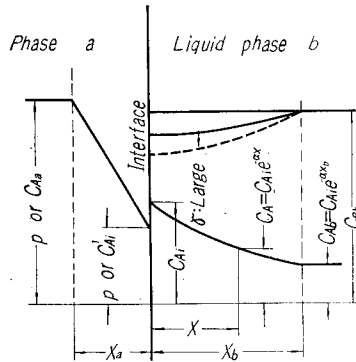


Fig. 17. Concentration Distribution in Case where  $av=1$  and  $\gamma$  is Small, and Diffusion and Chemical Reaction Control.

the total volume of the liquid ( $v'$ ) is constant in such a gas-liquid contact process.

Case (a) A case where  $\gamma$  is small

If  $\lambda$  is large,  $Y \approx \gamma$  from Equation (26). When  $(av)$  is small and  $\gamma^2$  is comparable in magnitude with  $\gamma(av)$ , we have from Equation (27)

$$\frac{C_{Ab}}{C_{Ai}} \approx \frac{1}{1 + \frac{\gamma^2}{2} + (av)\gamma} \quad (44)$$

Accordingly, from Equation (16)

$$\begin{aligned} \frac{N}{k_b C_{Ai}} &\approx 1 - \frac{1}{1 + \frac{\gamma^2}{2} + (av)\gamma} \frac{1}{1 + \frac{\gamma^2}{2}} \\ &\approx \frac{\gamma^2 + (av)\gamma}{1 + \gamma^2 + (av)\gamma} \\ &\approx \gamma^2 + (av)\gamma \end{aligned} \quad (45)$$

$$N = (X_b + v)kC_{Bb}^n C_{Ai} \quad (46)$$

Hence, for the case where  $(av) \gg \gamma$ , i. e.  $v \gg X_b$ , Equation (46) agrees with Equation (31). By substituting Equation (10) into Equation (9) and simplifying, the following relationship is derived.

$$N = \sqrt{kC_{Bb}^n D_A} \cdot C_{Ai} \left\{ \frac{Y}{\gamma} \left[ 1 + \frac{2}{\left\{ \frac{(av)(\gamma/Y) + 1}{(av)(\gamma/Y) - 1} \right\} e^{2\gamma(Y/\gamma)} - 1} \right] \right\} \quad (47)$$

where

$$(Y/\gamma) = (C_{BR}/C_{Bb})^{n/2} \quad (48)$$

In Equation (47), the value of  $\sqrt{kC_{Bb}^n D_A} \cdot C_{Ai}$  may not be changed by agitation intensity, and the ratio  $(C_{BR}/C_{Bb})$ , i. e. the ratio  $(Y/\gamma)$ , is uniquely determined for a specific value of  $\gamma$ . Hence the only value that may be directly affected by the change in agitation intensity is reduced to  $\gamma$  ( $= aX_b$ ).

Let the term in the parenthesis in Equation (47) be denoted as  $\Psi$ .

$$\Psi = \left\{ \frac{Y}{\gamma} \left[ 1 + \frac{2}{\left\{ \frac{(av)(\gamma/Y) + 1}{(av)(\gamma/Y) - 1} \right\} e^{2\gamma(Y/\gamma)} - 1} \right] \right\} \quad (49)$$

For the reaction of pseudo first order with  $C_A$ ,

$$\Psi = 1 + \frac{2}{\left( \frac{av+1}{av-1} \right) e^{2\gamma} - 1} \quad (49')$$

$\Psi$  is a measure which represents the effect of agitation intensity on the over-all rate of reaction. The authors called it "the agitation coefficient

for heterogeneous reaction" [refer to the previous paper (3, 6)].

Hence,

$$N = \sqrt{kC_{Bb}^n D_A} \cdot C_{A_i} \Psi \tag{50}$$

$$N/k_b C_{A_i} = \gamma \Psi = \beta^* \tag{51}$$

The authors made numerical calculations for Equation (49) in the case where  $\lambda = \infty$ , i.e. Equation (49) is reduced to Equation (49'), taking the value  $\alpha v [(kC_{Bb}^n/D_f)^{1/2} V/A]$  as the parameter, and obtained the relationship between  $\Psi$  and  $1/\gamma$  as shown by curve (1) in Figure 18. The other relationship between

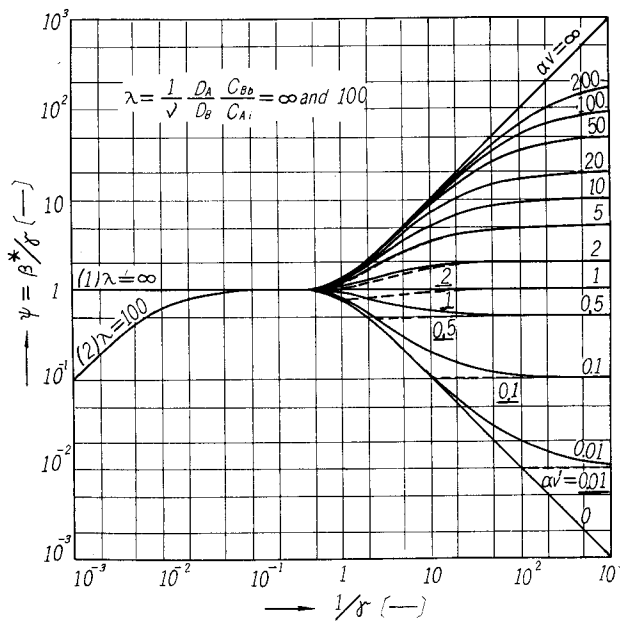


Fig. 18. Numerical Calculation of the Functional Relation Between  $\Psi$  vs.  $1/\gamma$  for  $\lambda = \infty$  and 100.

$\Psi$  and  $1/\gamma$  for various values of  $\lambda$  is similarly given as shown by Figures 18 to 23 for  $n=1$ . In Figure 18, the value of  $\Psi$  decreases as  $1/\gamma$  increases for the same value of  $\alpha v$  in the case where  $v \neq X_b$ . When the increase in  $1/\gamma$  is caused by the decrease in  $X_b$  as predicted by Equation (46), this corresponds to the decrease in the total volume of liquid so that the rate of over-all reaction decreases. In addition, the over-all rate decreases also in the case where the increase in  $1/\gamma$  is caused by the decrease in  $k$  or  $C_{Bb}$ . The change in  $N/k_b C_{A_i}$  due to the increase in  $\gamma$  is shown in Figures 2 to 7.

From a practical point of view, it is required to predict the change in the over-all rate of reaction caused by the decrease in  $X_b$ , i.e. by the increase

in agitation intensity. In this case, the thickness of the diffusion film ( $X_b$ ) decreases under the constant volume of total liquid ( $v$ ). The value of  $\alpha v$  increases as  $1/\gamma$  increases.

The concentration distribution within the diffusion film for this case is shown by Figure 24.

When  $v=0$ ,

$$N = kC_{Bb}^n C_{Ai} X_b \tag{52}$$

As Equation (31) is applicable for the range where  $\gamma \ll (\alpha v) \ll 1$  and also  $\gamma$  is very small, the state corresponds to the range  $R_1$  in Figure 10. Equation (52) is approximately applicable for the range where  $(\alpha v) \ll \gamma \ll 1$ , i.e. the range  $R_1'$  in Figure 10. This state appears, for example, when  $(\alpha v)=0.01$  as shown in Figures 2 and 3.

When  $(\alpha v)=0$  and  $\lambda$  is small, the limiting value of  $Y$  for  $\gamma \rightarrow \infty$  becomes small and the condition that  $Y=\gamma$  is no longer held for the case where  $\gamma$  is small.

Case (b) A case where  $\gamma$  and  $\lambda$  are large

The case is shown in the range  $R_4$  in Figure 10 and corresponds to the Case I (e).

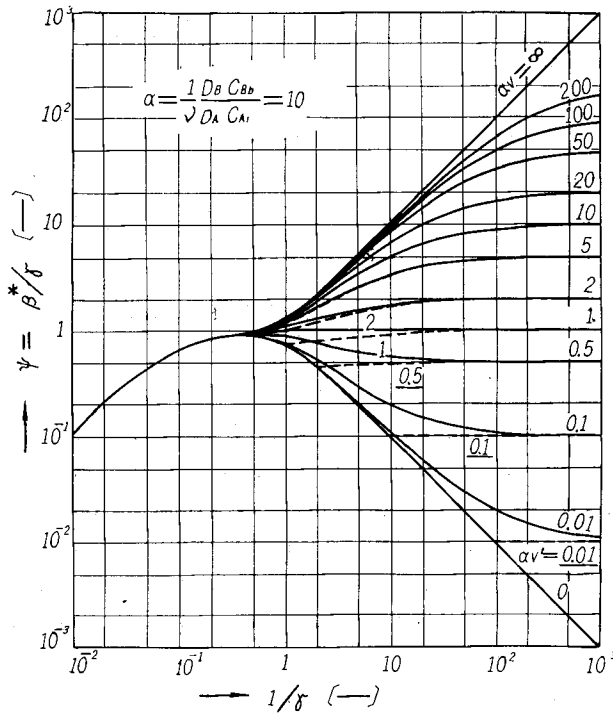


Fig. 19.  $\Psi$  vs.  $1/\gamma$  for  $\lambda=10$ .

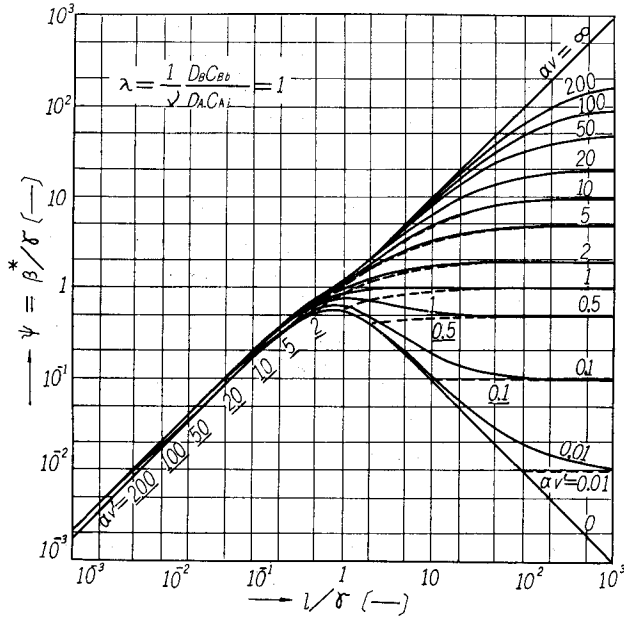


Fig. 20.  $\Psi$  vs.  $1/\gamma$  for  $\lambda=1$ .

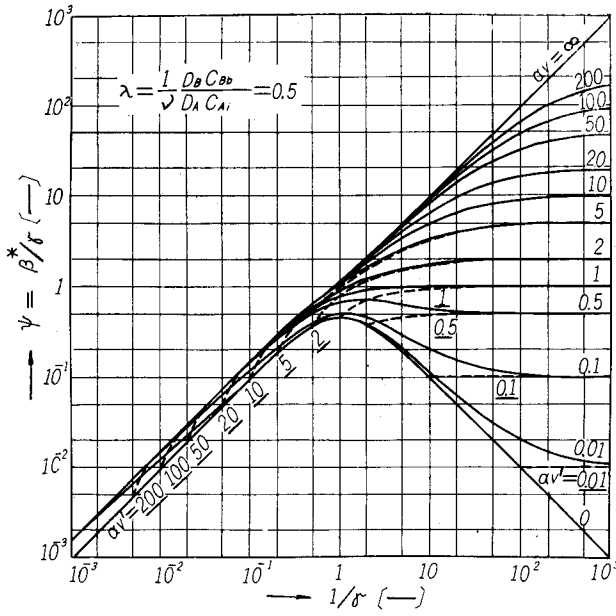


Fig. 21.  $\Psi$  vs.  $1/\gamma$  for  $\lambda=0.5$ .

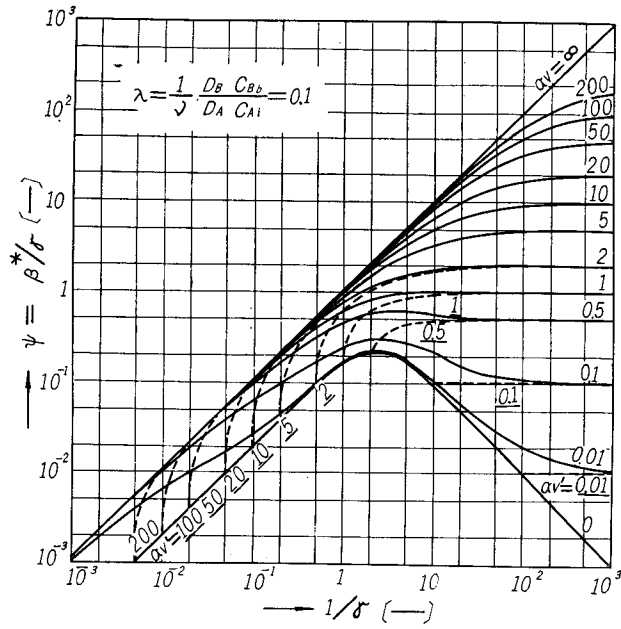


Fig. 22.  $\Psi$  vs.  $1/\gamma$  for  $\lambda=0.1$ .

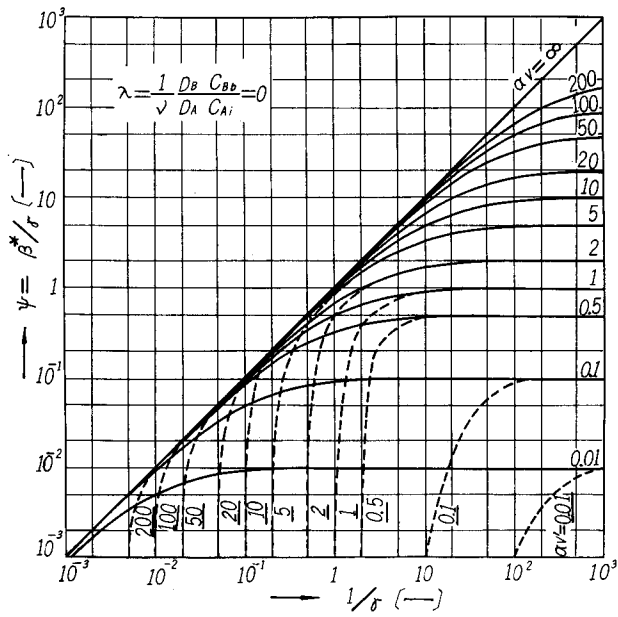


Fig. 23.  $\Psi$  vs.  $1/\gamma$  for  $\lambda=0$ .



This is the equation for the mass transfer by diffusion only. Figure 7 shows the limiting value of  $\lambda=0$ .

### Conclusion

Solutions of the differential equation for the over-all rate of reaction are derived, as shown by Equations (16) to (19), by applying an approximate concentration distribution for mass transfer at a steady state molecular diffusion accompanied by an irreversible  $(1+n)$ -th order reaction. In the present studies, the system consists of the diffusion film of finite thickness and of the bulk liquid of also finite volume which is uniformly mixed as may be encountered by an agitation vessel.

The relation between the over-all rate of reaction and reaction condition which may be the resistance to diffusion, the resistance to chemical reaction, the volume of the liquid, the interfacial contact area, etc. has been studied and the numerically calculated diagrams are presented as shown in Figures 2 to 7.

The concentration distribution of a reactant in the diffusion films is schematically shown in Figures 11 to 17, 24 and 25. Types of the overall reaction rate are classified into five steps as shown in Figures 8, 9 and 10, though some of them overlap each other or disappear.

The reaction conditions for these steps are discussed with reference to the corresponding rate equations. These equations agree well with the solutions given by S. Hatta, et al. (2) [refer to, Equations (21) and (22)], the solutions by D. W. van Krevelen (5) [refer to Equations (24) to (27)] and the solutions by S. Nagata and I. Yamaguchi (3) respectively in the corresponding conditions. Therefore, newly derived Equation (16)~(19) may be considered an approximate general solution.

### Acknowledgement

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### Notation

- $a$  = a phase in which the whole of the reactant  $A$  dissolved before contact
- $A$  = a reactant
- $A$  = total interfacial area between two phases  $a$  and  $b$ , (sq. m.)
- $b$  = a phase in which the whole of the reactant  $B$  dissolved before contact
- $B$  = a reactant



- $C_A$  = concentration of the reactant  $A$  in the diffusion film of the phase  $b$ ,  
(Kg-mole)/(cu. m.)
- $C_{Aa}$  = concentration of the reactant  $A$  in the bulk of the phase  $a$ , (Kg-mole)/  
(cu. m.)
- $C_{Ab}$  = concentration of the reactant  $A$  in the bulk of the phase  $b$ , (Kg-mole)/  
(cu. m.)
- $C_{Ai}$  = concentration of the reactant  $A$  at the interface in the phase  $b$ ,  
(Kg-mole)/(cu. m.)
- $C_{Ai}'$  = concentration of the reactant  $A$  at the interface in the phase  $a$ , (Kg-  
mole)/(cu. m.)
- $C_B$  = concentration of the reactant  $B$  in the diffusion film of the phase  $b$ ,  
(Kg-mole)/(cu. m.)
- $C_{Bb}$  = concentration of the reactant  $B$  in the bulk of the phase  $b$ , (Kg-mole)/  
(cu. m.)
- $C_{BR}$  = concentration of the reactant  $B$  in the assumed reaction zone of the  
phase  $b$ , (Kg-mole)/(cu. m.)
- $D_A$  = molecular diffusivity of the reactant  $A$  in the diffusion films of the  
phase  $b$ , (sq. m.)/(sec.)
- $D_B$  = molecular diffusivity of the reactant  $B$  in the diffusion film of the phase  
 $a$ , (sq. m.)/(sec.)
- $H$  = Henry's law constant, (Kg-mole)/(m.)<sup>3</sup>(atm.)
- $k$  = reaction rate constant for a  $(1+n)$ -th order reaction, (cu. m.) <sup>$n$</sup> /(Kg-  
mole) <sup>$n$</sup>  (sec.)
- $k_b$  = mass transfer coefficient in the diffusion film of the phase  $b$  (in the  
absence of chemical reaction or in the case of diffusion resistance  
controlling), (m.)/(sec.)
- $m$  = integration constant
- $n$  = integration constant, order of reaction
- $N$  = over-all rate of reaction, (Kg-mole)/(cu. m.) (sec.)
- $p$  = partial pressure of the gaseous reactant  $A$  in the bulk of the phase  
 $a$ , (atm.)
- $p_i$  = partial pressure of the gaseous reactant  $A$  at the gas-liquid interface  
in the phase  $a$ , (atm.)
- $R, S$  = reaction products
- $v = \frac{V}{A}$  = volume of the bulk of the phase  $b$  per unit interfacial area, (m.)
- $v' = \frac{V'}{A}$  = total volume of the phase  $b$  per unit interfacial area, (m.)
- $V$  = total volume of the bulk of the phase  $b$ , (cu. m.)

- $V$  =total volume of the phase  $b$ , (cu. m.)  
 $x$  =distance normal to the interface, (m.)  
 $X_a$  =thickness of the effective diffusion film in the phase  $a$ , (m.)  
 $X_b$  =thickness of the effective diffusion film in the phase  $b$ , (m.)  
 $X_R$  =thickness of the effective reaction zone in the phase  $b$ , (m.)  
 $Y$  = $\sqrt{kC_{BR}^n D_A/k_b}$   
 $\alpha$  = $\sqrt{kC_{Bb}^n/D_A}$ , (m.)<sup>-1</sup>  
 $\beta$  = $\gamma/\tanh \gamma$ =Hatta number  
 $\beta^*$  = $N/k_b C_{Ai} = \gamma \Psi$ =reaction coefficient for mass transfer in liquid phase heterogeneous reaction  
 $\gamma$  = $\sqrt{kC_{Bb}^n D_A/k_b} = \alpha X_b$   
 $\kappa$  = $X_R/X_b$   
 $\lambda$  = $(1/\nu)(D_B/D_A)(C_{Bb}/C_{Ai})$   
 $\nu$  =number of moles of the reactant  $B$  which reacts to one mole of the reactant  $A$   
 $\Phi$  = $C_{Ab}/C_{Ai}$ =degree of transitional saturation for the reactant  $A$   
 $\Psi$  =agitation coefficient for heterogeneous liquid phase reaction (3, 6)

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