- 8) Lange, N. A.: "Handbook of Chemistry", 10th ed., McGraw-Hill (1961)
- 9) Lee, K. and K. Kammermeyer: *Chem. Eng. Progr. Symposium Series*, **49**, (6), 99 (1953)
- 10) Lyster, W. N., et al.: *Petrol. Refiner*, **38**, 221 (1959)
- 11) Perry, J. H.: *Chemical Engineers' Handbook*", 4th. ed., McGraw-Hill (1963)
- 12) Sugie, H. and I. Yamada: *Kagaku Kōgaku* **32** 273 (1968)
- 13) Sadamoto, S., M. Kodama and M. Yorizane: *Kagaku Kōgaku*, **33**, 557 (1969)
- 14) Tanaka, S. and I. Yamada: *Kagaku Kōgaku (Chem. Eng., Japan)* **28**, 661 (1964)
- 15) The Society of Chemical Engineers, Japan: "Kagaku Kogaku Enshyu", Maruzen (Tokyo) 1969
- 16) Wilson, G.M.: *J. Am. Chem. Sci.*, **86**, 127 (1964)

FILM COEFFICIENTS OF MASS TRANSFER OF DILUTE SPHERE-PACKED BEDS IN LOW FLOW RATE REGIME*

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On the above subject the minimum Sherwood number is obtained by modelling a packed bed. From dimensional reasoning of the basic equations for flow of fluid and scalar transport, mass transfer process in steady Stokes flow is shown to be divided into two regimes of molecular diffusion controlling and of developing concentration boundary layer flow. The latter is observed only for liquid systems. The Sherwood number in the regimes is a sole function of the Péclet number for geometrically similar beds. By increasing the flow rate further, flow of fluid goes into the regime of developing laminar boundary layer flow, where mass transfer behaves according to the Carberry type formula. i_{Dh} vs. Re_h plot of gaseous film coefficients shows, for $2 \leq Re_h \leq 20$, anomalous behaviour which depends on the magnitude of ϵ_f . This anomaly is shown to be inherent only in dilute beds, and to come from flow transition.

1. Introduction

Heat or mass transfer between particles and fluid in packed beds is one of the important items of basic information necessary for various heat and mass transfer operations and chemical reactor design. It has been a target of many investigators during the past decades, giving various phenomenological and empirical correlations. Recently an empirical equation was presented⁶⁾ for data from various sources including lower flow rate regime, by introducing the ratio of particle size to bed height as a correlating parameter.

Of various beds studied previously, the behaviour of dilute beds (sometimes called extended beds) of spherical packings is treated here, where active and inactive spherical packings are mixed in the beds at a given ratio and packed uniformly. The dilution ratio $\bar{\gamma}$ is defined as the ratio of the total number of packings to the number of active ones, so that a bed of dummy spheres containing a single active sphere is expressed by $\bar{\gamma} \gg 1$. Since the behaviour of dilute beds is obviously different from that of usual beds of all active spheres, owing to the lack of interference between neighbouring active particles, scalar transport such as heat or mass is considered here for the former beds.

The limiting Sherwood number for zero flow rate is first considered, and mass transfer in the lower flow rate regime follows it.

2. Properties of Film Coefficient in Lower Flow Rate Regime

Rigorous analytical treatment is complicated for film coefficients due to the complicated geometry of a bed. Some informations useful in interpreting the rate data, however, are obtained from the equation of motion and that of continuity, as is discussed in what follows. A simplified modelling is then developed for the bed in zero flow rate regime.

2.1. Properties of the Sherwood number

Fluid is assumed incompressible, and the flow steady. Flow in packed beds is divided²⁾ into three regimes of a. Stokes flow or creeping flow for $Re = d_h \bar{u} / \nu \leq 2$, b. viscous boundary layer flow for $20 \leq Re \leq 200$, and c. turbulent flow for $Re \geq 2000$, where the numerical values are somewhat arbitrary. In the Reynolds numbers between each regime the flow is transitional from one regime to another.

For steady flow, the Navier-Stokes equations for fluid motion and the equations of continuity for scalar transport are given as follows¹⁹⁾ in dimensionless forms, where natural convection due to temperature or concentration difference is assumed absent:

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$$Re_p^*(V \mathbf{grad}) V = \nabla^2 V - 2f^* Re_p^* \mathbf{grad} P \quad (1)$$

$$(1/Pe_p^*) \nabla^2 c - V \mathbf{grad} c = 0 \quad (2)$$

where,

$$Re_p^* = d_p \bar{u} / \nu, \quad Pe_p^* = d_p \bar{u} / \mathcal{D}_M, \quad V = \bar{v} / \bar{u},$$

$$P = p / \pi, \quad \mathbf{grad} = d_p \mathbf{grad}, \quad \nabla^2 = d_p^2 \nabla^2 \quad (3)$$

and π is the pressure drop of packed bed per d_p . Also, the pressure drop is defined²⁾ on the basis of average interstitial velocity $\bar{u} (= U/\epsilon_f)$. Thus, $\pi = \Delta p(d/L) = 2f^* \rho \bar{u}^2$. Eq.(1) gives V and P when combined with

$$\mathbf{div} V = 0 \quad (4)$$

where $\mathbf{div} = d_p \mathbf{div}$. Several properties of geometrically similar packed beds are discussed as follows by utilizing the above relations.

a. The limiting case of $V \rightarrow 0$: The second term in the left-hand side of Eq.(2) is negligible compared with the first term, and

$$\nabla^2 c = 0 \quad (5)$$

The limiting Sherwood number, Sh_{po} , is obtained by solving this steady diffusion equation under proper boundary conditions. Eq.(5) has the same order as Eq.(2), and is able to satisfy all the boundary conditions necessary.

b. The steady Stokes flow regime: As is well known, the left-hand side of Eq.(1) is negligible compared with the right-hand side, so that the following equation is obtained by applying the Blake-Kozeny equation²⁾ for f^* :

$$\nabla^2 V - [150(1 - \epsilon_f)^2 / \epsilon_f^3] \mathbf{grad} P = 0 \quad (6)$$

For geometrically similar packed beds ϵ_f remains constant, and no parameter other than this is included in Eq.(6). Thus, the velocity field is maintained analogous for any Re_p^* in this flow regime, and the only parameter which specifies the concentration field in the beds is Pe_p^* from Eq.(2). Since the concentration fields remain analogous for the same Pe_p^* , a single correlating curve is obtained for the steady Stokes flow regime when Sh_p is plotted against Pe_p^* . This relation is quite helpful in interpreting experimental rate data.

c. The regime of viscous boundary layer flow:

The range of $Re_h = 2 \sim 20$ is the transition from steady Stokes flow to viscous boundary layer flow. For $Re_h \geq 20$, V is a function of Re_p^* from Eq.(1). The concentration field is, thus, a function of Re_p^* and Pe_p^* , leading to the relation that Sh_p is also a function of these two (as alternative parameters, one may take Re_p^* and Sc , or Pe_p^* and Sc).

Before going to the next step, the concentration driving force to define the film coefficient will briefly be mentioned here, since this has frequently been confused. Usually a packed bed is regarded as a medium with a film capacity coefficient $k_f a$, and a differential mass balance is taken for the flowing fluid through the bed. The mean concentration of fluid effective to this balance is obviously the flow-average or the cup-mixing concentration.³⁾ Thus, even for the limiting case of zero flow rate the mean fluid con-

A. Cross sectional view of a dilute bed
B. Concentric sphere model
C. Packed bed of all active spheres

Fig. 1 Modelling of packed beds

centration should be taken as the cup-mixing concentration, since normalized velocity V remains unchanged irrespective of the absolute value of $\bar{u}$ in steady Stokes flow.

2.2. Modelling of dilute bed in lower flow rate regime

A dilute packed bed in which active spheres are dispersed uniformly in dummy spheres may be expressed as shown in Fig. 1-A, where flow is steady and its direction is conveniently taken downward. The concentration of transferring material changes sharply around the active spheres, and only gradually apart from them, particularly in a location like ABCDE, shown in the figure. At the limiting case of zero flow rate the concentration change along the region BCDE is rather small, and may be approximated by a mean value of c_o . With this mean value, the scheme of mass transfer at zero flow rate is approximated by the model shown in Fig. 1-B, where mass transfer takes place steadily from the inner active sphere (surface concentration c_s , and radius a) to the concentric outer shell (concentration c_o , radius b^* , and assume $c_s > c_o$) through the spherical shell of dummy sphere bed with effective diffusivity $\mathcal{D}_{eff}$ for the transferring material.

With this modelling Sh_{po} is calculated in the next section to interpret the behaviour of film coefficient in the lower flow rate regime.

3. Sh_{po} for a Dilute Bed with Dilution Ratio τ

3.1. Formulation for Sh_{po}

As stated in 2.1.a, the basic differential equation, Eq.(5), to give Sh_{po} is as follows in spherical coordinates:

$$d^2(rc)/dr^2 = 0 \quad (5a)$$

The boundary conditions are (ref. Fig. 1-B)

$$c = c_s \text{ at } r = a, \text{ and } c = c_o \text{ at } r = b^* \quad (5b)$$

The solution of Eq.(5a) to satisfy Eq.(5b) is

Fig. 2 Effective diffusivity of packed beds

$$c = \left(\frac{1/r - 1/b^*}{1/a - 1/b^*} \right) c_s + \left(\frac{1/a - 1/r}{1/a - 1/b^*} \right) c_o \quad (7)$$

The rate of mass transfer on the surface of an active sphere is

$$N = -\mathcal{D}_{eff} \left(\frac{dc}{dr} \right)_{r=a} = \frac{\mathcal{D}_{eff}}{a} \cdot \frac{c_s - c_o}{1 - a/b^*} \quad (8)$$

On the other hand, the volume mean concentration $\bar{c}_V$ of the spherical shell from $r=a$ to $r=b^*$ is given by

$$\bar{c}_V = 4\pi \int_a^{b^*} r^2 c dr / \frac{4}{3} \pi (b^{*3} - a^3)$$

or

$$\frac{c_s - \bar{c}_V}{c_s - c_o} = \frac{1}{(1/a - 1/b^*)} \left(\frac{1}{a} - \frac{3}{2} \frac{b^{*2} - a^2}{b^{*3} - a^3} \right) \quad (9)$$

To define the film coefficient of mass transfer on the active surface, many workers^{8, 14, 15, 17, 21} utilize $(c_s - c_o)$ as the driving force. Thus, from Eq.(8) one has

$$N = k_{fo}(c_s - c_o) = \frac{\mathcal{D}_{eff}}{a} \frac{c_s - c_o}{1 - a/b^*} \quad (10)$$

or

$$Sh_{peo} = \frac{k_{fo} d_p}{\mathcal{D}_{eff}} = \frac{2}{1 - \xi^*}; \quad \xi^* = \frac{a}{b^*} \quad (11)$$

When $(c_s - \bar{c}_V)$ is taken as the driving force, one gets

$$Sh_{peo} = \frac{2}{1 - \frac{3}{2} \cdot \frac{1}{1 + 1/\xi^*(1 + \xi^*)}} \quad (12)$$

The rigorous driving force is $(c_s - \bar{c})$ as stated in 2.2 where $\bar{c}$ is the cup-mixing concentration, the determination of which is quite difficult. Since the concentration gradient is highest on the surface of the active sphere, and the velocity gradient effective to calculate $\bar{c}$ is also largest there, $\bar{c}$ is located somewhere in between c_o and $\bar{c}_V$. Therefore, simply by approximating $\bar{c}$ by the arithmetic mean of these two limiting values one has

$$c_s - \bar{c} = c_s - (c_o + \bar{c}_V)/2 \quad (13)$$

Fig. 3 Graphical expression of Eqs.(14), (19) and (20)

and

$$Sh_{peo} = \frac{k_{fo} d_p}{\mathcal{D}_{eff}} = \frac{2 + \xi^*}{1 - \xi^*} - \frac{\xi^*}{2 + \xi^*} \quad (14)$$

Also, from the definition of γ there is a relation that

$$\xi^* = \frac{a}{b^*} = \left(\frac{1 - \epsilon_f}{\gamma} \right)^{1/3} \quad (15)$$

3.2. Properties of Sh_{peo}

The effective diffusivity collected from several sources^{10, 13} is shown in Fig. 2 as the relation of $\mathcal{D}_{eff}/\epsilon_f \mathcal{D}_M$ vs. ϵ_f . In the same figure ξ defined as follows is also shown.

$$\xi = (1 - \epsilon_f)^{1/3} \quad (16)$$

where ξ is a parameter corresponding to the mean fluid thickness on the surface of spherical packings as shown in Fig. 1-C. For usual packed beds $\epsilon_f < 0.6$, and $\xi > 0.7$. This means that the channels through the usual beds are tortuous enough to justify the concept of Perkins and Johnston¹³. Thus, according to Hoogschagen⁵, $\mathcal{D}_{eff}$ is taken as follows:

$$\mathcal{D}_{eff}/\epsilon_f \mathcal{D}_M = 1/\chi, \quad \chi = 1.5 \quad (17)$$

Also, as obvious from Figs. 1-B and 1-C, b^* should be greater than about $2b$ for $\mathcal{D}_{eff}$ being approximated by Eq.(17). This restriction corresponds to the following relation from Eqs.(15) and (16):

$$\gamma = (\xi/\xi^*)^3 \geq 8 \quad (18)$$

When γ is greater than this approximate value, one has (with $Sh_{po} = k_{fo} d_p / \mathcal{D}_M$)

$$Sh_{peo} = (1.5/\epsilon_f) Sh_{po} \quad (19)$$

At the limiting case⁸ of $\xi^* \rightarrow 0$, $Sh_{peo} \rightarrow 2$ from Eq.(14), and all the driving forces of Eq.(10) through Eq.(13) converge to $(c_s - c_o)$. At another limiting case of $\gamma \rightarrow 1$ all the packings in the bed are active, and $a/b^*(=\xi^*)$ converges to $a/b(=\xi)$. Accordingly

the Sherwood number, Sh_{po} for this usual active bed is given from Eq.(14) by taking $\mathcal{D}_M$ and ξ instead of $\mathcal{D}_{eff}$ and ξ^* respectively, or

$$Sh_{po} = \frac{k_f d_p}{\mathcal{D}_M} = \frac{2 + \xi}{1 - \xi} - \frac{\xi}{2 + \xi} \quad (20)$$

Eqs.(14), (19) and (20) are shown graphically in **Fig. 3**, where $\tau=10^3$ roughly corresponds to the case of a single active sphere placed in a dummy sphere bed with $D_T/d_p \approx 10$ and $L/d_p \approx 10$. Sh_{po} is seen to be quite high for the usual bed with all active spherical packings.

4. Film Coefficient of Mass Transfer in Lower Flow Rate Regime

4.1. Literature survey

Theoretical approach to determine the film coefficient is rather rare in contrast to the many empirical correlations. Of these, Kitaura and Tanaka⁸⁾ give the following theoretical equation for the Stokes flow regime, by assuming an addition relation of the contributions from purely molecular diffusion and from convective transfer:

$$Sh_p = 2\epsilon_f^{3/2} + 1.775\epsilon_f f(\xi) Pe_p^{1/3} \quad (21)$$

where

$$f(\xi) = \left(\frac{1 - \xi^5}{2 - 3\xi + 3\xi^5 - 2\xi^6} \right)^{1/3}$$

This relation is applicable to the mass transfer of a single active sphere placed in an infinitely wide dummy sphere bed, where $\mathcal{D}_{eff}$ is approximated by $\epsilon_f^{3/2} \mathcal{D}_M$. For the same flow regime of all active sphere-packed beds Pfeffer¹⁴⁾ gives the following theoretical equation corresponding to the convective transfer, i.e., $Pe_p \gg 1$:

$$Sh_p = 1.26 f(\xi) Pe_p^{1/3} \quad (22)$$

Carberry et al.^{4,10)} derived Eq.(23) from the concept of developing boundary layer. Comparing it with experimental data, the equation is shown⁴⁾ applicable to $Re_p^* = 0.5 \sim 900$.

$$Sh_p = 1.15 (Re_p^*)^{1/2} Sc^{1/3} \quad (23)$$

Also, the following Frössling type equation is adopted by several authors^{8,16,18,20)} to correlate the data of wide flow regime. Of these Ranz obtains a good correlation by taking a jet flow with 10.73 times greater velocity than the superficial velocity.

$$Sh_p = A + B Re_p^{1/2} Sc^{1/3} \quad (24)$$

4.2. Preliminary phenomenological considerations

To correlate experimental film coefficients it is reasonable to divide the flow regimes into Stokes flow and developing laminar boundary layer flow. In the former flow regime Sh_p for geometrically similar beds is the sole function of Pe_p^* , as stated in 2.1.b. For a dilute bed shown in Fig. 1-A the thickness of diffusion layer r_f decreases gradually from b^* to, for example, r_1 as $\bar{u}$ (or Pe_p^*) gradually increases from zero to a certain value. As Pe_p^* increases further, r_f decreases more and more due to the increasing influence of convective transfer over

that of molecular diffusion. By way of r_2 and b as shown in Fig. 1-C, r_f finally shrinks to the space close to the surface of active sphere for $Pe_p^* \gg 1$. Accordingly, as a rough measure of mass transfer behaviour in the Stokes flow regime, three mass transfer mechanisms are considered to exist, i.e., (a) the regime of molecular diffusion controlling, corresponding to $r_f \geq r_2$, where Pe_p^* is smaller than about 10 as shown later, (b) that of convective diffusion controlling ($r_f \leq b$, and $Pe_p^* \gg 1$), where the concentration boundary layer is developing on the active surface, and (c) the regime of transition ($b \leq r_f \leq r_2$) from (a) to (b).

Since $Re_p^* \lesssim$ order 1 in the Stokes flow regime, the mechanism of convective diffusion controlling ($Pe_p^* = Re_p^* Sc \gg 1$) appears only in liquid systems ($Sc \gg 1$) and not in gaseous systems ($Sc \approx 1$). This is the greatest difference between gas and liquid. In other words, with increasing Re_p , the mechanisms for gaseous systems change from the molecular diffusion controlling to the developing laminar boundary layer flow, and for liquid systems there is an additional mechanism of convective diffusion controlling in between these two.

For geometrically dissimilar dilute beds with $\tau \geq 8$ the following correction seems useful in the molecular-diffusion controlling Stokes-flow regime. Here the representative length is taken as d_p , since a physically significant phenomenon to determine the Sherwood number is how many multiples of d_p the diffusion layer extends out of the active sphere. Also $\mathcal{D}_{eff}$ is taken as the effective diffusivity of the diffusion layer, and $\bar{u}$ as the effective convective velocity. With these quantities two dimensionless groups are defined as follows, and are utilized to establish the correlation of mass transfer data:

$$Sh_{pe} = k_f d_p / \mathcal{D}_{eff}, \quad Pe_{pe}^* = \bar{u} d_p / \mathcal{D}_{eff}$$

4.3. Correlation of mass transfer data available so far

The film coefficients of camphor sublimation⁹⁾ by downwards flowing air stream ($Sc = 2.8$) from single camphor sphere ($d_p = 10$ and 15 mm) placed in a dummy urea-resin sphere bed is shown in **Fig. 4** as the relation of Sh_{pe} vs. Pe_{pe}^* . ϵ_f utilized here is 0.260, 0.395 and 0.476. Points A_1 , A_2 and A_3 in the figure correspond to $Re_h = 20$ under given ϵ_f , and other points of B_1 , B_2 , and B_3 to $Re_h = 2$. Several properties of mass transfer are observed from the figure as follows: (a) For $Re_h \geq 20$ Sh_{pe} is proportional to $Pe_{pe}^{*1/2}$ or $Re_p^{*1/2}$, and is given by the Carberry type correlation, Eq.(23). The correlation is thus considered typical in the developing laminar boundary layer regime. (b) At point P , where $Pe_{pe}^* \approx 50$, three curves with different ϵ_f converge to a single curve C and it approaches the limiting Sherwood number Sh_{po} for $\tau \approx 10^3$ (ref. Eq.(20)) with decreasing Pe_{pe}^* further. The curve C located in the left-hand side of point P is thus considered the correlation curve for the molecular diffusion control-

Fig. 4 Sh_{pe} vs. Pe_{pe}^* plot for camphor sublimation by down-flowing air (data from Kitaura, et al.⁹)

Fig. 5 Sh_{pe} vs. Pe_{pe}^* plot for naphthalene sublimation by upflowing air (data from Bar-Ilan and Resnick¹¹); Three curves with $\epsilon_f = 0.260 \sim 0.476$ are from Fig. 4.)

ling Stokes flow regime. (c) The curves A_1B_1 , A_2B_2 and A_3B_3 have different gradients depending upon the magnitude of ϵ_f . These are the transition regime from Stokes flow to laminar boundary layer flow. Their upper and lower Pe_{pe}^* are bounded by upper and lower Re_h of 20 and 2, respectively. The

difference in the gradients thus means no more than a transition. (d) Smooth transition takes place for $\epsilon_f \approx 0.43$, since the gradient of transition curve is nearly the same as that of the Carberry type equation. This rather casual situation is considered responsible for the Carberry equation⁴) being apparently appli-

Fig. 6 Sh_{pe} vs. Pe_{pe}^* plot for liquid systems

Fig. 7 j_{Dh} vs. Re_h plot for gas and liquid systems

cable down to $Re_p^* \approx 0.5$. Finally (e) Sh_{pe} is not correlated by Pe_{pe}^* in the developing boundary layer regime.

Fig. 5 is the correlation of naphthalene sublimation data¹⁾ by up-flowing air stream ($Sc = 2.57$) from cylindrical naphthalene pellets ($d_p = 4.1$ and 8.2 mm, $\gamma \approx 5$). The data for $Pe_{pe}^* \geq 50$ are quite normal in parallel with those of Kitaura (ref. Fig. 4), since Sc is nearly the same in both cases. Points B_1^* and B_2^* correspond to $Re_h = 2$ under given ϵ_f of 0.402 and 0.468 , respectively. On the left-hand side of these points the flow is in the Stokes regime, and Sh_{pe} is seen decreasing

due to natural convection induced by density difference in the up-flowing air stream. Sh_{pe} decreases rapidly even below the limiting Sherwood number of about 4.6 for $\gamma = 5$. Fig. 6 is for liquid phase data,^{7,11)} showing a smooth transition at $Pe_{pe}^* \approx 50$ from the developing concentration boundary layer regime to the molecular diffusion regime (both in Stokes flow). This smooth transition is considered coming from a reason similar to the Carberry equation, since ϵ_f is at 0.40 . The data for the branch of $Pe_{pe}^* \leq 50$ are fairly close to those for gaseous systems, so that the reasoning given in section 4.2 is considered reasonable.

The right-hand side branch of $Pe_{pe}^* \gtrsim 50$ is for the developing concentration boundary layer regime characteristic of liquid systems, and is not encountered in gaseous systems.

The theory of Kitaura et al.⁸⁾, Eq.(21), is shown as dotted lines. Their theory assumes $\mathcal{D}_{eff}$ as the diffusivity outside of an active sphere, irrespective of the magnitude of Pe_{pe}^* . This assumption gives a sound approach for smaller Pe_{pe}^* , where the diffusion layer extends far from the active sphere, but reveals contradictions when $Pe_{pe}^* \gg 1$, where the diffusion layer shrinks to the surface of the active sphere and the effective diffusivity is not $\mathcal{D}_{eff}$ any more, but $\mathcal{D}_M$. Also, the assumption of smooth transition like Eq.(21) is still open to further study, as is obvious from the rather abrupt transition at $Pe_{pe}^* \approx 50$ for gaseous systems shown in Fig. 4. The Frössling type expression, Eq.(24), is also seen, for the same reason, to give a rough approximation of the transition.

Fig. 7 is an alternative expression of the above data as j_{Dh} vs. Re_h . The gas system is for the sublimation data by Kitaura et al.⁹⁾. The reason why the data for $\epsilon_f=0.260$ deviate rapidly from the correlation, $j_{Dh}=0.75/Re_h^{1/2}$, is seen to come from the transition to the molecular diffusion controlling Stokes flow regime and nothing more. The reason for the data for $\epsilon_f=0.476$ being located apparently on the correlation, $j_{Dh}=1.0/Re_h^{2/3}$ (this is for liquid systems of high Sc), comes also from the casual location of this kind of transition path. The data by Bar-Ilan¹⁾ also show a similar tendency for $Re_h \gtrsim 2$. Thus, this kind of behaviour is seen to be inherent to the transition encountered in dilute beds. For liquid systems shown in the figure no transition has been measured yet, although it is possible for quite small Re_h .

5. Conclusion

1. The minimum Sherwood number, Eq.(14), is obtained by modelling a packed bed as Fig. 1.
2. From the basic equations for flow of fluid and scalar transport, mass transfer in steady Stokes flow is shown to be divided into two regimes of molecular diffusion controlling (smaller Pe_{pe}^*) and developing concentration boundary layer controlling (higher Pe_{pe}^*). The Sherwood number in the regimes is shown to be a sole function of the Péclet number, and those in the developing laminar boundary layer flow regime a function of the Péclet and Schmidt numbers.
3. Two dimensionless numbers of Sh_{pe} and Pe_{pe}^* are found to correlate both gas and liquid data well for the molecular diffusion controlling regime, by an average single relation which approaches its limiting value, Sh_{peo} .
4. For gaseous systems the molecular diffusion controlling Stokes flow regime starts to transfer at $Re_h=2$, and ends at about $Re_h=20$, where the Carberry type relation is applicable. The transition path strongly depends on the magnitude of ϵ_f .

5. For liquid systems in Stokes flow there is a developing concentration boundary layer controlling regime when $Pe_{pe}^* \gg 1$, which is inherent only in liquid systems and is not encountered in gaseous systems.

6. j_{Dh} vs. Re_h plot of gaseous film coefficients shows, for $2 \lesssim Re_h \lesssim 20$, anomalous behaviour which depends upon the magnitude of ϵ_f , as indicated in Fig. 7. This anomaly is shown to be inherent only in dilute beds, and comes from flow transition.

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Nomenclature

D_T	= bed diameter	[cm]
$\mathcal{D}_M$	= molecular diffusivity	[cm ² /sec]
$\mathcal{D}_{eff}$	= effective diffusivity of packed bed	[cm ² /sec]
L	= bed height	[cm]
P	= p/π ; normalized pressure	[—]
Pe_p	= $U d_p / \mathcal{D}_M$; Péclet number	[—]
Pe_p^*	= $\bar{u} d_p / \mathcal{D}_M$; "	[—]
Pe_{pe}^*	= $\bar{u} d_p / \mathcal{D}_{eff}$; "	[—]
Re_p	= $d_p \bar{U} / \nu$; Reynolds number	[—]
Re_p^*	= $d_p \bar{u} / \nu$; "	[—]
Re_h	= $d_h \bar{u} / \nu$; "	[—]
Sc	= $\nu / \mathcal{D}_M$; Schmidt number	[—]
Sh_p	= $k_f d_p / \mathcal{D}_M$; Sherwood number	[—]
Sh_{po}	= Sh_p at $\bar{u}=0$	[—]
Sh_{pe}	= $k_f d_p / \mathcal{D}_{eff}$; Sherwood number	[—]
Sh_{peo}	= Sh_{pe} at $\bar{u}=0$	[—]
U	= superficial velocity	[cm/sec]
V	= $\bar{v} / \bar{u}$; normalized velocity vector	[—]
a	= radius of active sphere	[cm]
b	= ref. to Fig. 1-C	[cm]
b^*	= ref. to Fig. 1-A	[cm]
c	= concentration of transferring component	[g or mol/cc]
c_o	= c at $r=b^*$ or b	[g or mol/cc]
c_s	= c at $r=a$	[g or mol/cc]
$\bar{c}$	= flow rate mean concentration	[g or mol/cc]
$\bar{c}_V$	= volume mean concentration	[g or ol/cc]
d_h	= $[2\epsilon_f/3(1-\epsilon_f)]d_p$, hydraulic diameter	[cm]
d_p	= diameter of packing	[cm]
f	= friction factor of packed bed based on U	[—]
f^*	= same as above based on $\bar{u}$	[—]
k_f	= film coefficient of mass transfer	[cm/sec]
k_{fo}	= k_f at $\bar{u}=0$	[cm/sec]
p	= local pressure	[dyne/cm ²]
r	= radius	[cm]
$\bar{u}$	= U/ϵ_f , interstitial velocity	[cm/sec]
$\bar{v}$	= local velocity vector	[cm/sec]
div	= divergence operator	[1/cm]
div	= d_p div, dimensionless divergence operator	[—]
grad	= gradient operator	[1/cm]
grad	= d_p grad, dimensionless gradient operator	[—]
γ	= dilution ratio, [total number of bed spheres/ number of active spheres]	[—]
ϵ_f	= void fraction of packed bed	[—]
μ	= absolute viscosity	[poise]
ν	= μ/ρ , kinematic viscosity	[cm ² /sec]
ξ	= a/b , radius ratio	[—]
ξ^*	= a/b^* , radius ratio	[—]
π	= $\Delta p \cdot d_p / L$, press. drop per d_p for packed bed	[dyne/cm ²]
ρ	= density of fluid	[g/cc]
χ	= tortuosity factor of packed bed	[—]
Δp	= total press. drop of packed bed with height L	[dyne/cm ²]

∇^2 = Laplacian operator [1/cm²]
 ∇^2 = $d_p^2 \nabla^2$, dimensionless Laplacian operator [—]

Literature cited

- 1) Bar-Ilan, M. and W. Resnick: *Ind. Eng. Chem.*, **49**, 313 (1957)
- 2) Bird, R. B., W. E. Stewart and E. N. Lightfoot: "Transport Phenomena", p 198, 1st ed., John Wiley & Sons, Inc. (1960)
- 3) *ibid.*, p 391
- 4) Carberry, J. J.: *AIChE Journal*, **6**, 460 (1960)
- 5) Gunn, D. J.: *Trans. Inst. Chem. Engrs*, **47**, T351 (1969)
- 6) Kato, K., H. Kubota and C. Y. Wen: *CEP Symp. Ser.*, **66**, No. 105, 87 (1970)
- 7) Kawazoe, K., Y. Takeuchi and T. Hashimoto: *Kagaku Kōgaku* **32**, 175 (1968)
- 8) Kitaura, Y. and H. Tanaka: *ibid.*, **28**, 740 (1964)
- 9) Kitaura, Y., H. Tanaka, K. Harada and K. Araki: *ibid.*, **29**, 146 (1965)
- 10) Kimura, M., K. Ueda and T. Ofuka: *ibid.*, **21**, 2, (1957)
- 11) Mixon, F. O. and J. J. Carberry: *Chem. Eng. Sci.*, **13**, 30 (1960)
- 12) Miyauchi, T. and T. Nomura: *Kagaku Kōgaku*, paper submitted
- 13) Perkins, T. K., and E. C. Johnston: *Soc. Pet. Eng. Journal*, Mar. 70 (1963)
- 14) Pfeffer, Robert: *Ind. Eng. Chem., Fund.*, **3**, 380 (1964)
- 15) Pfeffer, R. and John Happel: *AIChE Journal*, **10**, 605 (1964)
- 16) Ranz, W. E.: *Chem. Eng. Prog.*, **48**, 247 (1952)
- 17) Rowe, P. N.: *Intern. J. Heat Mass Transfer*, **6**, 989 (1963)
- 18) Rowe, P. N. and K. T. Claxton: *Trans. Inst. Chem. Engrs*, **43**, T321 (1965)
- 19) Schlichting, Herman: "Boundary Layer Theory", translated by J. Kestin, 1st ed., p 52, McGraw Hill, New York (1955)
- 20) Shirai, Takashi: Ph. D. dissertation, Tokyo Inst. Tech. (1955)
- 21) Zabrodsky, S. S.: *Intern. J. Heat & Mass Transfer*, **6**, 23, 991 (1963)

GAS ABSORPTION WITH CHANGE IN INTERFACIAL AREA*

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The gas absorption rates in expanding and shrinking surfaces are measured with CO₂-water and CO₂-NaOH aqueous solution systems by using a liquid-film type absorber in which liquid flows along conical, reverse conical or hemispherical surfaces. The experimental results are compared with three theoretical models. MODEL II (stretch model) agrees best with the experiments in all cases.

Introduction

There are many cases of mass transfer through an interface in which area expands or shrinks. For example, mass transfer through the interface of a growing bubble or drop, gas absorption through an oscillating interface and others are such cases. When the bubble or drop is formed, large mass transfer rates through the interface are observed⁹⁾. In these phenomena, the change of interfacial area, the circulation of liquid, the instability of the interface, etc., have great influence on mass transfer rate, and it is difficult to treat all of them theoretically.

Regarding the change in interfacial area, a few models have been proposed. "Crude model" was used by Groothuis and Kramers⁵⁾ and Beek and Kramers²⁾ (MODEL I in this paper). In this model, it is assumed that a fresh surface element is formed by expanding the interfacial area, that the interface is wrapped with surface elements of different

ages, and that there is no mass transfer between these elements. "Stretch model" was used by Beek and Kramers²⁾ and Angelo et al.¹⁾ (MODEL II). In this model, the surface element is stretched by expanding the interfacial area, and a velocity component normal to the interface is produced.

In this paper, these models are applied to gas absorption with and without chemical reaction in a liquid film flowing along conical surfaces and a hemispherical surface, and the results are compared with experimental results.

Experimental Apparatus and Procedure

Experimental apparatus is shown schematically in Fig. 1. The liquid was fed from the level tank to the film-absorber through a thermostat controlled at 25°C. In the absorber, gas was absorbed by a liquid film, and the level of liquid leaving the absorber was adjusted by the level controller. The liquid flow rate was measured at the outlet of the level controller. CO₂ gas was fed from the gas-holder to the film-

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