Theory on Effective Diffusivities of Bi-disperse Porous Solids at Constant Pressure and Influence of an Inert Gas*

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Synopsis

For predicting effective diffusivities of bi-disperse porous media, an improved model in which tortuosity factors of the macro- and micropores are taken into account is proposed on the basis of the Wakao and Smith random pore model. The diffusion rates of binary gases at constant pressure and the effective diffusivity are derived according to the model.

By the use of the experimental data of Wakao and Smith and of Henry *et al.*, tortuosity factors of their porous solids are determined approximately on the basis of the model. The theoretical effective-diffusivities calculated by using the tortuosity factors agree better with the experimental ones over the pressure range 0.0006 to 12 atm than those calculated on the basis of the random pore model.

In order to examine the influence of an inert gas on the diffusion process, solutions to the Stefan-Maxwell equations for equimolar counter diffusion in a ternary gas mixture through a bi-disperse porous medium are derived on the basis of the model; the diffusion rate and the effective diffusivity in this system are determined reasonably.

The expressions for the simple one-dimensional diffusion mentioned above are extended to those for the radial diffusion in a spherical shell.

I. Introduction

Overall rate of gaseous reduction of iron oxide pellets is controlled not only by chemical reaction between iron oxide and reducing gas but also by counter diffusions of reducing and product gases through the gas film and the porous shell. And especially the latter diffusion step has a great influence on the overall rate in general.¹⁾ Therefore, evaluation of effective diffusivities of iron oxide pellets is important in order to analyze the overall rate quantitatively. There are many other solid-gas reactions in which diffusion through the porous body may play a role as the rate-controlling step; for example, gasification of coke and reaction processes with catalyst pellets.

Up to the present, many experimental results and theoretical analyses about diffusion rates through porous bodies and effective diffusivities have been reported.²⁻²¹⁾ Scott and Dullien²⁾ developed a parallel pore model; diffusion rates at constant pressure through capillaries or through the pores of a solid were derived from an equation of diffusion in a transition region where both molecular diffusion and Knudsen diffusion controlled together the overall rate of the system. Wakao and Smith⁴⁾ proposed a random pore model for bi-disperse porous solids which allowed for parallel and interconnected diffusion at constant pressure through the micro- and macropores in the transition region. Kawazoe *et al.*⁷⁾ and Henry *et al.*⁸⁾ showed that the parallel pore model predicted

experimental values of diffusion rates through bi-disperse porous bodies as well as mono-disperse ones better than the random pore model. However, their bi-disperse porous bodies can be regarded as mono-disperse ones. Therefore, their conclusion should be reexamined when both of the diffusions through macro- and micropores contribute to the overall rates in much the same degree. There were also some experimental analyses⁹⁻¹¹⁾ based on a dusty gas model which took into account the effect of pressure gradient but did not relate directly to the pore structure of a porous medium such as the pore-radii distribution and the tortuosity factors.

In the present paper, an improved model in which tortuosity factors of the macro- and micropores are taken into account is proposed on the basis of the random pore model.⁴⁾ The diffusion rates of binary gases at constant pressure through bi-disperse porous media and the effective diffusivities are derived according to the present model. The theoretical effective-diffusivities calculated by using experimental data reported previously^{4,8)} are compared with the experimental effective-diffusivities. In order to examine the influence of an inert gas on the diffusion process, solutions to the Stefan-Maxwell equations for equimolar counter diffusion in a ternary gas mixture at constant pressure through bi-disperse porous media are derived on the basis of the model; the diffusion rate and the effective diffusivity in this system are presented.

II. Effective Diffusivities of Bi-disperse Porous Media

Figure 1 illustrates the diffusion system for bi-disperse porous media at constant pressure. The dotted semisquares represent the unit constituent particles containing micropores and the spaces between them are the macropores. The area void fractions are assumed to be the same as the volume void fractions, as introduced in the random pore model.⁴⁾ Then the area fractions of macropores, micropores and solid on a plane perpendicular to the direction of diffusion are given by the respective volume fractions, namely, ϵ_{ma} , ϵ_{mi} , and ϵ_s . They are related as

$$\epsilon_{ma} + \epsilon_{mi} + \epsilon_s = 1. \quad \dots\dots\dots(1)$$

It is supposed after the random pore model⁴⁾ that the

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- 1: Diffusion through the macropores
- 2: Diffusion through the micropores
- 3: Diffusion through the macro- and micropores in series

Fig. 1. Diffusion mechanisms in bi-disperse porous media.

sample is cut at the plane and the two surfaces are rejoined. Then the diffusions through 1) the macropores, 2) the micropores, and 3) the macro- and micropores in series may be set up with respective areas of 1) ε_{ma}^2 , 2) $(1-\varepsilon_{ma})^2$, and 3) $2\varepsilon_{ma}(1-\varepsilon_{ma})$ per unit total area on the rejoined plane. In the second case, however, the effective void area of micropores per unit area in the particles is $\varepsilon_{mi}^2/(1-\varepsilon_{ma})^2$.

The Stefan-Maxwell equations for one-dimensional diffusion in a ternary gas mixture A-B-C at constant pressure through straight capillaries are given by^{6,22)}

$$\frac{P}{RT} \frac{dx_A}{dz} = -\frac{N_A^+}{D_{KA}} + \frac{x_A N_B^+ - x_B N_A^+}{D_{AB}} + \frac{x_A N_C^+ - x_C N_A^+}{D_{AC}}, \quad (2)$$

$$\frac{P}{RT} \frac{dx_B}{dz} = -\frac{N_B^+}{D_{KB}} + \frac{x_B N_A^+ - x_A N_B^+}{D_{AB}} + \frac{x_B N_C^+ - x_C N_B^+}{D_{BC}}, \quad (3)$$

where N^+ denotes diffusion rate per unit area in the capillaries; these equations are used in the *Chapters V* and *VI*. The mole fractions are related as

$$x_A + x_B + x_C = 1. \quad (4)$$

The equation of diffusion rate of component A in a binary gas mixture A-B is, therefore, given by Eqs. (2) and (4) as follows:^{2,4)}

$$N_A^+ = -\frac{P}{RT} \frac{1}{(1-\alpha^+ x_A)/D_{AB} + 1/D_{KA}} \frac{dx_A}{dz}, \quad (5)$$

where, $\alpha^+ \equiv 1 + N_B^+/N_A^+$, $\dots$ (6)

$$D_{KA} = (2/3)\bar{v}_A a = 9700a \sqrt{T/M_A}. \quad (7)$$

Now Eq. (5) is applied to the model of Fig. 1, by

adding the contributions to diffusion of A for each of the three mechanisms after taking into account tortuosity factors of the macro- and micropores. The resultant equation of diffusion rate per unit cross-sectional area of the porous body is (see *Appendix*)

$$N_A \frac{RT}{P} = -\left\{ \frac{\varepsilon_{ma}^2}{\tau_{ma}} \tilde{D}_{ma} + \frac{\varepsilon_{mi}^2}{\tau_{mi}} \tilde{D}_{mi} + \frac{4\varepsilon_{ma}(1-\varepsilon_{ma})}{\tau_{ma}/\tilde{D}_{ma} + \tau_{mi}[(1-\varepsilon_{ma})^2/\varepsilon_{mi}^2]/\tilde{D}_{mi}} \right\} \frac{dx_A}{dz}, \quad (8)$$

where,

$$\tilde{D}_{mj} \equiv [(1-\alpha x_A)/D_{AB} + 1/D_{KA,mj}]^{-1} \quad (mj = ma, mi), \quad (9)$$

$$\alpha \equiv 1 + N_B/N_A. \quad (10)$$

Integration of Eq. (8) from $z=0$ to L gives

$$N_A \frac{RTL\alpha}{PD_{AB}} = \sum_{mj=ma,mi,ma-mi} E_{mj} \times \ln \left\{ \frac{1-\alpha x_{A2} + D_{AB}/D_{KA,mj}}{1-\alpha x_{A1} + D_{AB}/D_{KA,mj}} \right\}, \quad (11)$$

where,

$$E_{mj} \equiv \begin{cases} \varepsilon_{mj}^2/\tau_{mj} & (mj = ma, mi), \\ \frac{4\varepsilon_{ma}(1-\varepsilon_{ma})}{\tau_{ma} + \tau_{mi}(1-\varepsilon_{ma})^2/\varepsilon_{mi}^2} & (mj = ma-mi), \end{cases} \quad (12)$$

$$D_{KA,ma-mi} \equiv \frac{\tau_{ma} + \tau_{mi}(1-\varepsilon_{ma})^2/\varepsilon_{mi}^2}{\tau_{ma}/D_{KA,ma} + \tau_{mi}[(1-\varepsilon_{ma})^2/\varepsilon_{mi}^2]/D_{KA,mi}}, \quad (13)$$

$$x_{A1} = x_A|_{z=0}, \quad x_{A2} = x_A|_{z=L}, \quad (14)$$

and $D_{KA,ma}$ and $D_{KA,mi}$ denote Knudsen diffusivities of a gas A in the macro- and micropores, respectively. When $\varepsilon_{ma}=0$ or $\varepsilon_{mi}=0$, Eq. (11) becomes much the same form as the following equation based on the parallel pore model:²⁾

$$N_A \frac{RTL\alpha}{PD_{AB}} = \frac{\varepsilon_{mj}}{\tau_{mj}^*} \ln \left\{ \frac{1-\alpha x_{A2} + D_{AB}/D_{KA,mj}}{1-\alpha x_{A1} + D_{AB}/D_{KA,mj}} \right\} \quad (mj = ma \text{ or } mi). \quad (15)$$

And when $\tau_{ma}=\tau_{mi}=1$, it agrees with the equation based on the random pore model.⁴⁾

Up to this time, the effective diffusivity defined below has been used for analyzing experimental and theoretical results on diffusion processes at nearly constant pressure*

$$N_A RT/P = -D_{eff} dx_A/dz. \quad (16)$$

Integration of this equation from $z=0$ to L gives

* The following equation is generally used for non-equimolar diffusion:

$$N_A RT/P = -\{D_e/(1-\alpha x_A)\} dx_A/dz. \quad (16-a)$$

After integrating this equation from $z=0$ to L at constant pressure, comparison of the resultant equation with Eq. (17) gives the following relation:

$$D_e = D_{eff} \alpha (x_{A1} - x_{A2}) \ln \{(1-\alpha x_{A1})/(1-\alpha x_{A2})\}. \quad (17-a)$$

Therefore the effective diffusivity generally used for non-equimolar diffusion, D_e , can be calculated from the present results by using Eq. (17-a). Equation (17) is used in this paper as the equation defining effective diffusivity, because it can be used in common with *Chapters V* and *VI* for equimolar counter diffusion in a ternary gas mixture.

$$N_A R T / P = D_{\text{eff}} (x_{A1} - x_{A2}) / L. \quad \dots\dots\dots(17)$$

Then, the effective diffusivity D_{eff} is written by combining Eqs. (11) and (17) as follows:

$$D_{\text{eff}} = \frac{D_{AB}}{\alpha(x_{A1} - x_{A2})} \sum_{mj=ma,mi,ma-mi} E_{mj} \times \ln \left\{ \frac{1 - \alpha x_{A2} + D_{AB}/D_{KA,mj}}{1 - \alpha x_{A1} + D_{AB}/D_{KA,mj}} \right\}. \quad \dots\dots\dots(18)$$

In the region of Knudsen-diffusion control at low pressures, namely, in the case of $D_{AB} \gg D_{KA,mj}$ ($mj=ma, mi$), Eq. (18) becomes

$$D_{\text{eff}} = \frac{\varepsilon_{ma}^2}{\tau_{ma}} D_{KA,ma} + \frac{\varepsilon_{mi}^2}{\tau_{mi}} D_{KA,mi} + \frac{4\varepsilon_{ma}(1 - \varepsilon_{ma})}{\tau_{ma}/D_{KA,ma} + \tau_{mi}[(1 - \varepsilon_{ma})^2/\varepsilon_{mi}^2]/D_{KA,mi}}. \quad \dots\dots\dots(19)$$

In the region of molecular-diffusion control at high pressures, namely, in the case of $D_{AB} \ll D_{KA,mj}$ ($mj=ma, mi$), Eq. (18) becomes

$$D_{\text{eff}} = \frac{D_{AB}}{\alpha(x_{A1} - x_{A2})} \left\{ \sum_{mj=ma,mi,ma-mi} E_{mj} \right\} \ln \left\{ \frac{1 - \alpha x_{A2}}{1 - \alpha x_{A1}} \right\}. \quad \dots\dots\dots(20)$$

Because D_{KA} is independent of pressure as shown in Eq. (7), D_{eff} of Eq. (19) is either. On the other hand, because D_{AB} is inversely proportional to pressure in general, D_{eff} of Eq. (20) also is.

In the case of the parallel pore model, combination of Eqs. (15) and (17) gives the following effective diffusivity:

$$D_{\text{eff}} = \frac{D_{AB}}{\alpha(x_{A1} - x_{A2})} \frac{\varepsilon_{mj}}{\tau_{mj}^*} \ln \left\{ \frac{1 - \alpha x_{A2} + D_{AB}/D_{KA,mj}}{1 - \alpha x_{A1} + D_{AB}/D_{KA,mj}} \right\} \quad (mj = ma \text{ or } mi). \quad \dots\dots\dots(21)$$

III. A Method for Determining Tortuosity Factors Concerning Macro- and Micropores

When effective diffusivity is estimated from Eq. (18), tortuosity factors τ_{ma} and τ_{mi} should be known beforehand; an approximate method for determining them is proposed below.

If an arbitrary value is tentatively given to β and the following relation is assumed:

$$\tau_{ma} = \tau_{mi}/\beta = \tau_m, \quad \dots\dots\dots(22)$$

then combination of Eqs. (11) and (22) gives

$$\tau_m = (H_{ma} + H_{mi} + H_{ma-mi}) PD_{AB} / (N_A R T L \alpha), \quad \dots\dots\dots(23)$$

where,

$$\left. \begin{aligned} H_{ma} &= \varepsilon_{ma}^2 \ln \left\{ \frac{1 - \alpha x_{A2} + D_{AB}/D_{KA,ma}}{1 - \alpha x_{A1} + D_{AB}/D_{KA,ma}} \right\} \\ H_{mi} &= \frac{\varepsilon_{mi}^2}{\beta} \ln \left\{ \frac{1 - \alpha x_{A2} + D_{AB}/D_{KA,mi}}{1 - \alpha x_{A1} + D_{AB}/D_{KA,mi}} \right\} \end{aligned} \right\}, \quad \dots\dots\dots(24)$$

$$\begin{aligned} H_{ma-mi} &= \frac{4\varepsilon_{ma}(1 - \varepsilon_{ma})}{1 + \beta(1 - \varepsilon_{ma})^2/\varepsilon_{mi}^2} \\ &\times \ln \left\{ \frac{1 - \alpha x_{A2} + D_{AB}/D_{KA,ma-mi}^*}{1 - \alpha x_{A1} + D_{AB}/D_{KA,ma-mi}^*} \right\}, \quad \dots\dots\dots(25) \\ D_{KA,ma-mi}^* &= \frac{1 + \beta(1 - \varepsilon_{ma})^2/\varepsilon_{mi}^2}{1/D_{KA,ma} + \beta[(1 - \varepsilon_{ma})^2/\varepsilon_{mi}^2]/D_{KA,mi}}. \quad \dots\dots\dots(26) \end{aligned}$$

Now, if

$$I_{mj} \equiv H_{mj} / (H_{ma} + H_{mi} + H_{ma-mi}) \longrightarrow 1 \quad (mj = ma \text{ or } mi), \quad \dots\dots\dots(27)$$

then Eq. (23) can be approximated as follows:

$$\tau_m \rightarrow \frac{H_{mj} P D_{AB}}{N_A R T L \alpha} \doteq \begin{cases} \tau_{ma} & (mj = ma), \\ \tau_{mi}/\beta & (mj = mi). \end{cases} \quad \dots\dots\dots(28)$$

Therefore, when values of τ_m are plotted as a function of I_{ma} or I_{mi} , τ_{ma} , or τ_{mi} can be evaluated approximately from a point of intersection of a line suitable for those plots and the line $I_{ma}=1$ or $I_{mi}=1$.

IV. Examination Based on the Previous Experimental Results

The validity of the above-mentioned method for estimating effective diffusivity on the basis of the improved random pore model is examined below by using the experimental data on counter diffusion of the binary system N_2 - H_2 through bi-disperse porous bodies by Wakao and Smith⁴⁾ and Henry *et al.*⁸⁾ (see Table 1).

Figure 2 exemplifies the values of τ_m calculated from Eq. (23) by using the above-mentioned data as a function of I_{ma} , and values of τ_{ma} are determined by the method proposed in the last section. When any appropriate value is given to β , it is found from the forms of Eqs. (27) and (28) that the value of τ_{ma} or τ_{mi} can be determined irrespective of the value of β as $I_{ma} \rightarrow 1$ or $I_{mi} \rightarrow 1$. Therefore, in this figure $\beta=1$ is given. However the values of τ_{ma} for some porous bodies and the values of τ_{mi} for all the porous bodies in Table 1 cannot be determined by this method, because there are no data available near the region $I_{ma} \approx 1$ or $I_{mi} \approx 1$ and/or because the plots scatter considerably. Therefore, in these cases unity is tentatively given to the tortuosity factors as shown in Table 1, although it is unsatisfactory.*

Theoretical values of effective diffusivity based on the improved model are calculated from Eq. (18) by using those values of tortuosity factors. As two extreme cases, effective diffusivities in the regions of Knudsen and molecular diffusion controls are evaluated from Eqs. (19) and (20), respectively. Experimental values of effective diffusivity can be obtained through Eq. (17) under the experimental conditions. Theoretical values of effective diffusivity based on the random pore model can be calculated from Eq. (18) by substituting $\tau_{ma} = \tau_{mi} = 1$.

* When unity is given to τ_{mi} , tortuosity factor of the micropores is not taken into account in the present model. When $\tau_{ma} = \tau_{mi} = 1$, the present model reduces to the random pore model.⁴⁾

Table 1. Physical properties and tortuosity factors of the porous solids used by Wakao and Smith⁴⁾ and by Henry *et al.*,⁸⁾ their experimental conditions and *J*-values.

Solid No.	<i>L</i> (cm)	ϵ_{ma} (—)	ϵ_{mi} (—)	a_{ma} (Å)	a_{mi} (Å)	τ_{ma} (—)	<i>P</i> (atm)	<i>J</i> _{ma} (%)	<i>J</i> _{mi} (%)	<i>J</i> _{ma-mi} (%)	τ_{mj}^* (—)
A	1.26	0.63	0.17	15 000	25	1.12	1.00~ 4.81	98.8~95.4	0.2~ 0.6	1.1~ 4.0	1.69
B	1.26	0.45	0.27	2 300	24	1.17	1.26~12.0	94.7~76.5	1.3~ 5.7	4.1~17.8	2.22
C	1.30	0.34	0.33	1 100	23	1.11	1.92~12.4	85.8~63.5	4.7~12.3	9.5~24.2	2.49
D	1.27	0.18	0.39	460	23	1	1.05~11.5	62.7~36.5	20.0~34.5	17.3~29.0	2.63
E	1.26	0.09	0.42	370	23	1	1.68~10.9	27.2~14.1	52.4~62.3	20.4~23.6	1.38
1	1.661	0.303	0.468	4 300	85	1.36	0.00060~0.79	85.1~65.1	5.5~13.0	9.4~21.8	3.75
2	1.244	0.233	0.492	20 000	37	1.29	0.00066~0.79	97.7~76.4	1.0~10.7	1.3~12.8	4.98
3	1.816	0.223	0.444	18 000	37	1.06	0.00198~0.78	98.1~83.1	0.9~ 7.9	1.0~ 9.0	4.38
4	1.548	0	0.302	—	85	—	0.00069~0.79	0	1	0	3.22

Binary gases: A(N₂)–B(He)
A~E: Wakao and Smith⁴⁾ (Alumina) 24°C, *PD*_{AB}=0.697 atm·cm²/s
1~4: Henry *et al.*,⁸⁾ (1~3: Alumina, 4: Vycor) 25.8°C, *PD*_{AB}=0.703 atm·cm²/s
*J*_{ma}, *J*_{mi}, *J*_{ma-mi}: macro, micro and series contribution factors calculated by Eq. (29).
 $\tau_{mi}=1$, $\tau_{mj}^*=\tau_{mi}^*$ for Solids Nos. E and 4, $\tau_{mj}^*=\tau_{ma}^*$ for the others.

Fig. 2. Estimation of tortuosity factors of the porous solids by means of Eqs. (27) and (28).

In order to calculate the theoretical values of effective diffusivity based on the parallel pore model, it is necessary to evaluate the value of τ_{mj}^* in Eq. (21) beforehand. First, which is the controlling step, macro- or micropore diffusion, is roughly decided by comparing the following values of *J*_{ma} and *J*_{mi}. The percentage of contribution of each diffusion process to the value of effective diffusion is defined on the basis of Eq. (18) as follows:

$$J_{mj} \equiv \frac{100}{D_{eff}} \frac{D_{AB}}{\alpha(x_{A1}-x_{A2})} E_{mj} \times \ln \left\{ \frac{1-\alpha x_{A2}+D_{AB}/D_{KA,mj}}{1-\alpha x_{A1}+D_{AB}/D_{KA,mj}} \right\} \quad (\%)$$

(mj = ma, mi, ma-mi).(29)

The contribution factors *J*_{mj} thus calculated are also shown in Table 1 with reference to the corresponding pressure range. Secondly, the value of τ_{mj}^* (mj=ma or mi, depending on the decision) is so determined that the experimental values of *D*_{eff} are well reproduced by the theoretical values of *D*_{eff} calculated from Eq. (21) over the experimental pressure range. The values of τ_{mj}^* thus obtained are also shown in

Table 1. Figures 3 and 4 show the four kinds of effective diffusivities as a function of pressure; those are theoretical values based on the improved model, the random pore model, and the parallel pore model as well as experimental values of Wakao and Smith⁴⁾ (see Fig. 3) or Henry *et al.*,⁸⁾ (see Fig. 4). On the whole, theoretical values based on the improved model show better agreement with the experimental values over the experimental pressure range than those based on the other models.

Figures 5 and 6 show comparison of theoretical curves calculated by Eq. (18) as substitutes for the experimental values with those calculated by Eqs. (19) and (20) under the experimental conditions carried out by Wakao and Smith⁴⁾ and Henry *et al.*,⁸⁾ respectively. Which region the experimental data belong to, Knudsen-diffusion-control, transition, or molecular-diffusion-control regions, is examined in consideration of Figs. 3 and 4; it is shown that the experimental data for solids 1~4, D, and E belong to the part of transition region which is adjacent to Knudsen-diffusion-control region, those for solid A belong to the part of transition region which is adjacent to molecular-diffusion-control region, and those for solids B and C belong to the central part of transition region. The former situations are considered to be caused by the facts that the experiments for solids 1~4 were done at fairly low pressures less than 1 atm and solids D and E had very small macropore-radii. The experimental results for solids A, B, and C are thought to have reasonable tendency by taking into account the pressure ranges and the macropore radii.

One of the criteria, under what conditions diffusion through a porous body is described by the simple equation for Knudsen or molecular diffusion, is to compare the values of *D*_{AB} and *D*_{KA,mj} (mj=ma, mi), but it will depend on the properties of the porous body and the experimental conditions. The other criterion is to compare the experimental data with the theoretical curves calculated by Eqs. (19) and (20)

Fig. 3. Effective diffusivities as a function of pressure; comparison between theory and experimental data of Wakao and Smith.⁴⁾

Fig. 5. Comparison of theoretical curves calculated by Eq. (18) with those calculated by Eqs. (19) and (20) under the experimental conditions carried out by Wakao and Smith.⁴⁾

Fig. 4. Effective diffusivities as a function of pressure; comparison between theory and experimental data of Henry *et al.*⁸⁾

Fig. 6. Comparison of theoretical curves calculated by Eq. (18) with those calculated by Eqs. (19) and (20) under the experimental conditions carried out by Henry *et al.*⁸⁾

in such a figure as Figs. 5 or 6. As exemplified by Fig. 6, Eq. (19) for Knudsen diffusion approximates to Eq. (18) within an error of about 5% below the pressure of 0.01 atm for solid 1, 0.003 atm for solids 2 and 3, and 0.7 atm for solid 4.

V. Influence of an Inert Gas on Equimolar Counter Diffusion through Bi-disperse Porous Media

It is shown in the last section that diffusion through bi-disperse porous media is well described by the equation based on the improved random pore model. Now, influence of an inert gas (component C) on equimolar counter diffusion through such a body is investigated analytically on the basis of this model.

In this case, the following relations

$$N_C^+ = 0, \quad N_A^+ + N_B^+ = 0 \quad \dots\dots\dots(30)$$

are added with the basic equations for straight capillaries, Eqs. (2) to (4). Substitution of Eq. (30) into Eqs. (2) and (3) yields

$$\frac{P}{RTN_A^+} \frac{dx_A}{dz} = -\frac{1}{D_{KA}} - \frac{x_A + x_B}{D_{AB}} - \frac{x_C}{D_{AC}}, \dots\dots\dots(31)$$

$$\frac{P}{RTN_A^+} \frac{dx_B}{dz} = \frac{1}{D_{KB}} + \frac{x_A + x_B}{D_{AB}} + \frac{x_C}{D_{BC}}. \dots\dots\dots(32)$$

Combination of Eqs. (4), (31), and (32) gives the following equation for diffusion rate of component A:

$$N_A^+ = \frac{P}{RT} \frac{1}{(1/D_{KA} - 1/D_{KB}) + (1/D_{AC} - 1/D_{BC})x_C} \frac{dx_C}{dz}. \dots\dots\dots(33)$$

Equation (33) is applied to the present model in the same manner as that for the case of a binary gas mixture and the resultant equation for the diffusion rate per unit cross-sectional area of the porous media is

$$\begin{aligned} N_A RT/P &= -N_B RT/P \\ &= \left\{ \frac{\epsilon_{ma}^2}{\tau_{ma}} \tilde{D}'_{ma} + \frac{\epsilon_{mi}^2}{\tau_{mi}} \tilde{D}'_{mi} \right. \\ &\quad \left. + \frac{4\epsilon_{ma}(1-\epsilon_{ma})}{\tau_{ma}/\tilde{D}'_{ma} + \tau_{mi}[(1-\epsilon_{ma})^2/\epsilon_{mi}^2]/\tilde{D}'_{mi}} \right\} \\ &\quad \times \frac{dx_C}{dz}, \dots\dots\dots(34) \end{aligned}$$

where,

$$\tilde{D}'_{mj} = [(1/D_{KA,mj} - 1/D_{KB,mj}) + (1/D_{AC} - 1/D_{BC})x_C]^{-1} \quad (mj = ma, mi). \dots\dots\dots(35)$$

Here also, the total pressure is assumed to be constant. Then, integration of Eq. (34) from $z=0$ to L gives

$$\begin{aligned} N_A(1/D_{AC} - 1/D_{BC})RTL/P &= \sum_{mj=ma,mi} E_{mj} \\ &\times \ln \left\{ \frac{(1/D_{KA,mj} - 1/D_{KB,mj}) + (1/D_{AC} - 1/D_{BC})x_{C2}}{(1/D_{KA,mj} - 1/D_{KB,mj}) + (1/D_{AC} - 1/D_{BC})x_{C1}} \right\}, \dots\dots\dots(36) \end{aligned}$$

where, $D_{KB,ma-mi}$ is given from Eq. (13) by substituting B into A and x_{C1} and x_{C2} are given from Eq. (14) by substituting C into A.

Hara *et al.*⁽²³⁾ showed in the region of molecular diffusion that the steady state diffusion caused a certain gradient of concentration of a stagnant inert gas C.

Equation (36) implies the same diffusion behavior even through bi-disperse porous media in the transition region as well as in the region of molecular diffusion.

VI. Influence of an Inert Gas on Effective Diffusivity

Although the effective diffusivity in such a ternary system as mentioned in the last section can be easily derived by combining Eqs. (17) and (36), the resultant expression is hard to use as it is, because it contains four mole fractions, namely, x_{A1} , x_{A2} , x_{C1} , and x_{C2} . Therefore, an approximate expression for the effective diffusivity is derived below.

Equations (31) and (32) are rewritten by using Eq. (4) as follows:

$$\frac{P}{RTN_A^+} \frac{dx_A}{dz} = -\frac{1}{D_{KA}} - \frac{1}{D_{AB}} + \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}} \right) x_C, \dots\dots\dots(37)$$

$$\begin{aligned} \frac{P}{RTN_A^+} \left(\frac{dx_A}{dz} + \frac{dx_C}{dz} \right) &= -\frac{1}{D_{KB}} - \frac{1}{D_{AB}} \\ &+ \left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}} \right) x_C. \dots\dots\dots(38) \end{aligned}$$

Combination of the above two equations gives

$$\begin{aligned} N_A^+ \frac{RT}{P} &= G \left\{ \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}} \right) \frac{dx_C}{dz} \right. \\ &\quad \left. - \left(\frac{1}{D_{AC}} - \frac{1}{D_{BC}} \right) \frac{dx_A}{dz} \right\}, \dots\dots\dots(39) \end{aligned}$$

where,

$$\begin{aligned} G &\equiv \left[\frac{1}{D_{KA}} \left(\frac{1}{D_{AB}} - \frac{1}{D_{BC}} \right) - \frac{1}{D_{KB}} \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}} \right) \right. \\ &\quad \left. + \frac{1}{D_{AB}} \left(\frac{1}{D_{AC}} - \frac{1}{D_{BC}} \right) \right]^{-1}. \dots\dots\dots(40) \end{aligned}$$

The equation of diffusion rate per unit cross-sectional area of a bi-disperse porous medium can be derived from Eq. (39) on the basis of the present model. Integration of the above-mentioned equation from $z=0$ to L gives

$$\begin{aligned} N_A RTL/P &= \left\{ \frac{\epsilon_{ma}^2}{\tau_{ma}} G_{ma} + \frac{\epsilon_{mi}^2}{\tau_{mi}} G_{mi} \right. \\ &\quad \left. + \frac{4\epsilon_{ma}(1-\epsilon_{ma})}{\tau_{ma}/G_{ma} + \tau_{mi}[(1-\epsilon_{ma})^2/\epsilon_{mi}^2]/G_{mi}} \right\} \left\{ \left(\frac{1}{D_{AB}} \right. \right. \\ &\quad \left. \left. - \frac{1}{D_{AC}} \right) (x_{C2} - x_{C1}) - \left(\frac{1}{D_{AC}} - \frac{1}{D_{BC}} \right) (x_{A2} - x_{A1}) \right\}, \dots\dots\dots(41) \end{aligned}$$

where G_{mj} ($mj=ma, mi$) is given by Eq. (40) after replacing D_{KA} and D_{KB} by $D_{KA,mj}$ and $D_{KB,mj}$, respectively.

Now, the equimolar counter diffusion in the ternary system, H_2 - H_2O - N_2^* at 800°C through the solid 2 shown in Table I is taken as an example. When the H_2O concentration at $z=L$ is zero ($x_{B2}=0$) and the one at $z=0$ is relatively small ($x_{B1} \ll 1$),[†] it is

*, † Reduction of an iron oxide pellet is supposed. In the region of Knudsen diffusion, it is estimated from a report of Hara *et al.*⁽²⁴⁾ that the pressure on the reaction interface is about 1.28 (1.07) times as much as the pressure on the outer surface of the pellet being reduced with H_2 (CO) at 800°C. Under usual experimental conditions the diffusion process is considered to be in the transition region, and therefore the pressure of the system can be approximated to be constant in some cases.

Fig. 7. Relation between x_{C1} and x_{A1} under the equimolar counter diffusion of components A (H_2) and B (H_2O) through a bi-disperse porous solid (Solid 2)⁸⁾ calculated by Eqs. (36) and (43); component C (N_2) is stagnant.

found from Fig. 7 that the relation between x_{A1} and x_{C1} can be approximated by a straight line, i.e.,

$$x_{C2} - x_{C1} \doteq l(x_{A2} - x_{A1}), \quad \dots\dots\dots(42)$$

where the gradient l is approximately determined by Eq. (43), which is derived by combining Eqs. (36) and (41).

$$l \doteq (dx_{C1}/dx_{A1})_{x_{C1}=x_{C2}} = \frac{1/D_{AC} - 1/D_{BC}}{\left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}}\right) - \frac{\sum_{mj=ma,mi,ma-mi} E_{mj} (1/D_{KA,mj} - 1/D_{KB,mj}) + (1/D_{AC} - 1/D_{BC})x_{C2}}{\frac{\epsilon_{ma}^2}{\tau_{ma}} G_{ma} + \frac{\epsilon_{mi}^2}{\tau_{mi}} G_{mi} + \frac{4\epsilon_m(1-\epsilon_{ma})}{\tau_{ma}/G_{ma} + \tau_{mi}[(1-\epsilon_{ma})^2/\epsilon_{mi}^2]/G_{mi}}}} \quad \dots\dots\dots(43)$$

Then, combination of Eqs. (17), (41), and (42) gives the following effective diffusivity:

$$D_{eff} = \left\{ \frac{\epsilon_{ma}^2}{\tau_{ma}} G_{ma} + \frac{\epsilon_{mi}^2}{\tau_{mi}} G_{mi} + \frac{4\epsilon_m(1-\epsilon_{ma})}{\tau_{ma}/G_{ma} + \tau_{mi}[(1-\epsilon_{ma})^2/\epsilon_{mi}^2]/G_{mi}} \right\} \times \{ (1/D_{AC} - 1/D_{BC}) - (1/D_{AB} - 1/D_{AC})l \}. \quad \dots\dots(44)$$

This expression can be reduced to the following form when the porous medium is mono-disperse and consists of macropores or when the porous medium is bi-disperse but can be considered to be a mono-disperse body composed of macropores:

$$D_{eff} = \left(\frac{\epsilon_{ma}^2}{\tau_{ma}} \right) / \left\{ \left(\frac{1}{D_{AB}} + \frac{1}{D_{KA,ma}} \right) - \left(\frac{1}{D_{AB}} - \frac{1}{D_{AC}} \right) x_{C2} \right\}. \quad \dots\dots\dots(45)^*$$

* This equation was used in Ref. 25) (see Eq. (21) in Ref. 25)) in order to evaluate effective diffusivity in the case of a mono-disperse porous iron-oxide-pellet being reduced with H_2 - N_2 mixture.

** Equation (31) after substituting $x_C = 0$ is applied to the diffusion through a mono-disperse porous medium by taking into account tortuosity factor of the macropores, and we obtain

$$N_A \frac{RT}{P} = - \frac{\epsilon_{ma}^2}{\tau_{ma}} \frac{1}{1/D_{AB} + 1/D_{KA,ma}} \frac{dx_A}{dz}. \quad \dots\dots\dots(34-a)$$

It is also supposed that the sample is cut at a plane and the two surfaces are rejoined, and therefore the term ϵ_{ma}^2 is included in this equation. Combination of Eqs. (34-a) and (16) gives Eq. (46).

Effective diffusivity for equimolar counter diffusion in a binary gas mixture through a mono-disperse porous medium composed of macropores is given** as follows:

$$D_{eff} = (\epsilon_{ma}^2/\tau_{ma}) / (1/D_{AB} + 1/D_{KA,ma}). \quad \dots\dots(46)$$

Therefore, Eq. (45) is the modified form of Eq. (46).

Influence of an inert gas on equimolar counter diffusion through mono- and bi-disperse porous media is considered to be expressed approximately by using effective diffusivities given by Eqs. (45) and (44), respectively.

VII. In the Case of Radial Diffusion in a Spherical Shell

The expressions for the simple one-dimensional diffusion mentioned up to this section are extended to those for the radial diffusion in a spherical shell as follows:

It is assumed that the effect of curvature is negligible because the unit constituent particles are very small in comparison with the porous body (see Fig. 1). Then, the diffusion rate n_A through a spherical shell from a reaction interface r_1 to the sample surface r_o can be derived on the basis of the expressions for the simple one-dimensional diffusion by using the follow-

ing relation between n_A and N_A :

$$N_A = n_A / (4\pi r^2). \quad \dots\dots\dots(47)$$

After substituting r for z in Eqs. (16) and (8) and using Eq. (47), integration of the resultant equations from $r=r_1$ to r_o yields the equations corresponding to Eqs. (17) and (11) respectively, i.e.,

$$n_A = 4\pi D_{eff} \frac{P}{RT} \frac{x_{A1} - x_{Ao}}{1/r_1 - 1/r_o}, \quad \dots\dots\dots(48)$$

$$\frac{n_A RT \alpha}{4\pi P D_{AB}} \left(\frac{1}{r_1} - \frac{1}{r_o} \right) = \sum_{mj=ma,mi,ma-mi} E_{mj} \times \ln \left\{ \frac{1 - \alpha x_{Ao} + D_{AB}/D_{KA,mj}}{1 - \alpha x_{A1} + D_{AB}/D_{KA,mj}} \right\}. \quad \dots\dots\dots(49)$$

The latter is the expression for diffusion rate of component A in a binary A-B through a bi-disperse porous

sphere. Combination of Eqs. (48) and (49) gives the effective diffusivity which is the same as Eq. (18) after replacing x_{A1} and x_{A2} by x_{A1} and x_{A0} , respectively. Therefore, Eqs. (19) and (20) in the regions of Knudsen- and molecular-diffusion control are valid for the case of radial diffusion when x_{A1} and x_{A2} in Eq. (20) is replaced by x_{A1} and x_{A0} , respectively.

After substituting r for z in Eq. (34) and using Eq. (47), integration of the resultant equation from $r=r_i$ to r_o yields the equation corresponding to Eq. (36), i.e.,

$$\frac{n_A R T}{4 \pi P} \left(\frac{1}{r_i} - \frac{1}{r_o} \right) \left(\frac{1}{D_{AC}} - \frac{1}{D_{BC}} \right) = \sum_{mj=ma, mi, ma-mi} E_{mj} \times \ln \left\{ \frac{(1/D_{KA, mj} - 1/D_{KB, mj}) + (1/D_{AC} - 1/D_{BC}) x_{Co}}{(1/D_{KA, mj} - 1/D_{KB, mj}) + (1/D_{AC} - 1/D_{BC}) x_{Ci}} \right\} \quad (50)$$

This is the expression for diffusion rate of component A in a ternary system A-B-C, where component C is inert and components A and B counter-diffuse equimolarly through a bi-disperse porous sphere. Effective diffusivities for this case and the same case except that the porous sphere is a mono-disperse body composed of macropores are also given by Eqs. (44) and (45) respectively after replacing x_{C2} by x_{C0} .

VIII. Conclusions

Effective diffusivities of bi-disperse porous media at constant pressure are derived theoretically and influence of an inert gas is discussed. Conclusions obtained are as follows:

(1) For predicting effective diffusivities of bi-disperse porous media, an improved model in which tortuosity factors of the macro- and micropores are taken into account is proposed on the basis of the Wakao and Smith random pore model.⁴⁾ The diffusion rates of binary gases at constant pressure and the effective diffusivity are derived according to the model. A method for approximately determining tortuosity factors concerning macro- and micropores is also proposed.

(2) By the use of the experimental data of Wakao and Smith⁴⁾ and Henry *et al.*,⁸⁾ tortuosity factors of their porous solids are evaluated. The values of τ_{ma} for some porous bodies and the values of τ_{mi} for all the porous bodies used by the above-mentioned investigators cannot be determined by this method, and therefore unity is tentatively given to them. The theoretical effective-diffusivities calculated by using those values of the tortuosity factors agree better with the experimental ones over the pressure range 0.0006 to 12 atm than those calculated on the basis of the random pore model.

(3) In order to examine the influence of an inert gas on the diffusion process, solutions to the Stefan-Maxwell equations for equimolar counter diffusion in a ternary gas mixture through a bi-disperse porous medium are derived on the basis of the present model; the diffusion rate and the effective diffusivity in this system are given.

(4) The expressions for the simple one-dimen-

sional diffusion mentioned above are extended to those for the radial diffusion in a spherical shell. Expressions of the effective diffusivities are similar to those for the simple one-dimensional diffusion.

The present paper gives the initial steps to evaluate diffusion rate, effective diffusivity, and influence of an inert gas on them in the case of intraparticle diffusion through a bi-disperse porous iron-oxide-pellet being reduced with gas.

Nomenclature

- a : pore radius (cm)
- D_{eff} : effective diffusivity defined by Eq. (16) (cm²/s)
- D_K : Knudsen diffusivity (cm²/s)
- $D_{KA, ma-mi}$: quantity defined by Eq. (13) (cm²/s)
- D_{XY} : binary bulk diffusivity for a system X-Y (cm²/s)
- E_{mj} : quantities defined by Eq. (12)
- G : quantity defined by Eq. (40) (cm⁴/s²)
- I_{mj} : quantities defined by Eq. (27)
- J_{mj} : quantities defined by Eq. (29) (%)
- L : geometrical length of a porous solid (cm)
- l : quantity defined by Eq. (42) or (43)
- M : molecular weight (g/mol)
- N : diffusion rate per unit area of a porous solid (mol/(cm²·s))
- N^+ : diffusion rate per unit area in a capillary (mol/(cm²·s))
- n : diffusion rate through a spherical shell (mol/s)
- P : total pressure (atm)
- R : gas constant (atm·cm³/(mol·K))
- r : radial distance in a sphere (cm)
- T : temperature (K)
- $\bar{v}$: average molecular velocity (cm/s)
- x : mole fraction
- z : distance in the direction of simple one-dimensional diffusion (cm)
- α : quantity defined by Eq. (10)
- β : quantity defined by Eq. (22)
- ϵ : volume fraction
- τ_m : quantity defined by Eq. (23)
- τ_{mj} : tortuosity factors in the present model
- τ_{mj}^* : tortuosity factors in the parallel pore model

Subscripts

- $mj=ma, mi$: quantities associated with macro- and micropores
- $ma-mi$: quantities associated with the diffusion through macro- and micropores in series

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Appendix

The diffusion rate through macropores N_{A1} (see Fig. 1) is given from Eq. (5) by taking into account the tortuosity factor τ_{ma} as follows:

$$N_{A1} \frac{RT}{P} = - \frac{\varepsilon_{ma}^2}{\tau_{ma}} \frac{1}{(1-\alpha_1 x_A)/D_{AB} + 1/D_{KA,ma}} \frac{\Delta x_A}{\Delta z} \quad \text{.....(A-1)}$$

The diffusion rate through micropores N_{A2} is similarly obtained in consideration of the effective void area of micropores per unit area in the particles as

$$N_{A2} \frac{RT}{P} = - \frac{(1-\varepsilon_{ma})^2}{\tau_{mi}} \frac{\varepsilon_{mi}^2}{(1-\varepsilon_{ma})^2}$$

$$\times \frac{1}{(1-\alpha_2 x_A)/D_{AB} + 1/D_{KA,mi}} \frac{\Delta x_A}{\Delta z} \quad \text{.....(A-2)}$$

The diffusion rate from macropores to micropores, as shown in Fig. 1, can be divided into two parts, *i.e.*

$$N_{A3,1} \frac{RT}{P} = - \frac{\varepsilon_{ma}(1-\varepsilon_{ma})}{\tau_{ma}} \times \frac{1}{(1-\alpha_{3,1} x_A)/D_{AB} + 1/D_{KA,ma}} \frac{\Delta x_{A,1}}{\Delta z/2} \quad \text{... (A-3)}$$

and

$$N_{A3,2} \frac{RT}{P} = - \frac{\varepsilon_{ma}(1-\varepsilon_{ma})}{\tau_{mi}} \frac{\varepsilon_{mi}^2}{(1-\varepsilon_{ma})^2} \times \frac{1}{(1-\alpha_{3,2} x_A)/D_{AB} + 1/D_{KA,mi}} \frac{\Delta x_{A,2}}{\Delta z/2} \quad \text{... (A-4)}$$

for upper and lower half, respectively. Here, $\Delta x_{A,1}$ and $\Delta x_{A,2}$ are the respective differences of mole fraction and relate as

$$\Delta x_{A,1} + \Delta x_{A,2} = \Delta x_A \quad \text{.....(A-5)}$$

The total diffusion rate through macro- and micropores in series N_{A3} is written as

$$N_{A3,1} = N_{A3,2} = N_{A3}/2 \quad \text{.....(A-6)}$$

It is easily found that

$$\alpha_{3,1} = \alpha_{3,2} = \alpha_3 \quad \text{.....(A-7)}$$

Now, the following approximate relation is assumed:

$$1 + N_{Bk}/N_{Ak} = \alpha_k \doteq \alpha = 1 + N_B/N_A \quad (k = 1, 2, 3) \quad \text{.....(A-8)}$$

Then N_{A3} is given by combining Eqs. (A-3) to (A-8) and (9) as follows:

$$N_{A3} \frac{RT}{P} = -2\varepsilon_{ma}(1-\varepsilon_{ma}) \times \frac{2}{\tau_{ma}/\bar{D}_{ma} + \tau_{mi}[(1-\varepsilon_{ma})^2/\varepsilon_{mi}]/\bar{D}_{mi}} \frac{\Delta x_A}{\Delta z} \quad \text{.....(A-9)}$$

Equations (A-1) and (A-2) are rearranged by using Eqs. (A-8) and (9), and the resultant equations and Eq. (A-9) are inserted into the following relation:

$$N_A = N_{A1} + N_{A2} + N_{A3} \quad \text{.....(A-10)}$$

and then Eq. (8) is obtained.