UNSTEADY STATE DIFFUSION WITHIN POROUS SOLID PARTICLES*

— Correlation between Solid Shapes and Diffusion Rates —

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The unsteady state diffusion mechanism has been applied to the analysis or the interpretation for various heterogeneous mass transfer processes such as adsorption^{12,15}, dissolution-extraction^{4,11}, and the intraparticle diffusion controlled reaction^{5,8}, for example, ion exchange^{6,16}, within porous solid particles. On the other hand, each mathematical solution for unsteady state diffusion and heat conduction within various porous solids; i. e. sphere, infinite cylinder, infinite flat plate, etc. has been obtained by many investigators^{2,3,7,13,14}.

However, as for a fundamental problem, the correlation between various solid shapes and intraparticle diffusion or heat conduction rates, the rigorous numerical examination has not yet been established.

In this work, for the purpose of the establishment of the shape correlation, the analytical solutions for the unsteady state diffusion within various shaped solids were derived under the simplified conditions, and then the detailed numerical calculations were carried out.

Furthermore, the approximate estimations for the overall intraparticle diffusion rates within mixed solid particles of different shapes and sizes were examined.

As these results, the correlative values were confirmed to be in good agreements with the analytical values.

Theoretical Equations

First consider a finite ring porous solid of inner radius R_i , outer radius R_o and length $2L$.

Introducing the intraparticle effective diffusivity, D_e , and assuming constant shape and constant temperature during the operation, a material balance over a differential volume element within a ring solid yields the following equation in cylindrical coordinates:

$$\frac{\partial W}{\partial \theta} = D_e \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial W}{\partial r} \right) + \frac{\partial^2 W}{\partial z^2} \right] \quad (1)$$

An initial condition for the uniform concentration distribution is

$$W = W_0; R_i \leq r \leq R_o, -L \leq z \leq L, \theta = 0 \quad (2)$$

A boundary condition for the negligible external mass transfer resistance is

$$W = 0; r = R_o, R_i, z = \pm L, \theta > 0 \quad (3)$$

The solution of Eq.(1) for these conditions, i. e. the unsteady state intraparticle concentration distribution is

determined by multiplying each solution for infinite ring and infinite flat plate as follows.

$$\frac{W}{W_0} = 2\pi \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{k_n} \cos\left(\frac{z}{L} k_n\right) \frac{J_0(\beta j_m)}{J_0(\beta j_m) + J_0(j_m)} \times [j_0(j_m r/R_o) Y_0(j_m) - J_0(j_m) Y_0(j_m r/R_o)] \times \exp[-(j_m^2 + k_n^2 \gamma^2)(D\theta)] \quad (4)$$

where

$$J_0(\beta j_m) Y_0(j_m) - J_0(j_m) Y_0(\beta j_m) = 0, m = 1, 2, \dots \quad (5)$$

$$k_n = (2n - 1)\pi/2, n = 1, 2, \dots \quad (6)$$

$$\beta = R_i/R_o, \gamma = R_o/L \quad (7)$$

$$D = D_e/R_o^2 \quad (8)$$

$D\theta$ corresponds to Fourier number for mass transfer.

Also, Eq.(4) can be reduced to the solutions for finite cylinder, infinite ring or infinite cylinder by introducing $\beta=0, \gamma=0$ or $\beta=0$ and $\gamma=0$, respectively.

Now, the fraction of a specified material to be transferred out of a porous solid, f is defined as the following expression.

$$\left. \begin{aligned} f &= 1 - \frac{\bar{W}}{W_0}, \\ \bar{W} &= \frac{1}{V_p} \iiint W dV_p \\ &= \frac{1}{2\pi(R_o^2 - R_i^2)L} \int_{R_i}^{R_o} \int_{-L}^L W(2\pi r \cdot dr \cdot dz) \end{aligned} \right\} \quad (9)$$

Then, by introducing Eq.(4) into Eq.(9), the analytical expression for f is obtained as Eq.(10) shown in Table 1.

The fractions for the other shapes were shown together in Table 1.

For the systems where a material transfers into a solid from the outer surface, Eqs.(16) and (17) are given as the initial and the boundary conditions instead of Eqs. (2) and (3). Although, of course, each analytical expression for f is given by Eqs.(10) through (15).

$$W = 0; \theta = 0 \quad (16)$$

$$W = W_0; \text{ on the outer surface, } \theta > 0 \quad (17)$$

Numerical Considerations

Fig. 1 represents curves of the fraction, f against $D\theta$, whose derivatives correspond to the intraparticle diffusion rates, according to Eqs.(10) through (15). It is found that these curves spread over the extremely wide range.

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Table 1 Analytical solutions of f against $D\theta$ in a single solid of various shapes

ring	$f_r = 1 - \frac{8}{1 - \beta^2} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{j_m^2 k_n^2} \cdot \frac{J_0(\beta j_m) - J_0(j_m)}{J_0(\beta j_m) + J_0(j_m)} \exp[-(j_m^2 + k_n^2 \gamma^2)(D\theta)]$ (10)	$J_0(\beta j_m) Y_0(j_m) = J_0(j_m) Y_0(\beta j_m)$ $k_n = (2n - 1)\pi/2$
cylinder	$f_c = 1 - 8 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{j_m^2 k_n^2} \exp[-(j_m^2 + k_n^2 \gamma^2)(D\theta)]$ (11)	$J_0(j_m) = 0$ $k_n = (2n - 1)\pi/2$
sphere	$f_s = 1 - 6 \sum_{n=1}^{\infty} \frac{1}{k_n^2} \exp[-k_n^2(D\theta)]$ (12)	$k_n = n\pi$
infinite flat plate	$f_p = 1 - 2 \sum_{n=1}^{\infty} \frac{1}{k_n^2} \exp[-k_n^2(D\theta)]$ (13)	$k_n = (2n - 1)\pi/2$
infinite cylinder	$f_{c'} = 1 - 4 \sum_{m=1}^{\infty} \frac{1}{j_m^2} \exp[-j_m^2(D\theta)]$ (14)	$J_0(j_m) = 0$
infinite ring	$f_{r'} = 1 - \frac{4}{1 - \beta^2} \sum_{m=1}^{\infty} \frac{1}{j_m^2} \cdot \frac{j_0(\beta j_m) - J_0(j_m)}{J_0(\beta j_m) + J_0(j_m)} \exp[-j_m^2(D\theta)]$ (15)	$J_0(\beta j_m) Y_0(j_m) = J_0(j_m) Y_0(\beta j_m)$

$$\beta = R_i/R_0, \quad \gamma = R_0/L, \quad D = D_e/R_0^2, \quad m, n = 1, 2, 3, \dots$$

Fig. 1 Calculation results of Eqs. (10) through (15)

Fig. 3 Effect of γ on f in a single ring or cylindrical solid

Fig. 2 Effect of β on f in a single ring solid; $\beta=0$ corresponds to a cylindrical solid

Effects of β and γ on f for an Arbitrary Ring and Cylinder

Fig. 2 shows curves of f against β at different values of $D\theta$. The variation of f according to the change of β can be quantitatively evaluated.

Also, Fig. 3 shows that f varies in approximate proportion to γ .

The relationships shown in both figures are available for the estimation of f for rings and cylinders of various values of β and γ .

Shape Correlation for an Arbitrary Shaped Solid

As shown in Fig. 1, each curve of f against $D\theta$ is apart far from one another. However, by adopting the ratio, V_p/S_0 as the characteristic dimension of an arbitrary shaped solid instead of R_0 in Eq. (8), i. e. Eq. (18) instead of Eq. (8),

$$D^* = D_e/(V_p/S_0)^2 \quad (18)$$

Fig. 4 Calculation results of Eqs. (10) through (15) correlated by Eq. (18) instead of Eq. (8)

these curves approach closely as shown in Fig. 4, although they differ in the strict sense from one another, even if each V_p/S_0 is the same. However, above all, curves for finite cylinders and a curve for spheres coincide with very good accuracy. Also, each analytical value of f for rings can be approximated by that for a sphere, an infinite flat plate or their mean value corresponding to the variation of β and γ .

It was found that the above conclusions are similar to the shape correlation between catalyst particle shapes and the steady state catalytic effectiveness factor^{1,9,10}. In other words, generally $D\theta$ corresponds to Thiele modulus $\phi_0 = R_0 \sqrt{k a_i c_f^{n-1}/D_e}$ in a n th order catalytic reaction, and $D^*\theta$ to modified modulus $\phi = (V_p/S_0) \sqrt{k a_i c_f^{n-1}/D_e}$.

Shape Correlation for a Mixture of Solid Particles of Different Shape-Sizes

When the unsteady state diffusion rates per unit solid mass or volume are measured with use of the plural solid particles, if the shape or the size of these solid particles is different in every operation, for example, cylindrical solids of various length are employed, the overall rates may be varied in every occasion, and eventually the considerable errors are introduced and the false conclusions may be drawn from the analysis of experimental results, unless the relations among solid shapes employed are quantitatively known.

However, it has not yet established, how to prescribe the characteristic dimension for such mixed systems of solid particles and so the arithmetic mean of particle dimensions appears to be often used. Thus, for obtaining a rational quantitative estimation of the overall rates, the approximations of the overall fraction to be transferred for mixed solids were examined by the numerical calculations.

Now, the general expression of the overall fraction,

f_0 for mixed heterogeneous solids is defined by

$$f_0 = 1 - \frac{\sum_{j=1}^a [(1/V_p)_j] \iiint W dV_p}{\sum_{j=1}^a (W_0 V_p)_j} = \frac{\sum_{j=1}^a (W_0 \cdot f \cdot V_p)_j}{\sum_{j=1}^a (W_0 \cdot V_p)_j} \quad (19)$$

If both W_{0j} and D_{ej} for each mixed solid particle are equal, respectively, i. e. if homogeneous solids are mixed, Eq. (19) can be simplified to Eq. (20).

$$f_0 = \sum_{j=1}^a (n_j \cdot f_j); \quad n_j = V_{pj} / \sum_{j=1}^a V_{pj} \quad (20)$$

Eq. (20) is the definition for mixed homogeneous solid particles. Accordingly, in order to determine f_0 , it is required that the volume fraction, n_j and the fraction, f_j for each particle are known. However, the more the number of mixed particles is, the more inconvenient to obtain n_j and f_j becomes. Thus, the numerical examinations were carried out by the approximate estimation corresponding to Eq. (20).

In this case, the characteristic dimension was remodified as the ratio $\sum_{j=1}^a V_{pj} / \sum_{j=1}^a S_{0j}$ and Eq. (21) was adopted instead of Eq. (18).

$$D_m^* = D_e / \left(\sum_{j=1}^a V_{pj} / \sum_{j=1}^a S_{0j} \right)^2 \quad (21)$$

Furthermore, for a mixture of ring shape solids, the following β_m and γ_m as the overall representative β and γ were adopted according to Eqs. (21) and (22).

$$\frac{\sum_{j=1}^a V_{pj}}{\sum_{j=1}^a S_{0j}} = \frac{\sum_{j=1}^a [\alpha_j^3 (1 - \beta_j^2) / \gamma_j]}{\sum_{j=1}^a \{ \alpha_j^2 (1 + \beta_j) [(2/\gamma_j) + (1 - \beta_j)] \}} = \frac{(1 - \beta_m)}{2 + (1 - \beta_m) \gamma_m} R_{01} \quad (22)$$

$$\beta_m = 1 - \frac{\sum_{j=1}^a [\alpha_j^3 (1 - \beta_j^2) / \gamma_j]}{\sum_{j=1}^a [\alpha_j^2 (1 + \beta_j) / \gamma_j]} \quad (23)$$

$$\gamma_m = \frac{\sum_{j=1}^a [\alpha_j^2 (1 - \beta_j^2)]}{\sum_{j=1}^a [\alpha_j^3 (1 - \beta_j^2) / \gamma_j]} \quad (24)$$

$$\alpha_j = R_{0j} / R_{01}, \quad \beta_j = R_{1j} / R_{0j}, \quad \gamma_j = R_{0j} / L_j \quad (25)$$

For the information, the followig parameters with the arithmetic mean of each V_p/S_0 were examined.

$$D_m^* = D_e / [(1/a) \sum_{j=1}^a (V_p/S_0)_j]^2 \quad (26)$$

$$\frac{1}{a} \sum_{j=1}^a (V_p/S_0)_j = \frac{1}{a} \sum_{j=1}^a \left[\frac{(1 - \beta_j) \alpha_j}{2 + (1 - \beta_j) \gamma_j} \right] R_{01} = \frac{(1 - \bar{\beta}_m)}{2 + (1 - \bar{\beta}_m) \bar{\gamma}_m} R_{01} \quad (27)$$

$$\bar{\beta}_m = \frac{\sum_{j=1}^a \left[\frac{\alpha_j \beta_j}{2 + (1 - \beta_j) \gamma_j} \right]}{\sum_{j=1}^a \left[\frac{\alpha_j}{2 + (1 - \beta_j) \gamma_j} \right]} \quad (28)$$

$$\bar{\gamma}_m = \frac{\sum_{j=1}^a \left[\frac{2 + (1 - \alpha_j) + (1 - \beta_j) \gamma_j}{2 + (1 - \beta_j) \gamma_j} \right]}{\sum_{j=1}^a \left[\frac{\alpha_j (1 - \beta_j)}{2 + (1 - \beta_j) \gamma_j} \right]} \quad (29)$$

Table 2 Calculation results of Eq.(12) correlated by Eqs.(21) and (26) for a mixture of three through ten spheres of different diameters

a [—]	$D^*\theta$ [—]				f_0 [—] [Eq.(20)]	$f_0(D_m^*\theta)$ [—] [Eq.(21)]	$f_0(D_m^*\theta)$ [—] [Eq.(26)]	$f_0(D_m^*\theta)/f_0$ [—]	$f_0(D_m^*\theta)/f_0$ [—]	$(V_p/S_0)_{max}/(V_p/S_0)$ [—]
3	0.09	0.18	0.27		0.3571	0.3589	0.3925	1.005	1.099	1.732
3	0.18	0.27	0.36		0.4468	0.4681	0.4841	1.003	1.037	1.414
3	0.27	0.36	0.45		0.5393	0.5402	0.5500	1.002	1.020	1.291
3	0.36	0.45	0.54		0.5950	0.5956	0.6020	1.001	1.012	1.225
3	0.09	0.18	0.9		0.3472	0.3510	0.4354	1.011	1.254	3.162
4	0.18	0.27	0.36	0.45	0.4832	0.4857	0.5104	1.005	1.056	1.581
4	0.18	0.27	0.36	1.8	0.4741	0.4794	0.5555	1.011	1.172	1.897
5	0.045	0.09	0.108		0.2821	0.2840	0.3149	1.007	1.116	2.236
	0.135	0.162								
5	0.18	0.27	0.36		0.4947	0.4998	0.5488	1.010	1.109	3.162
	0.45	0.9								
8	0.09	0.108	0.135		0.3729	0.3751	0.4154	1.006	1.114	2.236
	0.162	0.18	0.27							
	0.36	0.45								
10	0.045	0.09	0.108		0.3100	0.3141	0.3966	1.013	1.279	3.464
	0.135	0.162	0.18							
	0.27	0.36	0.45	0.54

Fig. 5 Error with variation of δ for a mixture of two spheres; $(D^*\theta)_1 > (D^*\theta)_2$

Fig. 6 Error with variation of volume fraction (n_1) and $D^*\theta$ for a mixture of many spheres of two kinds diameters

For a mixture of cylindrical solids, β_m and $\bar{\beta}_m$ in the above equations become zero.

The results calculated by Eqs.(10) through (12) and Eqs.(20) through (29) indicated great differences between Eq.(21) and Eq.(26), as shown in **Table 2** and **Figs. 5** through **9**.

Also, the overall fraction f_0 for a mixture of various shapes (for example, spheres, cylinders and rings) of

different sizes was approximated by the following equation instead of Eq.(20).

$$f_0 \doteq f'_0(D_m^*\theta) = [nf_0(D_m^*\theta)]_s + [nf_0(D_m^*\theta)]_c + [nf_0(D_m^*\theta)]_r \quad (30)$$

where n is the volume fraction of the respective groups of spheres, cylinders and rings. One of results calculated by Eq.(30) is shown in **Table 3** with the correlative values calculated by Eq.(31) etc..

Fig. 7 Error with variation of $D\theta$ for a mixture of two cylinders, and its comparison with correlative value from Eq. (12) for a sphere

Fig. 9 Error with variation $D\theta$ and δ for a mixture of two rings of different β

$f_0 \doteq f_0''(D_m^*\theta) = [nf_0(D_m^*\theta)]_{s,c} + [nf_0(D_m^*\theta)]_r$ (31)
where $[f_0(D_m^*\theta)]_{s,c}$ for spheres and cylinders were calculated by Eq. (12) for spheres, and $[f_0(D_m^*\theta)]_r$ for rings was obtained as the arithmetic mean value of Eq. (12) for spheres and Eq. (13) for infinite flat plates.

Conclusions

For the correlation between an arbitrary shape of porous solid particle and the unsteady state intraparticle diffusion rate, V_p/S_0 instead of R as the characteristic dimension can be generally used. Above all, it was

Fig. 8 Error with variation $D\theta$ and δ for a mixture of two rings of different γ

confirmed that the analytical values, f for finite cylinders and a sphere coincide with very good accuracy. Also, for a mixture of porous solids of various sizes and shapes, it was found that the analytical values, f_0 can be estimated with good accuracy by using $\Sigma V_p/\Sigma S_0$ instead of V_p/S_0 for a single solid, when the ratios, $(V_p/S_0)_j/(V_p/S_0)_i$ are between 1 and about 1.5.

Nomenclature

a	= number of solid particles mixed	[—]
a_i	= internal surface area per unit volume of catalyst particle	[cm ² /cm ³]
c_f	= concentration of reactant in fluid bulk phase	[mole/cm ³]
D	= intraparticle diffusion parameter, defined by Eq. (8)	[1/sec]
D_e	= intraparticle effective diffusivity	[cm ² /sec]
D^*	= modified intraparticle diffusion parameter, defined by Eq. (18) for a single particle	[1/sec]
D_m^*	= modified overall intraparticle diffusion parameter, defined by Eq. (21) for a mixture of particles	[1/sec]
$\bar{D}_m^*$	= average intraparticle diffusion parameter, defined by Eq. (26) for a mixture of particles	[1/sec]
E	= error = $1 - (\text{correlative value}/\text{analytical value}) \times 10^2$	[%]
f	= fraction of a specified material to be transferred, defined by Eqs. (9) etc. for a single particle	[—]
f_0	= overall fraction of a specified material to be transferred, defined by Eq. (20) for a mixture of particles = f_{0c}, f_{0r}, f_{0s} etc.	[—]
$f_{0p,s}$	= overall fraction calculated by the arithmetic mean of Eq. (13) for infinite flat plates, and Eq. (12) for spheres	[—]
$f_0(D_m^*\theta)$	= overall fraction calculated by Eq. (21) and Eqs. in Table 1	[—]
$f_0(\bar{D}_m^*\theta)$	= overall fraction calculated by Eq. (26) and Eqs. in Table 1	[—]
$f_0'(D_m^*\theta)$	= overall fraction calculated by Eqs. in Table 1, Eqs. (21) and (30)	[—]
$f_0'(\bar{D}_m^*\theta)$	= overall fraction calculated by Eqs. in Table 1, Eqs. (26) and (30)	[—]

Table 3 Calculation results of Eqs. (30) and (31) for a mixture of spheres, cylinders and rings

spheres ($a_s=8$) (Table 2) $D^*\theta$ [—]	cylinders ($a_c=8$) (Fig. 7) $D^*\theta$ [—]		rings ($a_r=8$) (Figs. 8 and 9) $D^*\theta$ [—]		
0.09	$\gamma=0.5$	0.0625	$\beta=0.25$	$\gamma=0.5$	0.1003
0.108		0.125			0.4011
0.135		0.25		$\gamma=1$	0.1344
0.162		0.375			0.5378
0.18	$\gamma=2$	0.16	$\beta=0.5$	$\gamma=0.5$	0.2025
0.27		0.32			0.81
0.36		0.64		$\gamma=1$	0.25
0.45		0.96			1.0
f_0 [—] [Eq. (20)]	$f_0'(D_m^*\theta)$ [—] [Eq. (30)]	$f_0''(D_m^*\theta)$ [—] [Eq. (31)]	$f_0'(D_m^*\theta)/f_0$ [—]	$f_0''(D_m^*\theta)/f_0$ [—]	
0.4008	0.4063	0.4067	1.014	1.015	

$f_0''(D_m^*\theta)$ = overall fraction calculated by Eqs. in Table 1, Eqs. (21) and (31) [—]

J_0 = first kind Bessel function

j_m = roots of Eq. (5) or $J_0(j_m) = 0$

k = intrinsic reaction rate constant

$$\left[\left(\frac{\text{cm}^3}{\text{mole}} \right)^{n-1} \cdot \text{cm/sec} \right]$$

L = half length of a ring or a cylinder [cm]

n = apparent volume fraction of each mixed particle or reaction order [—]

R_i = inner radius of a ring [cm]

R_0 = outer radius or half-thickness of each particle [cm]

R_{01} = maximum R_0 of particles mixed [cm]

r = radial length coordinate [cm]

S_0 = apparent external surface area of an arbitrary shaped particle [cm²/particle]

V_p = apparent volume of an arbitrary shaped particle [cm³/particle]

W = intraparticle concentration of a specified material to be transferred [g/cm³ of particle]

W_0 = initial intraparticle concentration [g/cm³ of particle]

Y_0 = second kind Bessel function

z = axial length coordinate [cm]

β = ratio of inner to outer diameter of a ring = R_i/R_0 [—]

β_m = overall representative β , defined by Eq. (23) [—]

$\bar{\beta}_m$ = average representative β , calculated by Eq. (28) [—]

γ = ratio of outer diameter to length of a ring or cylinder = R_0/L [—]

γ_m = overall representative γ , defined by Eq. (24) [—]

$\bar{\gamma}_m$ = average representative γ , calculated by Eq. (29) [—]

δ = ratio of (V_p/S_0) of two particles (1, 2); $[(D^*\theta)_1/(D^*\theta)_2]^{1/2} \geq 1$ [—]

θ = operation time [sec]

subscripts:

c = cylinder

p = infinite flat plate

r = ring

s = sphere

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