Steady-State Transport in Diluted Catalysts

The transport in composite media obtained by dispersing a porous active catalyst inside an inert porous medium has been considered here. Since such systems show a wide variety of advantages, it is necessary to obtain the correct transport equations. Very dilute systems are considered (volume fraction of catalysts $\ll \frac{1}{3}$), a condition that any one dispersed catalyst microsphere cannot feel the influence of others arises. An averaged conservation equation at steady state is obtained under the above condition as well as the condition that any one microsphere can be randomly placed in the medium. Similarly, an effective diffusion coefficient has been obtained.

The results differ from the ones previously in use. The enhancement in the reaction rate on diluting a catalyst is seen to be much less than the values previously suggested although a qualitative similarity exists.

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SCOPE

Very often it is desirable to disperse the active catalyst into an inert medium. An averaged conservation equation as well as an effective diffusion coefficient have been determined for such systems. These are the necessary tools for studying any process occurring in such media.

CONCLUSIONS AND SIGNIFICANCE

In a diluted catalyst where only diffusion takes place in the inert matrix and diffusion and reaction take place in the active catalyst inclusion, an appropriately averaged equation has been derived. The results have been obtained from the first principles, with an error $\sim\phi^2$, where ϕ is the volume fraction of the active catalyst. This complements a previous work (Neogi and Ruckenstein, 1980) which is applicable at moderately high volume fraction and inapplicable at low volume fractions. Together they provide a basis for handling problems of mass transfer in dispersions, when at least diffusion occurs in both phases.

Together with an averaged conservation equation, an effective diffusion coefficient is defined. This enables one to estimate the joint mass transfer resistance and its enhancement due to reaction in the dispersed phase which is of common occurance.

Recently, some attention has been paid to the diffusion in an inert porous medium containing active catalyst particles which are themselves porous and imbedded into the inert matrix (Ruckenstein, 1970; Varghese and Wolf, 1980). It has been shown that the effective reaction rate in such dilution catalysts can increase over the undiluted form when the diffusion and reaction occur under identical conditions (Ruckenstein, 1970), as well as increase the life times of the catalyst when the pore mouth poisoning occurs (Varghese and Wolf, 1980).

In a problem which can be extended to the above case, Neogi and Ruckenstein (1980) justified the model for the conservation equation popularly used. They obtained an ensemble averaged conservation equation. If the microspheres are imbedded randomly in the inert material, then a concentration field and a conservation equation can be obtained which is an average over the all possible ways in which the microspheres can be arranged inside the inert medium. This averaging is statistical, where it is necessary to know in principle the probabilities of all arrangements of the microspheres. It has been referred to as the ensemble average. However, their analysis also shows the conditions under which the above ensemble average is not valid, namely at large volume fractions of the microspheres where the number of arrangements become restricted as does the applicability of a statistical average. Further, at low dilutions the intermicrosphere distances become large and any one microsphere cannot "see" others. Hence, a probability density function for the arrangement of all the microspheres can no longer be defined. However, Hinch (1977) has shown that the ensemble average reduces to a tractable form at low dilutions and one of the objectives here is to obtain an appropriately averaged conservation equation at low dilution of the catalyst. It is important because some of the beneficial effects of catalyst dilution occur at low volume fractions of the catalyst.

Following Batchelor (1970) one may argue that since one microsphere cannot feel the presence of others, particle-particle interactions may be neglected as the first approximation. This produces an error comparable to ϕ^2, where ϕ is the volume fraction of the active catalyst. Further, since one microsphere cannot see its neighbors, the concentration field it sees at infinite distances is the average concentration field $\langle C \rangle$. This $\langle C \rangle$ can be treated as a "constant concentration at infinity boundary condition" under the assumption that the length scales through which $\langle C \rangle$ changes significantly is $\gg$ the length scales over which the detailed concentration field changes due to one microsphere. This can be defended only when ϕ is small and when no contradictions appear in the final results (Batchelor, 1970; Hinch, 1977). We note that the error $\sim\phi^2$ is a tolerable one; for $\phi = \frac{1}{3}$, the error is 11%, and finally point out the main difference in how a microsphere views the average concentration field in an ensemble average at high values of ϕ. In the latter effectively the microsphere is seen to observe the average concentration field on its surface as proved by Neogi and Ruckenstein (1980), which to a good approximation amounts to a point sink approximation for a microsphere. Here it sees the average value only at infinity.

The average now is defined as

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$$\langle C \rangle (\mathbf{r}) = \int_V P^*(\mathbf{r}^*) C(\mathbf{r}|\mathbf{r}^*) d\mathbf{r}^* \tag{1}$$

where C is the concentration which also could be any other quantity, P^* is the probability of finding a particle centered at $\mathbf{r}^*$. $C(\mathbf{r}|\mathbf{r}^*)$ is the concentration at $\mathbf{r}$ when the particle lies with its center at $\mathbf{r}^*$. If the distribution is random $P^*(\mathbf{r}^*)$ is a constant and equal to $\phi/\frac{4}{3}\pi r_i^3$, where ϕ is the volume fraction of the particles, i.e., the catalyst, and r_i is the radius of these spherical particles. This provides the appropriate average.

There is also a considerable difference of opinion between the roles of various diffusion coefficients in the model that serves for the conservation equation (Ruckenstein, 1970; Varghese and Wolf, 1980). Further, these authors have also attempted to define an effective diffusion coefficient D_e. Their definitions differ. Much of these will be cleared up once the correctly averaged concentration equation is established. D_e is *defined* simply as

$$\langle \mathbf{j} \rangle = -D_e \langle \nabla C \rangle \tag{2}$$

The determination of D_e is an old problem that merits consideration on its own. Note that in Eq. 2 D_e is not arrived at from the averaged conservation equation which deals in the averaged concentration $\langle C \rangle$, but has to be defined independently.

We assume now that our system is made of active porous catalysts (microspheres) imbedded into an inert porous matrix. Only diffusion occurs inside the inert material which has a diffusion coefficient D. Inside the microsphere both diffusion (with a diffusion coefficient D^*) and reaction occur. The reactant is adsorbed on the pore walls and reacts through a first order kinetics. The reaction is the controlling step and the reaction rate is kC where k is the effective rate constant involving adsorption coefficient, intrinsic rate constant, etc.

AVERAGING CONSERVATION EQUATION

Only one particle in the form of an inert porous solid with active catalyst imbedded in it, is under consideration and the detailed conservation equation can be written as

$$0 = \epsilon D \nabla^2 C(\mathbf{r}|\mathbf{r}^*) + m(\mathbf{r}|\mathbf{r}^*) \tag{3}$$

where m is the sink strength. m is zero in the inert solid and a lumped quantity in the active material which we intend to determine. Averaging Eq. 3, following Eq. 1, we get

$$0 = \epsilon D \nabla^2 \langle C \rangle (\mathbf{r}) + \langle m \rangle (\mathbf{r}) \tag{4}$$

Further, from Eq. 1

$$\langle m \rangle (r) = \frac{\phi}{\frac{4}{3}\pi r_i^3} \int_{V_p} m(\mathbf{r}|\mathbf{r}^*) d\mathbf{r}^* = \frac{\phi}{\frac{4}{3}\pi r_i^3} M \tag{5}$$

where M is the rate of mass transferred to a microsphere and ϵ is the pore void fraction in the inert material.

It is now necessary to evaluate M. Since the microsphere cannot "see" others, it observes at infinity the average concentration $\langle C \rangle_\infty$ where the subscript ∞ has been introduced for convenience. Thus, to evaluate M, one has to solve the detailed conservation equation for the concentration C_i inside the microsphere, with the concentration and the flux continuous across its bounding surface S_p with the outside concentration field C_o. This concentration field C_o has to satisfy the local conservation equation and have a value $\langle C \rangle_\infty$ at infinite distances. M may now be evaluated from either C_i or C_o.

EVALUATING *M*

The conservation equation outside the microsphere is

$$\nabla^2 C_o = 0 \tag{6}$$

subject to boundedness and the condition that as $r \to \infty$, $C_o \to \langle C \rangle_\infty$, and the conditions

$$C_o = C_i \text{ on } S_p \tag{7}$$

$$-\epsilon D \frac{\partial C_o}{\partial r} = -\epsilon^* D^* \frac{\partial C_i}{\partial r} \text{ on } S_p \tag{8}$$

where ∇^2 is the Laplacian operator and ϵ and ϵ^* are the void fractions in the inert medium and the active catalyst. The conservation equation inside the microsphere is

$$D^* \nabla^2 C_i = k C_i \tag{9}$$

which has to satisfy Eqs. 7–8 and the condition of boundedness.

The solution to Eq. 6 becomes (Hobson, 1931)

$$C_o = \langle C \rangle_\infty - \left(\frac{r_i}{r}\right) \frac{2\langle C \rangle_\infty x i_1(x)}{2x i_1(x) + \alpha i_o(x)} \cdot V_1(\mu,\phi) \tag{10}$$

where x is the Thiele modulus of the microspheres $r_i\sqrt{k/D^*}$, i_k the modified spherical Bessel function of the first kind of kth order (Abramowitz and Stegun, 1972), r is the radial distance from the center of the microsphere, μ is the cosine of the polar angle, ϕ is the azimutual angle and V_1 is the spherical surface harmonic of first order (Hobson, 1931). α is the ratio $\epsilon D/\epsilon^* D^*$.

The solution to Eq. 9 becomes

$$C_i = \frac{\alpha \langle C \rangle_\infty}{2x i_1(x) + \alpha i_o(x)} i_o\left(r\sqrt{\frac{k}{D^*}}\right) \tag{11}$$

when in deducing Eqs. 10–11, the orthogonality property of V_k (Hobson, 1931) and the relation $d/dx\, i_o(x) = i_1(x)$, have been used.

Now since

$$M = 2\pi r_i^2 \int_{-1}^{1} \left[-D^* \epsilon^* \frac{\partial C_i}{\partial r}\right]_{r=r_i} d\mu \tag{12}$$

we get from Eqs. 5, 11 and 12

$$\langle m \rangle = \frac{-\phi}{r_i^2} \alpha \epsilon^* D^* \frac{x i_1(x)}{2x i_1(x) + \alpha i_o(x)} \langle C \rangle_\infty \tag{13}$$

Dropping the subscript ∞ and substituting Eq. 13 into Eq. 4, we get

$$0 = \nabla^2 \langle C \rangle - \frac{\phi}{r_i^2} \frac{x i_1(x)}{2x i_1(x) + \alpha i_o(x)} \langle C \rangle \tag{14}$$

Now noting that $i_o(x) = \sinh(x)/x$, and $di_o(x)/dx = i_1(x)$, Eq. 14 becomes

$$0 = \nabla^2 \langle C \rangle - \frac{3\phi}{r_i{}^2} \frac{\langle C \rangle}{2 + \alpha[x \coth(x) - 1]^{-1}} \tag{15}$$

Equation shows that for an averaged conservation equation it is more important to define an average reaction rate than an average diffusion coefficient. Further, the form of this average reaction rate in Eq. 15 is substantially different from the previous work at higher concentrations (Ruckenstein, 1970; Varghese and Wolf, 1980; Neogi and Ruckenstein, 1980).

AVERAGING THE FLUX

We investigate the relation

$$\langle \mathbf{j} \rangle + \frac{\epsilon}{\epsilon^*} D \langle \nabla C \rangle = \int_V P^*(\mathbf{r}^*) \left(\mathbf{j} + \frac{\epsilon}{\epsilon^*} D \nabla C\right) d\mathbf{r}^* \tag{16}$$

where the flux $\mathbf{j} = -\epsilon/\epsilon^* D\nabla C$ in the inert material and $\mathbf{j} = -D^* \nabla C$ in the active catalyst. In Eq. 16, we have expressed the flux in terms of the gradient of concentration, the latter being based on the pore volume of the active catalyst. This has been done to facilitate comparison with the performance in undiluted catalyst. On substituting the expression for the flux in different regions, we get

$$\langle \mathbf{j} \rangle + \frac{\epsilon}{\epsilon^*} D \langle \nabla C \rangle = \frac{\phi}{\frac{4}{3}\pi r_i^3} \left(\frac{\epsilon}{\epsilon^*} D - D^* \right) \int_{V_p} \nabla C d\mathbf{r}^* \tag{17}$$

Further, using the divergence theorem Eq. 17 becomes

$$\langle \mathbf{j} \rangle + \frac{\epsilon}{\epsilon^*} D \langle \nabla C \rangle = \frac{\phi}{\frac{4}{3}\pi r_i^3} \left(\frac{\epsilon}{\epsilon^*} D - D^* \right) \int_{S_p} \mathbf{n}_p C dS \tag{18}$$

where $\mathbf{n}_p$ is the unit normal vector on the microsphere surface S_p.

It is now necessary to evaluate the surface integral on the right hand side in Eq. 18. The method is the same as before. The conservation equations inside and outside for a single microsphere (Eqs. 6 and 9) are solved subject to the condition of boundness, Eqs. 7 and 8, and the condition that as $r \to \infty$, C_o approaches the average concentration field which in this case is described by a constant $\langle \nabla C \rangle_\infty$. The subscript ∞ has been added for clarity.

EVALUATING THE SURFACE INTEGRAL

On integrating the boundary condition at infinity, we get as $r \to \infty$, $C_o \to C_\infty + \mathbf{r} \cdot \langle \nabla C \rangle_\infty$, where C_∞ is a constant of integration. We note that the microsphere is axisymmetric to the direction $\langle \nabla C \rangle_\infty$ and $\mathbf{r} \cdot \langle \nabla C \rangle_\infty$ is equal to $r |\langle \nabla C \rangle_\infty| \mu$ where $\|$ denotes the magnitude of a vector and μ is the cosine of the polar angle starting from the direction $\langle \nabla C \rangle_\infty$. This axisymmetry can also be exploited in Eqs. 6 and 9, where ∇^2 becomes

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \mu} \left[(1 - \mu^2) \frac{\partial}{\partial \mu} \right].$$

Solution to Eq. 9 subject to boundness now becomes

$$C_i = \sum_{k=0}^{\infty} a_k i_k \left(r \sqrt{\frac{k}{D^*}} \right) P_k(\mu) \tag{19}$$

where $\{a_k\}$ are constants $P_k(\mu)$ are Legendre polynomials of order k. The unit vector $\mathbf{n}_p$ being

$$\mathbf{n}_p = \mu \mathbf{e}_\| + (1 - \mu^2)^{1/2} \mathbf{e}_\perp \tag{20}$$

where $\mathbf{e}_\|$ and $\mathbf{e}_\perp$ are unit vectors parallel and perpendicular to $\langle \nabla C \rangle_\infty$, we note that the detailed calculations show that the surface integral in Eq. 18 is only due to the second term $k = 1$ from Eq. 19. This results in great simplification since only a_1 needs to be known (Carslaw and Jaeger, 1959).

The solution to Eq. 6 subject to boundedness is

$$C_o = \sum_{k=0}^{\infty} (b_k r^k + c_k r^{-k-1}) P_k(\mu) \tag{21}$$

where b_k and c_k are constants and $b_o = C_\infty$, $b_1 = |\langle \nabla C \rangle_\infty|$ and $b_k = 0$ for all $k > 1$. The above relations for b_k satisfy the condition at infinity. On satisfying Eqs. 7 and 8 with 21, we get from Eq. 19

$$C_i = \frac{C_\infty \alpha i_o \left(r \sqrt{\frac{k}{D^*}} \right)}{\alpha i_o \left(r_i \sqrt{\frac{k}{D^*}} \right) + r_i \frac{d}{dr_i} i_o \left(r_j \sqrt{\frac{k}{D^*}} \right)} + \frac{3\alpha |\langle \nabla C \rangle_\infty| r_i \mu i_1 \left(r \sqrt{\frac{k}{D^*}} \right)}{r_i \frac{d}{dr_i} i_1 \left(r_i \sqrt{\frac{k}{D^*}} \right) + 2\alpha i_1 \left(r_i \sqrt{\frac{k}{D^*}} \right)} \tag{22}$$

where the relation $P_1(\mu) = \mu$ has been used. Dropping subscripts from C_i, C_∞ and $|\langle \nabla C \rangle_\infty|$ in Eq. 22, substituting Eqs. 20 and 22 into Eq. 18 we get

$$\langle \mathbf{j} \rangle + \frac{\epsilon}{\epsilon^*} D \langle \nabla C \rangle = \phi \left(\frac{\epsilon}{\epsilon^*} D - D^* \right) \frac{3\alpha \langle \nabla C \rangle i_1(x)}{x \frac{di}{dx}{}_1(x) + 2\alpha i_1} \tag{23}$$

since $|\langle \nabla C \rangle| \mathbf{e}_\| = \langle \nabla C \rangle$. Simplifying the Bessel functions in terms of hyperbolic sines and cosines Eq. 23 becomes

$$\langle \mathbf{j} \rangle + \frac{\epsilon}{\epsilon^*} D \langle \nabla C \rangle = \phi \left(\frac{\epsilon}{\epsilon^*} D - D^* \right) \cdot \frac{3\alpha \langle \nabla C \rangle}{\left[\frac{2 + x^2 - 2x \coth x}{x \coth x - 1} \right] + 2\alpha} \tag{24}$$

Comparing Eq. 24 with Eq. 2, we get

$$\frac{D_e}{D^*} = \alpha - \phi \frac{3\alpha(\alpha - 1)}{\left[\frac{2 + x^2 - 2x \coth x}{x \coth x - 1} \right] + 2\alpha} \tag{25}$$

This completes our task.

RESULTS

On averaging the conservation equation for the diluted catalyst, Eq. 15 is obtained. The effect of the imbedded active catalysts appear lumped as a reaction term.

Originally, Ruckenstein (1970) had proposed diluting a catalyst where the reactant has a low diffusion coefficient D^*. Since D^* is small, the overall reaction rate is small as well. Consider the conservation equation in a sphere of active catalyst,

$$0 = D^* \nabla^2 C - kC \tag{26}$$

subject to the boundary conditions of boundedness and $C = C_o$ on $r = r_o$, where r_o is the radius of the sphere. From symmetry, $\nabla^2 = 1/r^2\, \partial/\partial r\, (r^2/(\partial/\partial r))$. The solution to Eq. 26 also provides the total consumption of the reactants as $-\epsilon^* D^* \partial C/\partial r|_{r=r_o}$ when integrated over the surface of the sphere of radius r_o. In contrast to this, one may consider the case of a diluted catalyst sphere of radius r_o, containing inclusions of active catalysts of radii r_i. The conservation equation for this pellet is given by Eq. 15. The pellet is also subject to the conditions of $\langle C \rangle = C_o$ on $r = r_o$ and of boundedness. From symmetry, we get $\nabla^2 = 1/r^2\, \partial/\partial r\, (r^2(\partial/\partial r))$. $\langle C \rangle$ can be solved for and the total consumption of the reactants obtained by calculating the flux $- \epsilon D \partial \langle C \rangle / \partial r|_{r=r_o}$ integrated over the surface of the sphere of radius r_o. Finally, a ratio η may be defined as

$$\eta = \frac{\text{total rate of uptake of the reactant for a diluted catalyst}}{\text{total rate of uptake of the reactant for active catalyst}}$$

obviously the ratio is being taken under identical conditions. These are that the diluted catalyst has a radius r_o and contains active catalyst microspheres of radius r_i and volume fraction ϕ and that the concentration at the outer surface is C_o. The uptake here is being compared with that in an active catalyst of radius r_o when the concentration at the outer surface is C_o. We note in passing that the uptake in an active catalyst is easier to determine. When multiplied by η derived below, it gives an easy means for calculating the uptake in a diluted catalyst pellet in a packed bed, when the surface concentration is known to be C_o. Thus η is a useful result and from Appendix

$$\eta = \frac{\alpha[\theta \coth(\theta) - 1]}{\left[\left(\frac{r_o}{r_i} \right) x \coth \left(\frac{r_o}{r_i} x \right) - 1 \right]} \tag{27}$$

where

$$\theta^2 = 3\phi \left(\frac{r_o}{r_i} \right)^2 \left[2 + \frac{\alpha}{x \coth(x) - 1} \right]^{-1}$$

In the limit $x \to \infty$,

$$\eta \to \alpha \left(\frac{r_i}{r_o} \right) \left[\sqrt{\frac{3\phi}{2\left(\frac{r_i}{r_o} \right)^2}} \cdot \coth \left(\sqrt{\frac{3}{2\left(\frac{r_i}{r_o} \right)^2}} \right) - 1 \right] \bigg/ x.$$

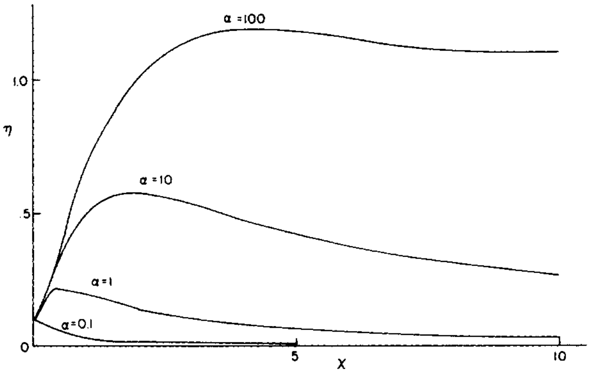

Figure 1. η against Thiele modulus x plotted from Eq. 27 for $\varphi = 0.1$ and $r_o/r_i = 20$. At large x, η goes to zero irrespective of α. At $x = 0$, η goes to $\phi = 0.1$.

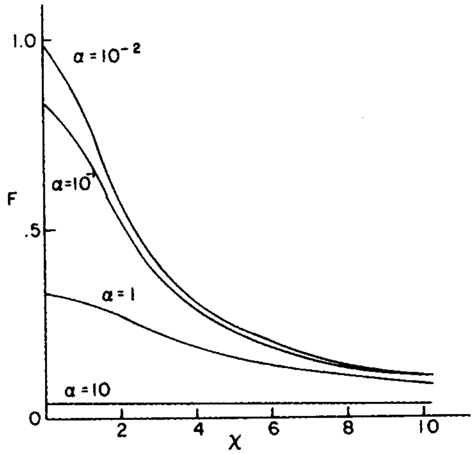

Figure 2. The function F defined before Eq. 28 plotted against x for different values of α.

With typical values of $\phi \sim 0.1$ and $r_o/r_i \sim 20$, we get

$$\sqrt{\frac{3\phi}{2\left(\frac{r_i}{r_o}\right)^2}} \sim 8,$$

which is a large quantity. This simplifies the limiting expression for η, which becomes $\eta \rightarrow \alpha/x\sqrt{3\phi/2}$. This is the case considered by Ruckenstein (1970) for small D^* (hence large x and large α). Similarly one may look at small reaction rates (or $x \rightarrow 0$), where it is seen that $\eta \rightarrow \phi$, thus underlining the importance of the volume fraction. Plots of η vs. x have been made in Figure 1 for various values of α, and for $\phi = 0.1$ and $r_o/r_i = 20$. It is seen that Ruckenstein's proposition of increasing the uptake by catalyst dilution can be realized at small volume fractions only for $\alpha \sim 100$ or greater.

As mentioned previously, our results can be valid up to a value of ϕ as large as ⅓ with an error of 11%. These results are in substantial disagreement with those of Ruckenstein (1970) when those results are extropolated outside their range of validity into the range of small ϕ. Some of Ruckenstein's results however extend to higher values of ϕ, where his governing equations are justifiable (Neogi and Ruckenstein, 1980) and the effects ($\eta > 1$) are unmistakable.

We are also able to clarify what an effective diffusion coefficient should be and quantitize D_e at low volume fractions ϕ of the active catalyst.

In analyzing the effective diffusion coefficient in Eq. 25, we note that D_e is greater than D^*, only if $\alpha > 1$, that is, the catalyst is diluted in a medium where the diffusion coefficient D is higher. Further, this is true sometimes only because the volume fraction ϕ is small. The above follows from the fact that the quantity

$$F = \left\{\left[\frac{2 + x^2 - 2x\coth x}{x\coth x - 1}\right] + 2\alpha\right\}^{-1}$$

in Eq. 25 is always positive and $F \rightarrow (1 + 2\alpha)^{-1}$ as $x \rightarrow 0$ and $F \rightarrow x^{-1}$ as $x \rightarrow \infty$. In the limit where there is no reaction $k \rightarrow 0$ and $x \rightarrow 0$, Eq. 25 becomes

$$\frac{D_e}{D^*} = \alpha - \phi\frac{3\alpha(\alpha - 1)}{(1 + 2\alpha)} \tag{28}$$

With some rearrangement Eq. 28 can be shown to be equivalent to the result of Rocha & Acrivos (1973) for equivalent thermal conductivity. The second important case occurs when $D^* \rightarrow 0$ and $x \rightarrow \infty$, Eq. 25 reduces to

$$\frac{D_e}{D^*} = \alpha - \phi\frac{3\alpha^2}{x} \tag{29}$$

In Figure 2, F has been plotted against x for various values of α.

NOTATION

C = concentration defined in terms of pore volume
D = diffusion coefficient
$\mathbf{e}_\parallel$ = unit vector parallel to the direction of the applied constant macroscopic concentration gradient $\langle\nabla C\rangle$
$\mathbf{e}_\perp$ = unit vector perpendicular to $\mathbf{e}_\parallel$
F = function of x and α defined before Eq. 28
i_k = modified spherical Bessel function of the first kind and k^{th} order
$\mathbf{j}$ = diffusive flux
k = first order reaction rate constant in the microspheres
n = number of microspheres per unit volume N/V
$\mathbf{n}_p$ = unit normal vector to the surface of a microsphere
N = number of microspheres in a volume V
r = radial distance from the center of a microsphere
r_i = radius of a microsphere
S = surface area
V = volume
x = Thiele modulus of a microsphere $r_i\sqrt{k/D^*}$

Greek Letters

α = ratio $\epsilon D/\epsilon^* D^*$
ϵ = void volume in the porous medium
μ = cosine of polar angle
ϕ = volume fraction of the catalyst

Subscripts

e = effective
P = microsphere

Superscripts

$*$ = microsphere

Symbols

$\langle\ \rangle$ = average
∇ = gradient operator
∇^2 = Laplacian operator

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APPENDIX

We solve here the equation

$$\nabla^2 C = \beta C \tag{i}$$

since both Eqs. 27 and 15 are of this form with constant β. C in Eq. i is subject to boundedness and to the condition that

$$C|_{r=r_o} = C_o \tag{ii}$$

where r_o is the radius of the macrosphere. Thus, C is a function of r only and the solution to Eq. i subject to Eq. ii becomes

$$C = C_o \frac{\sinh\,(r\sqrt{\beta})}{\sinh\,(r_o\sqrt{\beta})}\left(\frac{r_o}{r}\right) \tag{iii}$$

Then the total flux to the sphere is

$$F(\beta) = -\epsilon_\beta D_\beta 4\pi r_o^2 \left.\frac{\partial C}{\partial r}\right|_{r=r_o} \tag{iv}$$

and the ratio

$$\eta = \frac{\text{flux to the diluted catalyst}}{\text{flux to the undiluted catalyst}}$$

becomes

$$\eta = \alpha \frac{[\theta \coth\,(\theta) - 1]}{\left[\frac{r_o}{r_i} x \coth\left(\frac{r_o}{r_i} x\right) - 1\right]} \tag{v}$$

with

$$\theta^2 = 3\phi\left(\frac{r_o}{r_i}\right)^2 \frac{1}{2 + \alpha[x \coth(x) - 1]^{-1}}$$

on identifying β, D_β and ϵ_β from Eqs. 27 and 15

Dynamic Studies of Dispersion and Channeling in Fixed Beds

An experimental and theoretical study was carried out to relate the extent of channeling in a packed column to the response in the effluent gas to a tracer input. When the response curve showed a distinct peak associated with a channel, it was possible to establish the flow rate and void area of the channel from only the response curve. The experimental data provided new information on Peclet numbers in packed columns with nonuniform void fractions (low tube-to-particle diameter ratios).

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SCOPE

Nonuniform void regions in packed beds may be due to the influence of the column wall or may result when the packing process itself is nonuniform. Such nonuniformities cause channeling of flow with adverse performance: for example, reduced conversion or selectivity in fixed-bed catalytic reactors. While packing nonuniformities are usually random, the response curve to a tracer input provides some evidence of the specific characteristics of flow maldistribution. Thus, two, more-or-less distinct peaks in the response to a pulse input of tracer, or a peak with an elongated tail, are suggestive of channeling. However, the response can also be distorted by axial dispersion for a nonadsorbable tracer and, in addition, by adsorption for a tracer adsorbable on the packing.

For beds where nonuniform void fractions are suspected, it would be helpful to be able to determine quantitatively the extent of channeling from the overall response curve; that is, to determine the flow rate through the channels and their void areas. Our purpose in this paper is to report results of comparing predicted channeling with experimental measurements in beds prepared intentionally with a nonuniform distribution of voids. This was done in a simple way by packing glass beads in the annulus and core regions of a cylindrical column. The void fractions in the annulus and core could be varied by using different sizes of glass beads and by varying the width of the annulus and diameter of the core. To ensure large void fractions, and encourage channeling, low ratios (1.8 to 12) of width-(or diameter)-to-particle diameter were used. A nonadsorbing tracer (helium) was introduced into air (at 298 K and 101 kPa) entering the column, and the response curve measured in the combined effluent.

CONCLUSIONS AND SIGNIFICANCE

The experimental response curves for several bed arrangements showed two, more-or-less distinct peaks. In all cases these arrangements included a thin aluminum screen separating the core and annulus (noninteracting case). For such cases it was possible to estimate the effects of axial dispersion (Peclet numbers) on the response curves so that reliable values of the flow rates and void areas could be calculcated. The information required, in addition to the response curve, is the overall flow

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