POSTWITHDRAWAL DRAINAGE

This process can be described by the step function $f(t) = v_o$ for $0 < t < t_w$ and $f(t) = 0$ for $t > t_w$. With this choice, Equation (9) yields, as $T \to \infty$

$$Y = -H^2T + \frac{2}{3}H^4 + V_oT_w \qquad (16)$$

Apart from the inertial correction 2/3 H^4, which again makes its appearance, it can easily be checked that this is precisely the steady state postwithdrawal profile of Lang and Tallmadge (1971).

ACKNOWLEDGMENT

N. Annapurna is thankful to the Council of Scientific and Industrial Research for their financial assistance.

NOTATION

Lengths and times (denoted by lower case letters) are to be multiplied, respectively, by the factors $(g/\nu^2)^{1/3}$ and $(g^2/\nu)^{1/3}$ in order to obtain the corresponding dimensionless quantities (denoted by capitals).

g = acceleration due to gravity
h = liquid film thickness
Q = flux of the fluid entrained
t_w = withdrawal time in post withdrawal drainage
v = y component of the fluid velocity
v_o = constant withdrawal speed
Y_o = y coordinate of the top of the film
ν = kinematic viscosity of the fluid

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Manuscript received May 10, and accepted June 7, 1976.

The Effect of Cross Sectional Pore Shape on Knudsen Diffusion in Porous Materials

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The ideal model of a porous material would somehow combine the contradictory attributes of physical realism and mathematical tractability. Of the many attempts to provide such a model, the most popular has been the visualization of a porous material as a solid pierced by nonintersecting, randomly oriented, cylindrical pores possessing diameters ranging over perhaps several orders of magnitude. This model has achieved a reasonable success both in pore structure studies (Dullien and Batra, 1970) and in transport studies (Satterfield, 1970). Yet it is recognized that this model can have severe limitations, and other models are being proposed continually to remedy the defects in the cylindrical pore model. The Dullien-Batra review gives an account of many of those offered in pore structure studies, and examples of other models for transport are presented by Flood et al. (1952), Dullien (1975), and Neal and Nader (1976).

But before a defect is considered sufficiently serious to require a remedy, the probable error it will cause should be estimated if possible. For example, the presence of pore constrictions has been shown to be a serious factor in predicting transport rates through porous materials from both theoretical considerations (Petersen, 1958; Michaels, 1959; Haynes and Brown, 1971) and experimental implications (Brown et al., 1969). On the other hand, pore constrictions are not indicated as a serious problem when gaseous diffusion rates are predicted at one pressure from those measured at another pressure (Haynes and Brown, 1971).

Another possible flaw in the cylindrical pore model arises from the presence of pores with noncircular cross sections in real materials. While pores with circular cross sections are occasionally observed (Adair et al., 1972), the majority of porous materials appears to possess pores with highly irregular shapes (for example, Dullien and Mehta, 1972; Eklund, 1976). This note considers the effect of noncircular cross-sectional pores on transport through porous materials.

Most transport situations within porous materials involve one or more of three types of flow: bulk flow in the laminar flow regime, molecular diffusive flow, and Knudsen flow. In solids whose pores are not too small, combinations of the appropriate transport laws appear to predict the behavior very well (Mason et al., 1967; Gunn and King, 1969). The lower limit of pore size to which these laws can be applied appears to be about 50Å in radius (Omata and Brown, 1972), although it may be

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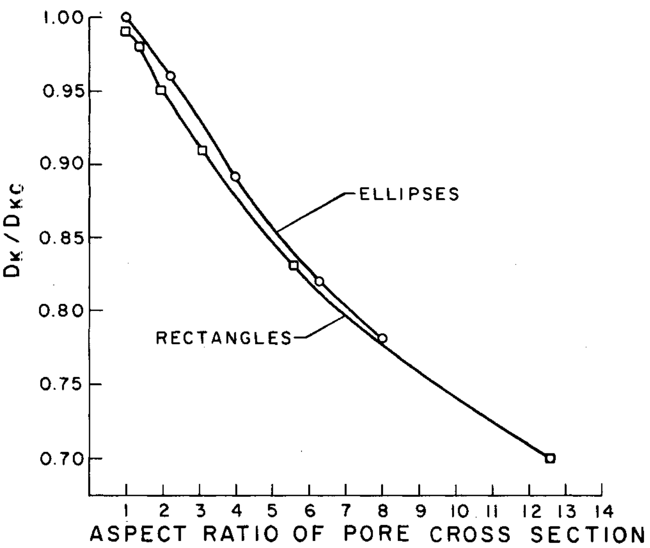

Fig. 1. Relationships between relative Knudsen diffusivities and pore aspect ratios.

significantly higher in some instances (Stoll and Brown, 1974; Spencer and Brown, 1975).

The only one of these three types of transport in which the effect of noncircularity of the pore cross section is not well-known appears to be Knudsen flow. In principle, the effect of irregular pore shape on laminar flow can be calculated by using the hydraulic radius. There should be no effect of irregular pore shape on molecular diffusion, because this type of flow depends only on total cross sectional void space and not at all on pore wall effects. For Knudsen flow, while the cylindrical pore formula derivation is presented in many places (for example, Kennard 1938), the effect of a noncircular cross section on the transport rate does not appear to have been considered quantitatively. This note presents the results of a short numerical study showing how the presence of a noncircular cross section would affect the observed rate vs. the rate predicted by assuming the pore to be circular.

APPROACH TO PROBLEM

The general equation for the Knudsen diffusion coefficient for a pore of arbitrary shape is

$$D_K = \frac{\bar{v}}{8A} \int_A \int_0^{2\pi} s\,d\theta\,dA \qquad (1)$$

and can be derived readily from formulas presented by Kennard (1938) or Present (1958). By using Equation (1), the diffusivity was determined for the following pore cross sections: a circle (to serve as a check on the numerical algorithm and computer program), various ellipses, a square, and various rectangles. All the cross-sectional shapes possessed the same area as the original circle.

RESULTS

The results of these calculations are presented in Figure 1, in which the ratio of the Knudsen diffusivity for the particular cross sectional pore shape to the circular Knudsen diffusivity is plotted as a function of the ratio of the major to the minor axis of the pore shape. (A term will be borrowed from the air-conditioning industry, and this latter ratio will be called the aspect ratio of the pore.) The figure shows that relatively large aspect ratios are necessary for severe departures from the Knudsen diffusivity of a circular pore to occur. If a significant deviation from the value of the circular diffusivity is defined as 10%, the figure indicates that the aspect ratio must exceed approximately 3.5 for the deviation to be significant. Thus a large fraction of the pores of a solid would have to possess rather large aspect ratios for noncircularity of the pore cross sections to have a significant effect. A quick scan of some pictures of porous materials (Dullien and Mehta, 1972; Eklund, 1976) shows that this condition is not fulfilled in general, and so it is felt that the presence of noncircular cross sections in pores usually does not have a significant effect on the Knudsen diffusion coefficient predicted on the assumption of a circular pore cross section. Exceptions can occur, quite obviously, and so it would be well to attempt to determine in some manner whether the particular porous solid under consideration is one of the exceptions.

The presence of surface roughness should not alter this conclusion. As long as the roughness dimensions are small compared with the mean free path of the diffusing molecules (the usual situation), the area of interest is the projected area of the pore wall, not the total area including the effect of surface roughness. There is one restriction, though, on Equation (1) which may be perceived from the derivations: all points on the projected surface of the pore must be seen by all other points on the pore surface.

The principal conclusion of this note is that the Knudsen equation for flow through circular pores may be used for most porous materials without fear that a noncircular pore cross section will alter the conclusions significantly. If the effect of pore intersections is about the same for both molecular and Knudsen diffusion rates, this means that the assumption of the same tortuosity factor for both molecular and Knudsen diffusion is a reasonable one. The near equality of these two tortuosity factors for a porous material with fairly large pores has been observed experimentally by Omata and Brown (1972).

NOTATION

A = cross-sectional area of pore, cm^2
D_K = Knudsen diffusion coefficient, cm^2/s
D_{KC} = Knudsen diffusion coefficient of a circular pore, cm^2/s
$\bar{v}$ = mean molecular velocity, cm/s
s = distance from the center of the area element dA to the perimeter of the pore at the angle θ, cm
θ = angle with respect to chosen coordinate of line connecting area element dA with point on perimeter of pore, radians

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Manuscript received April 20, and accepted June 15, 1976.

Diffusivities in Catalyst Pellets with Bidisperse Pores

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Recently (Dogu and Smith, 1975), a dynamic version of the Wicke-Kallenbach method was developed for measuring effective diffusivities (D_e) in single catalyst pellets. The theory was derived for diffusion through the macropores surrounding the particles from which the pellet was produced. Hence, the method was strictly applicable only to pellets made from nonporous particles. However, first moment measurements for a pellet made from alumina particles, which contained micropores, indicated that the method was also applicable to such bidisperse pellets. Verification was sought by obtaining data for pellets of the same macro (α) and micro (β) porosities but prepared from different size particles. These data resulted in the same values of D_e even though the length of the diffusion path in the micropores was presumably changed. On this basis it was concluded that micropore diffusion did not affect application of the method for obtaining macropore diffusivities. Here we show theoretically that the conclusion is correct by extending the original development to bidisperse pellets. This is important because the experimental test is uncertain. Even though different size particles were used, the pelletting process may have reduced the particles to about the same dimensions.

For a bidisperse pellet it is supposed that diffusion occurs through the macropores surrounding the particles and in series fashion into the micropores. Then, instead of the single mass conservation equation [Equation (4) of Dogu and Smith, 1975], separate expressions are written for the macropores (interparticle region)

$$D_e \frac{\partial^2 C}{\partial x^2} = \alpha \frac{\partial C}{\partial t} + D_{ei} \frac{3(1-\alpha)}{r_o} \left(\frac{\partial C_i}{\partial r} \right)_{r=r_o} \qquad (1)$$

and for the micropores (intraparticle region)

$$D_{ei} \left[\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \left(\frac{\partial C_i}{\partial r} \right) \right] = \beta \frac{\partial C_i}{\partial t} \qquad (2)$$

with the boundary condition

$$C_i(r_o, t) = C(t) \qquad (3)$$

relating the concentrations of diffusing component in the intraparticle and interparticle regions. The particles are assumed to be spherical of radius r_o and to have a micropore effective diffusivity D_{ei}. The pellet is cylindrical with diffusion in the axial direction (x) and with a length L. Initial and boundary conditions for the pulse experiments are the same as presented by Dogu and Smith (1975).

Linear Equations (1) and (2), with the boundary and initial conditions, were solved in the Laplace domain to give $\overline{C}(L, s)$. Then the first moment (retention time) of the response peak to an input pluse of diffusing substance is obtained from the expression

$$\mu_1 = \frac{m_1}{m_o} \qquad (4)$$

where

$$m_1 = -\lim_{s \to 0} \frac{d\overline{C}(L, s)}{ds} \qquad (5)$$

and

$$m_o = \lim_{s \to 0} \overline{C}(L, s) \qquad (6)$$

Carrying out the indicated operations yields

$$\mu_1 = \frac{L^2}{6D_e} [\alpha + \beta(1-\alpha)] \frac{3\dfrac{AD_e}{L} + F}{\dfrac{AD_e}{L} + F} \qquad (7)$$

This result is identical to that obtained by Dogu and Smith [their Equation (9)], since the term in brackets is the total porosity of the pellet.

An important feature of Equation (7) is that it does not contain the micropore diffusivity D_{ei}. Hence, micropore diffusivities cannot be obtained by this dynamic method, at least not from first moment information. The situation is analogous to pulse-response methods applied to fixed beds of particles through which a fluid is flowing. It has been shown (Schneider and Smith, 1968) that the first moment for that case is a function of the fluid

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