

θ	= cross angle of two laser beams at the measuring point
Λ^+	= nondimensional integral scale of transverse space correlation in wall turbulence
λ	= wave length
ν	= kinematic viscosity
ρ	= density
σ	= laser beam diameter at the focal point
σ_1	= length of the major axis of a scattering ellipsoid
σ_2, σ_3	= length of the shorter axes of a scattering ellipsoid
τ_w	= wall shear stress

LITERATURE CITED

- Achia, B. U., and D. W. Thompson, "Structure of the Turbulent Boundary in Drag-Reducing Pipe Flow," *J. Fluid Mech.*, **81**, p. 439 (1977).
 Barnard, B. J. S., and R. H. J. Sellin, "Grid Turbulence in Dilute Polymer Solutions," *Nature*, **222**, p. 1169 (1969).
 Berman, N. S., "Drag Reduction by Polymers," *Ann. Rev. Fluid Mech.*, **10**, p. 47 (1978).
 Berman, N. S., "The Effect of Sampling Probe Size on Sublayer Period in Turbulent Boundary Layers," *Chem. Eng. Commun.*, **5**, p. 337 (1980).
 Chiou, C. S., and R. J. Gordon, "Vortex Flow of Dilute Polymer Solutions," *Polym. Eng. Sci.*, **20**, p. 456 (1980).
 Fortuna, G., and T. J. Hanratty, "The Influence of Drag-Reducing Polymers on Turbulence in the Viscous Sublayer," *J. Fluid Mech.*, **53**, p. 575 (1972).
 George, W., and J. L. Lumley, "The Laser-Doppler Velocimeter and its

- Application to the Measurement of Turbulence," *J. Fluid Mech.*, **60**, p. 321 (1973).
 Hoyt, J. W., and J. J. Taylor, "Effect of Nozzle Shape and Polymer Additives on Water Jet Appearance," *J. Fluid Eng.*, **101**, p. 304 (1979).
 Laufer, J., "The Structure of Turbulence in Fully Developed Pipe Flow," NACA TN 2954 (1953).
 Little, R. C., R. J. Hansen, D. L. Hunston, O. Kim, R. L. Patterson, and R. Y. Ting, "The Drag Reduction Phenomenon. Observed Characteristics, Improved Agents, and Proposed Mechanisms," *Ind. Eng. Chem. Fund.*, **14**, p. 283 (1975).
 McComb, W. D., J. Allan, and G. A. Greated, "Effect of Polymer Additives on the Small-Scale Structure of Grid-Generated Turbulence," *Phys. Fluids*, **20**, p. 873 (1977).
 Mizushima, T., and H. Usui, "Reduction of Eddy Diffusion for Momentum and Heat in Viscoelastic Fluid Flow in a Circular Tube," *Phys. Fluids*, **20**, p. S100 (1977).
 Nakagawa, H., and I. Nezu, "Prediction of the Contributions to the Reynolds Stress from Bursting Events in Open-Channel Flows," *J. Fluid Mech.*, **80**, p. 99 (1977).
 Reishman, M. M., and W. G. Tiederman, "Laser-Doppler Anemometer Measurements in Drag-Reducing Channel Flows," *J. Fluid Mech.*, **70**, p. 369 (1975).
 Sellin, R. H. J., and B. J. S. Barnard, "Open Channel Applications for Dilute Polymer Solutions," *J. Hydraulic Res.*, **8**, p. 219 (1970).
 Sellin, R. H. J., and M. Ollis, "Polymer Drag Reduction in Large Pipes and Sewers," Soc. Rheol., Golden Jubilee Meeting, 37-6, Boston (1979).
 Ueda, H., and J. O. Hinze, "Fine-Structure Turbulence in the Wall Region of a Turbulent Boundary Layer," *J. Fluid Mech.*, **67**, p. 125 (1975).
 Usui, H., and T. F. Irvine, Jr., "Drag Reduction in a 90 Degree Triangle Open Channel," *J. Rheol.*, **24**, p. 525 (1980).
 Usui, H., and Y. Sano, "Turbulence Structure of Submerged Jet of Dilute Polymer Solutions," *J. Chem. Eng. Jap.*, **13**, p. 401 (1980).
 Virk, P. S., "Drag Reduction Fundamentals," *AIChE J.*, **21**, p. 625 (1975).

Diffusion of Gases in Porous Solids: Monte Carlo Simulations in the Knudsen and Ordinary Diffusion Regimes

Porous solids have been simulated in the computer as assemblages of spheres. When such assemblages contain spheres distributed in size and randomly arranged in space, the structure of the resulting solid resembles that of a real porous solid. Monte Carlo calculations of gas molecule trajectories through the assemblages were carried out for both the Knudsen and ordinary diffusion regimes. Tortuosities calculated from the simulated diffusion "data" fell in the range obtained experimentally by other investigators. Correlations were obtained that enable the prediction of diffusion rates from measurement of the porosity, mean pore size, and standard deviation of the pore size.

**M. H. ABBASI and
J. W. EVANS**

Department of Materials Science and
Mineral Engineering
University of California
Berkeley, CA

and

I. S. ABRAMSON
Department of Mathematics
University of California
San Diego, CA

SCOPE

The diffusion of gases within a porous solid is a phenomenon of practical interest in chemical engineering and metallurgical engineering, as well as in other engineering fields such as the production of energy. The presently available means for predicting rates of gaseous diffusion within porous solids are unreliable, even in the case where the structure of the porous solid is well characterized. Frequently, use is made of a "tortuosity

factor," which cannot be predicted from first principles and can only be estimated with little precision, yielding diffusivities which are likely to be erroneous.

The objective of the present investigation was to remedy this situation by performing a Monte Carlo simulation of the diffusion of gas molecules in porous solids. In this procedure a

porous solid is first simulated in the computer. The trajectory of a gas molecule diffusing through the solid is then calculated. Repetition of the trajectory calculation for a large number of molecules and use of the classical kinetic theory of gases then

yields the diffusivity of the gas in the solid. The diffusivity (or parameters related to it) could then be correlated with the structure of the porous solid. The latter was obtained by computer-based techniques.

CONCLUSIONS AND SIGNIFICANCE

Simulations of porous solids have been carried out; while some of the simulations are idealizations of real solids, others present the visual appearance of actual porous solids. The trajectories of large numbers of gas molecules within each porous solid could be computed for each solid with reasonable expenditure of computer time in both the Knudsen and ordinary diffusion régimes. When combined with the kinetic theory of gases, the results of the trajectory calculations enable the determination of an effective diffusivity for each solid.

It was found that the diffusion "data" from the simulations could be correlated by

$$\frac{k_o}{d} = 0.0093 + 0.1\epsilon - 0.0181 \frac{\sigma}{d}$$

for the Knudsen régime, where \bar{d} and σ are the mean and standard deviation of the pore size, ϵ is the porosity, and k_o is the

length parameter giving the Knudsen diffusivity, D_{AK} :

$$D_{AK} = \frac{4}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} k_o$$

where R is the gas constant, T temperature, and M molecular weight.

For the ordinary diffusion regime, the "data" could be correlated by

$$\tau = 1/\epsilon + 1.196 \sigma/\bar{d} \quad (28)$$

where τ is the tortuosity factor relating the effective diffusivity, D_{ABeff} , to the ordinary diffusion coefficient, D_{AB} , by the well-known equation:

$$D_{ABeff} = \frac{\epsilon}{\tau} D_{AB}$$

PREVIOUS INVESTIGATIONS

The diffusion of gases within a porous solid is a phenomenon of significance in many industrial processes. Examples are the reduction of iron ores to metal, the absorption of sulfur dioxide by lime (in proposed fluidized-bed coal combustors), and the many industrial reactions involving heterogeneous catalysis. Attempts to predict diffusion rates have hitherto yielded unsatisfactory results in that they have entailed a tortuosity factor (or similar parameter) that is not readily predicted from first principles. The research described in this paper was aimed at overcoming this difficulty and providing a means for prediction of diffusion rates from measurements of simple solid properties such as can be achieved by mercury penetration porosimetry.

Sandry and Stevenson (1970) have carried out a Monte Carlo simulation of the effusion of gases through a cylindrical hole. A simulation of Knudsen diffusion within cylindrical, unisized, nonintersecting pores has been performed by Jacobson (1981) while Knudsen diffusion in different solids has been simulated by Evans et al. (1980). The last named work has been exploited in a model of radiative heat transport through porous solids and packed beds by Evans and Abbasi (1982).

Many models have been proposed which purport to represent the diffusion of gases in porous solids. An example is the model of Johnson and Stewart (1965) which allowed for a distribution of pore sizes and assumed that each pore made its contribution to the diffusive flux independently of the others. The model of Wakao and Smith (1962) allowed for a bimodal distribution of pore sizes and is noteworthy in that it does not make use of a tortuosity factor or similar unknown. Cunningham and Geankoplis (1968) extended the model of Wakao and Smith to solids with a tridisperse pore-size distribution. Youngquist (1970) has reviewed the earlier models for pore diffusion of gases.

BASIS OF THE SIMULATION

Figure 1 depicts a porous plug separating a vacuum from a gas A at partial pressure, P_A from a space free of A. A molecule of A striking the left of the plug is either "transmitted" or "reflected" as shown in the figure. The flux of A molecules is given by

$$\text{flux} = \text{fraction transmitted} \times \text{number of moles impacting unit area per unit time}$$

$$= f_T \frac{P_A}{4RT} \left(\frac{8RT}{\pi M} \right)^{1/2} \quad (1)$$

where the rate of molecular impacts is obtained from the kinetic theory of gases.

For the Knudsen diffusion of gas A, an alternative equation for the flux is

$$\text{flux} = D_{AK} \frac{P_A}{RT} \left(\frac{1}{L} \right) \quad (2)$$

and elimination of the flux between the equations yields

$$f_T = 4D_{AK} \left(\frac{\pi M}{8RT} \right)^{1/2} \left(\frac{1}{L} \right) \quad (3)$$

For the ordinary diffusion of gases A and B in a porous plug it is usual to write (for the case of equimolar counterdiffusion)

$$\text{flux of A} = D_{ABeff} \frac{P_A}{RT} \left(\frac{1}{L} \right) \quad (4)$$

After again employing Eq. 1 to eliminate the flux, the following equation is obtained:

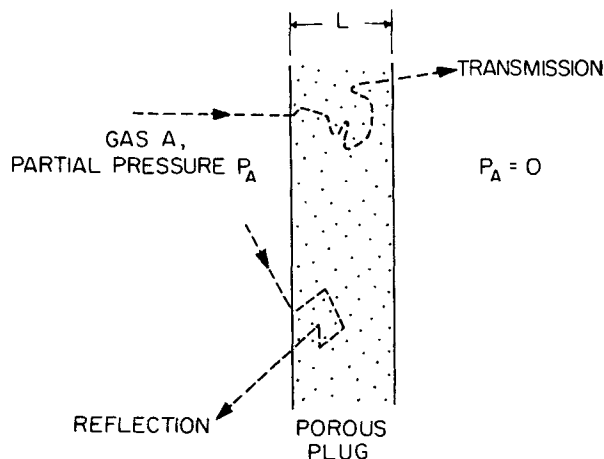


Figure 1. Schematic representation of the possible trajectories of gas molecules impacting a porous plug.

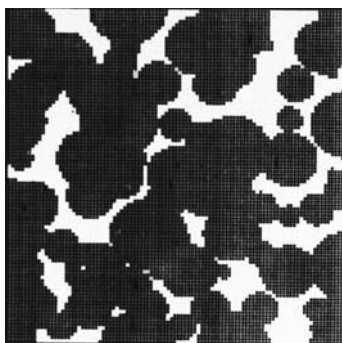


Figure 2. Computer-generated drawing of a plane passing through one of the simulated porous solids. In this case the spheres making up the solid are distributed in size and arranged in irregular positions.

$$f_T = 4D_{A\text{eff}} \left(\frac{\pi M_A}{8RT} \right)^{1/2} \left(\frac{1}{L} \right) \quad (5)$$

The basis of the simulation is that "random" molecular trajectories through simulated solids can be computed for large numbers of molecules. This yields a statistically significant value for the fraction transmitted, f_T , which when plotted against the reciprocal plug thickness yields a straight line. Diffusivities can be obtained from the slopes of these lines, using Eq. 4 or 5, for any temperature or molecular weight.

It is noted in passing that the trajectory calculations bear some resemblance to a random walk, and one might therefore expect a plot of $\ln f_T$ against L to yield a straight line. This was indeed found to be the case (Abbasi, 1981), and this latter approach is theoretically more satisfactory in that $f_T \rightarrow 1$ as $L \rightarrow 0$. The former approach yields $f_T \rightarrow \infty$ as $L \rightarrow 0$ because of the employment of Eq. 2 or 4 which (incorrectly) predict that the flux $\rightarrow \infty$ as $L \rightarrow 0$. In practical terms the former approach is more satisfactory in that it yields a well-established quantity of engineering interest (the diffusivity). The difference in the fit of the two approaches is negligible at the L values encountered in this paper and the former approach will be used in what follows.

COMPUTATIONAL PROCEDURE

The tasks entailed in the simulation are three: (a) simulation of a porous solid in a fashion readily acceptable to a computer; (b) characterization of the simulated solid (e.g. porosity determination); and (c) computation of molecular trajectories within the solid.

The solids were described as assemblages of large numbers of spheres, a complete description of the solid therefore consisting of a list of the coordinates and radii of all spheres in the solid. In many cases distributions of sphere sizes were employed. In some instances the centers of the spheres were in regular arrays while in other instances the spheres were randomly arranged. Particularly useful in the development of the porous solids was the work of Horsfield (1934). Following this work, a solid was "constructed" in the computer containing three sizes of spheres. The largest spheres were arranged in an hexagonal close-packed array with the smaller spheres occupying the hexagonal and tetragonal voids between the largest spheres. This solid is henceforth referred to as the "Horsfield solid." More realistic solids were obtained by perturbation of this solid. Such perturbations changed the radii of the spheres to various random distributions and, in some instances, moved the centers randomly. Figure 2 is a computer generated drawing of a plane drawn through the last kind of solid. In this case the radii of the spheres were all increased by an arbitrary amount (20%) following perturbation to reduce the porosity. It is suggested that the visual appearance of a real porous solid under the microscope is akin to that of Figure 2. The centers of the spheres were contained within the approximately cubical volume formed by six large spheres surrounding the assemblage. These "boundary spheres" were listed in the computer along with the spheres of the assemblage proper.

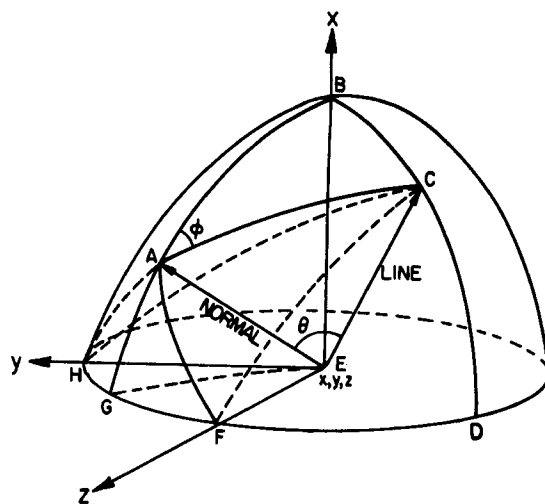


Figure 3. The geometry employed in calculating the trajectory of a gas molecule ("LINE") following impact with a sphere surface at point E.

The edge of the cube served to define the unit of length. Additional information concerning the construction of the porous solids may be found in a previous paper on this topic (Evans et al., 1980) or in the dissertation on which this publication is based (Abbasi, 1981).

Characterization of the simulated porous solids consisted of the determination of porosity, mean pore size, and standard deviation of pore size. The porosity was determined by generating approximately 3,000 random numbers with uniform probability between zero and one. Taken in groups of three these numbers served to define positions within the cube and the fraction of such positions lying within the pores is the porosity.

Two methods were available for obtaining the mean pore size of each solid. The first consisted of a computer-based version of a standard stereological technique wherein lines are cast randomly on a random plane through the solid (Fulman, 1953). The number of intercepts with the pore walls per unit length of line and the porosity can then be used to give a pore size. The second technique exploited the fact that during the Knudsen diffusion simulation the solid is traversed by random lines whose lengths can be conveniently stored in the computer. The mean lengths of such lines and the mean pore size from the first method were found to differ by only a few percent in test cases and consequently the second technique was used to obtain the mean pore size referred to below. The standard deviation of the line segment lengths was assumed to equal the standard deviation of the pore size.

For the Knudsen diffusion régime the molecular trajectories are made up of line segments from one sphere of the solid to another. A molecule originating at x, y, z and having direction cosines $\cos \alpha'$, $\cos \beta'$, $\cos \gamma'$ will intercept a sphere of radius r with center at x_c, y_c, z_c at a point x_i, y_i, z_i given by

$$x_i = p \cos \alpha' + x \quad (6)$$

$$y_i = p \cos \beta' + y \quad (7)$$

$$z_i = p \cos \gamma' + z \quad (8)$$

where

$$p = -(x_0 \cos \alpha' + y_0 \cos \beta' + z_0 \cos \gamma') - [(x_0 \cos \alpha' + y_0 \cos \beta' + z_0 \cos \gamma')^2 - (x_0^2 + y_0^2 + z_0^2 - r^2)]^{1/2} \quad (9)$$

and

$$x_0 = x - x_c \quad y_0 = y - y_c \quad z_0 = z - z_c$$

At any instant the line of the molecular trajectory will intersect many spheres; the intercept of physical interest is the closest one to the last gas molecules—sphere collision. On striking the sphere, the gas molecule is reflected from its surface at a random angle.

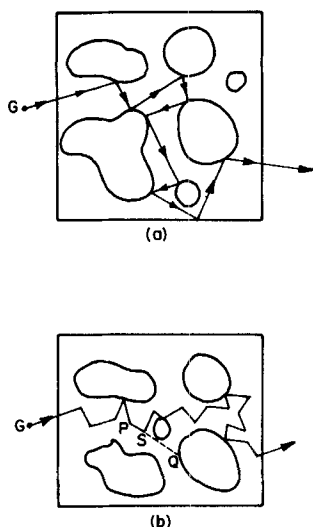


Figure 4. A schematic comparison of the diffusion of a gas molecule in: (a) the Knudsen régime; (b) the ordinary diffusion régime. In the latter case gas molecule-gas molecule collisions occur at P, S, etc.

Point x, y, z in Figure 3 is the point of impact. "LINE" in this figure represents the molecular trajectory following the collision; the normal to the sphere surface appears in the figure, as do the directions of the coordinate axes. It can be shown (Sarin, 1978) that the direction cosines of the molecule are given by

$$\cos \text{BEC} = \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \phi \quad (10)$$

$$\cos \text{HEC} = \cos \theta \cos \beta + \sin \theta \sin \beta \cos \text{HAC} \quad (11)$$

$$\cos \text{FEC} = [1 - \cos^2 \text{BEC} - \cos^2 \text{HEC}]^{1/2} \quad (12)$$

where

$$\text{HAC} = \pi/2 + (\text{sign } \cos \alpha)(\pi/2 - \phi) + (\text{sign } \cos \gamma) \text{HAC} \quad (13)$$

$$\text{HAG} = \cos^{-1} \left(\frac{\tan |\pi/2 - \alpha|}{\tan \beta} \right) \quad (14)$$

and $\cos \alpha, \cos \beta, \cos \gamma$ are the direction cosines of the normal, given by

$$\cos \alpha = \frac{x - x_c}{[(x - x_c)^2 + (y - y_c)^2 + (z - z_c)^2]^{1/2}} \text{ etc.} \quad (15)$$

The azimuthal angle θ is chosen randomly by the computer with a cosine probability distribution, whereas ϕ is chosen with a uniform distribution.

The computation of a molecular path therefore entails the alternate application of Eqs. 6 through 9 and Eqs. 10 through 15. The trajectory is started from a random position at the left of the plug and the progress of the molecule from sphere to sphere computed until the molecule impacted the boundary sphere at $x = 0$ (reflection) or $x = 1$ (transmission). Impacts with the other four boundary spheres were treated in the same manner as impacts with the spheres making up the solid. Typically the trajectories of two thousand gas molecules would be computed for each solid.

Consider a molecule attaining a penetration of half way through the plug before finally passing out at the $x = 0$ plane. This would constitute a reflection. However, such a molecule would count as a transmission for a plug of half the original thickness. Consequently, the maximum penetration of each molecule was stored in the computer and a plot of fraction of molecules penetrating to a reciprocal distance $1/L$ is equivalent to a plot of fraction transmitted against reciprocal plug thickness. By this artifice much computer time was saved.

The procedure used for the ordinary diffusion régime was based on an extension of that for the Knudsen régime. Consider Figure 4 where the two régimes are depicted schematically. For the ordinary régime the sphere to sphere trajectories are broken by gas

molecule—gas molecule collisions which are considered to randomize the direction of the gas molecule. For example, from point P the gas molecule proceeded towards Q. However, the distance PQ exceeded a free path length λ and after reaching point S (distance λ from P) the trajectory was broken and a new random direction computed. The distance λ was obtained from

$$\lambda = -\lambda_m \ln(\xi) \quad (16)$$

where λ_m is the mean free path and ξ is a random number chosen with uniform probability between zero and one. Equation 16 accounts for the fact that free paths are distributed in length.

Unfortunately the use of this simple extension of the Knudsen régime procedure into the ordinary régime results in excessive expenditure of computer time because much more computation is required for each traverse from sphere to sphere. This simple extension will henceforth be referred to as the "original simulation"; a more efficient procedure, referred to as the "pseudosimulation" will now be described.

Consider a list of positions within the solid $x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_j, y_j, z_j, \dots$ which represent the points of collision of a particular gas molecule with the spheres. The result of interest is the maximum value of x_j , i.e., the maximum penetration of the molecule into the plug. We may define

$$\Delta x_j = x_j - x_{j-1} \quad (17)$$

The original simulation can provide values of Δx_j . In fact much information on gas diffusion is garnered thereby; each gas molecule yields tens or hundreds of Δx_j values but only one maximum value of x_j . A technique exploiting the Δx_j values is therefore more efficient than one using merely the maximum value of x_j . The technique employed is to take the Δx_j values generated by a few gas molecules and fit them to a regression equation of the form

$$\Delta x_j = f(\Delta x_{j-1}, \Delta x_{j-2}, \dots, \Delta x_{j-n}, \epsilon_j) \quad (18)$$

where ϵ_j is an error term. Correct determination of the function and fitting constants then yields a "pool" of ϵ_j values. Consequently, Eq. 18 can be applied to calculate x_j values from the $n + 1$ values $x_{j-1}, x_{j-2}, \dots, x_{j-n-1}$ and an ϵ_j value selected randomly from the pool. This is a fast algorithm for moving the gas molecules through the solid, compared to the original simulation. The pseudosimulation could be extended to yield y_j and z_j values but these are not required. Each gas molecule in the pseudosimulation generates a maximum penetration, L (maximum x_j), which is stored by the computer.

The precise form of Eq. 18 used in this investigation was

$$\Delta x_j^{(k)} = c^{(k)} |\Delta x_{j-1}|^{\beta_1^{(k)}} |\Delta x_{j-2}|^{\beta_2^{(k)}} \text{sign}(\Delta x_{j-1}) \epsilon_j^{(k)} \quad (19)$$

This equation was obtained from a piecewise linear regression of the Δx_j values obtained from the original simulation, following a logarithmic transformation of Eq. 19. The Δx_j values were split into six classes (indicated by $k = 1, 2, \dots, 6$) based on the value of $|\Delta x_{j-1}|$ and the fitting coefficients, $c^{(k)}, \beta_1^{(k)}, \beta_2^{(k)}$ and error pool, $\epsilon_j^{(k)}$, stored for each class to be used in the subsequent pseudosimulation for this solid. During that simulation the appropriate class (k value) is selected, depending on the size of $|\Delta x_{j-1}|$. Table 1 contains values of the fitting parameters for the simple cubic solid.

The rationale behind the particular choice of the form of Eq. 19 is as follows. Multiplicativity was intended to capture the feature

TABLE 1. EXAMPLE OF RESULTS OF FITTING EQ. 19 TO SET OF Δx_j VALUES. Δx_j VALUES DIVIDED INTO SIX SETS DEPENDING ON MAGNITUDE OF Δx_{j-1} . SIMPLE CUBIC SOLID

Subset (k)	No. of Members of Subset	$c^{(k)}$	$\beta_1^{(k)}$	$\beta_2^{(k)}$
1	500	0.05	0.16	0.29
2	1,000	0.16	0.38	0.23
3	1,000	0.28	0.5	0.16
4	1,000	0.020	zero	zero
5	1,000	0.016	zero	zero
6	500	0.012	zero	zero

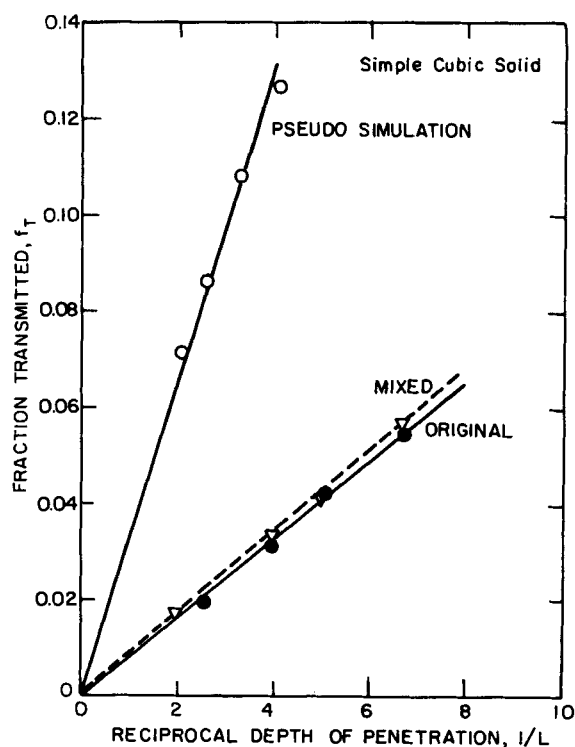


Figure 5. A comparison of the results of three simulation algorithms for Knudsen diffusion in the simple cubic solid. These simulations were carried out as a test of the mixed algorithm.

that the path segments would, for periods of time, be confined to particular cavities within the solid, the linear measure of which would govern the standard error of prediction by a proportion. Path behavior in a large pore would then be essentially a magnified version of that in a small one. Such physical behavior suggests a multiplicative scheme. As for the sign factor, that was incorporated so that, in conjunction with an asymmetry about zero in the pool of ϵ_i 's (in their "bootstrap distribution" in statistical parlance), a presumed tendency for direction reversal to occur on gas molecule-solid collisions could be embodied. The piecewise breakdown of the predictor variables into a few regions took account of gross nonlinearities that might be present in the autoregression, and a cross-validatory check was adopted to guard against overfitting.

The pseudosimulation is applicable to both the Knudsen and ordinary regimes and was tested on the Knudsen regime. In generating the Δx_i values for fitting to Eq. 18, the method originally employed for the Knudsen regime was used except that the gas molecules were "started" inside the solid. Approximately 5,000 Δx_i values were employed. Figure 5 compares the predictions of the original and pseudosimulation for the Horsfield solid. Clearly the pseudosimulation is inadequate in that it fails to agree with the original simulation. The reason for the discrepancy is as follows. The fraction of gas molecules transmitted through a plug

= probability of a gas molecule entering pore mouths \times probability of molecule (having entered) travelling along pores to other side of solid

Generation of the fitting parameters in Eq. 19 by starting gas molecules in the solid is equivalent to determining the second probability factor above and the pseudosimulation, by itself, makes no allowance for the first.

The difficulty can be overcome by allowing the gas molecule to enter the solid under the original simulation procedure and switching to the pseudosimulation once the molecule had penetrated beyond about one layer of spheres. The results of this "mixed simulation" are also included in Figure 5, and it is seen that this last procedure yields results close to the original simulation. In the case of ordinary diffusion it was found in preliminary trials that the

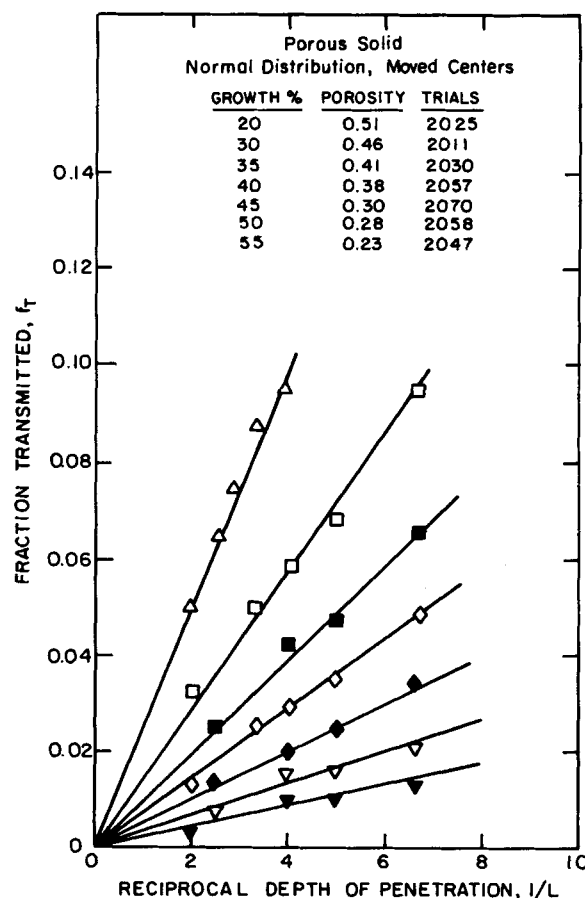


Figure 6. Plot of fraction transmitted vs. reciprocal depth of penetration for the solid with a normal distribution of sphere sizes and randomly moved centers at various levels of sphere "growth." Diffusivities are proportional to the slopes of the lines. Uppermost lines are higher porosity.

switch from the original to the pseudosimulation could be made after penetration to a depth of one-sphere radius without significant deviation from results calculated using the original simulation alone.

RESULTS AND DISCUSSION

Figure 6 depicts the result of simulations for the Knudsen diffusion regime. In this instance the spheres making up the solid have an approximately normal-size distribution. "Trials" is the number of gas molecules used in the simulation. The straight line relationship between fraction transmitted and $1/L$, expected from Eq. 3, is observed. A suite of results comparable to those of Figure 6, but for other simulated solids, is to be found in the dissertation on which this paper is based (Abbasi, 1981). The slopes of these lines can yield a Knudsen diffusivity for this solid by exploiting Eq. 3. However, a more general approach is to be preferred.

Mason et al. (1967) have provided the equation

$$D_{AK} = \frac{4}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} k_0 \quad (20)$$

based on the kinetic theory of gases. Elimination of various constants between Eqs. 3 and 20 yields

$$k_0 = \frac{3}{16} (f_T L) \quad (21)$$

the quantity in parentheses being the slopes of lines such as those of Figure 6. In these equations k_0 has dimensions of length. The simulations are carried out in terms of an arbitrary length scale and it follows that k_0 should be proportional to any suitably chosen length scale such as the mean pore size of the solid, determined by

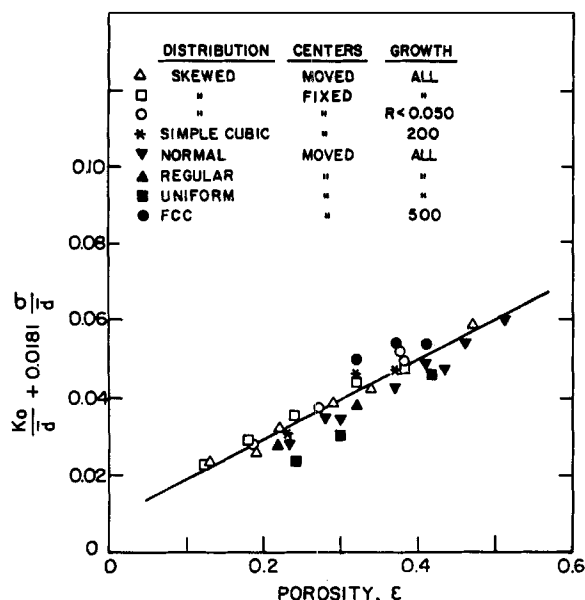


Figure 7. Plot indicating the precision of Eq. 22 which correlates the "data" for the Knudsen diffusion regime.

the technique described above. It is, therefore, expected that k_o/\bar{d} would be a function of dimensionless parameters such as the porosity, ϵ , and the dimensionless standard deviation of the pore size, σ/\bar{d} . Figure 7 represents the results of a least squares fit of the results of the correlation to the equation

$$k_o/\bar{d} = 0.0093 + 0.1 \epsilon - 0.0181 \sigma/\bar{d} \quad (22)$$

It is suggested that Eq. 22, in conjunction with Eq. 20, provides an estimate of the Knudsen diffusivity of a gas, given the mean pore

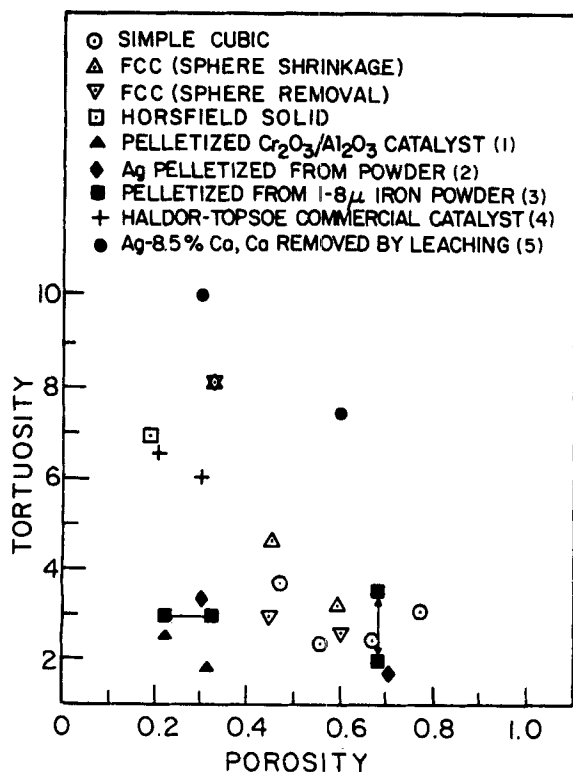


Figure 8. A comparison of tortuosities obtained experimentally by other investigators with those calculated using the Monte Carlo simulation in conjunction with the dusty gas model.

1 = Scatterfield and Saraf, 2 = Masamune and Smith,
3 = Hoogschagen, 4 = Satterfield and Cadle,
5 = Amberg and Echigoya

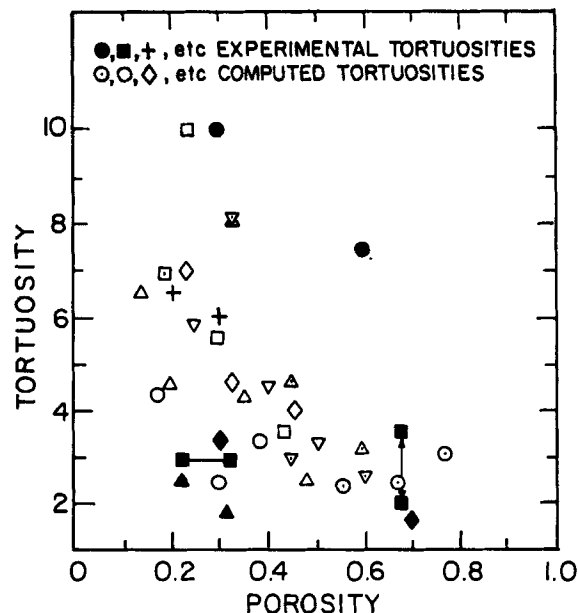


Figure 9. A comparison between experimental tortuosities and those obtained using the Monte Carlo simulation in conjunction with the cylindrical pore model.

size and standard deviation of pore size, for the solid in question, by such techniques as mercury penetration porosimetry. A less accurate fit to the "data" is provided by

$$\frac{k_o}{\bar{d}} = -0.0082 + 0.1 \epsilon \quad (23)$$

and requires only the determination of the mean pore size.

A comparison of the results of the simulation with experimental data can be achieved by means of the "dusty gas model" of Mason and coworkers (1967) for the case where the spheres do not overlap. Such a comparison is presented in Figure 8 and is based on a relationship, suggested by the aforementioned investigators, between tortuosity and k_o . It is noted that the simulated results apply to the Knudsen régime while the experimental measurements apply to the ordinary régime. The well-known cylindrical pore model described, for example, in Satterfield's book (1970), provides a means of comparison of computed and measured tortuosities for those simulated solids where the spheres overlap. Again the model provides a relationship between tortuosity and k_o . Figure 9 is a reproduction of the points from Figure 8 with the addition of tortuosities calculated in this way.

Figure 10 is a plot for the ordinary diffusion régime for a se-

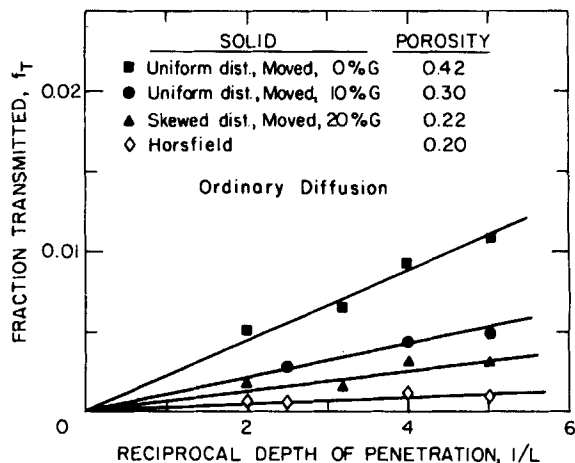


Figure 10. Typical results obtained for the ordinary diffusion régime for four different solids. The diffusivity can be obtained from the slopes of the straight lines.

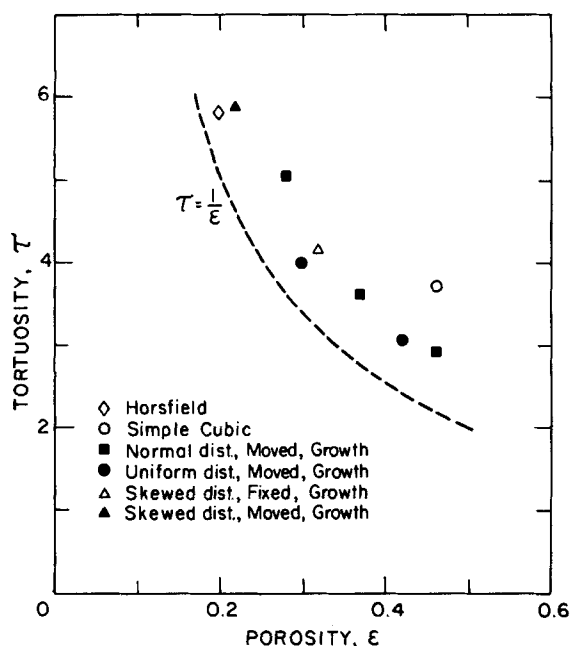


Figure 11. A plot of tortuosity vs. porosity from Monte Carlo simulations for various simulated solids. The broken line is a frequently employed relationship between tortuosity and porosity.

lection of solids. Additional plots of this nature may be found in the dissertation. The value of λ_m was set equal to one tenth of \bar{d} . The linearity expected from Eq. 5 is observed and permits the calculation of an ordinary diffusivity for these solids. Again, however, a more general approach is possible using the equation

$$D_{AB\text{eff}} = \frac{\epsilon}{\tau} D_{AB} \quad (24)$$

which serves to define the tortuosity factor, τ . Equations available in the literature (Hirschfelder et al., 1956) for the diffusivity of a gas provide the relationship

$$D_{AB} = 8,478 \lambda_m \sqrt{T/M} \quad (25)$$

where λ_m is in cm and T in K. Combining Eqs. 5, 24 and 25 yields

$$\tau = 2.35 \frac{\epsilon \lambda_m}{(f_T L)} \quad (26)$$

where again the slope of the straight line from the f_T vs. $1/L$ plot appears in parentheses. Figure 11 is a plot of tortuosity versus porosity, for various solids, calculated in this way. Also included in this plot is the line

$$\tau = 1/\epsilon \quad (27)$$

which is frequently regarded as yielding an approximate tortuosity (e.g., Wakao and Smith, 1962). Figure 11 should be compared with the experimental data of Figure 8. It was found that τ could be better correlated by introducing the dimensionless standard deviation of the pore size, σ/\bar{d} , and Figure 12 is a plot based on the correlation

$$\tau = 1/\epsilon + 1.196 \sigma/\bar{d} \quad (28)$$

obtained from a least squares fit of the "data." For the ordinary diffusion régime it is suggested that Eq. 28 in conjunction with Eq. 24 would yield an estimate of the diffusivity for solids where porosimetry data are available.

Table 2 provides a comparison of the tortuosities obtained from the dusty gas model, the cylindrical pore model and Eq. 28 for the various solids of this investigation. For the simple cubic solid the tortuosity of Eq. 28 is seen to be close to that of the cylindrical pore model. This is not unexpected in that in the simple cubic solid there are long, open pores traversing the width of the solid in the direction of the concentration gradient. For the Horsfield solid with its

TABLE 2. EXAMPLE OF TORTUOSITIES FOR THE CYLINDRICAL PORE MODEL, PRESENT MODEL, AND DUSTY GAS MODEL FOR VARIOUS SOLIDS

Solid	Tortuosity, τ		
	Cylindrical Pore Model	Present Model	Dusty Gas Model
Simple Cubic	3.5	3.7	5.6
Horsfield	3.7	5.8	6.9
Normal Dist., Moved, 30% G	3	2.9	NA
Normal Dist., Moved, 40% G	3.6	3.6	NA
Normal Dist., Moved, 50% G	5.25	5	NA
Uniform Dist., Moved, 0% G	3.5	3.2	NA
Uniform Dist., Moved, 10% G	4.6	4.1	NA
Skewed Dist., Fixed, 5% G	2.8	4.3	NA
Skewed Dist., Moved, 20% G	4.2	5.8	NA

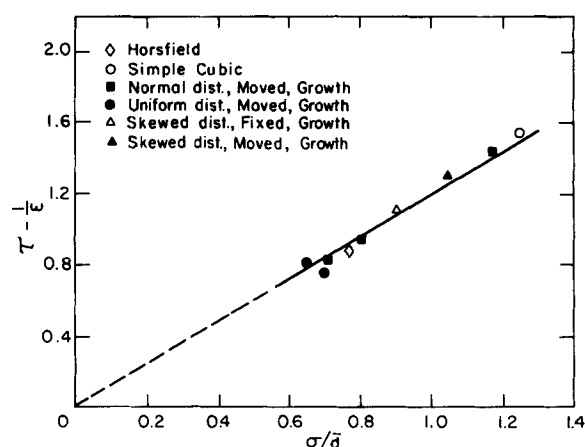


Figure 12. A plot indicating the precision of Eq. 28 which correlates the "data" for the ordinary diffusion régime.

more "closed" structure the tortuosity is closer to that of the dusty gas model. For other solids in Table 2 the dusty gas model cannot be applied since these structures contain overlapping spheres. The tortuosities obtained for the Knudsen diffusion régime employing the cylindrical pore model are seen to be approximately those calculated for the ordinary diffusion régime in most cases.

CONCLUDING REMARKS

In this paper the procedure and results have been presented for a Monte Carlo simulation of the diffusion of gases in porous solids. The simulation covers both the Knudsen and ordinary diffusion régimes. Results of the simulation have been empirically correlated with readily measurable properties of the porous solid, namely the porosity, mean pore size and standard deviation of the pore size. While some of the simulated solids used in this investigation represent idealizations of reality, it is encouraging that for such solids the results of the simulation fall close to those of more realistic solids (for example, Figure 12). The correlations arising from this work (Eq. 22 or 23 and Eq. 28), when combined with Eqs. 20 or 24, permit a prediction of pore diffusivities for any gas (of known ordinary diffusivity) at any temperature or pressure. However, it should be recognized that the present simulation has been carried out using solids of unimodal pore size distribution. The extension of this work to solids with a bimodal pore size distribution, such as are frequently encountered in heterogeneous catalysis, is conceptually straightforward (though requiring considerable computer time).

ACKNOWLEDGMENT

The research described in this paper has been partly supported by a Grant from the Office of Surface Mining, U.S. Department of the Interior, to the California Institute of Mining and Mineral Resources at the University of California, Berkeley.

NOTATION

$c^{(k)}$	= set of k fitting parameters in pseudosimulation (Eq. 19)
D_{AK}	= Knudsen diffusivity of gas A
D_{AB}	= diffusivity of gas pair A-B
D_{ABeff}	= effective diffusivity of gas pair A-B
d	= mean pore size
f_T	= fraction of molecules transmitted to depth L
k	= index in piecewise fit of Eq. 19
k_o	= characteristic length parameter for Knudsen diffusion
L	= thickness of porous plug (or maximum depth of penetration of a molecule)
M, M_A	= molecular weight of gas, of gas component A
P	= pressure
p	= defined by Eq. 9
R	= gas constant
r	= radius of sphere
T	= temperature
x, y, z	= spacial coordinates, the first representing distance from entry face of porous plug
x_c, y_c, z_c	= coordinates of sphere center
x_i, y_i, z_i	= coordinates of points of intersection of gas molecule with sphere
x_o, y_o, z_o	= defined following Eq. 9
Δx_j	= difference in x coordinate between successive gas molecule-sphere collisions
α, β, γ (or α')	= angles between gas molecule path and coordinate directions
$\beta_1^{(k)}, \beta_2^{(k)}$	= fitting parameters in pseudo-simulation (Eq. 19)
ϵ	= porosity
ϵ_j	= "error" term in pseudo-simulation (Eqs. 18 and 19)
λ, λ_m	= distance between gas molecule-gas molecule collisions, mean value
ϕ	= randomly chosen angle defining gas molecule path following collision with sphere (Figure 3)
σ	= standard deviation of pore size
θ	= randomly chosen angle between normal to surface

and gas molecule path (Figure 3)
= tortuosity

τ

LITERATURE CITED

- Abbasi, M. H., "A Monte Carlo Simulation of the Diffusion of Gases and Radiant Heat Transfer in Porous Solids," Ph.D. Dissertation, University of California, Berkeley (1981).
- Amberg, C. M., and E. Echigoya, "Pellitization and diffusivity studies on silver catalysts," *Can J. Chem. Eng.*, **39**, p. 215 (1961).
- Cunningham, R. D., and C. J. Geankoplis, "Effects of different structures of porous solids on diffusion of gases in the transition region," *Ind. Eng. Chem. Fund.*, **7**, p. 535 (1968).
- Evans, J. W., M. H. Abbasi, and A. Sarin, "A Monte Carlo simulation of the diffusion of gases in porous solids," *J. Chem. Phys.*, **72**(5), p. 2967 (1980).
- Evans, J. W., and M. H. Abbasi, "Monte Carlo Simulation of Radiant Transport through an Adiabatic Packed Bed or Porous Solid," *AIChE J.*, **28**, No. 6, p. 853 (Sept. 1982).
- Fulman, R. L., "Measurement of approximately cylindrical particles in opaque samples," *Trans. AIME*, **197**, p. 1267 (1953).
- Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1956).
- Hoogschagen, J., "Diffusion in porous catalysts and adsorbents," *Ind. Eng. Chem.*, **47**, p. 906 (1955).
- Horsfield, "The strength of asphalt mixtures," *J. Soc. Chem. Ind.*, **53**, p. 107T (1934).
- Jacobson, N. S., "The Diffusion of Gases in Capillaries," Ph.D. Dissertation, University of California, Berkeley (1981).
- Johnson, M. F. L., and W. E. Stewart, "Pore structure and gaseous diffusion in solid catalysts," *J. Catal.*, **4**, p. 248 (1965).
- Masamune, S., and J. M. Smith, "Pore diffusion in silver catalysts," *AIChE J.*, **8**, p. 217 (1962).
- Mason, E. A., A. P. Malinauskas, and R. B. Evans, "Flow and diffusion of gases in porous media," *J. Chem. Phys.*, **46**, p. 3199 (1967).
- Sandry, T. D., and F. D. Stevenson, "Molecular conductance from a curved surface through a cylindrical hole by Monte Carlo methods," *J. Chem. Phys.*, **53**, p. 151 (July, 1970).
- Sarin, A., "Simulation of the Diffusion of Gases in Porous Solids," M.S. Thesis, University of California, Berkeley (1978).
- Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," Chapter 1, M.I.T. Press, Cambridge, MA (1970).
- Satterfield, C. N., and P. J. Cadle, "Gaseous diffusion and flow in commercial catalysts at pressure levels above atmospheric," *Ind. Eng. Chem. Fund.*, **7**, p. 202 (1968).
- Satterfield, C. N., and S. K. Saraf, "Anisotropic diffusivities in pressed catalyst pellets," *Ind. Eng. Chem. Fund.*, **4**, p. 451 (1965).
- Wakao, N., and J. M. Smith, "Diffusion in catalyst pellets," *Chem. Eng. Sci.*, **17**, p. 825 (1962).
- Youngquist, G. R., "Diffusion and flow of gases in porous solids," *Ind. Eng. Chem.*, **62**, p. 52 (1970).

Manuscript received November 16, 1981; revision received July 19, and accepted August 27, 1982.