Knudsen Diffusion in Random Assemblages of Uniform Spheres

Experimental measurements have been conducted of Knudsen diffusion through a model porous medium fabricated by the pelleting of monodisperse silica spheres. Tortuosity factors for this random-assemblage-of-spheres porous solid are calculated and compared with values obtained from both theory and measurements made in the bulk diffusion regime. Evidence is presented to support the use of a mean pore radius calculated as twice the ratio of pore volume to surface area, as opposed to values obtained from mercury porosimetry or sorption isotherm analysis.

D. G. HUIZENGA

and D. M. SMITH

Department of Chemical Engineering
Montana State University
Bozeman, MT 59717

SCOPE

Knudsen diffusion of gases through porous media is of interest in a number of applications where the gas mean free path is much greater than the characteristic pore size. Effective Knudsen diffusivities for porous media are typically calculated using an expression for diffusion in a capillary in conjunction with a mean pore radius determined from mercury porosimetry or sorption isotherm analysis. To account for deviations in pore shape and direction, a tortuosity factor is also included. However, the tortuosity factor cannot be predicted from first principles. In addition, questions exist concerning the proper choice of the mean pore size, given that porosimetry and isotherm analysis are limited to providing information about the smallest constrictions in a pore. In comparison, one could use twice the ratio of pore volume to surface area to obtain a mean pore radius. This mean pore radius definition should be more descriptive for a transport process, such as Knudsen diffusion, which is dominated by molecule-pore wall collisions.

The objective of this work was to use a model porous solid with known geometry to address the questions of pore size and tortuosity factor. By pelleting a powder of monodisperse submicron solid spheres, a model porous medium can be fabricated with a pore structure known by analogy to the structure of randomly packed beds. By varying the solid sphere size, the characteristic pore size can be changed without changing the tortuosity factor. A permeability-type experiment was used to determine effective Knudsen diffusivities in our model porous medium. A series of pellets with different characteristic pore sizes were studied, thereby yielding information about the choice of pore size definition as well as tortuosity factors for this random-assemblage-of-spheres pore model.

CONCLUSIONS AND SIGNIFICANCE

A model porous medium has been fabricated by pelleting spheres of a very narrow size distribution and average radius ranging from 51 to 305 nm. The pore network surrounding this random assemblage of spheres is known from first principles by analogy to the random packing of uniform spheres in a packed bed. The average pellet porosity was 0.363 ± 0.030, which is in very close agreement with the literature values of 0.359–0.375 reported by Haughey and Beveridge (1969) for close random packings of uniform spheres.

Tortuosity factors in all pellets studied were found to range from 1.45 to 1.51 for Knudsen diffusion of argon, helium, hydrogen, and nitrogen. Plots of D_e/ϵ vs. $\sqrt{T/MW}$ and D_e/ϵ vs. $\bar{r}$ were linear, therefore indicating that the tortuosity was independent of sphere size and that no surface transport occurred. Effective diffusivities were independent of pressure over the range of 13.3 to 53.2 kPa, indicating that transport was in the Knudsen regime. The tortuosity factors were calculated using a mean pore radius equal to twice the ratio of pore volume to surface area. The fact that our tortuosity factors agree well with bulk diffusion tortuosities of 1.48 reported by Currie (1960) and 1.42 by Hoogschagen (1955) lends support to this definition for the mean pore radius. At least for random assemblages of spheres, this mean pore radius definition properly accounts for the effects of nonuniform pore shape on the transport rate. For random packings of spheres, one would expect the pore radius determined from mercury porosimetry or sorption isotherm analysis to be ~75% of the value of twice the ratio of pore volume to surface area. When combined with the common assumption of $\tau = 1/\epsilon$, (Satterfield, 1970), the predicted value of the effective Knudsen diffusivity will be only ~40% of the correct value.

Correspondence concerning this paper should be addressed to D.M. Smith.
The authors are presently at the Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, NM 87131.

INTRODUCTION

For Knudsen diffusion in long capillaries under conditions such that the mean free path of the gas is much greater than the pore diameter (i.e., $\lambda > d$), the diffusivity is given by (Knudsen, 1928):

$$D_k = \frac{4r}{3}\sqrt{\frac{2RT}{\pi MW}}\frac{(2-f)}{f} \tag{1}$$

For practical application, the sticking coefficient, f, is usually taken to be 1 and Eq. 1 is simplified in cgs units to:

$$D_k = 9{,}700\ r\sqrt{T/MW} \tag{2}$$

When Knudsen transport in porous media is considered, an effective diffusivity is usually defined as (Satterfield, 1970):

$$D_e = \epsilon\, D_k/\tau \tag{3}$$

The tortuosity factor, τ, is sometimes taken to be the product of a shape factor, S', and a length factor, L'. S' accounts for size and shape nonuniformity in the pore cross section. The length factor, L', accounts for the additional distance required for a molecule to travel in porous media relative to the mean direction of diffusion.

For predicting the effective Knudsen diffusivity in a particular porous solid, one must have information concerning the porosity, pore volume distribution (i.e., to calculate $\bar{r}$, and tortuosity for the material. However, defining the mean pore radius, $\bar{r}$, for porous media is not straightforward (Wang and Smith, 1983). The application of mercury porosimetry or capillary condensation techniques will provide information related to the size of the smallest restriction in a particular pore (Lowell, 1979). In contrast, defining the mean pore radius as twice the ratio of pore volume to surface area, as Satterfield (1970) suggests, takes the entire pore structure into account. For material with a pore network similar to an array of uniformity sized cylinders, these three methods should result in similar values for $\bar{r}$. However, for materials with nonuniform pore shapes and a distribution of pore sizes, the various means of defining $\bar{r}$ will result in different values for use with Eqs. 2 and 3.

BACKGROUND

Several studies of bulk diffusion in beds of randomly packed uniform spheres have been reported. Currie (1960) measured hydrogen diffusion in beds fabricated from smooth glass spheres of three diameters. Sample porosity was in the range of 0.375 to 0.405 and the tortuosity factor was found to be 1.48 ± 0.02. For beds fabricated from sand particles of a wider particle size distribution and more surface roughness, bed porosity varied from 0.355 to 0.424 and τ was 1.60 ± 0.03. For a bed fabricated of glass spheres with diameter 1.0–1.25 mm and a bed porosity of 0.43, Hoogschagen (1955) reports a tortuosity factor of 1.42. In a theoretical investigation of varying pore shape and size on bulk diffusion rates, Petersen (1958) concludes that the reduction in D_e due to pore constrictions for porosities greater than 0.4 are negligible (i.e., $S' \simeq 1$). This suggests that for bulk diffusion in beds of uniform spheres, $L' = \sqrt{2}$, which corresponds to a molecule traveling in a direction, on average, 45 degrees from the mean diffusion direction.

Monte Carlo simulation techniques have been used by several investigators to study Knudsen diffusion in porous media. Abbasi et al. (1980) and Evans et al. (1983) simulated porous solids by placing, in a mathematical sense, three different sphere sizes in a regular array. To obtain more realistic simulations, the coordinates of the various sphere centers were randomly moved. In this manner, a range of porosities is obtained. In the region of $\epsilon = 0.4$, the tortuosity was found to range between 2.5 and 5. A general expression for the effective Knudsen diffusivity derived from that series of simulations is:

$$D_e = \frac{4}{3}\sqrt{\frac{8RT}{\pi MW}}k_o \tag{4}$$

and the length parameter, k_o, is given by:

$$k_o = d\,(0.0093 + 0.1\epsilon) - 0.0181\,\sigma \tag{5}$$

The major problem with applying Eqs. 4 and 5 is the question of the characteristic pore size, d. The authors state that d may be obtained directly from mercury porosimetry measurements, but the scheme they describe for determining d for their simulated solids would appear to be analogous to taking twice the ratio of pore volume to surface area.

Smith and Huizenga (1984) have simulated Knudsen diffusion in beds of uniformly sized spheres. In that work, spatial coordinates of each sphere were selected at random with the constraint that the spheres not overlap. The mean pore size is defined as twice the ratio of pore volume to surface area. For beds of uniform spheres, $\bar{r}$ is a function of the porosity and sphere size only and is given by:

$$\bar{r} = \frac{2}{3}\frac{\epsilon}{(1-\epsilon)}r_s \tag{6}$$

Tortuosity values of 1.40 and 1.72 were calculated for bed porosities of 0.386 and 0.438 respectively.

Several investigations of the pore network contained in random packings of equal spheres have been reported. Dullien and Dhawan (1974) used mercury porosimetry to measure the pore volume distribution in beds of 250 μm dia. glass spheres. A very narrow pore size distribution was noted with a mean pore diameter of 75 μm corresponding to $\bar{r}/r_s \simeq 0.3$. Mason (1971) has performed a theoretical simulation of the pore network in random packings of equal spheres. He predicts that the mean pore radius as determined via mercury porosimetry or sorption isotherm analysis will be $0.275\ r_s$. In comparison, if twice the ratio of pore volume to surface area (Eq. 6) for a random packing of spheres (i.e., $\epsilon = 0.37$) is taken, then $\bar{r}/r_s$ is 0.39.

EXPERIMENTAL

Fabrication of a model porous medium with the desired properties required a source of uniform spheres with a narrow size distribution and average diameters of 100 to 1,000 nm. Materials with these properties were not available commercially, necessitating the production of spheres as part of this project. A search of the literature reveals that submicron-size spheres have been produced from a number of materials. For our work, silica was selected because of its excellent thermal and mechanical stability and well-characterized surface chemistry (Iler, 1955). Strober and Fink (1968) have detailed a procedure for fabricating uniform, colloid-size silica spheres via the hydrolysis of tetra-alkyl silicates with subsequent condensation of the silicic acid. The reaction is carried out using an alcohol solvent, with ammonia hydroxide as the catalyst. The size of the silica spheres produced with this scheme depends upon the alkyl group of the silicate, the type of alcohol solvent, and the concentrations of water and ammonia in the reaction mass.

To produce spheres in the size range of interest (100–1,000 nm), tetraethyl orthosilicate (Aldrich Chemical, technical grade) is reacted with ammonium hydroxide (reagent grade) and distilled water, using ethanol as a solvent. The reaction is undertaken at ambient temperatures in a 250 mL Erlenmeyer flask mounted on an Eberbach platform shaker [60 cycles/min (hz)]. The TEOS concentration is fixed at 0.28 M, corresponding to an intermediate value of the concentration range studied by Strober and Fink. After an invisible hydrolytic reaction forming silicic acid, the condensation of the supersaturated silicic acid was indicated by an increasing opalescence of the mixture starting 1–5 min after the addition of the TEOS. Subsequently, the transition to a turbid white suspension occurred within several minutes.

As a standard procedure, samples for electron microscope size analysis were taken 24 h after the initiation of the reaction. All sampling for size analysis was done by pipeting a drop of the suspension onto a Formvar-coated copper TEM grid. The grid was allowed to air dry and electron micrographs of the particles retained on the grids were obtained with a JEOL 100-CX transmission/scanning electron microscope. The average particle size and standard deviation were determined from the TEM micrographs using a Buehler Omnimet image analyzer. Typical sample sizes in the characterization ranged from 200 to 400 spheres.

Figure 1 is a TEM micrograph of silica spheres (batch 3) of average diameter equal to 98 nm shown at a magnification of 76,000. The high degree of sphere size and shape uniformity is quite apparent when viewed with the electron microscope. The size distribution for the same batch is illustrated in Figure 2. The standard deviation of sphere size was found to vary between 7 and 9% of the average diameter. This is slightly higher than the values reported by Strober and Fink but this may be attributed to their use of higher-purity reagents. For our investigation, size distributions such as Figure 2 were deemed to be quite satisfactory. In addition to the size measurements, the degree of eccentricity was studied. Within the limits of our measurements, the spheres were found to be perfectly round. This fact is illustrated in Figure 3, a TEM image of 650 nm dia spheres (× 76,000). Figure 3 also reveals a lack of large-scale surface roughness, which was consistent in all batches of spheres produced.

The reproducibility of the silica sphere growth scheme is excellent, as demonstrated in Table 1. In order to produce spheres of different sizes, the ammonium hydroxide and water concentrations were varied. The effects of changing these two variables is illustrated in Table 2.

Before pelleting, the sphere slurry was evaporated to dryness using a Buchi Rotovapor R110 rotary vacuum system operated at 303 K. The dried spheres were removed from the evaporator and placed in an agitation device for 24 h to break up small flakes and lumps that tended to form during the drying process. Samples were often taken at this point and subjected to the TEM size analysis techniques described above. The samples were found to be unaffected by the drying and agitation process (i.e., no fracturing or agglomeration).

To form pellets of porous media, the dried spheres were packed into stainless steel cylinders (0.475 cm ID × 1.2 cm length) using a hand pellet press. The use of packing pressures between 7 and 70 MPa was investigated and found to have little effect on the pellet porosity. Therefore, all pellet pressings were conducted at 70 MPa. Cadle and Satterfield (1968) report

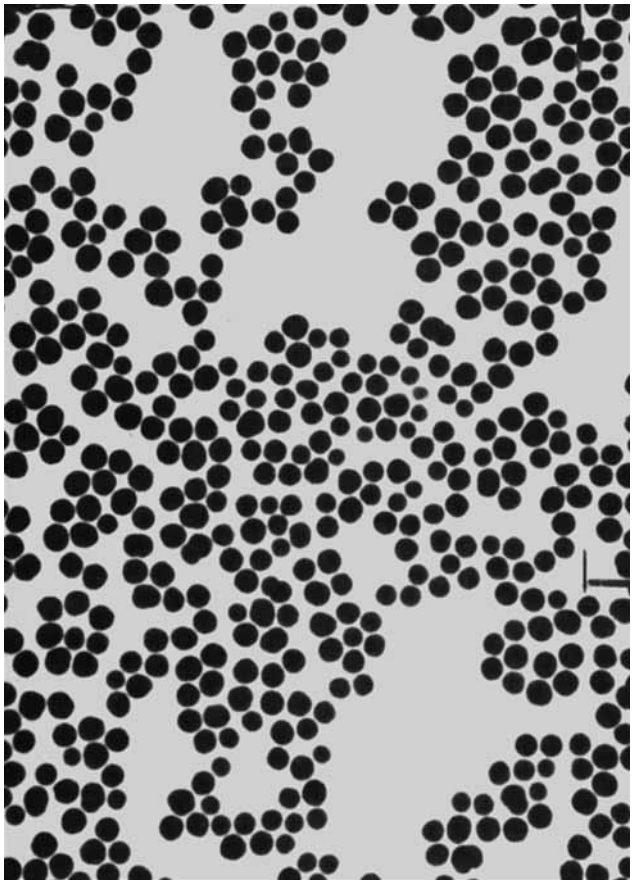

Figure 1. TEM micrographs of 98 nm silica spheres (×76,000).

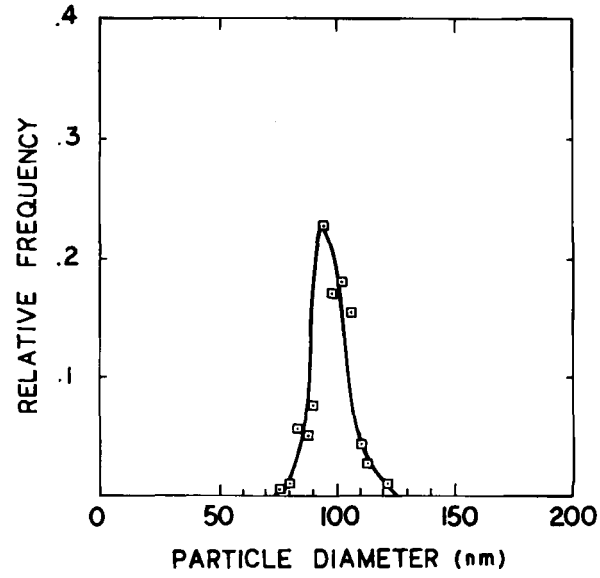

Figure 2. Typical sphere size distribution (dia. = 98 ± 8 nm).

TABLE 1. AVERAGE SPHERE RADIUS, SILICA SPHERES PRODUCED AT AN NH_4OH CONCENTRATION OF 0.55 M AND H_2O CONCENTRATION OF 3.0 M

Batch No.	No. Particles Measured	Sphere Radius nm
1	371	52 ± 5
2	499	49 ± 4
3	302	49 ± 4
4	444	54 ± 5

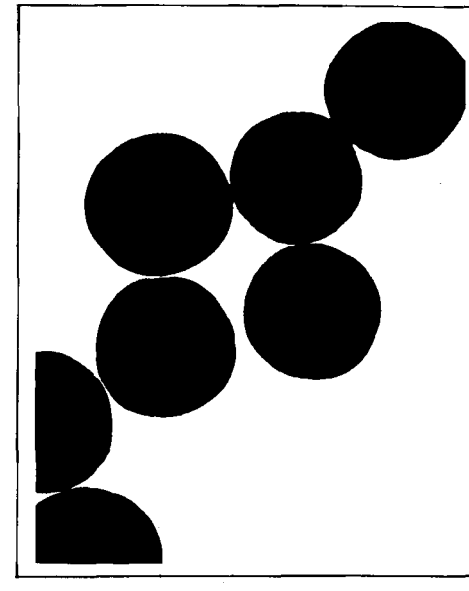

Figure 3. TEM closeup of 650 nm spheres (×76,000).

Table 2. Effect of Changing NH_4OH and H_2O Concentrations on Average Sphere Size

NH_4OH	H_2O	Sphere Radius, nm
0.55 M	3.0 M	50 ± 2*
1.0 M	2.4 M	50**
0.55 M	3.9 M	73 ± 3*
1.4 M	3.4 M	125 ± 8
1.6 M	3.8 M	160 ± 11
1.8 M	4.3 M	226 ± 21
2.0 M	4.8 M	306 ± 27

*Four-batch average.
**Estimated radius based on sample size of less than 20 particles.

that significant axial variations in pellet porosity may occur when powders are pressed without a die lubricant. To avoid this problem, each pellet was created in a series of steps by adding a small amount of powder and then pressing. This process was repeated between 20 and 35 times per pellet depending upon the sphere diameter. The porosity of each pellet was calculated using the known volume of the cylinder, the weight of spheres in a pellet and the true density of the silica powder as determined via methanol/water displacement measurements. To insure that the individual spheres remained intact under the 70 MPa forming pressure, samples were studied using scanning electron microscope (SEM) methods. A typical SEM cross section is shown in Figure 4 at a magnification of 40,000. This figure clearly shows that the individual spheres are intact. It should be noted that cross sections such as Figure 4 were taken at fracture planes in the porous structure, which explains the three-dimensional effect in the figure.

For pellets packed at 70 MPa, the average porosity was 0.363 ± 0.030. This value is in close agreement with the literature values of 0.359–0.375 reported by Haughey and Beveridge (1969) for a close random packing of uniform spheres. Table 3 indicates the expected independence of porosity with respect to sphere size, as well as the average pore radius calculated using Eq. 6. The slightly low value of 0.331 for the 51 nm spheres was thought to be caused by moisture contamination.

For the pellets described above, effective Knudsen diffusivities for hydrogen, helium, nitrogen, and argon were determined using the flow apparatus shown in Figure 5. From measurements of temperature, pressure, pellet size, and flow rate, the effective diffusivity may be calculated. All diffusion measurements were conducted at 303 K, a temperature low enough to minimize problems associated with sealing the pellets into the apparatus, but sufficiently high to avoid a surface diffusion contribution. At this temperature and a pressure of 13.3 kPa, the mean free path of the four gases studied ranged from 490 to 1,090 nm, as compared to our pore radius range of 17 to 114 nm. Complete details of the fabrication of the model porous media and the measurement of effective diffusivities in the pellets are reported by Huizenga (1984).

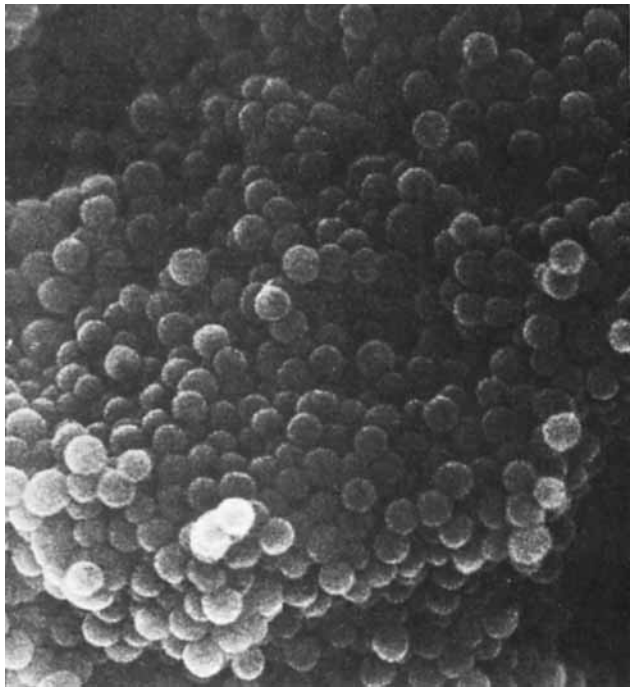

Figure 4. SEM micrograph of an interior surface for a pellet pressed at 70 MPa (×40,000).

Table 3. Physical Properties of Model Porous Media Pellets

Sphere Radius nm	No. Pellets Formed	Avg. Porosity	Avg. Pore Radius Eq. 6, nm
52 ± 4	8	0.331 ± 0.025	17
54 ± 5	5	0.377 ± 0.028	22
125 ± 8	6	0.381 ± 0.027	51
160 ± 11	7	0.366 ± 0.026	62
226 ± 14	9	0.364 ± 0.024	86
305 ± 27	7	0.359 ± 0.024	114

RESULTS AND DISCUSSION

To insure that effective diffusivity measurements were in the Knudsen regime, experiments were conducted over an inlet pressure range of 13.3 to 53.2 kPa. In all experiments, the exit pressure from the pellet was less than 13.3 Pa. For all gas and pellet combinations studied, the effective diffusivity was essentially independent of pressure. This indicates that gas-phase diffusion is indeed in the Knudsen regime, and is a strong indication that no measurable surface transport occurred. Since the ratio of the gas mean free path to pore radius is greatest at 13.3 kPa, for the pressure range we studied, and the possibility of surface diffusion is minimized at that pressure, we will report our findings for that inlet pressure only.

In order to examine the reproducibility of our diffusion measurement scheme, duplicate pellets were fabricated from the same batch of spheres. Small differences in pellet porosity were obtained in the pelleting process, which we account for by reporting our results in terms of D_e/ϵ. The results of these duplication experiments are reported in Table 4.

According to Eqs. 2 and 3, a plot of D_e/ϵ vs. $\sqrt{T/MW}$ should result in a straight line with slope proportional to $\bar{r}/\tau$. Figure 6 represents this plot for seven different pellets. As expected, the slope of each line increases with increasing sphere size. The discrepancies for the two 54 nm sphere pellets and the 52 nm sphere pellet are a result of a significant porosity difference and the resultant effect on $\bar{r}$ (see Eq. 6). Following Eqs. 2 and 3, our experimental findings for each particular sphere size do indeed fit a straight line. The fact that hydrogen and nitrogen behave similarily to the two inert gases (i.e., helium and argon) is further evidence that no surface transport occurred.

If one invokes a geometric similarity argument for pellets produced from random packings of different sphere sizes, the value of the tortuosity factor, τ, should be independent of sphere size. If the sphere radius which we define via Eq. 6 is indeed descriptive of the characteristic pore size, then a plot of D_e/ϵ for a particular gas (i.e., value of $\sqrt{T/MW}$) vs. $\bar{r}$ should be a straight line for pellets made from all sphere sizes. The value of the tortuosity factor is inversely proportional to the slope of this type of plot. Plotted in Figure 7 is D_e/ϵ vs. r for the two inert gases, helium and argon. For both gases, the data fit a straight line within the limits of our experimental measurements. In addition, when extrapolated to $\bar{r} = 0$, the line passes through $D_e/\epsilon = 0$ as would be expected from Eq. 2. Figure 8 is an analogous pair of plots for nitrogen and hydrogen. The fact that the data is fit by a straight line for all four

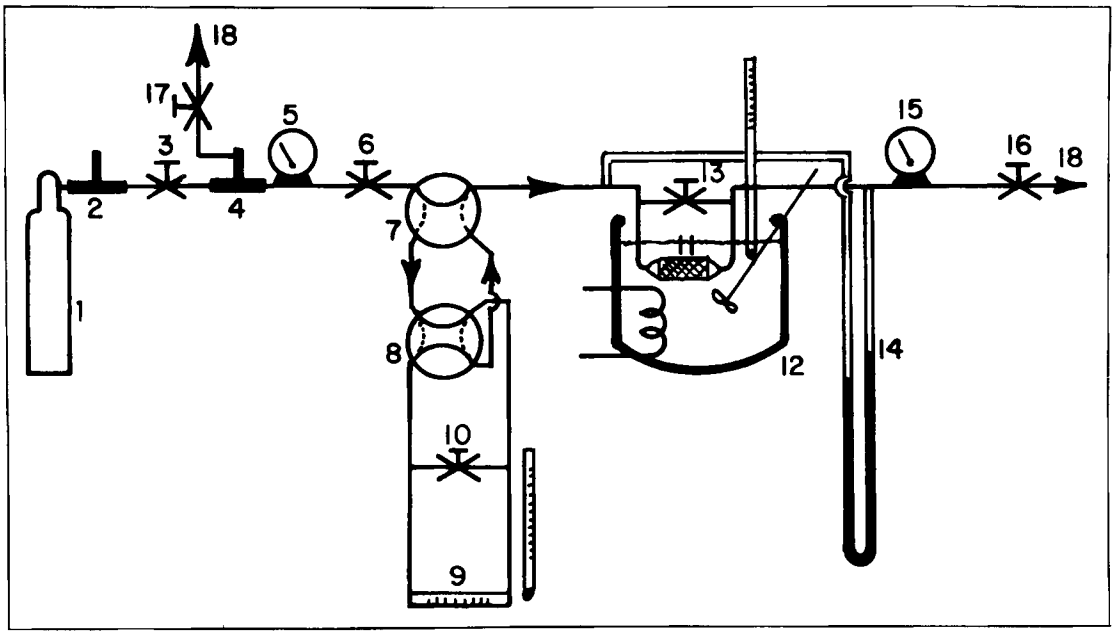

Figure 5. Diffusion apparatus schematic diagram.

1. Gas cylinder
2. High-pressure regulator
3. Feed valve
4. Low-pressure regulator
5. Vacuum gauge
6. Control valve
7. Flowmeter bypass valve
8. Flowmeter direction valve
9. Flowmeter
10. Flowmeter bypass loop
11. Sample pellet
12. Constant temperature bath
13. Sample bypass loop
14. U-tube Hg manometer
15. Thermocouple vacuum gauge
16,17 Vacuum valves
18. Vacuum pump

TABLE 4. DUPLICATION EXPERIMENT RESULTS

Pellet No.	Sphere Radius nm	ϵ	D_e/ϵ, cm^2/s Nitrogen	Helium	Hydrogen
6	160	0.367	-----	0.326	0.451
7	160	0.366	0.118	0.332	0.448
8	226	0.360	0.182	0.503	0.704
9	226	0.364	0.182	0.498	0.705

plots further indicates that $\bar{r}$ is an appropriate choice for the characteristic pore size.

Tortuosity factors have been calculated from the slope of the D_e/ϵ vs. $\bar{r}$ plots shown in Figures 7 and 8; they are given in Table 5. In general, one would not expect an effect of gas type on the magnitude of the tortuosity factor assuming that no surface transport is occurring. The small differences in τ evident in Table 5 are the result of the level of precision in our experiments. An error analysis indicates that τ values are accurate to ± 0.10. The largest contribution to this uncertainty arises from the pellet porosity determination.

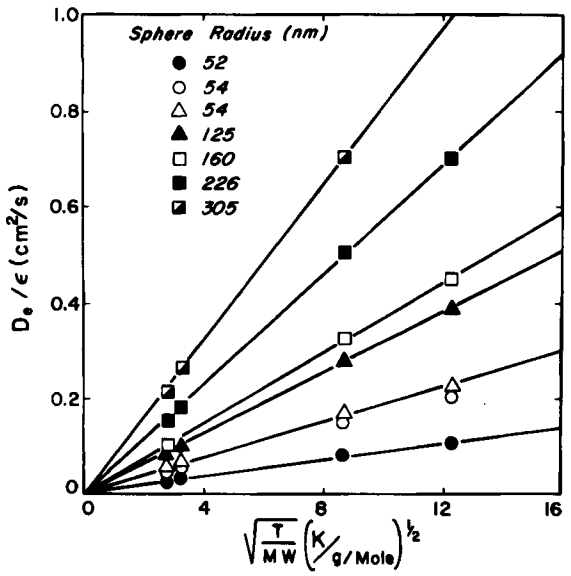

Figure 6. Effect of changing gas molecular weight on diffusivity.

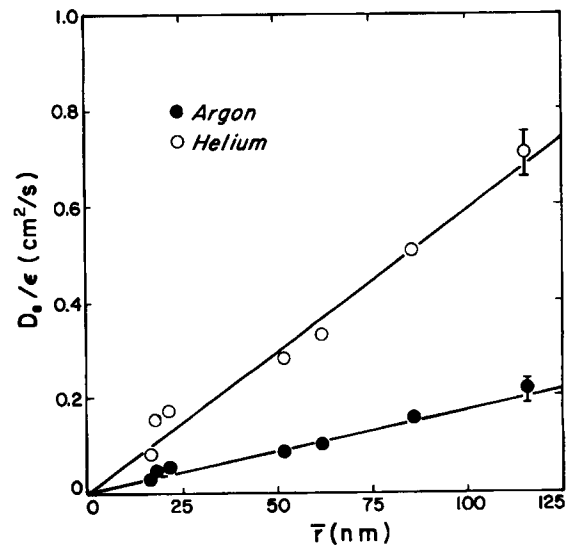

Figure 7. Mean pore radius dependency for helium and argon diffusion.

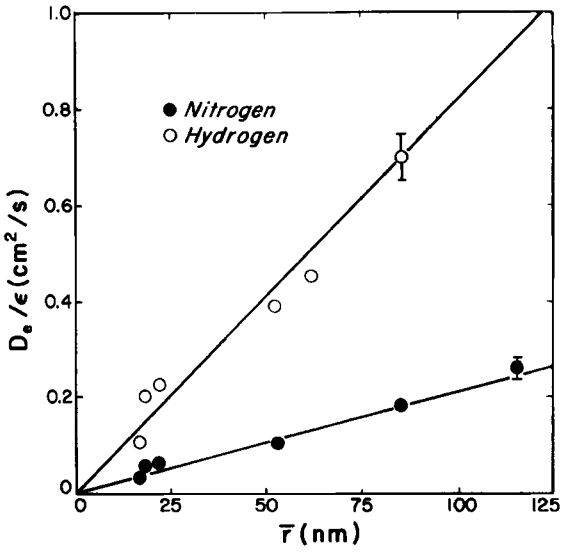

Figure 8. Mean pore radius dependency for hydrogen and nitrogen diffusion.

ANALYSIS

The average tortuosity factor was 1.47, which we find agrees reasonably well with values of 1.48 (Currie, 1960) and 1.42 (Hoogschagen, 1955) reported for bulk diffusion measurements. Our findings are also in close agreement with Monte Carlo simulations reported by Smith and Huizenga (1984). The fact that τ approximates $\sqrt{2}$ supports the theory that the shape factor, S', is unity and that the length factor, L', is identical for bulk and Knudsen diffusion (i.e., $L' = \sqrt{2}$). However, this is only true when we define the mean pore radius as twice the ratio of pore volume to surface area. If other means were used to obtain the pore radius, such as mercury porosimetry or sorption isotherm analysis, the value of the correct tortuosity factor would change with diffusion regime.

In the absence of actual measurements for Knudsen transport in a porous solid, the effective diffusivity is usually determined using the pore radius calculated from porosimetry/sorption analysis and a value of $\tau = 1/\epsilon$. For porous media which can be described as a random assemblage of spheres, this method would result in a predicted transport rate that is only 40% of the correct value.

A major limitation to making more general conclusions based upon this work is the fact that measurements could only be made over a very small porosity range. In future work, this problem will be rectified by using mixtures of uniform spheres. In addition, the question of whether the mean pore radius definition that we use will account for nonuniform pore shapes for other pore geometries should be investigated for Knudsen diffusion, as a parallel work to that performed by Petersen (1958) for bulk diffusion.

TABLE 5. CALCULATED AVERAGE TORTUOSITY FACTORS

Gas	Tortuosity Factor
Argon	1.51
Helium	1.46
Hydrogen	1.45
Nitrogen	1.48
Average for all gases	1.47

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of the MONTS program and the National Science Foundation (CPE-8404063). Support for D. G. Huizenga was provided by the Montana State University Engineering Experiment Station.

NOTATION

D_e = effective diffusivity
D_k = Knudsen diffusivity
d = mean pore diameter
f = sticking coefficient
k_o = length parameter used in Eqs. 4 and 5
L' = pore length parameter
MW = gas molecular weight
r = capillary radius
$\bar{r}$ = mean pore radius
r_s = solid sphere radius
R = gas constant
S' = pore shape factor
T = temperature

Greek Letters

ϵ = porosity
σ = standard deviation of pore size distribution
τ = tortuosity factor

LITERATURE CITED

Abbasi, M. H., J. W. Evans, I. S. Abramson, "Diffusion of Gases in Porous Solids: Monte Carlo Simulations in the Knudsen and Ordinary Diffusion Regimes," *AIChE J.*, **29**, 617 (1983).

Cadle, P. J., and C. N. Satterfield, "Anisotropic Diffusivities in Pressed Boehmite Pellets," *Ind. Eng. Chem. Fund.*, **7**, 192 (1968).

Currie, J. A., "Gaseous Diffusion in Porous Media. II: Dry Granular Materials," *British J. Appl. Phys.*, **11**, 192 (1960).

Dullien, F. A. L., and G. K., Dhawan, "Characterization of Pore Structure by a Combination of Quantitative Photomicrography and Mercury Porosimetry," *J. Colloid Interface Sci.*, **47**, 337 (1974).

Evans, J. W., M. H. Abbassi, and A. Sarin, "A Monte Carlo Simulation of the Diffusion of Gases in Porous Solids," *J. Chem. Phys.*, **72**, 2,967 (1980).

Haughey, D. P., and G. S. G. Beveridge, "Structural Properties of Packed Beds—A Review," *Can. J. ChE.*, **47**, 130 (1969).

Hoogschagen, J., "Diffusion in Porous Catalysts and Adsorbents," *Ind. Eng. Chem.*, **47**, 906 (1955).

Huizenga, D. G., "Knudsen Diffusion in Beds of Monodisperse Silica Spheres," MS Thesis, Montana State Univ., Bozeman (1984).

Iler, R.K., *The Colloid Chemistry of Silica and Silicates*, Cornell Univ. Press, Ithaca, NY, 21 (1955).

Knudsen, M., "The Laws of Molecular Flow and Viscous Flow of Gases through Tubes," *Annal. Phys.*, **28**, 73 (1928).

Lowell, S., *Introduction to Powder Surface Area*, Wiley, New York, 62 (1979).

Mason, G., "A Model of the Pore Space in a Random Packing of Equal Spheres," *J. Colloid Interface Sci.*, 35, 279 (1971).

Petersen, E. E., "Diffusion in a Pore of Varying Cross Section," *AIChE J.*, 4, 343 (1958).

Satterfield, C. N., *Mass Transfer in Heterogenous Catalysis*, MIT Press, Cambridge, MA, 41 (1970).

Smith, D. M., and D. G. Huizenga, "Simulation of Knudsen Diffusion in Porous Media," *Proc. 10th IASTED Symp. Appl. Modeling and Simulation*, ACTA Press, Anaheim, CA, 13 (1984).

Strober, W., and A. Fink, "Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range," *J. Colloid Interface Sci.*, **26**, 62 (1968).

Wang, C. T., and J. M. Smith, "Tortuosity Factors for Diffusion in Catalyst Pellets," *AIChE J.*, **29**, (1983).

Manuscript received Sept. 10, 1984, and revision received Feb. 21, 1985.