Marshall, R. D., and J. A. Storrow, "Dialysis of Caustic Soda Solutions," *Ind. Eng. Chem.*, **43**, 2934 (1951).

Pantell, K., "Versuche über Scheibenreibung," *Forsch. Gebiete Ingenieurw.*, **16**, 97 (1950).

Peterson, M. A., and H. P. Gregor, "Diffusion-Exchange of Ions and Nonexchange Electrolyte in Ion-Exchange Membrane Systems," *J. Electrochem. Soc.*, **106**, 1051 (1959).

Phipps, D. L., Jr., "Mass Transfer in a Mechanically Agitated Batch Dialyzer," S.M. thesis, Mass. Inst. Technol., Cambridge (1967).

Rogers, M. H., and G. N. Lance, "The Boundary Layer on a Disc of Finite Radius in a Rotating Fluid," *Quart J. Mech. Appl. Math.*, **17**, 319 (1964).

Scattergood, E. M., "Electrokinetic Membrane Processes," Ph.D. thesis, Univ. of Wisconsin, Madison (1966).

———, and E. N. Lightfoot, "Diffusional Interaction in an Ion-Exchange Membrane," *Trans. Faraday Soc.*, **64**, 1135 (1968).

Schultz-Grunow, F., "Der Reibungswiderstand rotierender Scheiben in Gehäusen," *Z. angew. Math. Mech.*, **15**, 191 (1936).

Seidell, A., Solubilities of Inorganic and Metal Organic Compounds. 3rd ed., Van Nostrand, New York (1940).

Smith, K. A., et al., "Convective Transport in a Batch Dialyzer: Determination of True Membrane Permeability from a Single Measurement," *Chem. Eng. Progr. Symp. Ser. No. 84*, **64**, 45 (1968).

Smith, K. A., and C. K. Colton, "Mass Transfer to a Rotating Fluid. Part I. Transport from a Stationary Disk to a Fluid in Bödewadt Flow," *AIChE J.*, **18**, 949 (1972).

Soo, S. L., "Laminar Flow Over an Enclosed Rotating Disk," *Trans. ASME*, **80**, 287 (1958).

Stokes, R. H., "An Improved Diaphragm-cell for Diffusion Studies, and Some Tests of the Method," *J. Am. Chem. Soc.*, **72**, 763 (1950).

Tomlan, P. F., and J. L. Hudson, "Flow Near an Enclosed Rotating Disk: Analysis," *Chem. Eng. Sci.*, **26**, 1591 (1971).

Wilson, E. E., "A Basis for Rational Design of Heat Transfer Apparatus," *Trans. ASME*, **37**, 47 (1915).

Manuscript received November 24, 1971; revision received May 19, 1972; paper accepted May 19, 1972.

Using the Dusty Gas Diffusion Equation in Catalyst Pores Smaller than 50 Å Radius

When the dusty gas diffusion equation is applied to materials containing pores with radii below 50 Å, the observed diffusion behavior in these smaller pore systems can be quite different from that predicted by the equation. Higher temperatures and in some cases higher pressures tend to lessen the deviations between prediction and experiment. The observed deviations are probably caused by surface transport and by momentum transfer between gas molecules and pore walls during molecular flight. For bimodal materials, an additional factor can be the inapplicability of the equation to systems of parallel micro- and macropores. Excellent agreement between theory and experiment occurs for large-pore unimodal systems.

HIROKAZU OMATA
and LEE F. BROWN

Department of Chemical Engineering
University of Colorado
Boulder, Colorado 80302

SCOPE

Diffusion and bulk transport of gases and liquids within porous materials can be of critical importance in catalysis, adsorption, and separation processes. Within recent years, investigation of the diffusion and transport of gases within porous materials has resulted in increasingly effective and rigorous correlation and prediction techniques. The heart of these techniques has been the so-called "dusty gas diffusion equation," independently derived by three sets of investigators. This equation covers the entire range from Knudsen diffusion through the transition region into bulk or molecular diffusion and as a result gives promise of extremely wide applicability to gaseous diffusion within porous materials under all types of process conditions.

Under the two limiting conditions of Knudsen diffusion and bulk diffusion and flow, equations have long existed which gave useful agreement between theory and experiment. But until the development of the dusty gas equation, mass transport in the transition region was not as well described. This was a critical lack because the transition region covers a wide range of pore sizes and process conditions. Using the dusty gas equation, Satterfield (1970) gave the range of pore sizes within the transition region for some binary gas mixtures at 300°C. and 1 atm. He listed pores as small as 8 Å and as large as 26,300 Å as lying within the transition region, depending on the gas composition. These sizes encompass the pores in most porous catalysts and adsorbents, with the exception of some molecular sieves and active carbons.

Thus the dusty gas equation appears to be necessary for describing gas-phase transport within a large number

---

Correspondence concerning this paper should be addressed to L. F. Brown. H. Omata is at #272 Hachimanmae-shataku, Mitsui Toatsu Chemicals, Inc., Mobara-shi, Chiba-ken, Japan.

of materials of real significance. But there should be a lower limit to the pore sizes where the dusty gas equation can be applied. All derivations of the equation assume that the forces exerted by the porous material's solid surface have a negligible effect on the flight paths of the gaseous molecules. The derivations also assume that the molecules are of insignificant size in comparison with the radius of the pore. Many commercial catalysts and adsorbents possess pores with radii below 50 Å, and this size is beginning to approach molecular dimensions. Somewhere around this size, therefore, the assumptions on which the equation are based should become unrealistic, and the equation's predictions should deviate from experimental observation.

This paper reports an experimental attempt to determine the lower pore size limit where the dusty gas equation can be applied, together with some theoretical discussion of factors which affect the applicability of the equation to porous materials.

As originally derived (Evans et al., 1961; Scott and Dullien, 1962; Rothfeld, 1963), the dusty gas equation described isothermal counterdiffusion of two gases within a porous substance with the gases under a constant total pressure. Later studies (Mason et al., 1967; Mason and Evans, 1969; Gunn and King, 1969) have added flow under temperature and pressure gradients to the diffusion phenomenon. To minimize the number of variables, the present study considers only the original situation, that is, only isothermal and isobaric systems with steady state counterdiffusion are treated in this paper.

The experimental program consisted of carrying out a steady state Wicke-Kallenbach type of experiment using three carefully selected porous materials. The Wicke-Kallenbach experiment consists of flowing two pure gases past opposing faces of a porous pellet. The circumferential surface of the pellet is sealed off, and the two gases are at the same temperature and pressure. Downstream from the pellet the compositions of the two streams are analyzed to determine the extent of crossflow (that is, diffusion) of the two gases through the porous pellet. For the present study, the two gases were helium and nitrogen.

Of the three porous materials chosen, the majority of the pores of two had radii below 50 Å (r_{mean} of 24 and 46 Å) and the third had considerably larger pores (r_{mean} of 550 Å) and was used for comparison. To simplify interpretation of the experimental results, all three materials had unimodal pore systems, that is, pore systems with reasonably uniform pore sizes.

All three materials were tested over a pressure range of 1-21 atm. and a temperature range of 26-146°C. The dusty gas equation was then applied to the experimental results from different aspects to examine its validity and utility in the small pore systems. In addition, the equation was applied to the data of Haynes (1969). He had measured the flux of helium diffusing through porous systems in the presence of nitrogen for nine different unimodal and bimodal porous materials, most of them containing pores with radii below 50 Å.

For the transition region between Knudsen and bulk diffusion, there appear to have been no comparisons as yet between theory and experiment concerning changes in pore diffusion with changes in temperature. This type of comparison was also made using the results of our experiments.

CONCLUSIONS AND SIGNIFICANCE

The dusty gas diffusion equation, for the system used in these experiments, predicts that the ratio of the fluxes of the counterdiffusing gases should be constant, irrespective of temperature or total pressure. This constant should be equal to the negative square root of the inverse ratio of the diffusing gases' molecular weights. The equation also predicts the manner in which the diffusing fluxes will change with changes in temperature and total pressure.

When unimodal porous materials containing pores with radii below 50 Å were tested, it was shown that the dusty gas equation can predict diffusion behavior significantly different from that experimentally observed for both flux ratios and changes of flux with changes of temperature or pressure. The deviations from theory appear to grow less severe as the pore radii become larger, and somewhere in the neighborhood of a 50 Å radius appears to be the place where the deviations become small enough to be neglected. The causes for the deviations are postulated to lie in the inapplicability of some of the basic assumptions used in deriving the equation. Principal factors are believed to be momentum transfer between gas molecules and pore walls during molecular flight within the molecule-wall dispersion force fields, and surface transport. In deriving the equation, both of these phenomena are assumed to be absent.

When applying the dusty gas equation to bimodal porous materials whose micropores have radii less than 50 Å, differences between prediction and experiment also appear. The differences appear to become greater as the micropore fraction of the total pore volume becomes larger. In addition to the difficulty of applying the dusty gas equation to pores with radii smaller than 50 Å, applying the equation in an overall manner to systems of parallel micro- and macropores may introduce additional error.

PREVIOUS WORK

The dusty gas equation tells how the flux of a diffusing gas within a porous medium depends upon pressure, effective molecular diffusivity, effective Knudsen diffusivity, and mole fraction gradient. The form of the equation resulting from integration between the limits y_{A0} and y_{AL}, which is the form applied in this paper, is (Scott and Dullien, 1962)

$$N_A = \left(\frac{D_{AB}}{\alpha L}\right)\left(\frac{P}{RT}\right)\ln\left[\frac{1 - \alpha y_{A0} + (D_{AB}/D_{kA})}{1 - \alpha y_{AL} + (D_{AB}/D_{kA})}\right] \tag{1}$$

As should be expected, this equation converges to the expressions for Knudsen or bulk diffusion under isothermal and isobaric conditions as the total pressure becomes very small or very large, respectively.

All of the models from which the dusty gas equation is derived also predict that the ratio of the fluxes of two counterdiffusing gases should be equal to the negative reciprocal of the square root of the two gases' molecular weights, that is,

$$\frac{N_A}{N_B} = -\sqrt{\frac{M_B}{M_A}} \qquad (2)$$

The theory predicts that this relationship should be true irrespective of temperature or total pressure, assuming the system is both isothermal and isobaric. The ratio of the fluxes of two gases counterdiffusing under these conditions within a porous medium has been experimentally measured, and most investigators reported that the theoretical flux ratio was observed within experimental error (Wicke and Hugo, 1961; Evans et al., 1961; Henry et al., 1967; Cunningham and Geankoplis, 1968; Horak and Schneider, 1971). There have been some exceptions, though. Hoogschagen (1955) and Satterfield and Cadle (1968) ascribed the deviations they observed to surface transport. The latter investigators observed that the deviations increased with increasing total pressure. Rothfeld (1963) discounted surface transport as a probable cause for the deviations he observed but offered no alternative explanation. Hwang and Kammermeyer (1969) observed deviations at low temperature (around 200 K), and the flux ratio approached the theoretical value at temperatures above 400 K.

The dusty gas equation has also been checked by some investigators for its ability to predict changes of flux with total pressure. Scott and Dullien (1962) and Henry et al. (1967) studied some unimodal materials, and Rothfeld (1963), Henry et al. (1967), and Cunningham and Geankoplis (1968) studied some bimodal materials. Satisfactory agreement within experimental error was reported in all cases between the predictions of the equation and the experimental data. The average radii of the unimodal pore systems ranged from 85 Å to 12,400 Å, and the average radii of the pore systems in the bimodal materials ranged from 37 Å to 20,000 Å, and all of these studies were carried out at pressures below atmospheric.

Studies of the limits of the transition region (Cadle, 1966; Haynes, 1969) indicate that for the gases used and the pressure ranges covered in these studies, pores with radii below 50 Å remain almost entirely within the Knudsen flow region. Thus the transition region behavior of the dusty gas equation was not tested for pores of this size range in these studies. Even though some of the bimodal materials had a pore system with an average radius below 50 Å, the transition region effects observed for these materials were almost certainly a result of the pores larger than 50 Å which were also present. The unimodal material with an average pore radius of 85 Å (Henry et al., 1967) showed only very slight transition region effects at the highest pressure studied (601 torr).

EXPERIMENTAL PROGRAM

Since the behavior of the dusty gas equation in the transition region apparently had not yet been examined using systems containing pores with radii below 50 Å, the experimental program mentioned earlier was devised to fill this gap to some degree. The three porous materials used were a ferric oxide gel catalyst of the type developed by Weitzel and Loebenstein (1960), with an average pore radius (r_{mean}) of 24 Å; a Harshaw alumina, type AL-1704 T 3/16, Lot 72, with an average pore radius of 46 Å; and a pelleted Aerosil with an average pore radius of 550 Å. Properties of the three materials are presented in Table 1 and pore-size distributions in Figure 1.

Both nitrogen sorption and mercury penetration techniques were used in the determination of the pore distributions. Nitrogen sorption isotherms were obtained on a Numinco-Orr adsorption apparatus. For determining the distributions, the method of Barrett et al. (1951) was applied to the adsorption branches of the isotherms, using the flat-surface *t*-curve recommended by Broekhoff and de Boer (1967). Mercury penetration measurements were carried out using an Aminco Model 5-7119 15,000 lb./sq.in. mercury porosimeter, which could measure the distribution of pores from the largest encountered to a minimum of 60 Å radius. A value of 60,200 (atm)(Å) was assumed for the product $(p)(r)$ in the calculation of the results.

Only nitrogen sorption methods were deemed necessary for the ferric oxide gel; the absence of any large pores in this particular batch was taken for granted because of extensive experience with this catalyst in our laboratories (for example, Barrick et al., 1965; Sterrett and Brown, 1968). Both nitrogen sorption and mercury penetration were used on the alumina. For the pelleted Aerosil, there was no curvature observable in the nitrogen isotherm *t*-plot below a relative pressure of 0.8. Applying the principles of analyzing the *t*-plot presented by de Boer et al. (1966) and Broekhoff (1969), this indicates that there were no pores present with radii below 70 Å. Mercury penetration results were therefore deemed sufficient for this material.

The total pore volumes reported in Table 1 were obtained by mercury-helium density measurements. The total pore volumes in Figure 1 were arrived at independently from the pore distributions. There is good agreement for the ferric oxide gel and the alumina, but the pelleted silica shows a significantly

TABLE 1. PROPERTIES OF POROUS MATERIALS

Porous material	Ferric oxide gel	Harshaw alumina	Pelleted Aerosil
Apparent density, g/cc	2.166	1.124	0.301
Density of solid, g/cc	4.816	3.238	2.632
Pore volume, cc/g	0.254	0.581	2.942
Surface area, m^2/g	218	254	201
Porosity	0.550	0.653	0.886
Average pore radii:			
r_{mean}, Å	24	46	550
r_W, Å ($= 2V_p/S_{BET}$)	23	46	293

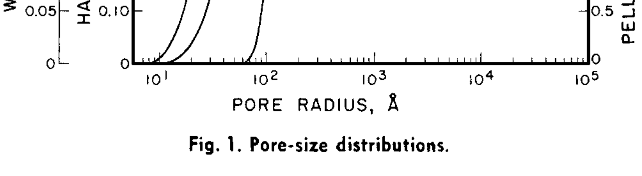

Fig. 1. Pore-size distributions.

lower total pore volume in the pore distributions. This is regarded as probably being caused by compression of this high porosity material during the mercury penetration measurement. This phenomenon has been reported before (Dickinson and Shore, 1968). The unusually high porosity and large pore sizes of the pelleted silica were probably caused by the low pelleting pressure used—only 270 atm. As a counterexample, Broekhoff (1969) used about 2400 atm. pelleting a similar material and the result was an average pore radius of approximately 80 Å.

One pellet was required for the Wicke-Kallenbach experiment. A particle of the ferric oxide gel catalyst was machined to size, a pellet of the Harshaw alumina was used as received, and the Aerosil was pelleted in situ in the center plate of the diffusion cell. The Wicke-Kallenbach experiment has been widely used and thoroughly described many times (for example, Scott and Dullien, 1962). The apparatus used for this study was originally built by Haynes (1969) and extensively modified by Bell (1971) and the details of the apparatus and procedure are available in these references. The data used for this paper, as well as some minor apparatus refinements required for the present study, are presented by Omata (1971). According to the analysis of Bell (1971), the random error in the measured flux using this apparatus should not have exceeded 2% of the reported value at any time.

The particle of the ferric oxide gel used for the diffusion experiments was from the same batch as the particles used for the pore structure measurements (that is, all the particles originated from the same large piece). For the Harshaw alumina, three pellets chosen at random from the same package were used for the pore structure measurements, and another pellet was used for the diffusion experiments. The same pellet of Aerosil which had been used for the diffusion experiments was used for the pore structure measurements.

Although it would have perhaps been desirable to use the same pellets in all cases for obtaining both diffusion data and pore structure data, it was not absolutely necessary. The pore structure data were not used in direct calculations involving the diffusion data; the pore structure results are rather used to indicate the general types of material that were studied, and for some rather inexact comparisons of numbers. The experimental procedures used were dictated by time scheduling of apparatus.

EXPERIMENTAL RESULTS

Flux Ratios

The theory predicts that the ratio of the fluxes of counterdiffusing helium and nitrogen should be 2.65, irrespective of temperature, pressure, or porous material. The ratios of the experimental fluxes obtained in this study are presented in Figure 2. In some circumstances there were wide deviations from the theoretical value. When the ferric oxide gel was used, the flux ratio was dependent on both temperature and pressure. At 26°C., there was a continuous change starting from well above the theoretical value at the lowest pressure to well below the theoretical value at the highest pressure. At the three higher temperatures, and above about 10 atm., the observed flux ratio appeared to be very close to the theoretical value, averaging slightly below (about 2.60). Below about 10 atm., there was a decrease in flux ratio with pressure at 66°C. and an increase with pressure at 106° and 146°C., the higher temperature showing the greater increase of flux ratio with pressure.

Using the Harshaw alumina catalyst, the results at the two lower temperatures were qualitatively the same, though quantitatively much less marked. At 26° and 66°C., there was a decrease of the flux ratio with increasing pressure. At the two higher temperatures, there was no apparent change of flux ratio with pressure. In the material containing the largest pores—the pelleted Aerosil—there was no change of the flux ratio with either temperature or pressure. All of the values for this large-pore material appeared to be slightly above the theoretical value, averaging approximately 2.75.

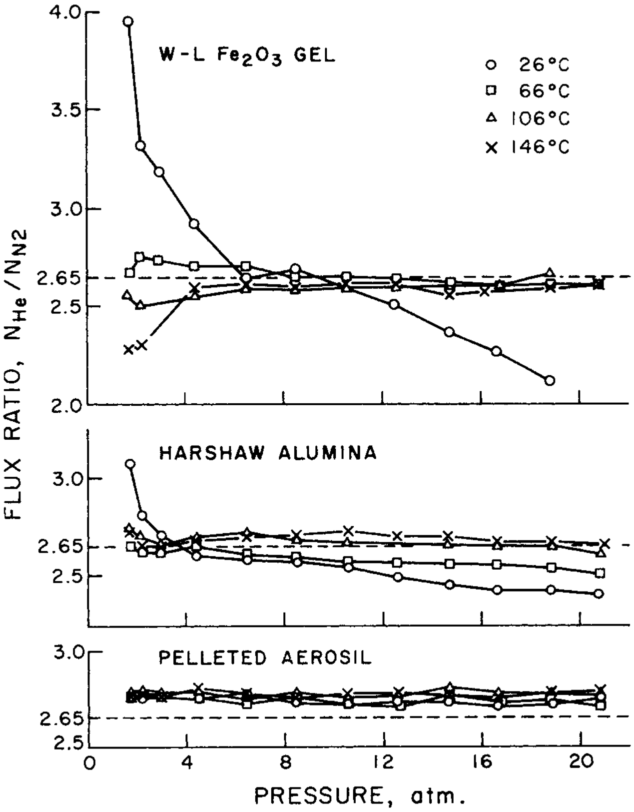

Fig. 2. Experimental flux ratios.

Thus large deviations of the flux ratio from the theoretically predicted behavior appear to be most prominent in small pores, and at lower temperatures and pressures. Small and almost constant deviations, independent of temperature and pressure, appear to be possible in almost any pore size.

Correlation of Equation with Data

The dusty gas equation contains both an effective Knudsen diffusivity and an effective molecular diffusivity. Any predicted diffusivities would be based on predicted transport rates, and present methods for predicting gas transport rates in porous materials are not particularly exact. (At best they are accurate only within an approximate factor of two (Satterfield and Cadle, 1968; Brown et al., 1969).) Equation (1) is therefore best regarded as possessing two adjustable parameters D_{kA} and D_{AB}. The effective Knudsen diffusivity should be independent of pressure, and the effective molecular diffusivity should be inversely proportional to it. At any particular temperature, then, two parameters independent of pressure would be D_{kA} and the product $D_{AB}P$.

For each material at every temperature, the fluxes of helium and nitrogen were measured at twelve different pressures within what was calculated to be the transition region. Using the twelve points, a nonlinear regression technique could be applied to the experimental results to determine numerical values of the two pressure-independent parameters. The numerical values obtained would be those which minimized the variance between the fluxes predicted by the equation and those experimentally measured. Since the fluxes of helium and nitrogen were both experimentally determined, values of the parameters could be obtained both for helium diffusing through the porous material in the presence of counterdiffusing nitrogen, and vice versa.

Sample results of these operations are presented in Figure 3, which compares the equation's behavior when optimum values of the parameters are used with the experimental results. The figure illustrates helium diffusing through all three materials at 66°C.; the comparisons using nitrogen were qualitatively the same as for helium (Omata, 1971). The temperature of 66° was chosen because it exhibited typical behavior (Omata, 1971).

There is a curvature in both theoretical and experimental lines in all cases. Since there were not particularly significant differences in the inlet and outlet compositions, a straight line with positive slope would have indicated that the data were following Knudsen flow characteristics; a straight line with zero slope would have indicated that molecular diffusion was dominant. The curvature indicates that either the data were indeed taken within the transition region or that other factors were affecting the transport rates.

In the figure, some deviation can be observed between the theoretical curve and the experimental data for the ferric oxide gel; practically no deviation can be observed between the curves and the data for the other two materials. To differentiate a little more clearly among the results for the three materials, the percent error is plotted as a function of pressure in Figure 4. This figure shows that there were systematic and significant deviations between the theoretical and observed diffusion behavior for the ferric oxide gel catalyst over the entire pressure range; there were also systematic but small deviations for the Harshaw alumina, but only at fairly low pressures; there were no observable systematic deviations for the pelleted Aerosil.

The values of the effective diffusivities obtained from the regression operations are presented in Table 2. The values of $D_{He\text{-}N2}$, although independently evaluated, should be identical for both helium and nitrogen if the theory is valid for the materials used. There appears to be a significant difference (greater than 5%) between the values for the two gases only at 26°C. and when using the ferric oxide gel and the Harshaw alumina. When the pelleted Aerosil was used, there was no significant difference at any temperature.

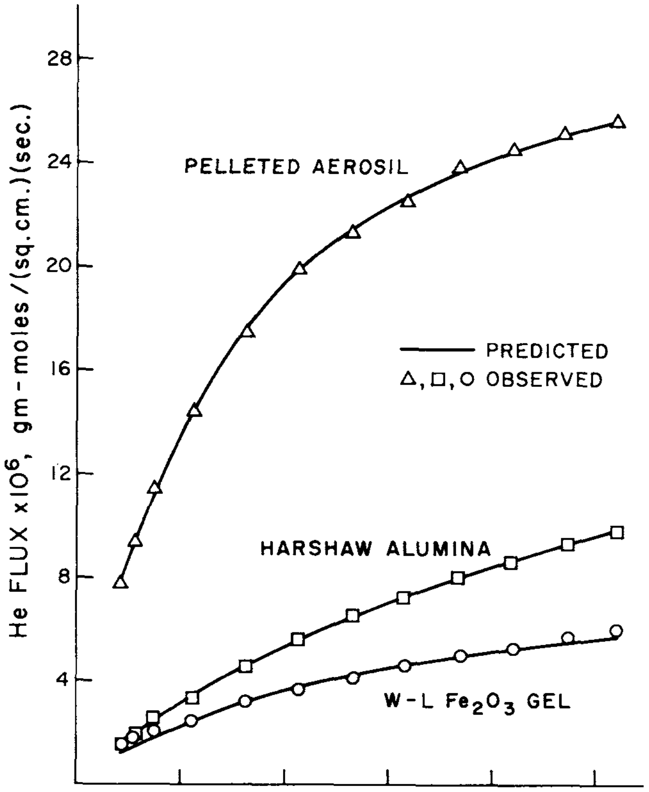

Fig. 3. Predicted and observed values of helium flux at 66°C.

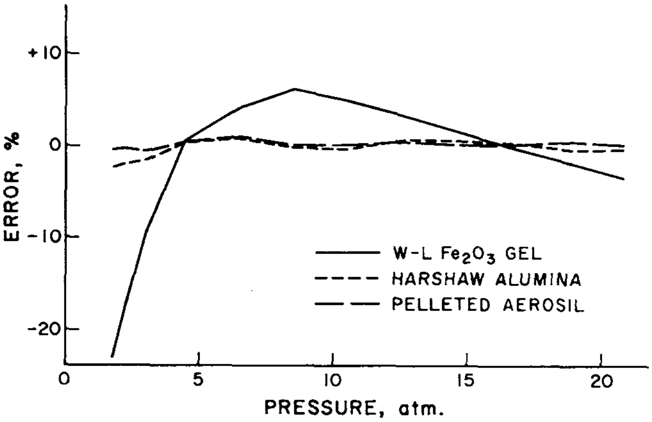

Fig. 4. Errors in predicted fluxes at 66°C.

The values of D_{kHe} and D_{kN2} obtained are also presented in Table 2. Theory predicts these values should differ by a factor of 2.65, which is the ratio of the square root of the gases' molecular weights. The ratios of D_{kHe}/D_{kN2} obtained from the ferric oxide data show a consistent trend with temperature, while the ratios for the alumina and silica materials show no apparent trend with temperature and average slightly higher than the theoretical value.

In the dusty gas equation, the effective diffusivities are related to the Knudsen diffusivity through a cylindrical capillary and to the gas-phase molecular diffusivity by

$$D_{kA} = \frac{\theta}{\kappa} \mathcal{D}_{kA} \tag{3}$$

$$D_{AB} = \frac{\theta}{\beta} \mathcal{D}_{AB} \tag{4}$$

The value of $\mathcal{D}_{He\text{-}N2}$ has been measured experimentally over the temperature range covered in this investigation (Seager et al., 1963). Using these experimental values and knowing the values of θ, the bulk diffusion tortuosity factors can be obtained for the three porous materials using Equation (4).

The expression for determining $\mathcal{D}_{kA}$ in Equation (3) is

$$\mathcal{D}_{kA} = \frac{2}{3} r_k \sqrt{\frac{8RT}{\pi M_A}} \tag{5}$$

From the derivation of this equation (Pollard and Present, 1948), the pore radius r_k results from the volume-to-surface ratio of the pore, and for a porous solid would be equal to $2V_p/S_{BET}$. The value of $\mathcal{D}_{kA}$ can then be calculated from Equation (5) and used together with the experimentally derived D_{kA} and θ to obtain the Knudsen diffusion tortuosity factor using Equation (3).

The values for these tortuosity factors are also presented in Table 2. They are valuable for comparison with expected values of tortuosity. At 26°C., for the ferric oxide gel and the alumina catalysts, the values of the tortuosity factors determined for the helium are different than for

TABLE 2. EFFECTIVE DIFFUSIVITIES, TORTUOSITY FACTORS, AND AVERAGE KNUDSEN RADII

Porous material	Temp, °C	$(D_{\text{He-N}_2})$ (P), (cm²/sec)(atm) He	N_2	D_k, cm²/sec He	N_2	$D_{k\text{He}}/D_{k\text{N}_2}$	β He	N_2	κ He	N_2
W-L ferric oxide gel	26	0.060	0.094	0.0087	0.0025	3.4	6.3	4.0	1.2	1.6
	66	0.076	0.079	0.0089	0.0032	2.8	6.0	5.8	1.3	1.3
	106	0.081	0.078	0.0088	0.0035	2.5	6.9	7.2	1.3	1.3
	146	0.095	0.090	0.0089	0.0036	2.5	7.2	7.5	1.4	1.3
Harshaw alumina	26	0.14	0.17	0.011	0.0040	2.8	3.2	2.7	2.3	2.4
	66	0.18	0.19	0.012	0.0044	2.7	3.0	2.9	2.2	2.3
	106	0.23	0.24	0.012	0.0045	2.7	2.9	2.8	2.4	2.4
	146	0.25	0.26	0.013	0.0047	2.8	3.2	3.1	2.3	2.4
Pelleted Aerosil	26	0.49	0.50	0.16	0.058	2.8	1.2	1.2	1.3	1.4
	66	0.61	0.62	0.17	0.063	2.7	1.2	1.2	1.4	1.4
	106	0.74	0.74	0.19	0.068	2.8	1.2	1.2	1.3	1.4
	146	0.88	0.88	0.20	0.071	2.8	1.2	1.2	1.3	1.4

the nitrogen; this reflects the differences in the effective diffusivities. The ferric oxide gel also shows significant changes in apparent tortuosity factors with temperature; the next section discusses the change of the effective diffusivities with temperature, and the apparent changes in tortuosity factors result from some abnormal temperature effects.

The authors see no particular reason why the tortuosity factors for Knudsen diffusion and bulk diffusion should be the same, yet in the pelleted Aerosil and the Harshaw alumina they were quite close. In the ferric oxide gel they were far different. The helium Knudsen diffusion tortuosity factors in this last case appear unusually low.

Outside of the anomalies mentioned, the tortuosity factors seem reasonable. The higher porosity materials possess lower tortuosity factors, as would be expected. There is no evidence of the onset of the extremely low effective diffusivities (and hence extremely high apparent tortuosity factors) observed in molecular sieves with pore radii in the 2-5 Å range (Satterfield, 1970). There is apparently no effect of temperature on the tortuosity factors of the alumina and silica materials.

In summary, the dusty gas equation appears to correlate the data very well for the largest pore material (the pelleted Aerosil), giving reasonable and consistent values for effective diffusivities and tortuosity factors at all temperatures. The data from the Harshaw alumina were correlated moderately well, showing some deviations from the equation's prediction at low pressures and some inconsistency in the effective diffusivities at the lowest temperature (26°C.). The smallest pore material (the ferric oxide gel) showed serious deviations from the equation's predictions and some inconsistency in the tortuosity factors at all temperatures and in the effective diffusivities at the lowest temperature.

Temperature Dependence of Effective Diffusivities

Since the effective diffusivities were obtained over the temperature range of 26 to 146°C. it was possible to determine the diffusivities' functional dependence on temperature over this range. It has been usual to assume that the presence of the porous material has no effect on the temperature dependence of the diffusivities; the temperature dependence of the effective diffusivities is regarded as being the same as that for the pure gases or for Knudsen flow in cylindrical capillaries (for example, Satterfield, 1970). Experimentally, Hawtin et al. (1969) observed that the effective molecular diffusivity of helium-nitrogen within porous graphites was proportional to T^n, with n lying between 1.50 and 1.61 for three graphites. The value of n for the free gas helium-nitrogen system was calculated by these authors to be 1.71 from available literature data. Agreement to about the same extent between free gas and pore molecular diffusivities were obtained for the helium-argon and the carbon dioxide-methane systems within some porous graphites.

For Knudsen diffusion, theoretically the diffusivity should be proportional to $T^{0.5}$ and experimental values for the exponent of 0.5 (Ash et al., 1970) and 0.6 (Brown and Haynes, 1969) have been reported.

By assuming the diffusivities were proportional to T^n and using linear regression to determine n, the experimental values of the exponent were obtained for both the helium and nitrogen molecular and Knudsen diffusivities. Again, it may be pointed out that the values for the two gases are independent. Table 3 shows that the exponents obtained using the smallest pore material (the ferric oxide) did not agree at all with the predictions; those obtained for the alumina and silica materials were quite close to those predicted.

DISCUSSION

Basic Assumptions

Several of the assumptions made in deriving the dusty gas equation should become invalid when small pores are involved. Two which appear to merit further discussion are:

1. There is no significant transport of adsorbed molecules along the surface.
2. Momentum transfer between the gas and the wall occurs only upon collision between the gas molecules and the wall.

Surface Transport

Table 4 presents estimated mean residence times for the molecules on the surface, estimated average molecule

TABLE 3. TEMPERATURE DEPENDENCE OF EFFECTIVE DIFFUSIVITIES

Values of exponent n in relationship: D & T^n

	$D_{\text{He-N}_2}$ He	N_2	D_k He	N_2
Pure gases	1.75	1.75	0.5-0.6(1)	
in *W-L* ferric oxide gel	1.3	—(2)	0.052	1.1
in Harshaw alumina	1.7	1.4	0.49	0.47
in pelleted Aerosil	1.7	1.7	0.61	0.59

(1) In porous carbon and porous Vycor.
(2) Four points were scattered randomly.

flight times between molecule-wall collisions, and ratios of the two. The surface residence times were estimated from the equation of de Boer (1953)

$$\tau_s \simeq 10^{-13}\, e^{-\Delta H_{ad}/RT} \tag{6}$$

using heats of adsorption of helium and nitrogen on graphite (Young and Crowell, 1962), as listed heats of adsorption do not appear to change radically with adsorbent surface. The flight times were estimated by considering the average distance of flight to be equal to the diameter of the pore and by using the kinetic theory velocity of a molecule.

For both the ferric oxide and the alumina materials, the fraction of time spent on the surface by the nitrogen appears significant at all temperatures. If the adsorbed nitrogen is mobile, then a significant portion of the total nitrogen transport within the ferric oxide and alumina may have taken place on the surface.

The possibility of significant nitrogen surface transport seems unlikely for nitrogen on the pelleted Aerosil, since the nitrogen spends only a small fraction of its total time on the surface. The same reasoning indicates the unlikelihood of significant helium surface transport when using any of the materials studied.

The presence of nitrogen surface transport would be reflected in a flux ratio below the theoretical value. Surface transport relative to gas phase transport increases with increasing pressure and decreases with increasing temperature (Satterfield, 1970). At constant temperature, therefore, its presence should cause the flux ratio to decrease with increasing pressure, and at constant pressure, the flux ratio should deviate most from the theoretical value at the lowest temperature.

Gas-Wall Momentum Transfer

Bird et al. (1960) state that when the intermolecular distance exceeds three times the collision diameter of the molecule, the energy of attraction has decreased to less than 1% of the maximum energy of attraction between the molecules. The collision diameters of helium and nitrogen listed by these authors are 2.58 and 3.68 Å, respectively, and so the distance over which the intermolecular forces have some effect is of the order of magnitude of 10 Å. If the pores within these materials are regarded as cylinders, this means that the volume fraction of the void space affected by gas molecule-wall interactions is about 66% for the ferric oxide gel, 40% for the Harshaw alumina, and 4% for the pelleted Aerosil. For noncylindrical pores, these percentages would be somewhat greater.

These molecule-wall interactions during flight should have a greater effect on nitrogen than on helium, because the nitrogen travels more slowly in flight. There is more time between collisions for the forces to affect the nitrogen molecule. This should keep more nitrogen molecules closer to the wall and increase the number of collisions of the nitrogen molecules with the wall, resulting in a decrease of nitrogen transport. This would be reflected in a value of the flux ratio above the theoretical.

The effects of molecule-wall interactions during flight should decrease both with increasing temperature and increasing pressure. With increasing temperature, the speed of the molecules increases, and so there is less time for the forces to act on the molecule between collisions. With increasing pressure, there are more molecules in the gas phase, also exerting their dispersion forces on the molecule being considered. These forces, which would average out to zero over the entire path of a molecule diffusing down a capillary, would tend to reduce the effect of the molecule-wall interactions during flight.

Other Assumptions

Two other assumptions considered as possibly invalid were diffuse reflection and equal effective voidage for the two diffusing molecules. Both of these assumptions should produce effects essentially independent of temperature. Since the observed flux ratio tended to approach the theoretical value as the temperature became higher, evidence is lacking for the invalidity of these assumptions.

Flux Ratios

Two of the assumptions on which the theoretically predicted flux ratio is based are seen to be very doubtful in small-pore systems. Violations of these assumptions have contrasting effects on the experimental flux ratio. If nitrogen surface transport is present, then the flux ratio should be below the theoretical value, and should decrease with increasing pressure. If molecule-wall interactions are significant during the time between molecule-wall collisions, then the flux ratio should be above the theoretical value, and should approach the theoretical value at higher pressure. A combination of these two effects can be invoked to explain qualitatively all the observed phenomena except the low pressure behavior of the flux ratio when using the ferric oxide gel at 106° and 146°C. This behavior implies that factors not discussed here are operative, and that further study in this area could be productive.

Use of the Equation for Unimodal Materials

The dusty gas equation can be used for correlating the data, for interpolation, and for extrapolation. For the first use, the two parameters are determined to obtain the "best" fit of the equation to the observed fluxes, as was done earlier in this paper. For interpolation or extrapolation, data are taken at two points for the calculation of the two parameters, and then the flux is predicted at a third point either within or outside the range covered by the two experimental points.

The behavior of the equation using these three methods is illustrated in Table 5. For the experimental work of this paper, the 66°C. data are again used as being typical. In addition, interpolation is used for two unimodal materials studied by Haynes (1969) at 21°C. The apparent accuracy of the equation changes both with method and

TABLE 4. ESTIMATED SURFACE RESIDENCE TIMES AND FLIGHT TIMES BETWEEN WALL COLLISIONS

		26°C		146°C	
		He	N_2	He	N_2
τ_s, sec		2×10^{-13}	9×10^{-12}	1.5×10^{-13}	2×10^{-12}
τ_f, sec	in *W-L* ferric oxide	4×10^{-12}	1×10^{-11}	3×10^{-12}	8×10^{-12}
	in Harshaw alumina	7×10^{-11}	2×10^{-11}	6×10^{-12}	2×10^{-11}
	in pelleted Aerosil	9×10^{-11}	2×10^{-10}	7×10^{-11}	2×10^{-10}
τ_s/τ_f	in *W-L* ferric oxide	0.05	1	0.05	0.3
	in Harshaw alumina	0.02	0.5	0.03	0.1
	in pelleted Aerosil	0.002	0.04	0.002	0.01

TABLE 5. APPLYING THE DUSTY GAS EQUATION TO UNIMODAL POROUS MATERIALS

	r_{mean}, Å	% error(1) at 10.5 atm using nonlinear regression	% error at 10.5 atm using two-point interpolation	% error at 20.8 atm using two-point extrapolation
Reference points		all points	1.7 and 20.8 atm	1.7 and 6.5 atm
Porous material				
W-L ferric oxide at 66°C	24	4.8	17.6	−29.0
Harshaw alumina at 66°C	45	0.5	2.8	−5.3
Pelleted Aerosil at 66°C	550	0.0	−0.7	−3.0
Girdler G-3B(2) at 21°C	380		0.0(3)	
Porous Vycor(2) at 21°C	43		11.2(3)	

(1) % error = [(predicted flux − observed flux)/observed flux] (100%).
(2) Data of Haynes (1969).
(3) Error at 10.2 atm; Reference points at 1.0 and 20.4 atm.

with porous material. Although the percent error may be quite small when judged by nonlinear regression analysis, errors of 20 to 30% might result if the equation is used for the interpolation or extrapolation of data.

This would be the case for the ferric oxide gel; quite good interpolation and extrapolation properties are exhibited when applying the equation to the Harshaw alumina and the pelleted Aerosil. The reason for the failure when using the ferric oxide is assumed to be the failure of the basic assumptions. But applying the equation to the Harshaw alumina gave rather good results, in spite of the small pores in this material and the significant deviations of the flux ratio from the theoretical values. It may be that the dusty gas equation is less sensitive to the failure of these assumptions than the flux ratio.

The applicability of the dusty gas equation is not determined solely by the pore size of the porous material; Table 5 shows that the behavior of the equation when the porous Vycor is used is considerably poorer than when the Harshaw alumina is used. The mean pore radius of these two materials is almost identical. Other factors must be significant here which have not been considered. For Haynes' large-pore unimodal material, the dusty gas equation was completely satisfactory, as for our large-pore material and in agreement with the studies of previous investigators.

Use of the Equation for Bimodal Materials

The materials considered thus far all possessed single pore systems. Many commercially used porous materials have more than one pore system, where particles containing very small pores are compacted together and the interstices between these particles form a second pore system. To study the use of the dusty gas equation for this type of system, two point interpolation was used to predict an interior point using diffusion data from the seven bimodal materials studied by Haynes (1969). The results are presented in Table 6. Of the seven porous materials, reasonable agreement between prediction and experiment (less than 5% error) was obtained for three, and poor agreement (greater than 5% error) was obtained for the other four.

A crude correlation exists between the percent error and the porosity data. The catalysts having a large micropore volume show a large error, and the ones having the majority of their pores in the macropore region show better agreement between prediction and experiment. Further refinement of this correlation does not seem to work, as a material with a micropore fraction of the total pore volume of 0.69 and an average pore radius of 38 Å gave a larger error (13.6%) than one with the higher micropore volume fraction of 0.76 and the smaller pore radius of 27 Å (11.6% error). Other details of the pore structure of both these and Haynes' unimodal materials may be found in the original references (Brown et al., 1969; Haynes, 1969).

The presence of pores with radii below 50 Å could alone justify the behavior for the bimodal materials. But some computer calculations demonstrated another possible cause. The total theoretical flux was calculated for a parallel pore system containing pores of two sizes—1000 Å radius and 30 Å radius. The total volume occupied by the large pores was equal to the total volume of the small pores. The flux was calculated over a range of pressures by using the dusty gas equation for each pore, and summing the individual contributions for the total flux. The dusty gas equation was then applied to the summations, using two-point interpolation. Only fair agreement was obtained in the latter case, as a 5% error was exhibited at 10 atm. (reference points, 1 and 20 atm.). Thus parallel flow within macropores and micropores can cause deviations when the dusty gas equation is applied to the system as a whole.

ACKNOWLEDGMENTS

The assistance of Dr. W. K. Bell, who gave detailed instruction on experimental technique, and many pertinent and helpful suggestions concerning data interpretation, is gratefully acknowledged. Porous materials were donated by D. H. Weitzel of the National Bureau of Standards, Boulder, Colorado, the Harshaw Chemical Company, and the Pigments Division of Degussa, Inc. During his study at the University of Colorado, Mr. Omata was supported by Mitsui Toatsu Chemicals.

TABLE 6. APPLYING THE DUSTY GAS EQUATION TO BIMODAL POROUS MATERIALS(1)

Porous material	Fraction of pore volume in micropores	r_{mean} of micro-pores, Å	% error at 10.2 atm(2)
Harshaw AL-1404	0.82	46	10.8
Girdler G-35	0.76	27	11.6
Catalysts and chemicals C-46-2	0.45	34	4.1
Girdler G-56B	0.19	32	4.3
Girdler T-126	0.69	38	13.6
Harshaw ZN-0103	0.15	39	2.9
Catalysts and chemicals C-20-6A	0.81	39	8.0

(1) Using data of Haynes (1969).
(2) Reference points at 1.0 and 20.4 atm.

NOTATION

D = effective molecular diffusivity within porous material, cm.^{2}/sec.
D_k = effective Knudsen diffusivity within porous material, cm.^{2}/sec.
$\mathcal{D}$ = gas-phase molecular diffusivity, cm.^{2}/sec.
$\mathcal{D}_k$ = Knudsen diffusivity of pure gas within a capillary, cm.^{2}/sec.
ΔH_{ad} = enthalpy change of adsorption, cal/mole
L = axial distance through pellet of porous material, cm.
M = molecular weight, g./g.-mole
N = flux of diffusing material, g.-moles/(cm.^{2}) (sec.)
P = pressure, atm.
R = gas constant, (atm.) (cm.^{3})/(g.-mole) (K) or cal/g.-mole
r = pore radius, cm. or Å
r_k = effective capillary radius for Knudsen diffusion, cm. or Å
r_{mean} = radius where cumulative pore volume is 50% of total pore volume, cm. or Å
r_W = average pore radius from gross measurements ($= 2\ V_p/S_{BET}$), cm. or Å
S_{BET} = porous material surface area measured by BET method, m^2/g. or cm.^{2}/g.
T = absolute temperature, K
V_p = total pore volume of porous material, cm.^{3}/g.
y = mole fraction in gas phase, dimensionless

Greek Letters

α = the quantity $1 + (N_A/N_B)$, dimensionless
β = tortuosity factor for bulk diffusion, dimensionless
θ = porosity of material, dimensionless
κ = tortuosity factor for Knudsen diffusion, dimensionless
τ = average residence time of molecule in particular mode, sec.

Subscripts

A = of substance A
AB = of substance A in the presence of substance B
B = of substance B
f = in flight between collisions with the pore wall
He = of helium
N2 = of nitrogen
L = condition at exit side of pellet
0 = condition at entrance side of pellet
s = on the surface

LITERATURE CITED

Ash, R., et al., "Diffusion of Helium through a Microporous Membrane," *Surface Science*, **21**, 265 (1970).

Barrett, E. P., et al., "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms," *J. Am. Chem. Soc.*, **73**, 373 (1951).

Barrick, P. L., et al., "Improved Ferric Oxide Gel Catalysts for Ortho-Para Hydrogen Conversion," Advances in Cryogenic Engineering, Vol. 10, K. D. Timmerhaus, (ed.), pp. 181-9, Plenum Press, New York (1965).

Bell, W. K., "Interactions between a Mobile Adsorbed Phase and Diffusing Gases in Porous Media," Ph.D. thesis, Univ. Colorado, Boulder (1971).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, pp. 23, 744, Wiley, New York (1960).

de Boer, J. H., The Dynamical Character of Adsorption, pp. 30-36, Oxford, London (1953).

———., B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A.v.d. Heuvel, and T. J. Osinga, "The t-Curve of Multimolecular N$_2$ Adsorption," *J. Colloid Interface Sci.*, **21**, 405 (1966).

Broekhoff, J. C. P., "Adsorption and Capillarity," Ph.D. thesis, Technical Univ. Delft, The Netherlands (1969).

———., and J. H. de Boer, "Calculations of Pore Distributions from the Adsorption Branch of Nitrogen Sorption Isotherms in the Case of Open Cylindrical Pores. B. Applications," *J. Catalysis*, **9**, 15 (1967).

Brown, L. F., and H. W. Haynes, Jr., "Gaseous Diffusion and Flow in Commercial Catalysts at Pressure Levels Above Atmospheric" (Correspondence), *Ind. Eng. Chem. Fundamentals*, **8**, 600 (1969).

———., and W. H. Manogue, "The Prediction of Diffusion Rates in Porous Materials at Different Pressures," *J. Catalysis*, **14**, 220 (1969).

Cadle, P. J., "Diffusion of Gases in Pelleted Catalysts," Sc.D. thesis, Mass. Inst. Technol., Cambridge (1966).

Cunningham, R. S., and C. J. Geankoplis, "Effects of Different Structures of Porous Solids on Diffusion of Gases in the Transition Region," *Ind. Eng. Chem. Fundamentals*, **7**, 535 (1968).

Dickinson, J. M., and J. M. Shore, "Determination of Porosities in Graphites," *Carbon*, **6**, 937 (1968).

Evans, R. B., III, et al., "Gaseous Diffusion in Porous Media at Uniform Pressure," *J. Chem. Phys.*, **35**, 2076 (1961).

Gunn, R. D., and C. J. King, "Mass Transport in Porous Materials under Combined Gradients of Composition and Pressure," *AIChE J.*, **15**, 507 (1969).

Hawtin, P., et al., "The Diffusion of Gases through Graphite," *Trans. Inst. Chem. Engrs.*, **47**, 109 (1969).

Haynes, H. W., Jr., "Models for Predicting the Diffusion Rates of Gases in Porous Catalysts and Adsorbents," Ph.D. thesis, Univ. Colorado, Boulder (1969).

Henry J. P., Jr., R. S. Cunningham, and C. J. Geankoplis, "Diffusion of Gases in Porous Solids over a Thousand-Fold Pressure Range," *Chem. Eng. Sci.*, **22**, 11 (1967).

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

Horak, Z., and P. Schneider, "Comparison of Some Models of Porous Media for Gas Diffusion," *Chem. Eng. J.*, **2**, 26 (1971).

Hwang, S.-T., and K. Kammermeyer, "Gaseous Diffusion and Flow in Commercial Catalysts at Pressure Levels Above Atmospheric" (Correspondence), *Ind. Eng. Chem. Fundamentals*, **8**, 601 (1969).

Mason, E. A., and R. B. Evans III, "Graham's Laws: Simple Demonstrations of Gases in Motion, I. Theory," *J. Chem. Ed.*, **46**, 358 (1969).

Mason, E. A., et al., "Flow and Diffusion of Gases in Porous Media," *J. Chem. Phys.*, **46**, 3199 (1967).

Omata, H., "Diffusion Rates of Gases in Porous Catalysts and Adsorbents Containing Small Pores," M.S. thesis, Univ. Colorado, Boulder (1971).

Pollard, W. G., and R. D. Present, "On Gaseous Self-Diffusion in Long Capillary Tubes," *Phys. Rev.*, **73**, 762 (1948).

Rothfeld, L., "Gaseous Counterdiffusion in Catalyst Pellets," *AIChE J.*, **9**, 19 (1963).

Satterfield, C. N., Mass Transfer in Heterogeneous Catalysis pp. 41-56, MIT Press, Cambridge, Mass. (1970).

———., and P. J. Cadle, "Gaseous Diffusion and Flow in Commercial Catalysts at Pressure Levels above Atmospheric," *Ind. Eng. Chem. Fundamentals*, **7**, 202 (1968).

Scott, D. S., and F. A. L. Dullien, "Diffusion of Ideal Gases in Capillaries and Porous Solids," *AIChE J.*, **8**, 113 (1962).

Seager, S. L., et al., "Temperature Dependence of Gas and Vapor Diffusion Coefficients," *J. Chem. Eng. Data*, **8**, 168 (1963).

Sterrett, J. S., and L. F. Brown, "The Application of Theoretical Diffusion Models in the Presence of a Catalytic Reaction," *AIChE J.*, **14**, 696 (1968).

Weitzel, D. H., and W. V. Loebenstein, "Conversion of Ortho-to Parahydrogen," U.S. Patent 2,943,917 (July 5, 1960).

Wicke, E., and P. Hugo, "Gleitungserscheinungen bei der Gasdiffusion," *Z. Phys. Chem.* (*N.F.*), **28**, 401 (1961).

Young, D. M., and A. D. Crowell, Physical Adsorption of Gases, pp. 30, 32, 42 Butterworths, London (1962).

Manuscript received September 23, 1971; revision received April 13, 1972; paper accepted April 13, 1972.