$\mathbf{h}_i$ = viscous force per unit volume that phase i exerts upon the pore walls and the other fluid phases contained within S. Defined by Equation (7)
$\mathbf{I}$ = identity tensor
$\mathbf{n}$ = unit normal that is outwardly directed with respect to S_i
p = pressure
p_0 = constant reference pressure
$\mathcal{P}$ = modified pressure defined by $\mathcal{P} \equiv p + \rho\varphi$
s_i = local saturation of phase i. If there are n fluid phases present then $s_i \equiv \dfrac{V_i}{\sum_{j=1}^{n} V_j}$
S = an arbitrary closed surface that is associated with every point in the porous medium
S_i = closed boundary surface of V_i
S_{fi} = portion of S_i that coincides with the pore walls
S_{mi} = portion of S_i that coincides with the boundaries of the other moving and deforming phases present
$\mathbf{T}$ = stress tensor
$\overset{i}{\overline{\mathbf{v}}}$ = average over V of the velocity of phase i
V = volume of S
V_i = volume of pores containing phase i that are enclosed by S

Greek Letters

ρ = density; ρ_i is the density of phase i
φ = potential energy per unit mass
ψ = porosity. If there are n fluid phases present, then

$$\psi \equiv \frac{1}{V}\sum_{j=1}^{n} V_j$$

Special Symbols

$\overline{\ldots}$ average over V of a quantity associated with phase i. For example, $\overline{B}$ is an average over V of a quantity B associated with phase i:

$$\overset{i}{\overline{B}} \equiv \frac{1}{V}\int_{V_i} B dV$$

$<\ldots>^i$ Average over V_i of a quantity associated with phase i. For example, $<B>^i$ is an average over V_i of a quantity associated with phase i:

$$<B>^i \equiv \frac{1}{V_i}\int_{V_i} B dV$$

LITERATURE CITED

Blair, P. M., and C. F. Weinaug, "Solution of Two-phase Flow Problems Using Implicit Difference Equations," *Soc. Petrol. Engrs. J.*, **9**, 417 (1969).

Douglas, J., Jr., et al., "A Method For Calculating Multi-Dimensional Immiscible Displacement," *Trans. Am. Inst. Min. Metall. Engrs.*, **216**, 297 (1959).

Muskat, M., et al., "Flow of Gas-Liquid Mixtures Through Sands," *Trans. Am. Inst. Min. Metall. Engrs.*, **123**, 69 (1937).

Rapopart, L. A., and W. J. Leas, "Properties of Linear Water Floods," *ibid.*, **198**, 139 (1953).

Scheidegger, A. E., The Physics of Flow Through Porous Media, p. 216, Macmillan, N. Y. (1960).

Slattery, J. C., "Flow of Viscoelastic Fluids Through Porous Media," *AIChE J.*, **13**, 1066 (1967).

———., "Multiphase Viscoelastic Flow Through Porous Media," *ibid.*, **14**, 50 (1968).

———., "Two-phase Flow Through Porous Media," *ibid.*, **16**, 345 (1970).

———., Momentum, Energy, and Mass Transfer in Continua, pp. 191 and 194, McGraw-Hill, New York (1972).

Terwilliger, P. L., et al., "An Experimental and Theoretical Investigation of Gravity Drainage Performance," *Trans. Am. Inst. Min. Metall. Engr.*, **192**, 285 (1951).

Manuscript received March 1, 1972; revision received May 24, 1972; note accepted May 24, 1972.

Predicting Diffusion Rates in Some Materials with Abnormal Pore Structures

HIROKAZU OMATA and LEE F. BROWN

Department of Chemical Engineering
University of Colorado, Boulder, Colorado 80302

Many models and methods have been proposed for a priori prediction of diffusion rates in porous materials. None of these is completely ideal, and it is important to define both their areas of suitability and their limitations. The most certain way of accomplishing this is to apply the models and methods to a large amount of experimental data, with the data covering as wide a range of process conditions, diffusing substances, and types of porous material as possible. This note applies the method currently most popular to recent data taken on some unusual porous materials over a reasonably wide range of temperature and pressure.

PREVIOUS WORK

Recently, the more popular models have been examined by Satterfield and Cadle (1968a, b), by Brown et al. (1969), and by Haynes and Brown (1971). An exhaustive review of various models and their applications has been presented by Haynes (1969). These studies concluded that the method proposed by Johnson and Stewart (1965) is currently the best available. The observed diffusion rates were usually within a factor of two of those predicted, and good extrapolation properties with pressure were obtained without exception. The latter property means that if one experiment (probably near atmospheric pressure) is used to obtain an empirical tortuosity factor, this tortuosity factor is reasonably valid at any other pressure.

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

Table 1. Properties of Porous Materials

Porous material	Ferric oxide gel	Harshaw alumina	Pelleted Aerosil
Apparent density, g/cm^3	2.17	1.12	0.301
Density of solid g/cm^3	4.82	3.24	2.63
Pore volume, V_P, cm^3/g	0.254	0.581	2.942
Surface area, S_{BET}, 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

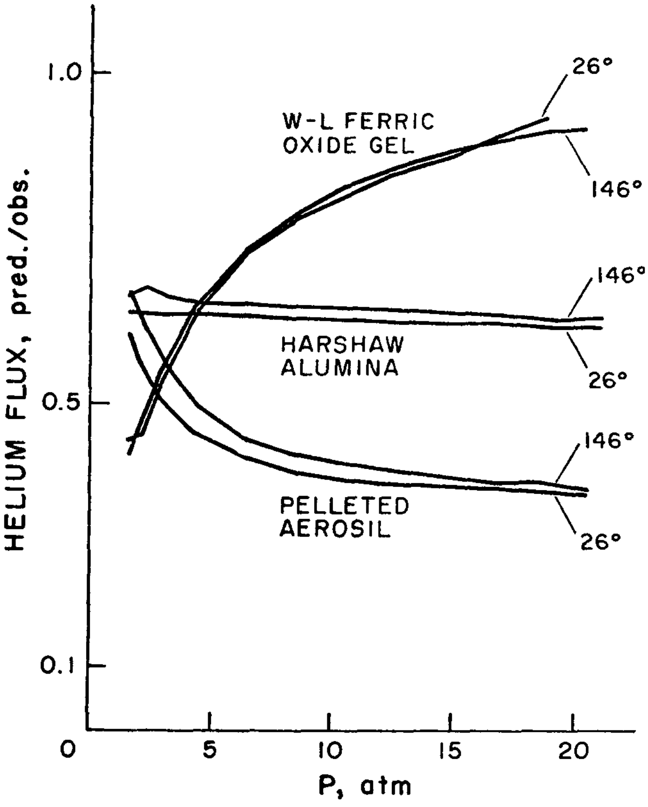

Fig. 1. Ratio of predicted to observed fluxes.

Some exceptions have been noted to the ability of this model to predict diffusion rates within a factor of two (Satterfield and Cadle, 1968a; Brown et al., 1969), and the latter investigators ascribed these exceptions to the presence of severe pore constrictions. No other cause has been advanced for the occasional failure of this method (3 samples out of the total of 56 studied by Johnson and Stewart, Satterfield and Cadle, and Brown et al.). As stated above, no exception has been noted to the good extrapolation properties of this method.

EXPERIMENTAL WORK

The data used are those of Omata (1971), who measured the counterdiffusion of helium and nitrogen through porous materials under isothermal and isobaric conditions, using a Wicke-Kallenbach apparatus. The pressure range of the experiments was 1 to 21 atm, and the temperature range was 26 to 146°C. Three different porous materials were used. Detailed properties and pore-size distributions of the three materials have been presented by Omata and Brown (1972), along with greater experimental detail.

The porous materials all had unimodal pore systems. One was a ferric oxide gel catalyst of the type developed by Weitzel and Loebenstein (1960), with an average pore radius of 24 Å; another was a Harshaw alumina with an average pore radius of 46 Å; the third was a pelleted Aerosil with an average pore radius of 550 Å. Both the ferric oxide and the alumina materials had very narrow pore distributions, but the pelleted Aerosil had the pores distributed over a very wide range—from about 70 Å to about 30,000 Å. In addition, the pelleted Aerosil had the unusually high porosity of 0.886. Other properties of the materials are presented in Table 1.

In the case of the pelleted Aerosil, the pore-size distribution and other pore structure properties were measured on the same pellet as that used for the diffusion experiments. For the ferric oxide, different particles from the same batch (that is, the particles were broken off the same large piece) were used for the diffusion experiments and measurement of pore structure properties. Pellets of the Harshaw alumina used for determining the pore structure properties were taken from the same jar as those used for the diffusion experiments, and were listed as being from the same batch.

RESULTS

The results of applying the Johnson and Stewart method to the diffusion data are presented in Figure 1. The plots are presented in the form of predicted flux over observed flux as a function of pressure, with temperature as a parameter in the curves. The figure presents the data for helium diffusing in the presence of nitrogen; the results for nitrogen diffusing in the presence of helium were qualitatively very similar (Omata, 1971).

The ratios of predicted to observed flux increased from about 0.4 at the lowest pressure to 0.9 at the highest pressure (an increase of 125%) for the ferric oxide gel; for the alumina, the value stayed practically constant around 0.65 at all pressures; for the pelleted Aerosil, the ratio was approximately 0.65 at the lowest pressure, decreasing to 0.37 at the highest pressure (a decrease of 43%).

DISCUSSION

The Harshaw alumina had a pore structure rather typical of many porous catalysts and adsorbents. For this material, the Johnson-Stewart predictions showed behavior in agreement with previous studies which applied this model to diffusion data, that is, observed transport rates within a factor of two of those predicted, and good extrapolation of the predictions with pressure.

The other two materials had pore systems somewhat unusual in porous catalysts and adsorbents. The Weitzel-Loebenstein ferric oxide gel had a very small average pore radius, and the pelleted Aerosil had an unusually high void fraction of pores. For both of these materials, the Johnson-Stewart predictions showed poorer reliability than previously reported.

The Johnson-Stewart model assumes that the pore structure consists of randomly oriented, nonintersecting cylindrical pores, whose radii are distributed in accordance with the pore-size distribution determined from nitrogen sorption and/or mercury penetration methods. The total flux is predicted by summing the predicted fluxes for the individual pores, using the dusty gas diffusion equation for predicting the fluxes in the individual pores. The inadequacy of the Johnson-Stewart predictions for the ferric oxide gel is probably caused by the inadequacy of the dusty gas diffusion equation in very small pores; it has been shown that the equation could not be applied reliably to pores as small as those present in the ferric oxide gel (Omata and Brown, 1972). The inadequacy of the predictions for the pelleted Aerosil is probably caused by a high order of intersections of the pores within this material;

there must be many intersections with so high a porosity, and the Johnson-Stewart model neglects the volume of these intersections .

It is concluded that application of the Johnson-Stewart method for predicting diffusion rates may be hazardous for porous materials either containing abnormally small pores or having abnormally high porosities. For materials having pore structures of types more frequently encountered, the behavior of the Harshaw alumina reinforces previous conclusions of reasonable a priori predictability and good extrapolation properties with pressure.

It may also be noted that the effect of temperature on the predictive capability of the Johnson-Stewart method was very slight.

ACKNOWLEDGMENTS

Porous materials were donated by Mr. 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.

LITERATURE CITED

Brown, L. F., et al., "The Prediction of Diffusion Rates in Porous Materials at Different Pressures," *J. Catalysis,* **14**, 220 (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).

———., and L. F. Brown, "Effect of Pressure on Predicted and Observed Diffusion Rates in Constricted Pores—A Theoretical Study," *AIChE J.*, **17**, 491 (1971).

Johnson, M. F. L., and W. E. Stewart, "Pore Structure and Gaseous Diffusion in Solid Catalysts," *J. Catalysis,* **4**, 248 (1965).

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

———., and L. F. Brown, "Using the Dusty Gas Diffusion Equation in Catalyst Pores Smaller Than 50 Å Radius," *AIChE J.*, **18**, 000 (1972).

Satterfield, C. N., and P. J. Cadle, "Diffusion in Commercially Manufactured Pelleted Catalysts," *Ind. Eng. Chem. Process Design Develop.*, **7**, 257 (1968a).

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

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

Manuscript received May 15, 1972; paper accepted June 7, 1972.

Impact Tube Gas Velocity Measurement at High Temperatures

F. E. CARLETON and R. H. KADLEC

University of Michigan, Department of Chemical Engineering
Ann Arbor, Michigan 48104

Impact tubes (Pitot tubes) are frequently used to determine the line or velocity of a flowing fluid at a point. The inviscid model, or Bernoulli equation, can be successfully applied in gas flows at reasonable temperatures, but when extremely high temperatures are encountered this model becomes suspect. Because gas viscosities increase with temperature, and because of compressibility effects, the usual impact tube results no longer apply.

When temperatures exceed those normally found in flames (1,000-2,000 K), such conditions may be encountered. The impact tube must then be internally cooled, or destruction will result. Thus the phenomenon of heat transfer also enters the picture. A model of an impact tube must correctly predict both heat and momentum transfer when the cooled tube is immersed in an extremely hot gas (plasma).

STAGNATION STREAMLINE FLOW

For isentropic, inviscid deceleration of an incompressible fluid along a stagnation streamline, the stagnation pressure P_0 as measured with an impact (Pitot) tube is given in terms of the free stream quantities—static pressure P_∞, density ρ_∞, and velocity U—by the Bernoulli equation

$$P_0 = P_\infty + \frac{\rho_\infty U^2}{2} \tag{1}$$

If the fluid is compressible, the equation for isentropic, inviscid deceleration becomes

$$P_0 = P_\infty \left(1 + \frac{\gamma - 1}{2} M_\infty^2 \right) \frac{\gamma - 1}{\gamma} \tag{2}$$

where M_∞ is the free stream Mach number and γ is the ratio of specific heats C_p/C_v.

For viscous fluids flowing at Reynolds numbers above 100 (the characteristic length chosen to be the radius of the impact tube), the viscous forces acting on the fluid are very small in comparison to the inertia forces and the above equations are valid. As the Reynolds number is decreased below 100, however, the measured impact pressure departs from the true stagnation pressure based on isentropic, inviscid deceleration, and it is no longer possible to ignore the effects of viscosity. This departure of the impact pressure from the Bernoulli pressure is known as the Barker (1922) effect and has been observed experimentally by Hurd (1953), MacMillian (1954), Schowalter and Blaker (1961), and Sherman (1953). It shows

---

Correspondence concerning this note should be addressed to R. H. Kadlec. F. E. Carlton is with the Atlantic Richfield Company, Dallas, Texas.