JOURNAL OF CATALYSIS 4, 248–252 (1965)

Pore Structure and Gaseous Diffusion in Solid Catalysts

MARVIN F. L. JOHNSON

From the Sinclair Research, Inc., Harvey, Illinois

AND

WARREN E. STEWART

From the University of Wisconsin, Madison, Wisconsin

Received July 28, 1964; revised October 7, 1964

A method is given for predicting the rate of diffusion of a binary gas mixture through a porous solid at constant temperature and pressure. The rate of diffusion in each pore is predicted by the "dusty gas" theory of Evans, Watson, and Mason, and the total diffusion rate is predicted by integration over the pore-size distribution. Because of possible anisotropy and related effects, a diffusion or Knudsen permeability measurement is needed to allow accurate predictions; however, approximate predictions can be made from the pore-size distribution alone.

Axial diffusion rates are reported for H_2 through N_2 in tableted alumina catalysts. The measured rates range from 0.15 to 0.42 times the rates predicted for parallel pore alignment; this ratio, κ, is predicted to be 1/3 for randomly oriented cylindrical pores with no dead ends.

I. INTRODUCTION

The prediction of gaseous diffusion in pore systems is a fundamental problem in catalysis. The problem is exceedingly complex; besides the complications of pore geometry, one may have to deal with several transport mechanisms, such as viscous flow, ordinary diffusion, and Knudsen diffusion, whose relative contributions vary with the pore size. Predictions of diffusion rates are most difficult for solids with wide pore-size distributions, e.g., for pelleted or extruded catalysts.

Considerable work has been done on diffusion in solids with nearly uniform pore sizes. Weisz and Schwartz (*1*) have given a simple theory which agrees fairly well with observed rates of Knudsen diffusion in such materials. Evans, Watson, and Mason (*2*), Scott and Dullien (*3*), and Rothfeld (*4*) have given theoretical analyses of isothermal, isobaric diffusion for the full range from Knudsen diffusion (small pores) to ordinary diffusion (large pores); the results of the three analyses are compatible and agree well with binary diffusion measurements. These analyses, strictly speaking, are for solids of uniform pore size, though they have been curve-fitted to diffusion and permeability data on other types of materials (*2–4*).

The present work deals with the effects of pore-size distribution and pore orientation on diffusion rates. Surface diffusion is neglected. For simplicity only isothermal, isobaric conditions are considered, in the theory as well as in the measurements.

II. MEASUREMENTS

Diffusion rates of hydrogen through cylindrical pills of various γ-alumina catalysts were measured in the presence of counter diffusing nitrogen, at 745 mm Hg total pressure and 25°C. The method of measurement was similar to that of Weisz (*5*) except for the pill holder. For each experiment, 10 pills of the catalyst were randomly selected, measured with a micrometer, and inserted into holes drilled in a gum-rubber disc. The holes were half as large in diameter as the pills, and about 50% greater in length. The rubber disc was clamped between two glass chambers to form a diffusion cell, in which pure nitrogen was passed across one face of the disc and pure hydrogen across the other. The nitrogen-rich effluent was metered and analyzed continuously to determine the hydrogen concentration and hydrogen diffusion rate; the hydrogen-rich effluent was analyzed occasionally to determine its nitrogen concentration, which was negligible for the present purposes. A Gow-Mac thermal conductivity cell was used for the analyses, and was calibrated at the steady state conductivity reading after each experiment. Steady state was essentially reached within an hour and readings were continued for two additional hours. The steady state data were reported in terms of the pseudodiffusivity

$$D_e = N_{Az}L/(c_{A0} - c_{AL}) \tag{1}$$

where N_{Az} is the molar flux of hydrogen through the pills (g moles cm^{-2} sec^{-1}), $1/L$ is the mean of their reciprocal lengths (cm), and $c_{A0} - c_{AL}$ is the hydrogen concentration difference across them (g moles cm^{-3}).

Measurements of D_e were normally reproducible within a few per cent. The spread between paired tests on separate sets of 10 pills from the same catalyst sample was less than 4% for 60% of the samples, and greater than 10% for only 10% of the samples. Blank tests with 1/8-inch metal rods inserted in place of the pills showed negligible leakage.

Pore-size distributions were calculated from nitrogen adsorption data by the BJH (*6*) method, modified for IBM computation by treating their c as a continuous function. The techniques for determining nitrogen adsorption–desorption isotherms have been previously described (*7*); these data are believed reliable up to $p/p_0 = 0.99$, which corresponds to a pore radius of 1000Å. When larger pores are present, a mercury porosimeter (*8*) is necessary; for this purpose we have built one which operates up to 2000 psig and measures pores greater than 530Å in radius. A contact angle of 140° was used in analyzing the porosimeter data. The complete pore-size distributions were determined by splicing the BJH and mercury porosimeter curves at a pore radius of 500Å.

The total pore volumes obtained from the adsorption and porosimeter data agree fairly well with those obtained by He–Hg displacement, i.e., within 0.04 cm^3/g. The agreement on pore volume is believed to be within the uncertainty of the He–Hg method in view of the complications that arise (*9*) from the finite radius of the helium atom and the unknown forces between the helium atom and the walls of the pores.

The samples studied were essentially pure alumina, prepared by a number of different methods, formed into tablets, and calcined at 900°F to γ alumina.

III. THEORY

Consider a binary gas mixture in a single pore segment, and measure the coordinate l along this segment. Let $N_i^{(p)}$ be the molar flux of species i along the pore in the positive l direction, based on the pore cross section. Then, if the temperature and pressure are uniform, the results of refs. (*2*), (*3*), or (*4*) can be applied locally to give the equations

$$N_A^{(p)}/N_B^{(p)} = -(M_B/M_A)^{1/2} \tag{2}$$

and

$$\frac{dx_A}{dl} = -N_A^{(p)} \left\{\frac{1 + x_A[(M_A/M_B)^{1/2} - 1]}{c\mathfrak{D}_{AB}} + \frac{1}{c\mathfrak{D}_{AK}}\right\} = -N_A^{(p)}\beta \tag{3}$$

Here β is the term in brackets, $\mathfrak{D}_{AB}$ is the binary gaseous diffusion coefficient, and $\mathfrak{D}_{AK}$, the Knudsen diffusivity of species A in the pore (cm^2 sec^{-1}), is given by

$$\mathfrak{D}_{AK} = (9.7 \times 10^{-5})r(T/M_A)^{1/2} \tag{4}$$

for a cylindrical pore of radius r angströms and a temperature of T°K.

Equation (2) implies a corresponding equation

$$N_{Az}/N_{Bz} = -(M_B/M_A)^{1/2} \tag{5}$$

for the ratio of the fluxes in the z direction based on the external pill dimensions. This equation, first derived by Hoogschagen (*10*), has been confirmed by many experiments (*2, 3, 10*); it predicts a net molar flow through the pill unless $M_A = M_B$.

Further assumptions are needed to calculate the individual fluxes N_{Az} and N_{Bz}. For simplicity we assume that the concentrations along the pore axes depend only on the distance z from one end of the pill. Then, for a pore inclined at an angle θ to the z axis, Eq. (3) becomes

$$(dx_A/dz)\cos\theta = -(N_{Az}^{(p)}\beta/\cos\theta) \qquad (6)$$

where $N_{Az}^{(p)}$ is the z component of the pore flux $N_A^{(p)}$.

Now, if $f(\theta,r)d\theta dr$ is the fraction of open area (in a plane of constant z) occupied by pores with inclinations between θ and $\theta + d\theta$ and radii between r and $r + dr$, the flux N_{Az} averaged over the void and solid area of the plane is

$$N_{Az} = \int_0^\infty \int_0^{\pi/2} N_{Az}^{(p)} f(\theta, r)d\theta dr \qquad (7)$$

In view of Eq. (6) this becomes

$$N_{Az} = -\frac{dx_A}{dz}\int_0^\infty \int_0^{\pi/2} \beta^{-1}\cos^2\theta f(\theta, r)d\theta dr \qquad (8)$$

which holds for an anisotropic pore system under the present assumptions.

If the pore orientations are uncorrelated with pore size, then $f(\theta,r) = f(\theta)f(r)$ and Eq. (8) gives

$$N_{Az} = -\kappa\frac{dx_A}{dz}\int_0^\infty \beta^{-1}f(r)dr \qquad (9)$$

Here $f(r)dr$ is the void fraction in pores with radii between r and $r + dr$, and is obtainable from the pore volume measurements described in Section II. The geometric constant κ, according to our cylindrical pore model, is determined by the pore orientation function $f(\theta)$ and would have the value 1/3 for isotropic pore systems; for accurate work κ should, of course, be measured experimentally.

Integration of Eq. (9) from $z = 0$ to $z = L$ gives

$$\begin{aligned} N_{Az}L &= -\kappa\int_{x_{A0}}^{x_{AL}}\int_0^\infty \beta^{-1}f(r)dr dx_A \\ &= -\kappa\int_0^\infty\int_{x_{A0}}^{x_{AL}} \beta^{-1}dx_A f(r)dr \qquad (10)\end{aligned}$$

Inserting β from Eq. (3) and evaluating the inner integral, one obtains

$$N_{Az}L = \kappa\frac{c\mathfrak{D}_{AB}}{[(M_A/M_B)^{1/2} - 1]}\int_0^\infty \ln \left\{\frac{1 + x_{A0}[(M_A/M_B)^{1/2} - 1] + (\mathfrak{D}_{AB}/\mathfrak{D}_{AK})}{1 + x_{AL}[(M_A/M_B)^{1/2} - 1] + (\mathfrak{D}_{AB}/\mathfrak{D}_{AK})}\right\} f(r)dr \qquad (11)$$

which can be used to evaluate κ from experimental measurements, or to predict the diffusion rate if κ is known.

Equation (11) can be derived more simply by assuming that the pores are straight and nonintersecting, with no dead ends; that a volume fraction κ of each pore size is aligned with the z axis; and that the remaining pores are perpendicular to the z axis. Such a model, however, appears less useful for reaction conditions than the one we have used.

The integration with respect to r can be written in closed form if one assumes the pore-volume distribution $f(r)$ to consist of one or more sharp peaks (δ functions); thus for a single peak one gets the formula for N_{Az} given in refs. (*2*), (*3*), and (*4*). We have integrated Eq. (11) numerically, since this procedure is easier to mechanize.

Predicted values of D_e, for κ of 1/3, were obtained by integrating Eq. (11) over the pore-volume distribution of each catalyst and inserting the results in Eq. (1). The increments of r used in the integration were those reported in the pore-size distribution, and ranged from 12 to 20 in number. For each increment $\mathfrak{D}_{AK}$ was calculated using an average value of r, and $f(r)\Delta r$ was found by multiplying the incremental pore volume $\Delta V(\text{cm}^3/\text{g})$ by the pill density. The gas-phase diffusivity $\mathfrak{D}_{AB}$ at the test conditions was taken as 0.76 cm²/sec. The results of these calculations are summarized below.

IV. Results

In Fig. 1 are shown pore-distribution data for a series of catalysts made from the same alumina (I) by tableting to different densities. Such data are classified here in terms of micropores and macropores, whose size and volume are found at the points of maximum and minimum slope, respectively, on the distribution curve. These distributions are trimodal or bimodal; the sum of the micropore volumes is approximately constant, while the macropore size and volume vary. Table 1 shows the diffusivities D_e as measured, and as predicted from Eq. (11) with $\kappa = 1/3$. For this series, the ratio of observed to predicted values is nearly constant, averaging 0.84. If κ is obtained for each catalyst as D_e (obs.)/$3D_e$ (pred.), the agreement becomes exact and one can expect an improvement in predictions of diffusion rates at other conditions.

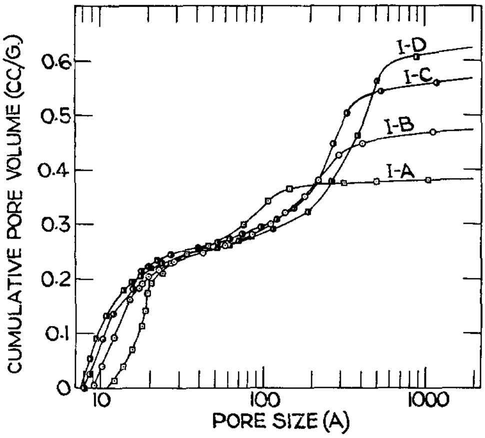

Fig. 1. Alumina I tablets, varying density.

Another series of samples was prepared by tableting sedimentation-separated fractions of Alumina II, with the results shown in Table 2. Again a nearly constant ratio is observed, averaging 1.08 for this alumina. The Alumina-II samples vary only in macropore size, whereas the Alumina-I samples vary both in macropore size and volume. It is noteworthy that the data of Table 2 show a definite effect of pore size even in this relatively high range.

Similar data for a variety of aluminas are presented in Table 3. Again, a given value of κ appears to be characteristic of a given alumina; the values of κ are not far from 1/3 except for Aluminas IV and V. Deviations of 3κ from unity are attributed to deviations from the idealized pore geometry of Eq. (9), or to anisotropy.

V. Discussion

It is clear from the preceding results that effective diffusion coefficients for porous catalysts can be predicted with fair accuracy from pore-size distribution data. The accuracy can be improved by evaluating κ from a diffusion measurement, before at-

TABLE 1
Alumina-I Tablets,[a] Varying Density

Sample	Micropores Vol. (cc/g)	Macropores Size (Å)	Macropores Vol. (cc/g)	D_e (cm²/sec) Obs.	D_e (cm²/sec) Pred.	Obs./Pred. = 3κ
I-A	0.25	85	0.13	0.0103	0.0120	0.86
I-B	0.255	230	0.22	0.0226	0.0249	0.91
I-C	0.265	300	0.30	0.0279	0.0336	0.83
I-D	0.255	450	0.39	0.0369	0.0488	0.76

[a] 1/8-inch diameter × 1/8-inch length.

TABLE 2
Tablets[a] from Fractions of Alumina II

Sample	Micropores Vol. (cc/g)	Macropores Size (Å)	Macropores Vol. (cc/g)	D_e (cm²/sec) Obs.	D_e (cm²/sec) Pred.	Obs./Pred. = 3κ
II-A	0.25	650	0.24	0.0456	0.0455	1.00
II-B	0.26	940	0.27	0.0663	0.0599	1.11
II-C	0.26	1300	0.25	0.0658	0.0589	1.12

[a] 1/8-inch diameter × 1/16-inch length.

TABLE 3
Tableted Aluminas[a]

Sample	Micropores		Macropores		D_e (cm²/sec)		Obs./Pred. = 3κ
	Size (Å)	Vol. (cc/g)	Size (Å)	Vol. (cc/g)	Obs.	Pred.	
III-A	58	0.73	—	0	0.0259	0.0217	1.19
III-B	56	0.83	—	0	0.0321	0.0278	1.16
III-C	97	1.03	—	0	0.0449	0.0369	1.22
IV-A	[b]	0.08	59	0.30	0.0066	0.0138	0.48
IV-B	[b]	0.10	70	0.34	0.0094	0.0195	0.48
IV-C	[b]	0.08	135	0.55	0.0186	0.0423	0.44
V	[b]	0.05	85	0.51	0.0127	0.0240	0.53
VI	38	0.59	4500	0.03	0.0204	0.0274	0.74
VII	65	0.91	—	0	0.0246	0.0275	0.89
VIII	105	0.72	—	0	0.0281	0.0287	0.98
IX	110	0.83	—	0	0.0280	0.0300	0.93
X	80	0.71	—	0	0.0318	0.0230	1.38
XI	[b]	0.05	160	0.86	0.0390	0.0380	1.02
XII	[b]	0.05	180	0.98	0.0396	0.0465	0.85
XIII	120	1.15	—	0	0.0445	0.0392	1.13
XIV	30	0.19	650	0.58	0.0627	0.0776	0.81
XV	20	0.10	1000	2.09	0.105	0.114	0.92
XVI	[b]	0.13	2300	0.50	0.116	0.115	1.01
XVII	[b]	0.15	1500	0.53	0.124	0.108	1.25

[a] 1/8-inch diameter × 1/16-inch length.
[b] Pores of undefined size, below 20 Å.

tempting to predict diffusion rates at other conditions.

The quantity κ is assumed to be a constant for a given catalyst. It includes not only the pore orientation effects considered in our model, but also the effects of dead ends and noncylindrical pores, which we have neglected in the pore-size analysis and in the diffusion model. In anisotropic catalysts, of course, the radial and axial diffusion will be governed by different values of κ; this question will be treated at another time.

ACKNOWLEDGMENTS

The authors wish to acknowledge the cooperation of Sinclair Research, Inc., in obtaining and publishing these data. One of us (W.E.S.) wishes to acknowledge the financial support of the National Science Foundation (Grant 86-3354) during his phase of the work.

REFERENCES

1. Weisz, P. B., and Schwartz, A. B., *J. Catalysis* **1**, 399 (1962).
2. Evans, R. B., III, Watson, G. M., and Mason, E. A., *J. Chem. Phys.* **35**, 2076 (1961).
3. Scott, D. S., and Dullien, F. A. L., *A.I.Ch.E. J.* **8**, 113 (1962).
4. Rothfeld, L. B., *A.I.Ch.E. J.* **9**, 19 (1963).
5. Weisz, P. B., *Z. Physik. Chem. (Frankfurt)* **11**, 1 (1957).
6. Barrett, E. P., Joyner, L. G., and Halenda, P. P., *J. Am. Chem. Soc.* **73**, 373 (1951).
7. Ries, H. E., Johnson, M. F. L., and Melik, J. S., *J. Phys. Colloid Chem.* **53**, 657 (1949).
8. Ritter, H. L., and Drake, R. C., *Ind. Eng. Chem. Anal. Ed.* **17**, 787 (1945).
9. de Boer, J. H., private communication.
10. Hoogschagen, J., *Ind. Eng. Chem.* **47**, 906 (1955).