Diffusion Rates in Porous Catalysts

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Rates of diffusion of helium, nitrogen, and carbon dioxide through alumina pellets were measured at atmospheric pressure and room temperature. The cylindrical pellets, ¾ in. diameter and ⅜ in. in length, were prepared from α-alumina particles with a mean pore radius of 65 Å. Surface area and pore volume data indicated that the corresponding mean pore radius of the micro and macropores in the whole pellet was 96 Å.

The results showed that Knudsen type of diffusion was the controlling transport process despite the large fraction of void volume in the macropores. Carbon dioxide diffused more rapidly than expected, suggesting the possibility of migration of physically adsorbed molecules along the pore walls.

The diffusion rates were about 16% higher than predicted, with a mean pore radius (Wheeler model) based upon the void volume of both micro and macropores used. However there is no logical basis for using this mean pore radius for a pellet having widely separated, micro and macropore size distributions.

More information is needed about pore diffusion in order to interpret reaction rate data on porous catalysts. While the effective pore radius for diffusion is not the same as that for diffusion and reaction in a catalyst particle, the two radii are related. Diffusion and pore geometry information are needed to establish this relationship. Published diffusion data include Weisz's (5) measurements for hydrogen, Hoogschagen's (3) studies on oxygen, and Wicke and Kallenbach's (8) work using compressed zinc oxide tablets. Wheeler (7) has reviewed the subject and presented a modified model of the pore system supplementing his earlier work (6). For predicting diffusion rates the important feature of the model is the effective pore radius, particularly for small pores where Knudsen diffusion occurs. The purpose of this paper is to present experimental data on diffusion in a high-porosity pellet prepared by compressing porous γ-alumina particles.

The pore system in any pellet must present a number of parallel paths for diffusion. The individual paths follow a tortuous course and have a continuously changing shape and size. In a homogeneous porous bed such as a gel, the parallel paths would be expected to be similar. In other words if each unit pore were assigned an average radius, the distribution of radii would be over a small range. Pellets of low porosity appear to fit into this framework. Such particles may be of two classes: Pellets formed of nonporous particles of relatively large size. These pellets have a small surface area and interstitial pores large enough for diffusion to be of the bulk type. Pellets of large surface area which are fused porous materials, such as Vycor glass, with small pores in which diffusion is of the Knudsen type and gel type of materials, such as silica gel. Here the mean pore size is very small and the surface area correspondingly large.

Observed diffusion rates in the first class of particles are less than those predicted on the basis of a model consisting of parallel, straight, circular pores with the same area and volume as the pellet. Hoogschagen (3), from experimental data on ammonia catalyst, attributed the deviation to the tortuous nature of the pores and determined numerical values of a tortuosity correction factor. Peterson (4) showed that the low bulk diffusion rates could be accounted for by variations in cross-sectional area of the pore along its length.

In treating diffusion in the second class of low porosity particles an estimate of the effective pore size is critical. This is indicated by the following equation for free molecule, or Knudsen, diffusion in a long capillary tube of radius r:

$$N = 9.7 \times 10^{3} \pi r^{3} \sqrt{\frac{T}{M}} \left(\frac{\Delta C}{L} \right)$$

$$= a \pi r^{3} \frac{\Delta C}{L} \quad \ldots \quad (1)$$

where

$$a = 9.7 \times 10^{3} \sqrt{\frac{T}{M}} \text{ cm./sec.}$$

To use this equation for a pellet it is necessary to estimate the radius r_e of an equivalent circular pore and the number of such hypothetical pores in the pellet. Wheeler (7) postulated that the pellet contained n cylindrical pores of a single constant radius but that these pores might intersect and also have rough walls. For this model the constant radius, or mean pore radius, which would give the same pore volume and surface area is

$$\bar{r} = \frac{2\,V_g}{S_g} \text{ (r.f.)} (1 - \epsilon) \ldots . (2)$$

This concept of mean pore size is thus based upon purely geometrical considerations and does not involve diffusion. The roughness factor (r.f.) cannot greatly exceed 2. Hence for low porosity materials (ϵ from 0.30 to 0.50), the product (r.f.)$(1 - \epsilon)$ is close to unity. For this reason the simple relationship

$$\bar{r} = \frac{2\,V_g}{S_g} \quad \ldots\ldots \quad (3)$$

has been widely used as a measure of the mean pore size.

Catalyst pellets prepared from porous powders constitute a third class of materials which may be described as follows: pelleted materials consisting of particles containing micropores surrounded by macropores. This type of pellet is characterized by a high porosity (0.5 to 0.9).

In this third class of pellets it is conceivable that Knudsen diffusion in the micropores could be affected significantly by bulk diffusion in the macropores. In addition to this complication there is uncertainty in predicting the correct, effective pore radius for diffusion. It is advantageous to define an effective pore radius in terms of V_g and S_g, as in Equation (3), since these are commonly measured physical properties of the pellet. However two values of $\bar{r}$ can be so computed. For example in the alumina sample used in this investigation $\bar{r} = 96$ Å based upon the pore volume of the whole pellet, while $\bar{r} = 65$ Å for the micropore alone. The experimental work described in

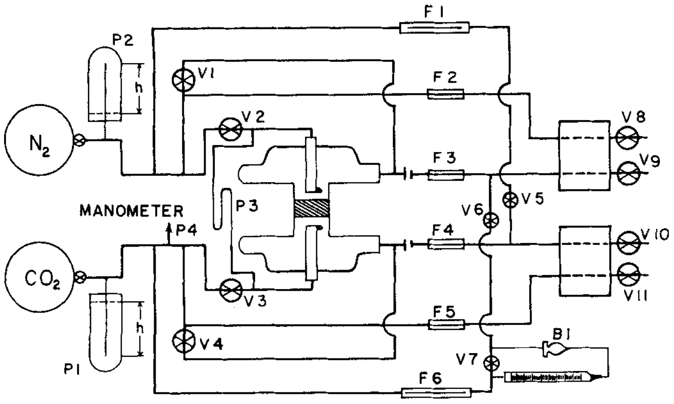

Fig. 1. Schematic flow system.

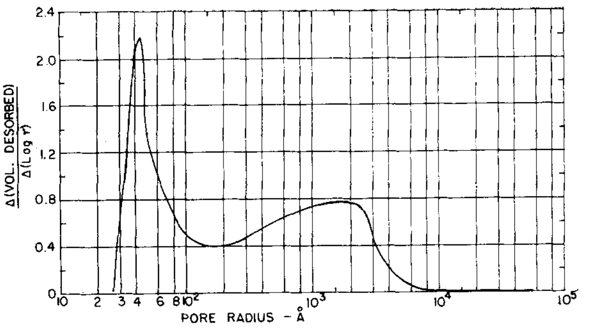

Fig. 2. Pore size distribution for alumina pellet.

the next section was designed so as to be able to evaluate the effective diffusion radius for comparison with that calculated from Equation (3).

EXPERIMENTAL

Diffusion rates were measured for pelleted alumina particles having the following properties:

Density of γ-alumina

ρ = 3.2 g./cc. (1)

Micropores

V_g = 0.882 cc./g.

S_g = 266 to 273 sq. m./g.

$\bar{r}$ = 65.3 Å [from Equation (3)]

ϵ = 0.738 (calculated from V_g and ρ)

Pellet (as a whole)

V_g = 1.35 cc./g.

S_g = 280 sq. m./g.

$\bar{r}$ = 96.4 Å [from Equation (3)]

ϵ_p = 0.812 (calculated from V_g and ρ)

The surface area was determined with a modified Brunauer-Emmett-Teller apparatus, and pore volumes were measured by the water penetration method.

Data were obtained at approximately atmospheric pressure and room temperature for each gas in the two systems: helium-nitrogen and helium-carbon dioxide. Approximate preliminary measurements were also made for the nitrogen-carbon dioxide system.

The pellets, cylinders ¾ in. in diameter and ⅜ in. in length, were mounted in slightly undersize tubing and clamped in place to prevent leakage around the outside, cylindrical surface. Preliminary measurements made with varying pressures on the clamp served as a test for leakage. The apparatus, including the diffusion cell, is shown schematically in Figure 1. The figure illustrates the setup for the nitrogen-carbon dioxide system. Pure gas is fed across the top of each face of the pellet. To prevent a stagnant layer (and therefore a diffusional resistance) from building up on each face, a small glass tube was attached to each side of the cell. The flow of gas through the tube was thus directed parallel to the face of the pellet. A U-tube connection (P3) across the two sides of the cell equalized the pressure and eliminated flow through the pellet by a total pressure gradient.

The rates of flow and pressures through the two sides of the diffusion cell and through the thermal conductivity cells were measured and maintained constant by valves and flowmeters (designated with the symbols V and F in Figure 1). Flow rates through the diffusion and thermal conductivity cells were controlled at about 400 cc./min. The flow meters were capillary tubes, calibrated with a wet test meter or by volumetric displacement. The calibrations were checked at intervals and believed to be accurate to 2%.

The sample stream to each thermal conductivity cell was the gas flowing over the pellet face, while the reference stream was the pure gas, as indicated in Figure 1. The cells were enclosed in a constant temperature bath held at 90°F. and operated at constant current conditions (80 ma. for the helium stream, 125 for the nitrogen, and 110 for the carbon dioxide stream).

The rate of diffusion was measured by first noting the emf readings of each thermal conductivity cell when steady state was reached. For example in the nitrogen-carbon dioxide measurements the emf reading is noted for the sample gas from the nitrogen side of the diffusion cell. Then this stream is shut off (with valve V2), and pure nitrogen is allowed to flow through the sample side of the thermal conductivity cell through valve V1. Now pure carbon dioxide is added to this stream before it enters the thermal conductivity cell through valve V6. The amount of carbon dioxide necessary to obtain the same emf readings is noted on the flowmeter $B1$. This is the required diffusion rate of carbon dioxide through the pellet into the nitrogen stream. A similar procedure was used to determine the simultaneous diffusion of nitrogen in the opposite direction into the carbon dioxide stream. This arrangement eliminates the necessity for calibrating the thermal conductivity cells and tends to eliminate errors in their use. A run, carried out in this manner, provided an independent measurement of the diffusion rate of each gas through the pellet.

TABLE 1. CHARACTERISTICS OF ALUMINA PELLETS USED FOR DIFFUSION MEASUREMENTS

Pellet no.	Length L_p, cm.	Mass m_p, g.	Cross-sectional area A_p, sq. cm.
1	0.900	1.902	3.50
2	0.898	1.987	3.49
3	0.896	1.961	3.48

RESULTS

The experimental results consisted of a measured volume of each gas diffusing through the alumina pellet at a recorded temperature and pressure. In general three runs were made for each of three pellets. The characteristics of the pellets are shown in Table 1 and the diffusion results in Table 2. The differences between runs for a given pellet did not exceed 1%, thus establishing the reproducibility of the data. Average, volumetric diffusion rates for each pellet are given in the second and third columns of Table 2.

EFFECTIVE PORE RADIUS FOR DIFFUSION

Wheeler's model of the catalyst particle leads to the following expression for the number of pores:

$$n = \frac{m_p S_g^2}{4\pi V_g L_p} \qquad (4)$$

This equation, along with Equation (3) for $\bar{r}$, describes the geometry of the pores on a volume and surface area basis. To explain diffusion suppose that the same model is used, except that the mean radius is $\bar{r}_e$. Then the total diffusion rate through a pellet is given by applying Equation (1) to a pore with this effective diffusion radius $\bar{r}_e$ and then multiplying by the number of pores in the pellet. If N_p is the total rate of diffusion, the result is

$$N_p = \frac{m_p S_g^2}{4\pi V_g L_p^2} a \pi \bar{r}_e^{-3} \Delta C_p \qquad (5)$$

This expression defines $\bar{r}_e$ and also may be used to evaluate numerical values

TABLE 2. DIFFUSION DATA AND RESULTS

A. Helium—nitrogen system

Pellet no.	Vol. diffusing cc./sec.		Pressure, mm.	Temp., °F.	$PQ/\Delta P$—cc./sec.		$\overline{r}_e$—Å	
	N_2	He			N_2	He	N_2	He
1	0.109	0.292	779.6	83	0.116	0.311	102	103
2	0.106	0.283	779.5	86	0.112	0.300	100	100
3	0.101	0.287	778.9	87	0.110	0.304	99	101
Average							100	102

B. Helium—carbon dioxide system

Pellet no.	Vol. diffusing cc./sec.		Pressure, mm.	Temp., °F.	$PQ/\Delta P$—cc./sec.		$\overline{r}_e$—Å	
	CO_2	He			CO_2	He	CO_2	He
1	0.104	0.277	775.7	87	0.110	0.293	108	100
2	0.100	0.274	777.3	86	0.106	0.286	105	98
3	0.0974	0.275	778.1	88	0.103	0.290	105	99
Average							106	99

employing the diffusion rates reported in Table 2. If the gas mixtures are assumed to be ideal, $\breve{N}_p$ can be expressed in terms of the volumetric diffusion rate. Then Equation (5) takes the form

$$\overline{r}_e = 4\left[\frac{PQ}{\Delta P}\,\frac{V_g L_p^{\,2}}{a\, m_p\, S_g^{\,2-}}\right]^{1/3} \qquad (6)$$

The data in the first columns of Table 2 were used in Equation (6) to compute the values of $\overline{r}_e$ presented in the last column of the same table.

There are several points of interest in the results. The first is concerned with the magnitude of $\overline{r}_e$. Based upon the microporous particles in the pellet the geometric mean radius is 65 Å, while for the nitrogen-helium system the diffusion mean radius is 101 Å. Thus $\overline{r}$ for the micropores would predict diffusion rates only $(65/101)^3$, or 0.28, as large as observed. This could be due to pore interconnections in the micropores and small diffusion resistances in the much larger macropores. It is not possible to determine the relative significance of these two factors from the data.

It is noted that the mean pore radius for the whole pellet, 96 Å, is surprisingly close to the effective diffusion value of 101 Å. for the nitrogen-helium system. However, this is not particularly significant, because $\overline{r}$ for a pelleted particle is not a realistic quantity but simply the result of averaging two, separated, pore size distribution functions. This is illustrated by Figure 2, which shows a pore size distribution function for the alumina pellet studied in this investigation.[*] On this plot the measure of the number of pores is reported in terms of volume of nitrogen desorbed, that is as (Δ volume desorbed)/(Δ log r). It is evident that there are relatively few pores in the region of 96 Å but that this value happens to be the average of large numbers of macropores (1,000 to 2,000 Å) and micropores (30 to 80 Å).

The second point is the equality of the values of $\overline{r}_e$ for nitrogen and helium. Since these radii were obtained from a Knudsen diffusion supposition, Equation (1), the results indicate that the Knudsen process, rather than bulk diffusion, controls the mass transfer through the pellet. If bulk diffusion had been controlling, the volumetric flow rates of nitrogen and helium would have been the same. Instead the data in Table 2 show that the rates are approximately in the inverse ratio of the square roots of the molecular weights, as required by Equation (1).

The effective radius for helium diffusing in the carbon dioxide-helium system is also about the same as the value for helium-nitrogen system. However the radius for carbon dioxide is higher (106 vs. 99 Å). This is contrary to the possibility of the molecular diffusivity influencing the process, since then the diffusion rate for carbon dioxide would be less than that for helium. This suggests that the diffusion of carbon dioxide is augmented by a third process, different from both Knudsen and bulk diffusion. A possibility is that carbon dioxide is transported to a significant extent by adsorption and migration along the pore walls. This type of transport has been observed in a number of instances [for example by Carman (2)]. In a qualitative way the slight decrease in effective radius for helium diffusion in the carbon dioxide system can be explained in terms of the obstruction offered by the adsorbed carbon dioxide molecules on the pore walls (that is decrease in cross-sectional area of the pores).

Diffusion data are needed on a number of types of porous materials in order to determine if the observations reported here are widely applicable. Particularly it would be desirable to have measurements for several types of pelleted materials to find the influence of macro and micropore size distributions.

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NOTATION

a = constant in Knudsen diffusion equation, cm./sec.
C = concentration, g. moles/cc.
L = pore length
m_p = mass of pellet, g.
M = molecular weight
n = number of equivalent pores in the cross section of the pellet
N = rate of diffusion, g. moles/sec.
P = total pressure, mm.
r = pore radius
$\overline{r}_e$ = mean effective pore radius for diffusion, based upon Knudsen diffusion
$\overline{r}$ = geometric mean pore radius, defined by Equation (3)
Q = volume rate of diffusion cc./sec.
S_g = surface area per gram, cc./g.
T = absolute temperature, °K.
V_g = pore volume per gram, cc./g.
ΔP = partial pressure difference across pellet for diffusion component, mm.

Subscript

ϵ = void fraction
ρ = density of the solid phase of a porous particle, g./cc.
p = pellet as a whole

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