A Dynamic Method for Catalyst Diffusivities

It is shown that a pulse-response technique can be used with the Wicke-Kallenbach type of diffusion cell to determine effective diffusivities in catalyst pellets. The diffusivity is a function of the retention time of the pulse of diffusing gas in the pellet. Experimental values obtained with an alumina pellet agreed well with expected results for this type of material.

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SCOPE

Diffusion rates in catalyst pellets are necessary for design of many types of catalytic reactors. Prediction methods based upon the geometrical properties of the porous pellet are available (Satterfield, 1970), but their accuracy is about 50 to 100%. Hence, experimental methods are needed, particularly those that are rapid, accurate, and simple enough to be used as a standard procedure in catalyst laboratories. Diffusivities customarily have been determined by steady state methods: either from diffusion data (Brown et al., 1969; Rothfeld, 1963; Satterfield and Cadle, 1968) or indirectly from combined reaction and diffusion measurements in large catalyst pellets (Rao and Smith, 1963; Satterfield et al., 1968). While dynamic methods have seldom been used for gases, they have potential advantages. They can be very rapid, require but small quantities of diffusing component, and can provide more information, for example, about the importance of dead-end pores. The objective of the research reported here was to develop and evaluate a dynamic method based upon the Wicke-Kallenbach diffusion cell (Smith, 1970). The procedure consists of introducing a pulse of diffusing gas to one end face of the catalyst pellet and measuring the concentration vs. time response peak leaving the other end face.

CONCLUSIONS AND SIGNIFICANCE

It is shown that the diffusivity D_e of a catalyst pellet can be related to the retention time of a pulse of diffusing gas in the pellet. Other quantities involved are the porosity, length, and cross-sectional area of the pellet, and the flow rate F of gas across the face of the pellet. For very large values of F, the expression for D_e is simplified to one requiring only the retention time, porosity, and length of the pellet. With this equation it is possible to evaluate D_e from but one run at high F, determining the retention time from a single response peak. Alternately, response peaks can be measured for several flow rates and D_e established by comparing the retention time vs. flow rate data with the derived equation.

The method was evaluated with experimental data at 24°C and one atmosphere for the diffusion of helium (in nitrogen) in an alumina pellet of 0.48 porosity. The results indicate that an accurate value of D_e can be obtained. The apparatus is simple and the time required is short so that the procedure could be attractive for use on a routine basis in catalysis laboratories. The equations were developed for a nonadsorbing gas such as helium. The result for the nonadsorbing gas gives a tortuosity factor for the pellet. This tortuosity factor can then be used to calculate the diffusivity for any diffusing component, as long as surface diffusion is insignificant. Hence, diffusivities for adsorbing as well as nonadsorbing gases can be obtained by the proposed method.

The dynamic version of the Wicke-Kallenbach diffusion cell is shown in Figure 1. The end faces of the cylindrical catalyst pellet are exposed to the flow of different gases through the upper and lower chambers. In the steady state procedure the two streams consist of different pure gases. The diffusion rates are determined from the flow rates and analyses of the streams leaving the two chambers. In the dynamic method both end faces are exposed to the flow of the same reference (or carrier) gas B. Then a pulse of diffusing gas A is introduced in the stream entering the upper chamber. A suitable detector in the exit stream from the lower chamber is used to determine the retention time of the part of the pulse of A that diffuses through the pellet. The diffusivity is calculated from the retention time. The same pressure must be maintained in the two chambers to eliminate convective transport through the pellet. Application of the method is illustrated with data obtained for an alumina pellet.

With a sensitive detector the input pulse can consist of but a small concentration of A in carrier B. Even with a pulse of pure A, its concentration decreases sharply in the direction of diffusion through the pellet. For example, Fujita (1952) has shown this by numerical calculation of the concentration profile in a porous material as described by an equation equivalent to Equation (4). Hence, the average concentration of A in the pores is low; values of about 1% are easily attainable. This is a significant advantage of the dynamic method because the effective diffusivity D_e then becomes independent of concentration. For constant pressure diffusion of a binary system in a capillary, the diffusive flux is given by (Rothfeld, 1961)

$$N_A = -D\frac{dC_A}{dx} \tag{1}$$

where the composite diffusivity is

$$\frac{1}{D} = \frac{1-\alpha y_A}{D_{AB}} + \frac{1}{D_{KA}} \tag{2}$$

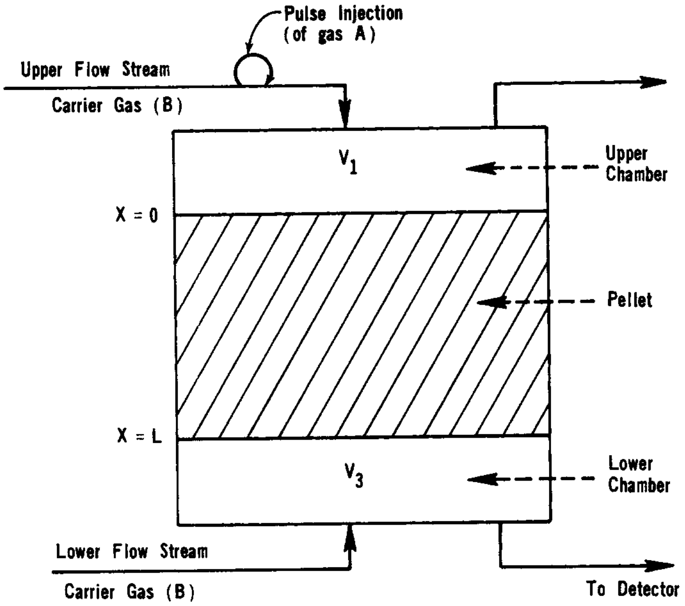

Fig. 1. Schematic diagram of the single pellet system.

and

$$\alpha = 1 + \frac{N_B}{N_A} = 1 - \left(\frac{M_A}{M_B}\right)^{1/2} \tag{3}$$

If the mole fraction y_A approaches zero, the $\alpha\, y_A$ term in Equation (2) becomes negligible and D_e is independent of concentration.

Effective intrapellet diffusivities for gases can be measured dynamically in fixed beds of catalyst pellets by pulse-response techniques (Schneider and Smith, 1968). However, axial dispersion and fluid-to-particle mass transfer in the bed must be accounted for before D_e is obtainable. Furthermore, the variance (second moment) of the response pulse is required, while in the single-pellet method proposed here only the retention time (first moment) is needed. For both of these reasons the single-pellet procedure can give more accurate results.

The origin of the method is the earlier work of Barrer (1953) in which the rate of pressure increase with time was measured in a closed, originally evacuated volume such as the lower chamber in Figure 1. Such data did not give diffusivities but provided information about permeability. The pulse technique in single pellets was first used for diffusion studies by Suzuki and Smith (1972). In their procedure the lower chamber was a permanently closed volume, originally filled with carrier gas, and in which was located the detector. While diffusivities could be obtained with this arrangement, instabilities of the response of the closed chamber to composition changes required very careful and time consuming experiments. In contrast, the flow system depicted in Figure 1 gives stable and easily reproducible response peaks.

THEORY

For a nonadsorbed gas the conservation equation applied to a section of the pellet is

$$\epsilon_p \frac{\partial C_A}{\partial t} = D_e \frac{\partial^2 C_A}{\partial x^2} \tag{4}$$

where D_e has been assumed to be independent of composition in accordance with the argument previously advanced for neglecting the term $\alpha\, y_A$ in Equation (2). The boundary and initial conditions are (see Figure 1):

$$\text{Input pulse:} \quad C_A = M\,\delta(t) \quad \text{at} \quad x = 0 \tag{5}$$

$$-A\,D_e\left(\frac{\partial C_A}{\partial x}\right)_{x=L} = V_3\left(\frac{d\,C_{AL}}{dt}\right) + F\,C_{AL} \tag{6}$$

$$C_A = 0 \quad \text{at} \quad t = 0 \quad \text{for} \quad 0 < x \leq L \tag{7}$$

Equation (6) implies complete mixing in the lower chamber and negligible mass transfer resistance between pellet face and gas at $x = L$. In the application described later, these requirements were approached by reducing V_3 to 0.5 cm^3 and by passing the flow stream directly over the pellet face. For a lower flow rate F of 60 cm^3/min. (an intermediate value) and a pellet thickness of 2.44 cm, the average residence time of the diffusing species in V_3 was small (about 0.5 s) in comparison with the diffusion time through the pellet (about 10 s). Also order of magnitude analysis for F = 60 cm^3/min. and V_3 = 0.5 cm^3 indicated that the accumulation term in Equation (6) could be neglected since it was but 4% of $F\,C_{AL}$.

Equations (4) to (7) can be solved in the Laplace domain for $\overline{C}_A = f(x, s)$. Then using the relation

$$m_n = (-1)^n \lim_{s\to 0} \frac{d\,\overline{C}_A}{ds^n} \tag{8}$$

gives theoretical expressions for the moments. For the first normalized moment for the pellet itself, the result is (Dogu, 1974)

$$(\mu_1)_{\rm Corr} = \frac{m_1}{m_0} = \frac{L^2\epsilon_p\left(3\frac{A}{L}D_e + F\right)}{6\,D_e\left(\frac{A}{L}D_e + F\right)} \tag{9}$$

The limiting value of μ_1 as the lower flow rate increases is

$$(\mu_1)_{\rm Corr} = \frac{L^2\epsilon_p}{6\,D_e} \tag{10}$$

Experimental values of the first moment can be determined from the observed response peaks using the equation

$$(\mu_1)_{\rm obs} = \frac{\int_0^\infty C_A\,t\,dt}{\int_0^\infty C_A\,dt} \tag{11}$$

To obtain the moments for the pellet itself the observed values should be corrected for the retention time in the dead volumes between injection point and the upper face, and between the lower face of the pellet and the detector, and for the injection time of the pulse, according to the equation

$$(\mu_1)_{\rm Corr} = (\mu_1)_{\rm obs} - (\mu_1)_{\rm d.v.} - \frac{t_0}{2} \tag{12}$$

The values of $(\mu_1)_{\rm Corr}$ determined from Equation (12) may then be used in Equation (9) or (10) to determine the effective diffusivity. The method is applied to experimental data for helium diffusing through an alumina pellet in the following sections.

EXPERIMENT

The apparatus (Figure 2) consisted of the diffusion cell enclosed in a constant temperature oven, pulse injection valve, thermal conductivity detector, and flow metering and controlling equipment. The diffusion cell is shown in detail and with dimensions in Figure 3. The upper stream was brought to the top of the pellet through a 0.165-cm I.D., 9-cm long tube, flared on the end, so as to minimize the upper dead volume and to create a rapid flow of gases across the upper face of the pellet. Similarly, the lower stream was passed directly across the lower face in the volume V_3 ($V_1 = 0.45$ cm^3 and $V_3 = 0.50$ cm^3). The volumes in the lines (Figure 2) between pulse injection and catalyst holder and between the lower chamber V_3 and the detector were minimized in order to reduce the corrections to the observed first moment required by Equation (12).

The pressure was maintained constant on both sides of the pellet by adjusting valve V_9 and observing the pressure difference with the manometer (Figure 2). After obtaining equal pressures the manometer was disconnected prior to pulse injection to eliminate an additional contribution to the dead volume.

Nitrogen was used as the carrier gas and 1 cm^3 pulses of pure helium were introduced to the upper stream. The measurements made at 24°C and 1 atm consisted of the flow rates and the recorded response peak from the detector. The upper flow rate was maintained at 60 cm^3/min while response peaks were measured for lower flow rates from about 20 to 150 cm^3/min. Measurements with the detector placed in both upper and lower streams indicated that about 20% of the helium in the pulse diffused through the pellet.

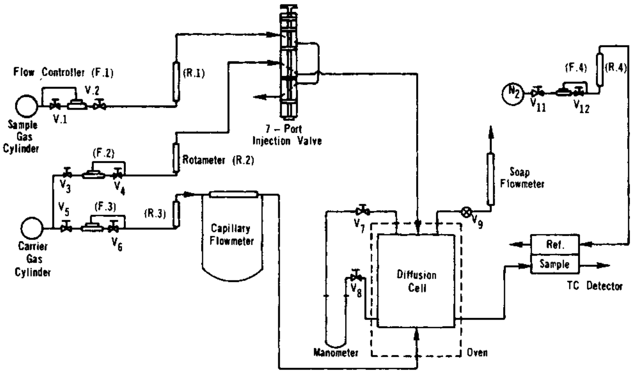

Fig. 2. Schematic diagram of the apparatus.

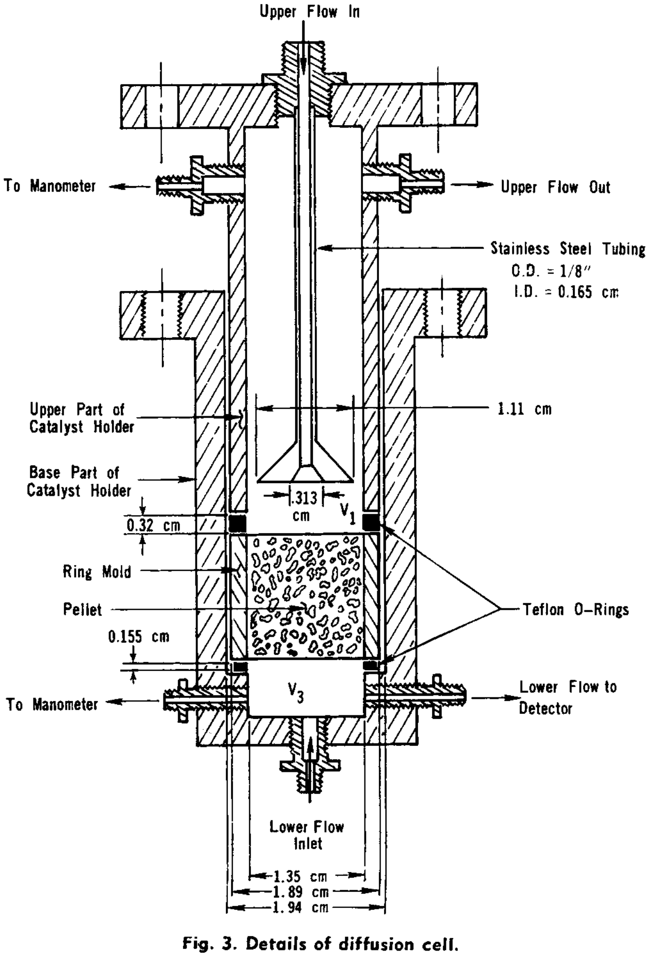

Fig. 3. Details of diffusion cell.

The alumina pellet was made by compressing porous (micropores) Boehmite particles in a stainless steel mould. The particles were heated at 325°C for 18 hours in air prior to the pelletting process. The surface area of the Boehmite was 339 m^2/g, determined by nitrogen adsorption (Otani and Smith, 1966). Other properties of the cylindrical pellet are: length = 2.44 cm, diameter = 1.35 cm, total porosity = 0.771 (from helium pycnometer) and macropore porosity = 0.480 (from mercury porosimeter). The macropores are considered to be those with radii greater than 150Å and are contained primarily in the interparticle space in the pellet. The average macropore radius determined from pore-volume distribution measurements was 2990 Å. Prior to the pulse experiments the pellet was heated at 300°C for 6 hours with nitrogen flowing on both sides of the pellet.

RESULTS

The observed moments were computed by numerical integration of the response peaks according to Equation (11). Since the response of the thermal conductivity cell was directly proportional to the concentration, it was not necessary to calibrate the cell to obtain the moments; the proportionality constant cancels in the numerator and denominator of Equation (11). The dead volumes were estimated from the geometry of the experimental arrangement to be 1.0 cm^3 for the upper dead volume and 1.3 cm^3 for the lower dead volume. These volumes introduced an average correction to the observed first moment of about 20%.

Figure 4 illustrates how the corrected first moment varies with lower flow rate. After the first run the pellet was again heated at 300°C for 6 hours with nitrogen. Then the pulse tests with helium were repeated. The agreement of the two sets of data is indicative of the type of results that can be obtained in these kinds of experiments.

The diffusivity was calculated from the data in Figure 4 in two ways. First, Equation (10) was used, estimating $(\mu_{1\infty})_{\text{Corr}}$ to be 9.8 s from Figure 4. This method gave $D_e = 0.078$ cm^2/s. In the second method Equation (9) was written in linear form as

$$F(\mu_1)_{\text{Corr}} = K_1 F + K_2 (\mu_1)_{\text{Corr}} + K_3 \tag{13}$$

where

$$K_1 = \frac{L^2 \epsilon_p}{6 D_e} \tag{14}$$

$$K_2 = -\frac{A}{L} D_e \tag{15}$$

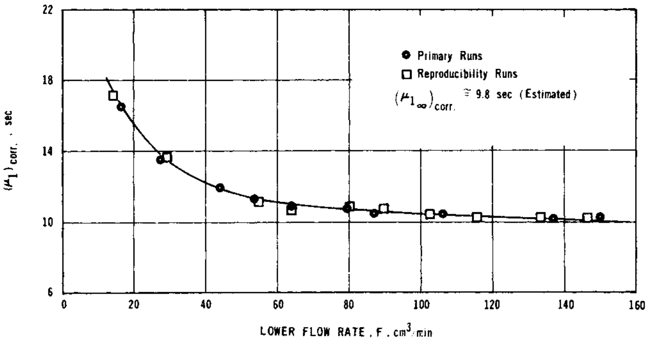

Fig 4. First absolute moment data for He-N_2 system (upper flow rate = 60 cm^3/min).

$$K_3 = \frac{L A \epsilon_p}{2} \qquad (16)$$

Then the data for all flow rates were used with least square analysis to determine the best value of K_1. Using all the data points shown in Figure 4 gave $K_1 = 9.63$ s. Then from Equation (14), $D_e = 0.079$ cm^2/s.

Both methods lead to diffusivities that are well within the limits of accuracy of the data. The first has some advantages as a rapid procedure for obtaining the diffusivity since measurements need be made only for high values of F to determine $(\mu_{1\infty})_{\text{Corr}}$.

DISCUSSION

To check the validity of the experimental results the tortuosity factor τ_a was calculated from D_e from the expression

$$D_e = \frac{\epsilon_a D}{\tau_a} \qquad (17)$$

The composite diffusivity was evaluated from Equation (2) with $\alpha\, y_A \to 0$ and for molecular and Knudsen diffusivities of 0.713 cm^2/s and 2.49 cm^2/s for helium in nitrogen at 24°C and 1 atm pressure. The Knudsen diffusivity was evaluated at the mean macropore radius of 2990Å. The molecular diffusivity was obtained from the experimental data of Fuller et al. (1956). The resultant value of $\tau_a = 3.34$ agrees well with the figure of 4 suggested by Satterfield (1970) after examination of available data for alumina and other catalyst pellets. Macropore porosity is used in Equation (17) because the diffusion occurs predominantly in the macropores. This was verified by making measurements for two pellets of nearly the same total porosity but made from particles of different average diameters, 48 and 70 microns. The diffusivities for the two pellets agreed within 1%. Hence, Equation (17) gives a macropore tortuosity factor. For more dense pellets micropore diffusion could be significant.

Suzuki and Smith (1972) for a pellet of the same Boehmite, but with a porosity $\epsilon_a = 0.51$, obtained $D_e = 0.082$ cm^2/s at 24°C vs. 0.079 cm^2/s for the present pellet ($\epsilon_a = 0.48$).

These results suggest that the pulse-response technique reported here can be used to determine reasonably accurate effective diffusivities in catalyst pellets. For most accurate results the pellet length should be relatively large and the dead volumes and volume of the lower chamber as small as possible. By reducing these volumes, measurements can be made using catalyst pellets of customary length ($\sim$ 8 mm). The basic requirement is to design the apparatus so that the retention time in the dead volumes is small with respect to the diffusion time in the pellet. The experimental procedure is rapid and the apparatus simple. For a complete study response peaks should be measured over a range of lower flow rates, but an approximate diffusivity can be obtained from a single measurement at a high flow rate.

A nonadsorbing gas can be used for the diffusing component in the experimental studies. The resultant tortuosity factor then can be used to calculate pore-volume diffusivities for other components using Equation (17).

NOTATION

A = area of end face of pellet, cm^2
C_A = concentration of tracer gas A, moles/cm^3
$\overline{C}_A$ = Laplace transform of the function $C_A(t, x)$
C_{AL} = concentration of A at $x = L$, moles/cm^3
D = composite (of molecular and Knudsen diffusion) diffusivity in a capillary, defined by Equation (2), cm^2/s
D_e = effective diffusivity in the pellet, based upon void plus nonvoid area, cm^2/s
D_{AB} = molecular diffusivity in binary system of A and B, cm^2/s
D_{KA} = Knudsen diffusivity of A, cm^2/s
F = volumetric flow rate through lower chamber, cm^3/s at $p = 1$ atm and $t = 24$°C
K_1, K_2, K_3 = parameters defined by Equations (14) to (16)
L = pellet length, cm
M = strength of input pulse, moles s/cm^3
M_A, M_B = molecular weights of A and B
m_n = nth moment about the origin, defined as

$$m_n = \int_0^\infty C\, t^n\, dt$$

s = Laplace variable, s^{-1}
t = time, s; t_0 = injection time of pulse
N_A = diffusion flux of A, moles/cm^2 s
V_1, V_3 = volume of upper and lower chambers (Figure 3), cm^3
x = coordinate in direction of diffusion in pellet, cm
y_A = mole fraction A in gas mixture

Greek Letters

α = function of flux ratio, defined by Equation (3)
$\delta(t)$ = Dirac delta pulse, s^{-1}
ϵ_p = total porosity of pellet
ϵ_a = macropore porosity
μ_1 = first absolute moment, m_1/m_0, s; $(\mu_1)_{\text{obs}}$ = measured value; $(\mu_1)_{\text{d.v.}}$ = value for dead volumes; $(\mu_1)_{\text{Corr}}$ = value for pellet (corrected for dead volumes and injection time; s
τ_a = tortuosity factor in macropores of pellet

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