Diffusion and Adsorption in Arrested-Flow Chromatography

Moonsoo Oh
J. M. Smith
B. J. McCoy
Department of Chemical Engineering
University of California
Davis, CA 95616

Arrested-flow chromatography has proven successful for measuring gas-phase diffusion coefficients in open tubes (McCoy and Moffat, 1986), and intraparticle diffusion coefficients in columns packed with large-pore particles (Park et al., 1987). The approach was verified experimentally by measurements with nonadsorbing species. For small-pore particles with nonadsorbing gases, the intraparticle transport was too small to yield accurate intraparticle diffusivities. The present work shows that this limitation to large-pore particles can be overcome by using an adsorbing gas.

Suppose adsorption rates are very large with respect to diffusion rate, for example, as in physical adsorption. Then the expression for the spatial variance of a chromatographic peak that has broadened during a period of arrested flow (Park et al., 1987) is:

$$s = s_0 + 2D_e t_B/\epsilon \tag{1}$$

The spatial variance is equal to the observed temporal variance, divided by the square of the peak velocity. For adsorbing gases, the total capacity of the column now includes the adsorption equilibrium coefficient, K, i.e.,

$$\epsilon = \alpha + (1 - \alpha)(\beta + \rho_p K) \tag{2}$$

From data for the variance, s, at various values of stopped time, t_B, we can calculate the effective diffusion coefficient for the packed column, D_e, provided that ϵ, and hence, the adsorption equilibrium constant, is known.

The experimental apparatus used for arrested-flow experiments with adsorbing gases, Figure 1, was similar to that used by Park et al. (1987). After a pulse of the adsorbing tracer gas is injected into the packed column, the flow of carrier gas is stopped for the time, t_B, and the band is allowed to broaden by stationary (nonconvective) diffusion. Then the flow is started and the diffusion band is measured in the effluent from the bed at the detector. The variance (second central moment) is determined from the width of the eluted band at its half-height.

Four different particles were employed but only one (T-126 alumina) had small pores characteristic of most catalyst particles. Properties of the particles are given in Table 1. The column void fraction, α, was determined from measurements of the empty column volume, the weight of the packed column, and the particle density. Particle densities, ρ_p, were measured with a helium pycnometer, and the pore-size distribution, with a mercury porosimeter. The small pores of T-126 prevented nonadsorbing gases from penetrating sufficiently to yield measureable values of the intraparticle diffusivity.

Conventional flow chromatographic runs (Schneider and Smith, 1968) were made to determine the equilibrium adsorption coefficient, K, from the first temporal moment. Measurements were made for three tracer gases: methane, carbon dioxide, and helium. A 0.25×10^{-6} m^3 sample loop was used in all cases. Tracer gas pulses were injected with the six-port valve, Figure 1. Irreversibly adsorbing sites were first saturated with several injections of pure adsorbing gas. The resulting values of K are listed in Table 2. Negligible adsorption was observed for all the large-pore particles, except for CO_2 on Alcoa alumina. The heat of adsorption for methane on T-126 particles was determined to be $\Delta H = -10.4$ kJ/mol from a linear regression of ln K versus $1/T$.

Figure 2 shows experimentally-measured values of variance, plotted versus stopped-time, for nonporous glass beads (Park et al., 1987) and for the three large-pore particles (the three upper, and the lower lines). The adsorbing gas was methane except where noted. Carbon dioxide adsorbed strongly on the large surface area of T-126 particles, and desorbed too slowly to provide a measureable peak. Nitrogen was the carrier gas in all cases.

Figure 2 also displays (four intermediate lines) the measured

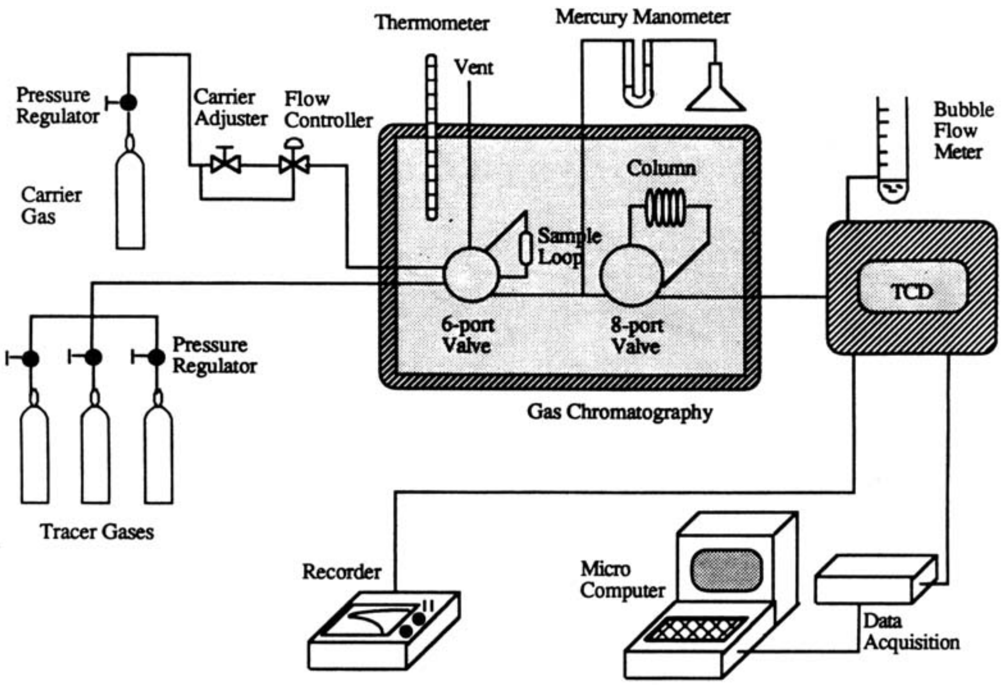

Figure 1. Apparatus for arrested-flow chromatography.

variance for the methane-T-126 system at temperatures from 313 to 373 K. Only these results were used for calculating internal tortuosity factors for porous particles, defined as

$$\tau = \beta D_c / D_i \qquad (3)$$

Here, D_i is the effective intraparticle diffusivity calculated from D_e (obtained from Eq. 1), with either the Maxwell, Burger, Rayleigh, or Jeffrey models for diffusion in a composite medium (Park et al., 1987). These calculations require a value for the external tortuosity factor applicable for the void region in the bed. This was found to be 1.50, from the data for glass beads by Park, and confirmed with additional experiments in this study. The composite molecular diffusion coefficient inside the pores, D_c, is in general, a combination of molecular and Knudsen diffusivities, and was calculated from the pore-size distribution by the method of Wang and Smith (1983). Values of D_c, based upon the volume-average of the pore sizes, were within 7% of those shown in Table 3. Results of the calculation with Burger's model are listed in Table 3, and for the other models, in Table 4. Internal tortuosity factors are, as expected, essentially independent of temperature. These results for τ agree well with the average of 3.7 in the literature for T-126 particles, as reported by Satterfield (1970).

Table 1. Properties of Particles Measured by He-Pycnometer and Hg-Porosimeter

	Solid Density $\rho_s \cdot 10^{-3}$ kg/m^3	Particle Density $\rho_p \cdot 10^{-3}$ kg/m^3	Porosity β	Pore Diameter $d \cdot 10^{10}$, m
Common Fire Brick	2.54	1.93	0.24	960 ~ 17,000
Varian Fire Brick	2.19	0.765	0.65	1,500 ~ 27,000
Alcoa Alumina	4.15	1.05	0.747	290 ~ 10,000
T-126 Alumina	3.02	1.38	0.541	29 ~ 1,900

As mentioned, adsorption was negligible in columns packed with particles of Varian firebrick and Alcoa alumina, Table 2. The intraparticle diffusivity, calculated by the method of Park et al. (1987) for a nonadsorbing gas, gave essentially the same values as reported by Park.

To test consistency with earlier results, one experiment was done with adsorbing CO_2 in a column packed with large-pore particles of Alcoa alumina. The result for intraparticle diffusivity was identical to that reported by Park et al. (1987), when Eq. 2 is used for the capacity of the column for the adsorbing gas.

It is concluded from this study that the arrested-flow method can be utilized with adsorbing gases to determine intraparticle diffusivities for small-pore particles for some systems.

Table 2. Adsorption Equilibrium Constants of Gases in Particle Pores

Tracer Gases	Particles	Temperature K	Adsorption Equilibrium Constant K · 10^3, m^3/kg
Methane	Common F.B.	313 ~ 373	0
	Varian F.B.	313 ~ 373	0
	Alcoa Alumina	313 ~ 373	0
	T-126 Alumina	313	0.38
		343	0.26
		373	0.19
Carbon Dioxide	Common F.B.	313 ~ 373	0
	Varian F.B.	313 ~ 373	0
	Alcoa Alumina	313	1.00
Helium	All Particles	313 ~ 373	0

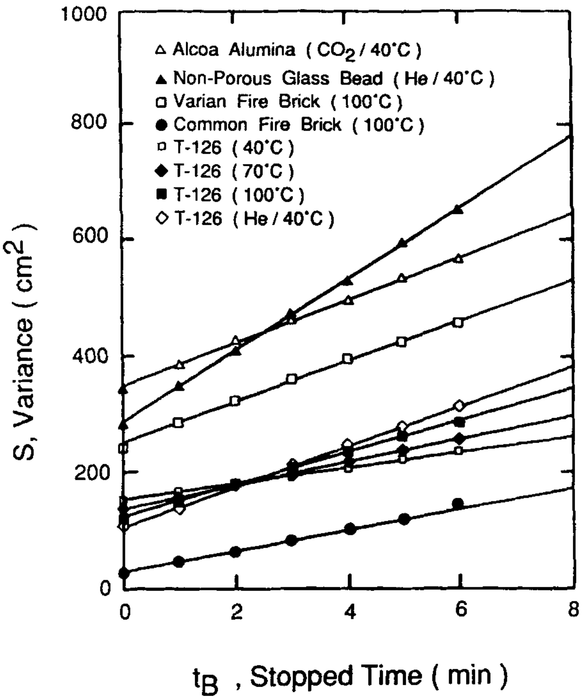

Figure 2. Variance of response curve for different particles vs. stopped time.

Carrier gas is nitrogen; tracer is methane, except where noted.

Table 3. Internal Tortuosity Factors of T-126 Particles Calculated by Burger's Model

	Temperature, K		
Parameters	313	343	373
Slope of Variance	8.19	10.67	13.3
Effective Diffusivity			
$D_e \cdot 10^4$, m^2/s	0.071	0.084	0.097
Molecular Diffusivity			
$D_i \cdot 10^4$, m^2/s	0.234	0.276	0.321
Intraparticle Diffusivity			
$D_m \cdot 10^4$, m^2/s	0.0164	0.0188	0.0217
Average Composite Diffusivity			
$D_c \cdot 10^4$, m^2/s	0.126	0.147	0.152
Internal Tortuosity Factor, τ_{int}	4.2	4.2	3.8

Table 4. Internal Tortuosity Factor of T-126 Particles Calculated by Parallel, Maxwell, Burger, Rayleigh or Jeffrey's Model

	Temperature, K		
Model	313	343	373
Parallel	3.4	3.4	3.3
Maxwell	4.7	4.6	4.4
Burger	4.1	4.1	3.9
Rayleigh	5.0	4.9	4.7
Jeffrey	4.9	4.9	4.7

Notation

D_c = composite diffusivity, m^2/s

D_e = effective diffusion coefficient for column packed with porous particles, m^2/s

D_i = effective intraparticle diffusion coefficient, m^2/s

K = adsorption equilibrium constant, m^3/kg

s = spatial variance of peak at exit of chromatographic column, including contributions due to flow and time, t_B; s_0 = variance for $t_B = 0$

t_B = time that flow is arrested, s

Greek letters

α = external void fraction

β = intraparticle porosity

ϵ = total capacity of column as volume fraction capacity of column

ρ_p = particle density, kg/m^3

ρ_s = solid-phase density, kg/m^3

τ = internal tortuosity factor

Literature Cited

B. J. McCoy, and A. J. Moffat, "Arrested-Flow Chromatography Measurement of Diffusion Coefficients," *Chem. Eng. Comm.*, **47**, 219 (1986).

I. S. Park, B. J. McCoy, and J. M. Smith, "Intraparticle Diffusion Coefficients in Packed Columns: Measurement by Arrested-Flow Gas Chromatography," *AIChE J.*, **33**, 1102 (1987).

C. N. Satterfield, "Mass Transfer in Heterogeneous Catalysis," p. 66, M.I.T. Press, Cambridge, MA (1970).

P. Schneider, and J. M. Smith, "Chromatographic Study of Surface Diffusion," *AIChE J.*, **14**, 886 (1968).

C. T. Wang, and J. M. Smith, "Tortuosity Factors for Diffusion in Catalyst Pellets," *AIChE J.*, **29**, 132 (1983).

Manuscript received Nov. 8, 1988, and revision received Jan. 23, 1989.