Intraparticle Diffusion Coefficients in Packed Columns: Measurement by Arrested-Flow Gas Chromatography

Arrested-flow chromatography was used to determine intraparticle diffusivities of large-pore particles packed in columns. Particle and column tortuosity factors were determined for helium tracer in nitrogen carrier gas at 40°C and atmospheric pressure. Semiempirical modifications of Maxwell's, Burger's, Jeffrey's, and Rayleigh's relations for the composite diffusivity of spherical particles in a stationary medium are proposed for the effective composite diffusion coefficient for a packed bed of porous particles. The equations, modified to represent accurately the extraparticle void diffusion based on measurements for beds of nonporous particles, are used to evaluate intraparticle diffusivities from experimental data obtained by arrested-flow chromatography.

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Introduction

Much effort has been directed toward the theory and measurement of intraparticle diffusion coefficients and the effective diffusivities of packed beds of porous particles (Dullien, 1979). A related problem is to describe mathematically the conduction, e.g., of heat or electricity, through a porous medium composed of discrete particles (Crank, 1975).

One method to measure intraparticle diffusion coefficients is flow chromatography, in which a pulse of tracer is convected through a column packed with porous particles (Furusawa et al., 1976). Moments of the tracer concentration at the column exit are related to the transport parameters of the process, including axial dispersion, fluid-to-particle mass transfer, and intraparticle diffusion. The moment equations suggest doing repeated experiments for particles of different radii and accounting for the dispersion and film mass transfer processes (Schneider and Smith, 1968). For particles with large pores, intraparticle convection (pressure-driven flow in the pores) may require special treatment (Rodriques et al., 1982). These difficulties are circumvented in arrested-flow chromatography, which requires for the given geometry a relationship between the effective diffusivity of the porous medium and the continuous phase diffusivity.

Arrested-flow chromatography was first described by Knox and McLaren (1964), who measured diffusion coefficients for gas pairs in open columns and in packed columns. Maynard and Grushka (1975), in their review of gas chromatographic measurement of diffusion coefficients, discussed arrested-flow chromatography, and Choudhary (1974) commented on the higher precision of the arrested-flow method. McCoy and Moffat (1986) revived the method recently to measure gas-pair diffusivities in open tubes.

In arrested-flow chromatography the flow of a band of solute gas in a carrier gas is stopped when the band reaches the midregion of the column. The band spreads by stationary (nonconvective) diffusion during the period of arrested flow, and is then eluted by resuming the flow. In the absence of adsorption or chemical reaction the diffusive and dispersive processes are linear, and band-spreading effects are superimposed. Subtraction of variances for eluted bands, as in the determination of the slope of variances vs. delay time, will cancel convective dispersion and entrance and exit effects. From the slope of this line the effective diffusion coefficient for the column can be calculated (Knox and McLaren, 1964; McCoy and Moffat, 1986). The elimination of entrance and exit effects, and of convective dispersion and mass transfer, is an attractive feature of arrested-flow chromatographic measurement of packed-bed diffusivities.

An objective of this work is to evaluate the method of arrested-flow chromatography for determination of effective diffusivities for packed columns of porous particles. Another objective, to determine the intraparticle diffusivity from the effective column diffusivity, requires having a relationship for the combined effects of intraparticle and extraparticle (column void) diffusion. We discuss the validity of several such equations, and propose a semiempirical modification to correct for inaccuracies in the equations. The shortcomings of the equations are due to the common assumption in their derivations that particles are widely separated, so that the resulting expressions are power-series expansions in the particle number density. For densely packed beds of nonporous particles the equations do not accurately describe diffusion in the extraparticle voids. Our proposal is that data for diffusion in beds of nonporous particles be used to correct the approximate equations so as to describe more accurately the diffusion in the extraparticle voids. This procedure allows the modified equations to yield reasonable values of intraparticle diffusion from experimental data for diffusion in a bed of porous particles.

An empirical procedure is described in this paper to correct the theoretical equations of Maxwell, Burger, Jeffrey, and Rayleigh by replacing their predictions for dense beds of nonporous particles with the experimentally measured extraparticle diffusion coefficient, expressed in terms of the external tortuosity factor. With external diffusion accurately quantified, we are able to calculate values of intraparticle diffusivity from the modified equations, and thus evaluate the internal tortuosity. The four equations provide reasonably consistent values of internal tortuosity for several kinds of particles.

The present study is restricted to large-pore particles with no adsorption. A limitation of the method of arrested-flow chromatography for measuring diffusion coefficients in porous particles is that the pore diffusion must be significant in magnitude compared to diffusion in the external voids. Thus, the method cannot totally replace flow chromatography or single-pellet methods, which are more suitable when the particle porosity or pores are small. In this investigation we determined diffusion coefficients for relatively large-porosity particles, for which intraparticle diffusion was a substantial contribution. Such particles are of recent interest for such processes as hydrodesulfurization where metal deposition can cause closure of small pores.

Theory

The differential mass balance equation expressed in terms of an effective diffusivity D_e, for a packed bed of porous particles is

$$\epsilon \partial c/\partial t = D_e \partial^2 c/\partial z^2 \tag{1}$$

where, in terms of the void fraction α and the particle porosity β the total porosity is

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

The effective diffusivity D_e accounts for combined diffusion through the extraparticle voids and the particle pores. The initial condition is

$$c(t = 0, z) = c_o(z) \tag{3}$$

and the boundary conditions are

$$c(t, z = \pm\infty) = 0 \tag{4}$$

As explained by McCoy and Moffat (1986), and by Knox and McLaren (1964), the spatial variance s of a pulse at the column exit is the superposition of the variance, s_o, due to the flow and reflow periods, and that due to diffusion during the stopped-flow period of duration t_B,

$$s = s_o + 2D_e t_B/\epsilon \tag{5}$$

To convert from the temporal variance, measured at the column exit, to the spatial variance, we multiply by the square of the pulse velocity, which is given by

$$v_p = v_o/\epsilon \tag{6}$$

in terms of the superficial velocity v_o. The pulse velocity is defined in terms of the total porosity ϵ, since v_p depends on the total volume capacity of the column.

According to Eq. 5, a plot of spatial variance s vs. stopped time t_B yields a slope equal to $2D_e/\epsilon$. This relation for the slope is readily solved to obtain D_e, given the value (usually experimentally determined) of ϵ.

The time scale for radial gas diffusion inside a particle (e.g., $R^2/D_i \sim (10^{-1}\text{cm})^2/10^{-1}\text{cm}^2/\text{s} = 10^{-1}$ s) is, during flow chromatography, of the same order of magnitude as the time for flow of a pulse past a particle (e.g., $R/v \sim 10^{-1}\text{cm}/10^0\text{cm/s} = 10^{-1}$ s). Radial intraparticle diffusion is, therefore, a significant contribution to band-broadening in flow chromatography (Schneider and Smith, 1968). For arrested-flow gas chromatography, in contrast, broadening of a pulse requires minutes, and the relaxation of radial diffusion transients within the particles is relatively much faster than the stationary pulse broadening. We consider, therefore, steady state models of D_e for analyzing arrested-flow chromatography data for diffusion through two-phase porous media composed of spheres.

There is a vast literature on the steady state theory of conduction through heterogeneous materials (Crank, 1975). For interpretation of our experimental data, we focus on theories leading to closed-form equations, rather than theories that require numerical solutions to the partial differential equations. The principal theoretical relations between the intraparticle diffusion coefficient D_i and the diffusion coefficient D_m of the gas are next presented.

Maxwell (1873) derived an expression applicable for the composite diffusivity of a porous material composed of spherical particles randomly distributed in a continuous medium and in low number densities,

$$D_e/D_m = 1 + 3\gamma(1 - \alpha)/[1 - \gamma(1 - \alpha)] \tag{7}$$

in terms of

$$\gamma = (D_i - D_m)/(D_i + 2D_m) \tag{8}$$

Equation 7, based on particles widely separated, is only valid to first order in the particle volume fraction, $1 - \alpha$ (Jeffrey, 1973; Acrivos and Chang, 1986).

Burger (1919), using ideas similar to those of Maxwell, attempted to account for particle shape with the equation,

$$D_e/D_m = \eta + (1 - \eta)D_i/D_m \tag{9}$$

where

$$\eta = \alpha/(\alpha + k(1 - \alpha)) \tag{10}$$

and $k = 1.5$ for spherical particles. Suzuki and Smith (1972) proposed Burger's equation as the low-velocity limit for axial dispersion in packed columns.

Jeffrey (1973), extending Maxwell's treatment, included corrections for number density by accounting for conduction between two particles. Acrivos and Chang (1986), applying an averaging procedure, derived the same expression as Jeffrey,

$$D_e/D_m = 1 + 3\gamma(1-\alpha) + 3\gamma^2(1-\alpha)^2(1+2\gamma\delta) \quad (11)$$

where the nearly constant parameter δ is given by Jeffrey as 0.22, 0.21, 0.25 for $D_i/D_m = 0$, 1, and ∞, respectively. Equation 11 reduces to Maxwell's Eq. 7 when terms of order $(1-\alpha)^2$ are ignored in both equations.

Rayleigh (1892), analyzing the case when spherical particles are arranged in a cubic array, derived an equation that is also an expansion in the particle volume fraction, $1-\alpha$,

$$D_e/D_m = 1 + \frac{3\gamma(1-\alpha)}{1-\gamma(1-\alpha) + \dfrac{\gamma d(1-D_i/D_m)(1-\alpha)^{10/3}}{4+3D_i/D_M}} \quad (12)$$

The value of d was computed by Runge (1925) to be 1.57.

External and internal tortuosity factors are defined (Cerro and Smith, 1970; Satterfield, 1970) in terms of the extraparticle void diffusivity D_v, and the intraparticle diffusivity D_i, as

$$\tau_{ext} = \alpha D_m/D_v \quad (13)$$

and

$$\tau_{int} = \beta \bar{D}/D_i \quad (14)$$

If the particle pore diameter a is distributed such that

$$\beta = \int_0^\infty f(a)\,da \quad (15)$$

the diffusion coefficient $\bar{D}$ for the internal tortuosity factor τ_{int} in Eq. 14 is represented (Wang and Smith, 1983; Dullien, 1979) by

$$\bar{D} = \int_0^\infty D(a) f(a)\,da \Bigg/ \int_0^\infty f(a)\,da \quad (16)$$

where

$$1/D(a) = 1/D_m + 1/D_K(a) \quad (17)$$

in terms of $D_K(a)$, the Knudsen diffusivity. If molecular diffusion is the predominant mechanism, then Eq. 17 reduces to $D(a) = D_m$. Values of $\bar{D}$ for the particles used in experiments are listed in Table 5.

Since the foregoing models for effective diffusivities are restricted by the dilute particle limit, they not only are approximate for densely packed porous particles, but also for nonporous particles, for which $D_i = 0$. Since the models apply to particles spaced far apart, they overestimate the contribution of diffusion in the extraparticle voids. Maxwell's Eq. 7, for example, predicts a value for the external tortuosity of 1.3 when $\alpha = 0.4$, whereas for packed beds, according to our experiments, τ_{ext} falls in the neighborhood of 1.5. For a bed of nonporous particles, Maxwell's Eq. 7, and Burger's Eq. 9 as well, reduce to

$$D_e = D_v = 2\alpha D_m/(3-\alpha) \quad (18)$$

or with Eq. 12,

$$\tau_{ext} = (3-\alpha)/2 \quad (19)$$

As it is possible to measure accurately the effective diffusivity for a column of nonporous particles, for example with arrested-flow chromatography, an empirical method to correct dilute particle equations is suggested: replace the predicted value of τ_{ext} with the experimentally measured value. If we assume that D_v for a bed of nonporous particles equals that of porous ones, we can replace $(3-\alpha)/2$ from Eq. 19 with τ_{ext}. Equations 7 and 9 in terms of τ_{ext} lead to the semiempirical equation:

$$D_e = D_m\alpha/\tau_{ext} + D_i(1-\alpha/\tau_{ext})/f \quad (20)$$

where the factor f is a different function for each model. For Maxwell's equation,

$$f = 1 + (D_i/D_m - 1)\alpha/3 \quad (21)$$

and for Burger's model,

$$f = 1 \quad (22)$$

For Jeffrey's and Rayleigh's models, through a similar procedure, we can obtain Eq. 20 with the following equations for f. For Jeffrey's model,

$$f = \frac{1.5 - 0.75(1-\delta_o)(1-\alpha)}{1.5(1-\gamma) - 0.75(1-\delta_o)(1-\alpha)}\,\frac{1}{F} \quad (23)$$

$$F = \left[1 - \frac{\gamma^2(1+2\delta\gamma)}{0.25(1-\delta_o)}\right] \Bigg/ (D_i/D_M)$$

and for Rayleigh's model,

$$f = \frac{1 - \gamma(1-\alpha) + \gamma d\left(\dfrac{1-D_i/D_M}{4+3D_i/D_M}\right)(1-\alpha)^{10/3}}{(1+2\gamma)/(D_i/D_M) - 7/4 \cdot [\gamma d/(4+3D_i/D_M)](1-\alpha)^{10/3}} \quad (24)$$

Equation 20 shows that for the limit $D_i/D_m = 1$, we have $D_i = D_m$ for all the models because all the expressions for f converge to unity as D_i/D_m approaches unity.

The factor f for the case of $\alpha = 0.40$ is plotted against D_i/D_m in Figure 1 for Eqs. 21, 22, 23, and 24. For this parameter ($\alpha = 0.4$) typical of packed columns, the agreement of the modified Maxwell, Jeffrey, and Rayleigh models is good. The agreement is most satisfactory when D_i/D_m is nearly one, i.e., for particles of large porosity. Arrested-flow chromatography is especially recommended for large-porosity particles, since flow chromatography will manifest convective flow within the pores of such particles (Rodrigues et al., 1982). The inadequacies of the modi-

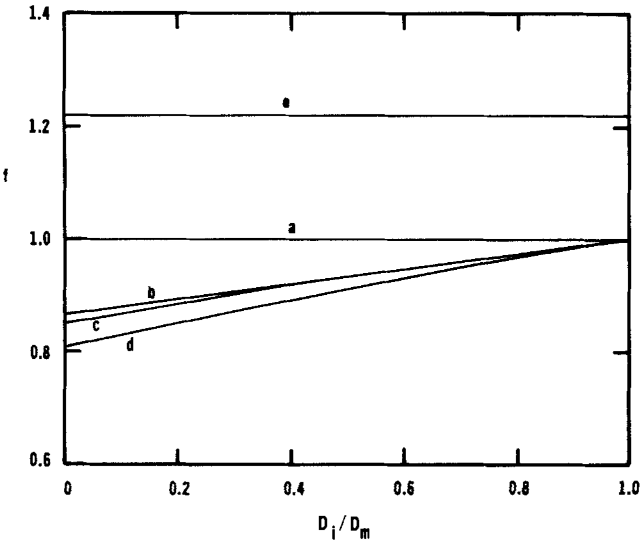

Figure 1. Corrective factor f vs. ratio of effective intraparticle diffusivity to molecular diffusivity D_i/D_m.

Packed bed; $\alpha = 0.4$, $\tau_{ext} = 1.5$
Models: a, modified Burger; b, Maxwell; c, Jeffrey; d, Raleigh; e, parallel diffusion

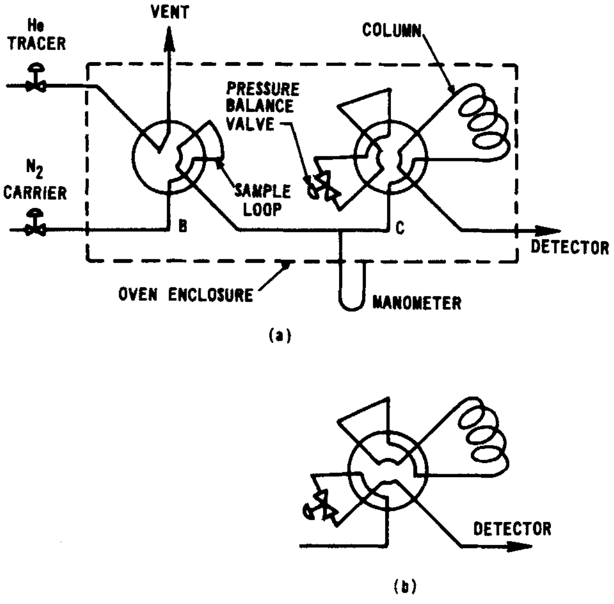

Figure 2. Valve arrangements.

a. Flow modes; B, sample valve; C, eight-part switching valve
b. Switching valve in stopped-flow mode

fied Burger model, shown in Figure 1, stem from its oversimplifications in treating the fundamental transport problem, e.g., the assumption of proportional gradients in voids and particles.

We consider next a parallel diffusion model for which the concentration gradient in particles equals that in the voids,

$$D_e = D_v + (1 - \alpha)D_i \tag{25}$$

With Eq. 13, D_v can be expressed in terms of the experimentally determined value τ_{ext} in the same manner used for the other models. This approximate model, however, does not account for the interactions of concentration profiles at the surface of the porous particles, and is not expected to be as reliable as the modified Maxwell, Jeffrey, or Rayleigh models. Modified as the others, the parallel diffusion model gives

$$f = (1 - \alpha/\tau_{ext})/(1 - \alpha) \tag{26}$$

whose plot, Figure 1, with $\tau_{ext} = 1.5$ is substantially different from those of the modified theoretical models.

It is possible to use Eq. 25 to calculate D_i or to derive an expression for f. Values of f on this new basis do not, however, converge to unity with increasing D_i/D_m, and are judged less acceptable than those based on Eq. 9. It is interesting, though, that f values for this approach differ by less than 20% from those in Figure 1 for the range of D_i/D_m between 0 and 1.

Experiments

The experimental apparatus consisted of a chromatograph (Varian model 1420) with a thermal conductivity detector. The analytical column was replaced with an eight-port valve attached to a column packed with either porous or nonporous particles. The flow through the six-port sample valve and the eight-port column valve is shown in Figure 2 for flow and arrested-flow modes. A 1.53 m (5.02 ft.) long stainless steel tube of 4.83×10^{-3} m (0.190 in.) dia. was formed into a 0.13 m (5 in.) dia. coil and placed in the constant temperature chromatograph oven. In an experiment in which the column was replaced with a very short length of tubing, the dead volume of the apparatus was found to be 3.73×10^{-6} m^3. Tracer gas from a 0.25×10^{-6} m^3 sample loop was injected into the column with the six-port valve. The pressure drop across the column was measured with a

Table 1. Properties of Particles Used in Experiments

Particle	$\rho_s \times 10^{-3}$ k$_g$/m^3	$\rho_p \times 10^{-3}$ k$_g$/m^3	β	$\bar{a} \times 10^{10}$ m	Pore Range $a \times 10^{10}$ m
Quartz chips	2.05	2.05	0	—	—
Glass beads	0.939	0.939	0	—	—
T-126	3.02	1.38	0.541	76.0	$2.9 \times 10 \sim 1.9 \times 10^3$
Varian FB*	2.19	0.765	0.650	6.85×10^3	$1.5 \times 10^3 \sim 2.7 \times 10^4$
Common FB	2.54	1.93	0.240	3.22×10^4	$9.6 \times 10^2 \sim 1.7 \times 10^5$
CSS-1,000LDS	4.15	1.05	0.747	3.64×10^3	$2.9 \times 10^2 \sim 1.0 \times 10^4$
Macropore (>2,900 Å) = 48%		—	—	5.95×10^3	—
Micropore (<2,900 Å) = 52%		—	—	1.40×10^3	—

Properties measured by helium and mercury displacement. Average pore diameter given by: $a = (1/V) \int a\,dV$, in terms of pore volume V.
*Based on assumptions that $\beta = 0.650$ (from total porosity data in Table 4 and $\alpha = 0.4$), and that any interparticle space is larger than the largest pore within particles.

Table 2. Molecular Diffusivities Measured in Empty Tube by Arrested-flow Chromatography

Column No.	Temp. K	$\left(\frac{PD_m}{P_o}\right) \times 10^4$ m^2/s	Error* %	ΔP kPa
E-1	313	0.802	+5.1	0.85
E-2	313	0.802	+5.1	0.85
E-3	343	0.941	+5.0	0.95
E-4	343	0.952	+6.3	1.00

$P_o = 1.013 \times 10^2$ kPa
*Compared to correlation of Fuller et al. (1966)

manometer, and the gas flow rate was determined with a downstream soap-film flowmeter and corrected to the operating temperature (40 or 70°C) and the mean pressure of the column. All arrested flow runs for each column were performed at the same flow rate and at a constant temperature and atmospheric pressure with helium tracer in nitrogen carrier gas. Tables 1–4 provide properties of the systems studied in this work.

The properties of particles used in these experiments are summarized in Table 1. Varian firebrick is a chromatographic support (Varian Aerograph Co.), CSS-1,000LDS (99% Al_2O_3, ⅛ in. [3 mm] dia. spheres) is a commercial demetallization catalyst (Aluminum Company of America), Common FB is construction firebrick, and T-126 is a γ-alumina (Girdler Chemical, Inc.). The particle density, porosity, solid density, and pore size distribution of particles were measured with a 60,000 psi (413.4 MPa) mercury porosimeter and helium pycnometer. Pore size distributions are shown in Figure 3. Properties of nonporous particles, sieved to be of the same size as porous particles, are shown in Table 3.

The values of total porosity, ϵ, of the packed beds, displayed in Table 4, were determined in two ways: by using Eq. 2 with known values of α and β, as in Table 4, and by measuring the first moment, μ, for a chromatographic flow experiment. μ is related to ϵ by

$$\mu = L\epsilon/v_o \tag{27}$$

Table 3. External Tortuosity Factors for Columns Packed with Nonporous Particles, $T = 313$ K

Column No.	Packing Material	α	Mesh Size	Sieve Opening $\times 10^3$ m	τ_{ext}	ΔP kPa
I	Quartz chips	0.410	60/65	0.229	1.50	6.8
II	Quartz chips	0.406	60/65	0.229	1.45	6.8
III	Quartz chips	0.408	60/65	0.229	1.46	2.5
IV	Glass beads	0.406	28/35	0.505	1.47	1.7
V	Glass beads	0.421	28/35	0.505	1.56	1.7
VI	Glass beads	0.421	28/35	0.505	1.55	0.68
Average		—	—	—	1.50 ± 0.11	—

in terms of the column length, L. Mechanical vibration applied during the column packing process ensured uniform packing.

Results and Discussion

The variance of each response pulse was determined from the width of the peak at its half-height, which is 2.3548 times the square root of the variance (McCoy and Moffat, 1986). This method, valid for Gaussian curves, avoids difficulties of tailing and baseline drift that affect determination of variance by numerical integration.

According to Eq. 5, a graph of variance vs. stopped time t_B should yield a straight line. Typical cases are shown in Figure 4, including one plot, with noticeably larger slope, for an empty column. Slopes of the lines, from which diffusivities were calculated, were determined by linear regression; correlation coefficients were all greater than 0.999.

The molecular diffusion coefficients for He in N_2 at two different temperatures were determined by arrested-flow chromatography in the open column. For an open tube, D_e in Eq. 5 is equal to D_m. The results are displayed in Table 2. The differences between the measured values and D_m from the correlation equation of Fuller et al. (1966) were less than 6%. A similar small uncertainty was reported by McCoy and Moffat (1986) in their study of arrested-flow chromatography in open tubes.

Application of Eq. 5 for variances measured for columns packed with nonporous particles gives D_v. Then τ_{ext} can be cal-

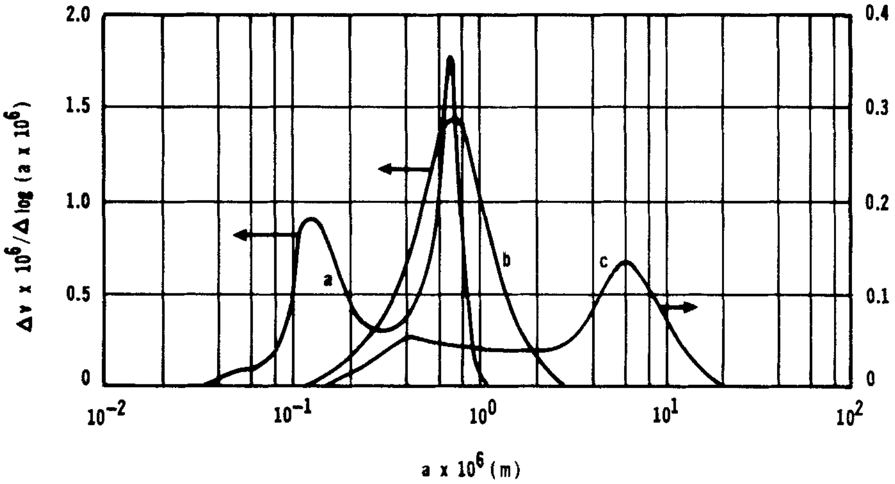

Figure 3. Pore size distribution.
a. CSS-1,000LDS; b. Varian firebrick; c. common firebrick

Table 4. Properties of Columns Packed with Porous Particles

Column No.	Packing Material	Temp. K	ΔP kPa	α	β	ϵ*	Mesh Size	Sieve Opening $\times 10^3$ m	$D_m \times 10^4$** m^2/s	$D_e \times 10^4$ m^2/s	$\frac{\alpha D_m}{D_e}$
VII	Varian FB†	313	7.8	0.400	0.650	(0.796)	80/100	0.161	0.770	0.413	0.746
VIII-1	Varian FB†	313	7.8	0.400	0.650	(0.778)	80/100	0.161	0.771	0.395	0.781
VIII-2	Varian FB†	343	7.8	0.400	0.650	(0.780)	80/100	0.161	0.910	0.463	0.786
IX-1	Common FB	313	3.2	0.453	0.240	0.584 (0.576)	28/35	0.505	0.783	0.264	1.34
IX-2	Common FB	343	3.4	0.453	0.240	0.584 (0.588)	28/35	0.505	0.924	0.311	1.35
X	Common FB	313	3.4	0.456	0.240	0.587 (0.582)	28/35	0.505	0.784	0.275	1.30
XI	Common FB	313	1.7	0.450	0.240	0.582 (0.575)	28/35	0.505	0.793	0.267	1.34
XII	CSS-1000LDS	313	2.5	0.384	0.747	0.844 (0.826)	20/28	0.715	0.788	0.398	0.760
XIII	CSS-1,000LDS	313	2.5	0.389	0.747	0.845 (0.822)	28/35	0.505	0.789	0.418	0.734
XIV	CSS-1,000LDS	313	2.7	0.383	0.747	0.844 (0.825)	28/35	0.505	0.787	0.397	0.759
XV	CSS-1,000LDS	313	2.7	0.390	0.747	0.846 (0.823)	28/35	0.505	0.789	0.416	0.740
XVI-1	T-126	313	6.8	0.378	0.541	0.715	28/35	0.505	0.772	0.201	1.45
XVI-2	T-126	313	3.4	0.378	0.541	0.715	28/35	0.505	0.781	0.201	1.47

*Values in parentheses are from first temporal moment data.
**Corrected to barometric pressure and ΔP.
†Values based on assumptions made in footnote of Table 1.

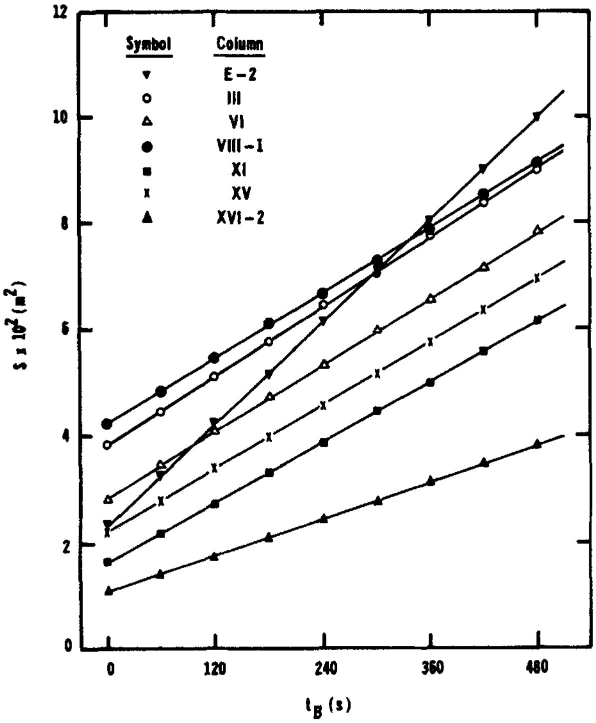

Figure 4. Graphs of variance vs. stopped time for columns packed with porous or nonporous particles.
Column E-2 is empty

culated from D_m and Eq. 13. The experimental results are displayed in Table 3. The average value of τ_{ext} for the beds of quartz chips and glass beads was 1.50 ± 0.11, comparable to the frequently used approximation $\sqrt{2}$ (Cerro and Smith, 1970). The value $\tau_{ext} = 1.5$ was used in the calculations of τ_{int} in Table 5.

For tubes packed with porous particles, the variance data and Eq. 5 gave values of the effective composite diffusivity D_e. The experimental results are shown in Table 4. With these values for D_e, and appropriate expressions of f, Eq. 20 yields the intraparticle diffusivity D_i. The tortuosity factors τ_{int} for the porous particles are then obtained from Eq. 14. The results are given in Table 5. Uncorrected equations of Maxwell, Burger, Jeffrey, and Rayleigh, because they overestimate the contribution of diffusion in the extraparticle voids, were found actually to predict negative values for the intraparticle diffusion coefficients of the Common FB. These relations are therefore not accurate for estimating intraparticle diffusion coefficients from data of the kind obtained from arrested-flow chromatography. The empirically modified equations, however, prove acceptable. For all the models cited, Eq. 20 provides reasonable values for intraparticle tortuosities when compared with those reported by Satterfield (1970), which are in the range 2 to 6. The results are also in reasonable agreement with the relations of the spherical-cell pore model (Weisz and Schwartz, 1962),

$$\tau_{int} = \sqrt{3}/1.5\beta \tag{28}$$

and of the random-pore model (Wakao and Smith, 1962),

$$\tau_{int} = 1/\beta \tag{29}$$

Table 5. Internal Tortuosity Factors for Porous Particles

Column No.	Packing Material	$\bar{D} \times 10^4$ m^2/s	$\tau_{int} = \beta \bar{D}/D_i$				
			Parallel Diffusion Eq. 26	Modified Maxwell Eq. 21	Modified Burger Eq. 22	Modified Rayleigh Eq. 24	Modified Jeffrey Eq. 23
VII	Varian FB	0.620	1.16	1.56	1.42	1.62	1.56
VIII-1	Varian FB	0.620	1.28	1.72	1.56	1.78	1.73
VIII-2	Varian FB	0.715	1.27	1.71	1.55	1.77	1.71
IX-1	Common FB	0.744	3.55	5.29	4.53	5.55	5.74
IX-2	Common FB	0.873	3.59	5.35	4.58	5.61	5.81
X	Common FB	0.746	2.66	3.97	3.40	4.15	4.22
XI	Common FB	0.753	3.42	5.07	4.35	5.32	5.49
XII	CSS-1000LDS	0.554	1.30	1.72	1.57	1.79	1.72
XIII	CSS-1000LDS	0.555	1.19	1.58	1.44	1.63	1.58
XIV	CSS-1000LDS	0.554	1.30	1.72	1.57	1.79	1.73
XV	CSS-1000LDS	0.555	1.20	1.59	1.45	1.65	1.60

Table 6. Tortuosity Factors*

Packing Material	Tracer/ Carrier	ϵ	$D_m \times 10^4$ m^2/s	τ_{ext}	$\tau_{int} = \beta D_m/D_i$				
					Parallel Diffusion Eq. 26	Modified Maxwell Eq. 21	Modified Burger Eq. 22	Modified Rayleigh Eq. (24)	Modified Jeffrey Eq. 23
Firebrick	C_2H_4/N_2	0.80	0.165	1.65	3.17	4.52	4.01	4.76	4.60
Celite	C_2H_4/N_2	0.88	0.165	1.65	1.18	1.60	1.49	1.63	1.60

*From data of Knox and McLaren (1964); $T = 291$ K; $P = 1.00 \times 10^2$ kPa (750 mm Hg); $\alpha = 0.4$ (assumed value).
Values of τ_{ext} based on reported data for a bed of glass beads.

The four different models yield values of intraparticle diffusion coefficients that are nearly the same in magnitude. The modified equation based on the parallel diffusion model yields values of τ_{int} that are no more than 20% lower than other values in Table 5.

Table 6 shows the analysis of the Knox and McLaren (1964) data by Eq. 20. In our notation D_e/ϵ is equivalent to γD_g in Knox and McLaren. The value of τ_{ext} is based on their data for a bed of glass beads with $\alpha = 0.38$. The modified equations yield reasonable values of τ_{int} that are nearly the same for the two kinds of particles.

For particles with very small pores, such as particles of T-126 alumina, the contribution of intraparticle diffusion is so small that determining D_i accurately is not possible. As shown in Table 4, the ratio $\alpha D_m/D_e$ in that case is not significantly different from the average of τ_{ext} in Table 3, which implies that diffusion in the voids dominates the band-broadening process. The arrested-flow method, therefore, is particularly useful for large-pore and large-porosity particles, for which other methods might be less satisfactory because of intraparticle flow.

The final issue to be addressed in this study is the prediction of composite effective diffusion coefficients. As the contribution of intraparticle diffusion is considerably smaller than overall diffusion through the packed bed, this prediction is not as severe a test of the theories as calculating the intraparticle diffusion coefficient from measurements of the overall effective diffusivity. Thus, given D_m and D_i for the conditions of this work, all the unmodified equations, as well as all the modified ones, yield fairly good estimates for composite diffusion for packed beds of porous particles.

Notation

a = pore diameter, m
$\bar{a}$ = volume average pore diameter, m
$c(z, t)$ = effective concentration in heterogeneous media, mol/m^3
$c_o(z)$ = initial concentration profile, Eq. 3, mol/m^3
$D(a)$ = composite diffusivity in pore space, Eq. 17, m^2/s
D_e = effective composite diffusivity in heterogeneous media, m^2/s
D_i = effective intraparticle diffusivity, m^2/s
$D_K(a)$ = Knudsen diffusivity, m^2/s
D_m = molecular diffusivity, m^2/s
D_v = effective interparticle diffusivity, m^2/s
$\bar{D}$ = average of $D(a)$, Eq. 16, m^2/s
d = constant, Eq. 12
f = correction factor, Eqs. 21–24 and 26
$f(a)$ = pore size distribution function, Eq. 15
k = shape factor, Eq. 10
L = length of bed, m
P = column operating pressure, kPa
P_o = 1.013×10^2 kPa
ΔP = pressure drop, kPa
R = particle radius, m
s = second central spatial moment, m^2
s_o = second central spatial moment of flow period, m^2
T = absolute temperature, K
t = time variable, s
t_B = time period of stopped flow, s
V = pore volume, m^3
v = interstitial velocity of fluid, m/s
v_o = superficial velocity of fluid, m/s
v_p = pulse velocity, Eq. 6, m/s
z = distance variable, m

Greek letters

α = void fraction in bed
β = porosity of particle

γ = diffusivity ratio function, Eq. 8
δ = function of D_i/D_m, Eq. 11
δ_o = δ at $D_i/D_m = 0$
ϵ = total porosity of bed, Eq. 2
η = function of α and k, Eq. 10
μ = first absolute temporal moment, s
ρ_p = particle density, kg/m^3
ρ_s = solid density, kg/m^3
τ_{ext} = external tortuosity factor, Eq. 13
τ_{int} = internal tortuosity factor, Eq. 14

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