Dynamic Analysis of Viscous Flow and Diffusion in Porous Solids

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In case of nonisobaric diffusion, the total flux of a gas through a porous solid is expressed in terms of the summation of diffusion and viscous flow terms. The diffusion flux is generally considered to be inversely proportional to the series combination of molecular and Knudsen resistances. On the other hand, viscous flow is expressed by the Darcy equation.

In some applications with porous catalysts, diffusion with a pressure gradient is of interest. A detailed review of diffusion and flow of gases in porous solids was reported by Youngquist (1970). Evans et al. (1961), following a dusty gas model, have shown the flux relationships. Scott and Dullien (1962) used the simple kinetic theory of gases to derive the flow equation in a capillary. Wakao et al. (1965) and Otani et al. (1965) derived the governing equations of diffusion and flow in fine capillaries in the presence of significant pressure gradients.

The theory of mass transport in porous materials under combined gradients of composition and pressure was developed by Gunn and King (1969). Mason et al. (1967) and Gunn and King (1969) considered the viscous flow term to be independent of the diffusive flux and wrote down the total flux as the summation of diffusive and Darcy fluxes. This assumption, which is implicit in the use of the classical convective diffusion equation, was later verified by Allawi and Gunn (1987). Asaeda et al. (1981) and Nakano et al. (1986) also reported some diffusion rate data at nonisobaric conditions.

Single-Pellet moment technique is one of the fastest and dependable methods for the measurement of intraparticle rate parameters. The method was introduced by Doğu and Smith (1975, 1976) and was used to determine effective diffusion coefficients, adsorption equilibrium, and rate parameters in porous catalysts. Hashimoto et al. (1976), Doğu and Ercan (1983), and Doğu et al. (1987) showed that this method can also be used to determine the macro- and micropore diffusion coefficients as well as adsorption parameters. Moffat (1978), Baiker et al. (1982), and Wang and Smith (1983) used this technique for evaluation of effective diffusivities and tortuosities. Doğu (1984) and Doğu et al. (1986) illustrated the use of single-pellet moment technique for the measurement of surface reaction rate constants for catalytic and noncatalytic gas-solid reactions. In this work, a method was introduced for the study of relative significance of diffusion and viscous flow in porous catalysts using the single-pellet moment approach. The method allows the measurement of Darcy coefficient together with effective diffusion coefficient in a porous solid.

Method and Theory

In the single-pellet moment method used in this study, dynamic version of the Wicke-Kallenbach type of a diffusion cell was used for the evaluation of relative significance of diffusion and viscous flow terms. The schematic diagram of the diffusion cell was shown in Figure 1. A pulse of an inert tracer was injected into the carrier gas flowing past the upper face of the single pellet, and the response was detected at the outlet of the lower stream carrier gas by a TC detector. These experiments were repeated at different pressure differences between the upper and lower faces of the pellet (Figure 1). The experimental values of the zeroth and first absolute moments were determined from the observed response peaks using the equations,

$$m_n = \int_0^\infty C(t)t^n\,dt; \quad n = 0, 1, \ldots \tag{1}$$

$$\mu_1 = m_1/m_0 \tag{2}$$

The effective flux of the inert tracer in the porous pellet was expressed as

$$N_{A_e} = -D_e \frac{\partial C_A}{\partial z} - \frac{C_e}{\mu} C_A \frac{dP}{dz} \tag{3}$$

where D_e is the effective diffusivity and C_e is the effective Darcy coefficient. Both D_e and C_e depend upon the pore structure of the solid. In dilute systems (small amount of tracer injected), both of these parameters can be taken as constant. Also considering a constant pressure gradient throughout the pellet, the differential mass balance for the transport of the diffusing component A (tracer) was written as

$$\epsilon_p \frac{\partial C_A}{\partial t} = D_e \frac{\partial^2 C_A}{\partial z^2} - \gamma \frac{\partial C_A}{\partial z} \tag{4}$$

where

$$\gamma = \frac{C_e}{\mu}\left(-\frac{dP}{dz}\right). \tag{5}$$

In general, the effective diffusion coefficient was expressed as $D_e = D_T(\epsilon_p/\tau)$, where D_T was calculated from Eq. 6.

$$D_T = 1/[(1 - \alpha y_A)/D_{AB} + 1/D_{K_A}] \tag{6}$$

In the prediction of D_T, either average pore radius can be used or D_e can be estimated by the integration of $D_T(a)$ throughout the pore-size distribution.

$$D_e = \frac{1}{\tau}\int_0^\infty D_T(a) f(a)\, da \tag{7}$$

Wang and Smith (1983) showed that prediction of D_e from Eq. 7 provides better results. In this work, D_T values were estimated at the mean pressure within the pellet. As discussed later in this paper, the variation of D_T with pressure is not large in the pressure range used in this work. Also, by carrying out pulse response experiments with different sample sizes of inert tracer He (ranging from 0.1 cm^3 to 10.0 cm^3), it was shown that the concentration dependency of D_e is negligible for the experimental conditions used in this work (Pekediz, 1988).

The initial and boundary conditions for the system (Figure 1) are:

$$t = 0; \quad 0 < z < L; \quad C_A = 0 \tag{8}$$

$$z = 0; \quad C_A = M\,\delta(t) \tag{9}$$

$$z = L; \qquad -A\left[D_e \frac{\partial C_A}{\partial z} - \gamma C_A\right]_{z=L} = FC_A\big|_{z=L} \tag{10}$$

Justification of similar boundary conditions corresponding to isobaric diffusion was given by Doğu and Smith (1975, 1976).

The zeroth and first absolute moment expressions were determined from the solution of Eq. 4 and Eqs. 8–10 in the laplace domain (Pekediz, 1988).

$$m_0 = \lim_{s\to 0} \bar{C}_A\big|_{z=L} = \frac{Me^D}{\cosh D + \left(\frac{FL}{AD_e} - D\right)\frac{\sinh D}{D}} \tag{11}$$

and

$$\mu_1 = \left(\frac{\epsilon_p L^2}{2D_e}\right)\frac{\left[\frac{\sinh D}{D} + \left(\frac{FL}{AD_e} - D\right)\frac{(D\cosh D - \sinh D)}{D^3}\right]}{\left[\cosh D + \left(\frac{FL}{AD_e} - D\right)\frac{\sinh D}{D}\right]} \tag{12}$$

In these equations, a new dimensionless group D is defined as

$$D = \frac{\gamma L}{2D_e} = \frac{C_e(-\Delta P)}{2\mu\, D_e} \tag{13}$$

and its value is proportional to the ratio of viscous flow contribution to effective diffusion in the porous pellet. The limit of Eqs. 11 and 12 as $D \to 0$ gave the corresponding equations applicable for isobaric diffusion reported by Doğu and Smith (1975).

$$\lim_{D\to 0} m_0 = m_{00} = M \Bigg/ \left(\frac{FL}{AD_{e_0}} + 1\right) \tag{14}$$

$$\lim_{D\to 0} \mu_1 = \mu_{10} = \left(\frac{\epsilon_p L^2}{6D_{e_0}}\right)\frac{\left[3\frac{A}{L}D_{e_0} + F\right]}{\left[\frac{A}{L}D_{e_0} + F\right]} \tag{15}$$

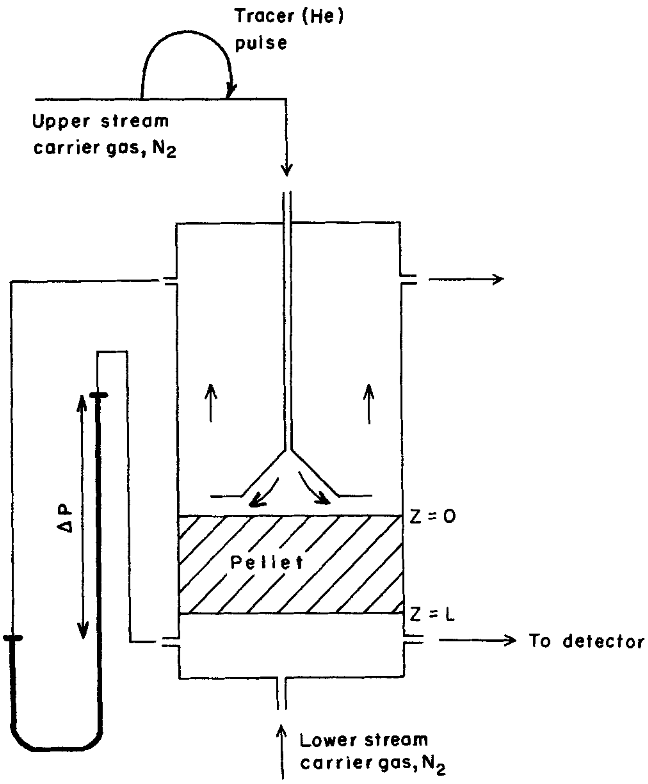

Figure 1. Single-pellet system.

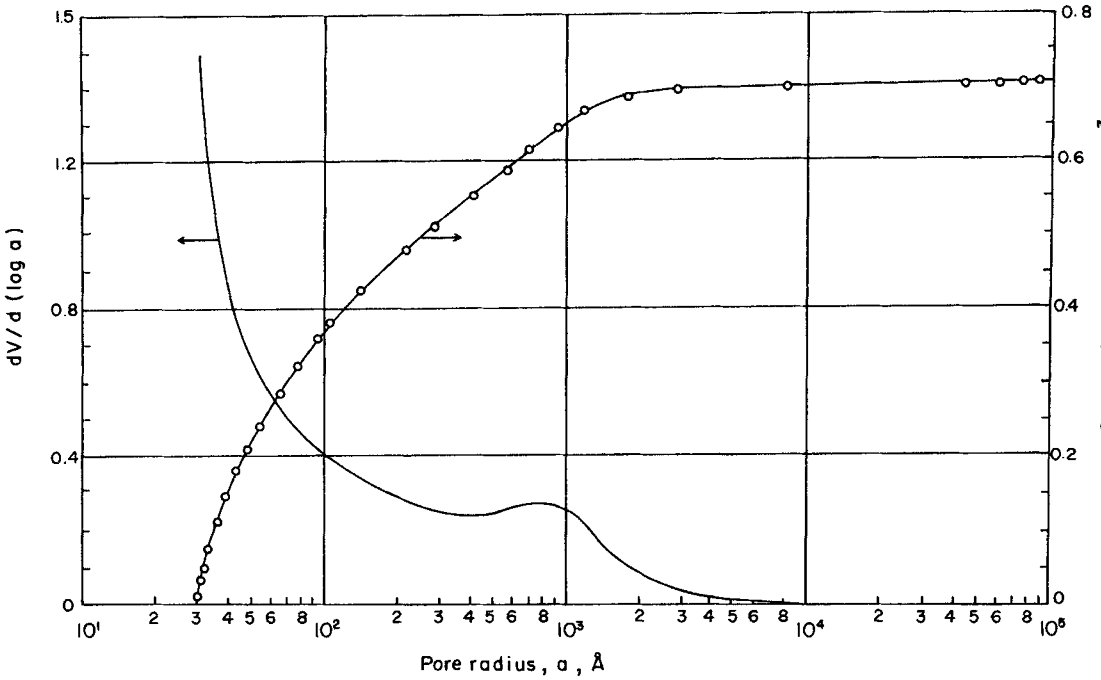

Figure 2. Pore-size distribution of the Al_2O_3 pellet used.

The ratio of m_{00} to m_0 was then expressed as,

$$\frac{m_{00}}{m_0} = \frac{\cosh D + \left(\frac{FL}{AD_e} - D\right)\frac{\sinh D}{D}}{\left(\frac{FL}{AD_{e_0}} + 1\right)e^D} \tag{16}$$

For high values of the lower stream carrier gas flow rate (F), m_{00}/m_0 and μ_1 expressions reach a constant limit.

$$\lim_{F\to\infty} \frac{m_{00}}{m_0} = \left(\frac{m_{00}}{m_0}\right)_\infty = \left(\frac{D_{e_0}}{D_e}\right)\frac{\sinh D}{De^D} \tag{17}$$

$$\lim_{F\to\infty} \mu_1 = (\mu_1)_\infty = \left(\frac{\epsilon_p L^2}{2D_e}\right)\left(\frac{D\cosh D - \sinh D}{D^2 \sinh D}\right) \tag{18}$$

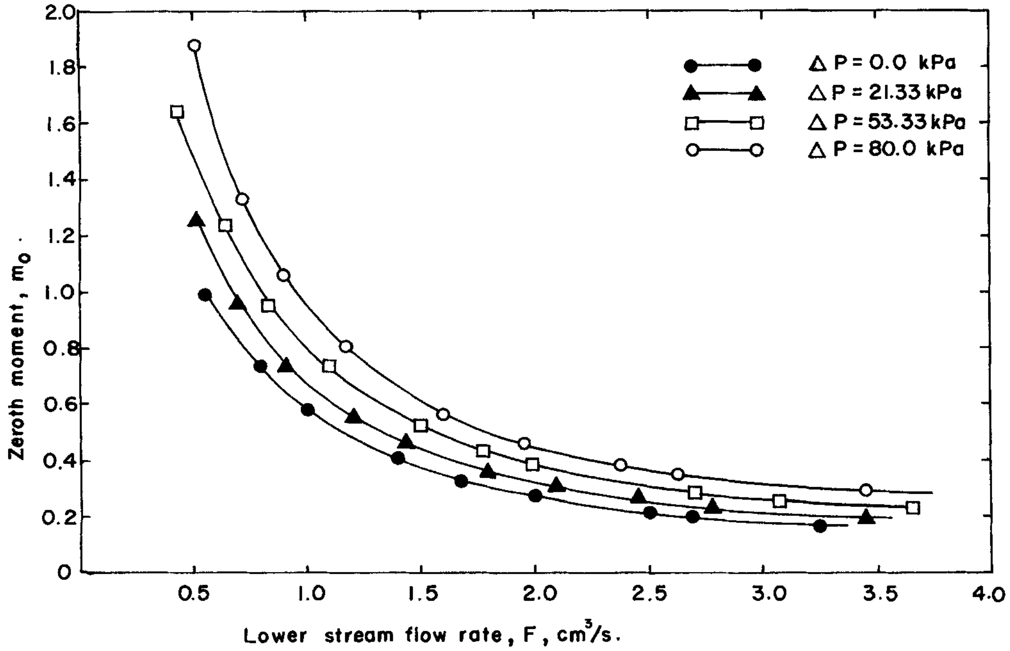

Figure 3. Relative values of zeroth moments of He tracer at different pressure drops across the pellet.
$T = 45°C$, sample size = 1 cm³

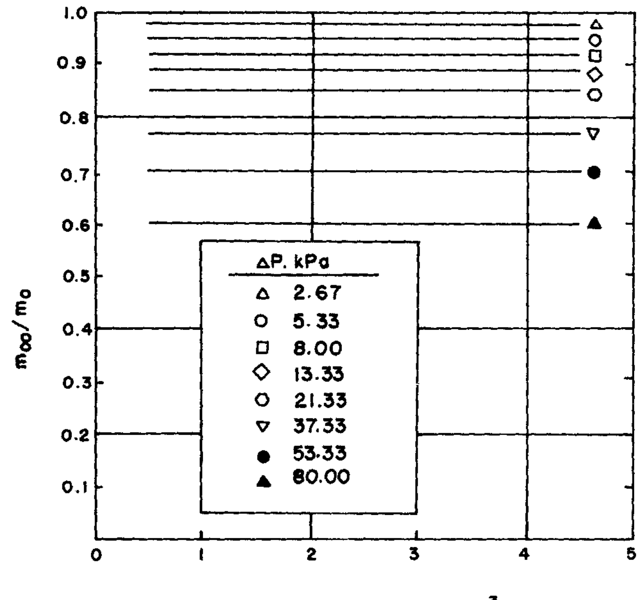

Figure 4. Variation of m_{00}/m_0 with respect to F for different pressure drop values across the pellet.
$\epsilon_p = 0.68$, $L = 1.3$ cm, $T = 45°C$

Experimental Work

The experimental set-up used is similar to the one used by Doğu and Smith (1975), and Doğu et al. (1986). Nitrogen was used as the carrier gas flowing past both upper and lower faces of the pellet. Helium was used as the tracer. The pellets were made from α–alumina powder obtained from American Cyanamid Co. The pore-size distribution of the pellets were measured by a micrometrics pore–sizer. The total porosity of the pellets used was $\epsilon_p = 0.68$, while the porosity corresponding to pores having radia greater than 30 Å was 0.57. The pore-size distribution of the pellet is given in Figure 2.

The response curves were measured by a (Varian 6000) gas chromatograph. Pulse response experiments were repeated at nine different pressure differences ranging from zero to 80 kPa (60 cm Hg) between the upper and lower faces of the pellet. The pressure at the lower face of the pellet was kept at atmospheric pressure in all experiments. The change of zeroth-moment values with the lower stream flow rate were shown in Figure 3 at some typical pressure differences between the faces of the pellet ($L = 1.3$ cm and $A = 1.54$ cm^2). The experimental values reported in this figure were obtained at 45°C, and the zeroth moment of the response curve corresponding to $\Delta P = 0$ and $F = 0.5$ cm^3/s was taken arbitrarily as unity. All the other zeroth-moment values are relative values with respect to that. The ratio of zeroth moment obtained at $\Delta P = 0$ to zeroth-moment values obtained at different pressure drops (m_{00}/m_0) were found to be essentially independent of flow rate (Figure 4). As expected, as ΔP increases the amount of tracer passing through the pellet and consequently its zeroth-moment value increases. The general form of m_{00}/m_0 (Eq. 16) and the high flow rate limit of this expression, which is independent of F (Eq. 17), contain the parameter D and the effective diffusivities at atmospheric pressure (D_{e_0}) and at the higher mean pressure (D_e) (for different ΔP values). In order to evaluate D from Eq. 17 using the data reported in Figure 4, D_{e_0}/D_e values should be known.

The effective diffusivity, D_{e_0}, was determined using a similar method suggested by Doğu et al. (1986). The difference of first absolute moment values obtained from pulse response experiments carried out at atmospheric pressure (isobaric runs) in the diffusion cell with two pellets of identical physical properties but of different lengths ($L_1 = 1.3$ cm and $L_2 = 0.3$ cm) were analyzed to determine the value of D_{e_0} (Pekediz, 1988) using the following equation.

$$\lim_{\substack{F\to\infty \\ \delta\to 0}} \Delta\mu_1 = \frac{\epsilon_p(L_1^2 - L_2^2)}{6D_{e_0}} \tag{19}$$

The dead volume contributions to the first moments were eliminated by taking the differences of first absolute moment results obtained with these two pellets. For the pellet used, the effective diffusivity of He in N_2 was found to be 0.0234 cm^2/s at 45°C.

The isobaric runs were repeated at different temperatures (Pekediz 1988), and the tortuosity factor of the pellet was determined from Eq. 9 using the pore-size distribution data. Results were reported in Table 1. The tortuosity factor values were found to be very close to the value of 4, which is recommended by Satterfield and Cadle (1968).

The effective diffusivity values corresponding to the mean pressures in the pellet in the nonisobaric runs were calculated from Eq. 7 using the tortuosity factor of 3.95. Then, D values were determined by analyzing the data reported in Figure 4 using Eq. 17 and the results were tabulated in Table 2.

As shown in Table 2, the value of the dimensionless parameter D changed from 0.05 to 0.77 as ΔP was increased from 2.67 kPa to 80 kPa. This indicated that, at $\Delta P = 80$ kPa, the relative significance of viscous flow term was close to the diffusion flux

Table 1. Tortuosity Factor Values Obtained at Different Temperatures

T, °C	45	60	70	80	95	105
τ	3.95	3.72	4.08	3.92	4.07	3.87

Table 2. D and D_e Values Measured at Different Pressure Gradients Along the Pellet*

$(-\Delta P)$ (kPa)	2.67	5.33	8.00	13.33	21.33	37.33	53.33	80
D_e(cm^2/s)**	0.0233	0.0231	0.0230	0.0227	0.0224	0.0217	0.0210	0.0201
D	0.05	0.065	0.10	0.15	0.22	0.37	0.51	0.77
D_e(cm^2/s)†	0.024	0.024	0.022	0.023	0.023	0.022	0.020	0.019

*D_e values correspond to mean pressure in the pellet.
**Predicted from Eq. 7.
†From first moment data.

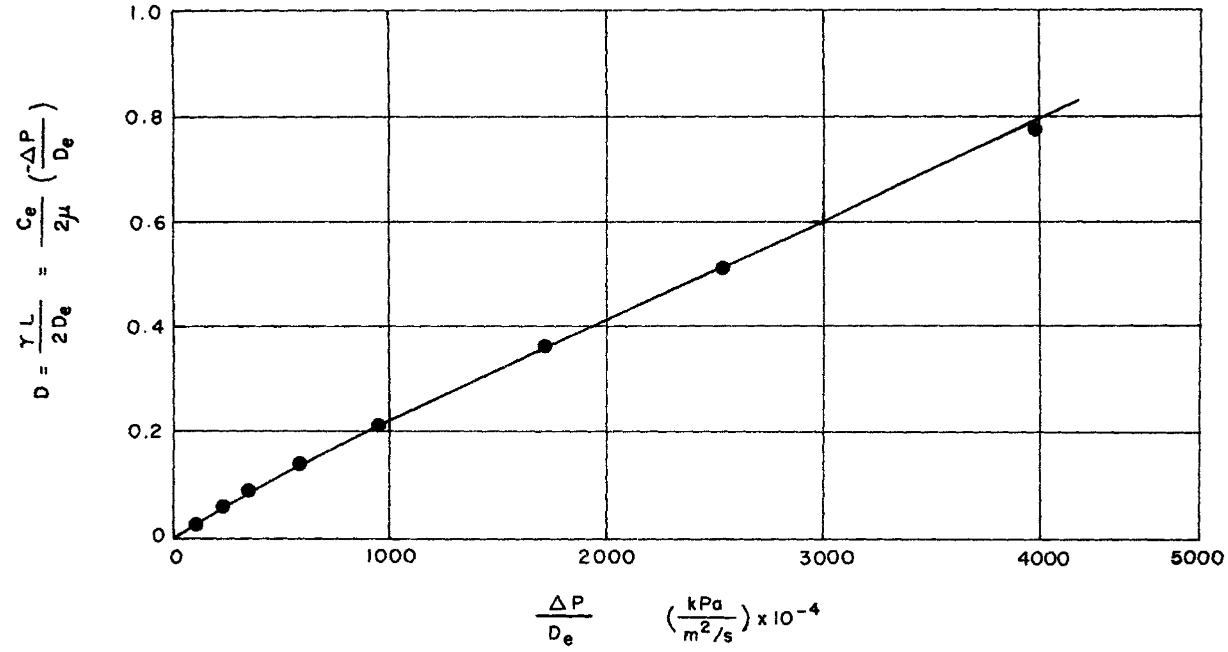

Figure 5. Variation of D with respect to $-\Delta P/D_e$ in nonisobaric runs.

term in the pellet studied in this work. The dependence of D on ΔP was shown in Eq. 13. D values reported in Table 2 were then plotted with respect to $-\Delta P/D_e$ (Figure 5). From the slope of the linear relationship between D and $-\Delta P/D_e$, the Darcy flow parameters C_e was determined as $C_e = 0.069 \times 10^{-14}$ m^2.

The first absolute moment values were also determined in the nonisobaric runs (Pekediz, 1988). A typical set of first absolute moment values obtained at $(-\Delta P) = 80$ kPa with two pellets of different lengths but of same physical properties were reported in Figure 6. Knowing the value of D from zeroth-moment analysis, D_e values at the mean pressures in nonisobaric runs were then determined from the analysis of difference of first absolute moment data reported in Figure 6. In this analysis, Eq. 18 was used for the high flow rate limit of μ_1 for the two pellets used. The D_e values determined from this analysis gave good agreement with the corresponding values predicted from Eq. 7 (Table 2). The agreement of the diffusion coefficients from the isobaric and flow tests and the agreement between the predicted and observed D_e's at different pressures supports the independence of the two types of flow.

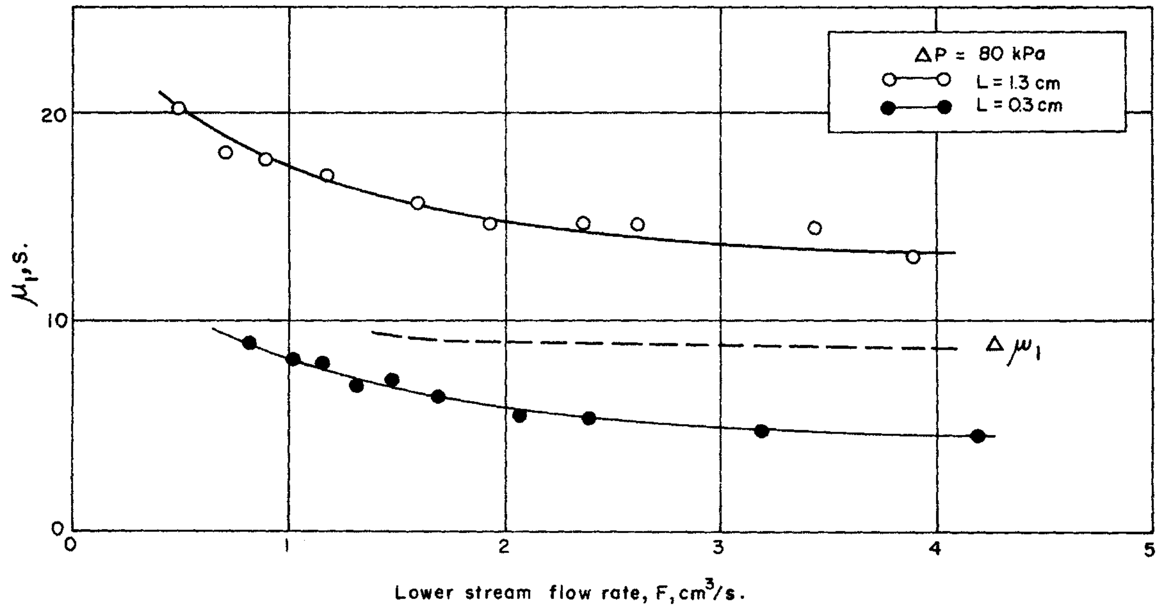

Figure 6. Variation of first absolute moment values with respect to lower stream flow rate for two pellets of different lengths.

$\epsilon_p = 0.68$, $T = 45°C$

Results of this work showed that the viscous flow contribution to the flux of a species in a porous solid and consequently Darcy flow parameter can be measured together with effective diffusivity using the single-pellet moment technique. The new dimensionless parameter, $D = [C_e(-\Delta P)]/2\,\mu\, D_e)$, which physically gives us the relative significance of viscous flow contribution with respect to diffusion was found to increase with ΔP as expected, and it is found out that at $\Delta P/L = 61.5$ kPa/cm its value reached 0.77.

Notation

a = pore radius
A = cross-sectional area of the pellet
C_e = effective Darcy parameter
D = dimensionless group defined by Eq. 13
D_{AB} = molecular diffusion coefficient
D_e = effective diffusion coefficient
D_{e_0} = effective diffusion coefficient at atmospheric pressure
D_{K_A} = Knudsen diffusion coefficient of A
D_T = defined by Eq. 6
$f(a)da$ = volume of pores between a and $a + da$, in unit pellet volume
F = lower stream flow rate of carrier gas
L = pellet length
m_n = nth moment
m_{00} = zeroth moment at atmospheric pressure
M = strength of the input pulse
N_{A_e} = effective molar flux
ΔP = pressure difference across the pellet
y_A = mole fraction of A

Greek Letters

$\alpha = 1 - (M_A/M_B)^{1/2}$
$\delta(t)$ = Dirac delta function
ϵ_p = porosity of the pellet
γ = defined by Eq. 5
μ = fluid viscosity
μ_1 = first absolute moment
τ = tortuosity factor

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