A Simple Technique for Dead Volume Residence Time Evaluation

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INTRODUCTION

The determination of the effective diffusivity in porous catalyst particles is necessary for the evaluation of fluxes in these particles and the associated effectiveness factors. Most investigators have employed a diffusion cell of the Wicke-Kallenbach (1941) type to determine diffusivity either by the steady state method or by using the pulse tracer method. If the latter technique is used and the diffusivities are estimated by the moment method, errors arise because of the dead volumes between injector and pellet and between the pellet and the detector, which cause an increase in observed residence time. It is difficult to eliminate (or even minimize) these dead volumes from the system, as was found by Gibilaro et al. (1970) when they altered their equipment from steady state to a dynamic mode. Suzuki and Smith (1972), using a similar unsteady-state method, assumed that in the first dead volume plug flow conditions were attained, but neglected the second dead volume. This restriction was recognized by Burghardt and Smith (1979), who modified the equipment and used an approximate formulation to obtain the second dead volume. In comparing their results with those of Suzuki and Smith, they found that up to 45% error in the effective diffusivities was obtained if the second dead volume was not accounted for. Unfortunately, in order to employ this technique both a high flow rate and pellets of low or medium porosity had to be employed. Recently Wang and Smith (1983) suggested an improved technique in which a trial-and-error procedure was used that involved more lengthy experimental runs and a theoretical approximation.

In the present work, some of the above methods or a combination of them were tried, but with unsatisfactory results. This was probably due to the much smaller size of the piping compared to the cell and the tangential positioning of inlets and outlets from the diffusion cell, which together make the assumption of plug flow rather doubtful. Further complications occur if measurements are attempted at higher temperatures since the injection valve and cell are now at different temperatures.

Conventionally, if the moment technique is employed to characterize the response curves, following the injection of a tracer pulse, the total moment (μ_T), not the net moment (μ_N), is determined from the distribution curve. This value includes all the component transit times of the pulse within the flow system and porous particle, i.e.,

$$\mu_T = \mu_N + \frac{t_o}{2} + t_1 + t_2 \qquad (1)$$

where $t_o/2$ is the injection time

t_1 is the time required for the pulse to reach the face of the pellet

t_2 is the time required for the pulse to travel from the other face of the pellet to the detector

When plug flow is assumed, t_1 and t_2 can be calculated simply by taking

$$t_1 = V_1/F_1 \quad \text{and} \qquad (2)$$
$$t_2 = V_2/F_2$$

where V_1 and V_2 are the respective dead volumes, and F_1 and F_2 are the carrier and reference gas flow rates.

Because plug flow was doubtful in the present equipment and because of the temperature effects noted above, a new technique was developed which does not rely on mensuration of the dead volumes and the assumption of plug flow.

Instead of estimating the dead volumes, the method adopted is to evaluate the total residence time for these dead volumes directly using a specially made pellet in the same system. Basically, a cylindrical metal pellet of the same size replaces the porous sample pellet. This metal pellet has a small bore hole drilled along its axis which enables the tracer gas to pass through. Details of the pellet as well as the sealing method can be found in the work of Al-Rqobah (1981).

The reference gas stream carries the pulse to one side of the pellet and through the hole drilled in this to the other side and to the detector. The total residence time, t_d, which includes the injection time $t_o/2$, the elution time in the dead volumes,

t_1 and t_2, and the time to traverse the metal pellet, t_3, can now be determined. Thus

$$t_d = \frac{t_o}{2} + t_1 + t_2 - t_3 \quad (3)$$

and (4)

$$\mu_N = \mu_T - t_d$$

As the conditions for calibration and effective diffusivity measurements are identical except for the path through the pellet, more reliable results can be expected.

RESULTS AND DISCUSSION

Using the drilled metal pellet, both reference and carrier gas flow rates were kept the same as those used in the determination of the effective diffusivity with a porous pellet. The characteristics of the temperature effect on the moments are found to be similar to those of the flow rates. As the effects on the net moment due to changes in carrier or reference gas flow rates are well documented in the literature, they are not repeated here. The values of the total moment and net moment are plotted against temperature and are illustrated in Figure 1. Curve *A* represents the reduction in total moment with temperature for a helium pulse in nitrogen at atmospheric pressure through a silica-alumina pellet of total porosity 0.64. The corresponding net moments are indicated in curves *B* and *C* for the plug flow assumption and the present technique, respectively. When plug flow is assumed, there are only negligible differences in the dead volume residence time for both methods below 350 K. However, as the operating temperature is increased, the difference increases and may in some cases be as high as the values of the total moment. Curve *B* shows the characteristics of the resultant net moment with temperature when plug flow is assumed. As can be seen, there is a more rapid decrease for curve *B* compared with curve A at higher temperatures due to the thermal effect. When the temperature attains a certain value, the net moment becomes negative, which illustrates the dubiousness of this method. In contrast, when the new method described above is adopted (curve *C*), a monotonic reduction in the net moment with rise in temperature was observed, following a parallel path to that for the total moment. This correspondence between the two curves validates the use of the method, especially at higher temperatures.

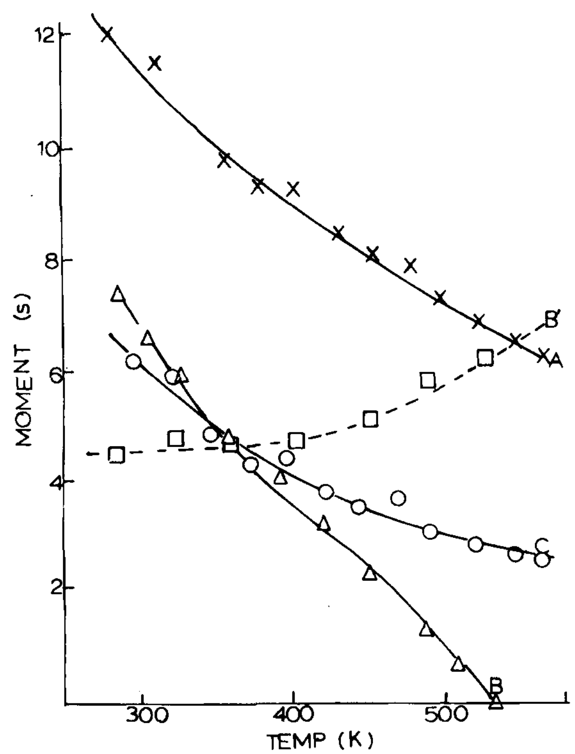

Figure 1. Effect of temperature on moments. A, total moment; B, net moment assuming plug flow; C, net moment using present procedure; B', residence time assuming plug flow.

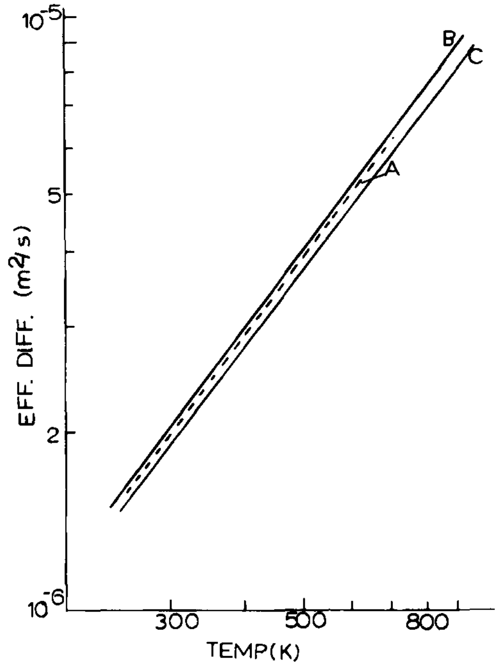

Figure 2. Comparison of effective diffusivities. A, present method; B, Johnson and Stewart model; C, Wakao and Smith model.

Also plotted in Figure 1 is the residence time estimated using the plug flow assumption, curve B^1. This is obtained by subtracting the values of curve *B* from those of curve *A*. The increase in residence time with temperature is small below 350 K but increases more rapidly above this temperature. At 520 K the residence time equals the total moment, resulting in a zero net moment at this temperature. At temperatures beyond 520 K the resultant net moment becomes negative, as demonstrated above.

To illustrate the applicability of the present method, a comparison has been made in Figure 2 between the effective diffusivities obtained from the parallel pore model of Johnson and Stewart (1965), and the random pore model of Wakao and Smith (1962) represented by curves *B* and *C*, respectively, in Figure 2. Since both axes are log scales, straight-line plots of D_e against temperature are obtained in the range 298–578 K. Values predicted from the random pore model are slightly higher than those from the parallel pore model, while the present experimental measurements (corrected for dead volume by the method above) lie between the two predictive curves. These results indicate that the present method gives reliable results, which has been proved for gas pairs other than the helium-nitrogen system described in Figure 2 (Al-Rqobah, 1981).

CONCLUSIONS

A simple experimental technique has been developed to evaluate the dead volume residence time for the dynamic Wicke-Kallenbach diffusion apparatus. Apart from the use of a drilled metal pellet no other equipment modification is required. Moreover, the procedure used to determine the dead volume residence time is identical to that for the total moments and hence no additional theoretical consideration is necessary.

The experimental results obtained using this method are in excellent agreement with predictions from the well-proven models developed by Wakao and Smith (1962) and Johnson and Stewart (1964). The application of this simple method is not limited solely to the evaluation of effective diffusivities. Other physical and chemical phenomena such as diffusion coupled with adsorption, or diffusion with adsorption plus reaction can also be considered. Some results for the case of diffusion with adsorption have already been obtained (Al-Rqobah, 1981).

NOTATION

F_1 = reference flow rate, m^3/s
F_2 = carrier flow rate, m^3/s
$t_o/2$ = injection time, s
t_1 = first dead volume residence time, s
t_2 = second dead volume residence time, s
t_3 = residence time in pellet tunnel, s
t_d = total dead volume residence time, s
V_1 = first dead volume, m^3
V_2 = second dead volume, m^3
μ_N = net moment, s
μ_T = total moment, s

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Manuscript received Jan. 24, 1985, and revision received Apr. 15, 1985.