

# Mixing Effects in Chemical Reactors—III —Dispersion Model

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## OBJECTIVES

At the completion of this module, the student should be able to:

1. Define the concept of axial dispersion.
2. Outline the principal assumptions that underlie the dispersion model, derive the fundamental dispersion model equation, and recognize the conditions of validity and limitations of the model.
3. Estimate an effective axial dispersion coefficient or a Peclet number from a dimensionless correlation, and apply the estimated value to the design or analysis of a tubular flow reactor.
4. For a given reaction system, estimate the conditions under which dispersion effects on conversion may be neglected.

5. Determine the value of the Peclet number from a measured impulse response or from inlet and outlet tracer response peaks by the method of moments.

## PREREQUISITE MATHEMATICAL SKILLS

1. Elementary calculus.

## PREREQUISITE ENGINEERING AND SCIENCE SKILLS

1. Understand the concept of a reactor model (Module E4.5) and the uses of impulse responses for reactor modeling (Modules E4.4 and E4.5).

Suppose a reaction  $A \rightarrow B$  takes place in a plug flow reactor of length  $L$  (m) in which fluid velocity is  $\bar{u}$  (m/s). Since  $A$  is continuously consumed, its concentration decreases steadily with axial position in the reactor, so that a plot of  $C_A$  versus  $z$  appears as in Figure 1. The existence of a gradient in the concentration of  $A$  gives rise to a diffusive motion of  $A$  from the reactor inlet to the outlet, which is superimposed on the convective motion of the bulk fluid phase. The performance of the reactor, specifically, the reactant conversion attainable for a given feed and reactor volume, differs from that which would be predicted, assuming ideal plug flow (negligible diffusion), with the magnitude of the difference depending upon the relative rates of diffusion and convection.

To visualize the effect of diffusion on reactor behavior, let us consider what happens to a group of

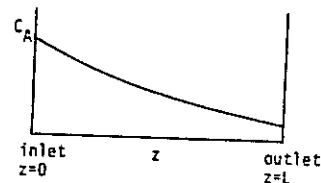


Figure 1.

molecules which enter the reactor at a given instant of time. For the sake of discussion, this module will refer to them collectively as tracer molecules, although they could equally well be molecules of any species in the feed to the reactor.

Shortly after injection, the tracer is contained in a relatively small volume. If the reactor is in ideal plug flow, the tracer cloud then moves through the reactor

without distortion (Figure 2), and emerges in a burst to give the characteristic ideal PFR impulse response, shown in Figure 3, where  $Rdt$  is proportional to the fraction of the outflow around time  $t$  which consists of tracer molecules. However, if diffusion does take place, the tracer spreads away from the center of the cloud in both the upstream and downstream directions. At various times from injection, the cloud might occupy the positions in the reactor shown in Figure 4. Further suppose that the concentration of tracer molecules in the reactor effluent can be monitored. The measured values would depend on the length of the reactor, the mean fluid velocity, and the rate of diffusion; however, the characteristic shape of a concentration versus time plot is easily envisioned. The response begins when the tracer which has diffused ahead of the centroid of the cloud emerges from the reactor, builds up to a maximum when the bulk of the tracer emerges, and decreases as the trailing portion of the cloud passes the detector. The responses which might be measured for reactors of increasing length are shown in Figure 5.

The spreading in the tracer cloud (or to put it another way, the distribution of tracer molecule residence times in the reactor) is a consequence of molecular diffusion, and also of turbulent mixing, if the Reynolds number exceeds a critical value. In addition, a nonuniform velocity profile causes different portions of the tracer cloud to move at different rates, which also results in a spreading of the measured response at

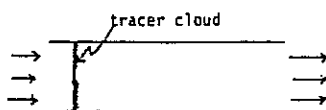


Figure 2.

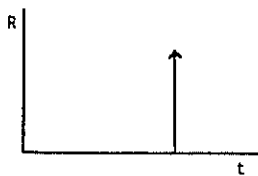


Figure 3.



Figure 4.

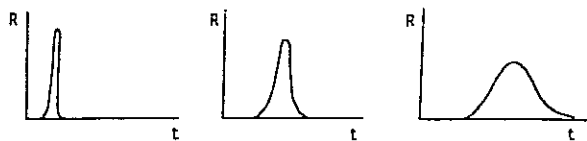


Figure 5.

the reactor outlet. The term *dispersion* is used to denote the combined action of all phenomena—diffusion and nonuniform velocities—which give rise to a distribution of residence times in a reactor. The term *backmixing* is also used frequently.

There are several questions to be considered regarding the role of dispersion in the design and analysis of chemical reactors:

1. Are there systems where in dispersion has a significant influence on reactor performance?
2. How can one model a reactor in which dispersion is significant?
3. How does the performance of the reactor depend on the model parameters?
4. How can the degree of dispersion in a flow unit be measured?

These questions will be considered in turn in the sections that follow. To keep the analysis from getting overly complex, our attention will be restricted to isothermal reactors in which no expansion occurs (liquid-phase reactions, or gas-phase reactions with no mole changes at constant pressure).

## THE DISPERSION MODEL:

### The Model Equation

According to Fick's law, the rate of diffusion of a substance  $A$  is proportional to the negative of the concentration gradient of  $A$ . In any tubular reactor, either empty or packed, reactant depletion and nonuniform flow velocity profiles give rise to concentration gradients, and hence diffusion, in both axial and radial directions. In addition, in turbulent flow eddy transport takes place, tending to level out gradients in all directions to an even greater extent than does molecular diffusion.

A reactor model which accurately reflects these phenomena is difficult to derive, and even more difficult to analyze. What is often done instead is to model the reactor making the following two assumptions:

1. *The reactor is in plug flow* (but not ideal plug flow); radial uniformities are presumed to exist, and the process fluid moves through the reactor at a uniform velocity  $\bar{u}$  equal to the mean velocity of the fluid in the reactor being modeled.
2. *Dispersion occurs in the axial direction.* The extent of the dispersion is sufficient to account for the combined effects of all dispersive phenomena (molecular and turbulent mixing, and nonuniform velocities) in the real reactor. This representation of a flow reactor is termed the *dispersed plug flow model*, or simply the *dispersion model*. As has been shown in the literature, it can successfully simulate the behavior of reactors in which complex radial and axial flow and transport patterns exist (3).

To derive the model equation, let us consider Figure 6, a cross section of a dispersed plug flow reactor at steady-state. Suppose that the mean fluid velocity is  $\bar{u}$ (cm/s) (in a packed bed reactor,  $\bar{u}$  is the superficial

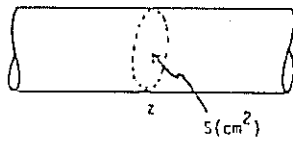


Figure 6.

velocity), and that  $D_e$  ( $\text{cm}^2/\text{s}$ ) is the constant of proportionality between the dispersive flux of a reactant  $A$  and the negative gradient of  $A$  in the  $z$  direction ( $-dC_A/dz$ ). The rate at which  $A$  traverses the cross section is the sum of the rate at which it is carried through by the convective (bulk) flow of the fluid, plus the rate at which it passes through by dispersion:

$$J_{\text{total}} \left( \frac{\text{mol}}{\text{s}} \right) = \bar{u} \left( \frac{\text{cm}}{\text{s}} \right) S \left( \text{cm}^2 \right) C_A \left( \frac{\text{mol}}{\text{cm}^3} \right) - D_e \left( \frac{\text{cm}^2}{\text{s}} \right) S \left( \text{cm}^2 \right) \frac{dC_A}{dz} \left( \frac{\text{mol}}{\text{cm}^3} \right) \quad (1)$$

The reactor may be considered to be in ideal plug flow to the extent that the second term is negligible relative to the first.

Let us further suppose that  $A$  is involved as a reactant, and that the rate at which it reacts is  $-r_A$  ( $\text{mol}/\text{cm}^3 \cdot \text{s}$ ). The steady-state material balance on  $A$  in the reactor may be derived by considering a differential element from  $z$  to  $z + \Delta z$ . See Figure 7. The balance takes the form *input = output + consumption*, where the input term is the rate at which  $A$  enters the element at  $z$  by convection and dispersion, the output term is the rate of passage of  $A$  through the cross section at  $z + \Delta z$ , and the consumption term is the volumetric rate of consumption ( $-r_A$ ) times the volume of the differential element ( $S\Delta z$ ). If the input and output terms are expressed by Equation 1, the result is

$$\bar{u} S C_A \Big|_z - D_e S \left( \frac{dC_A}{dz} \right) \Big|_z = \bar{u} S C_A \Big|_{z+\Delta z} - D_e S \left( \frac{dC_A}{dz} \right) \Big|_{z+\Delta z} - r_A S \Delta z \quad (2)$$

Upon division by  $S\Delta z$  and rearrangement of terms, this equation becomes:

$$\bar{u} \frac{C_A \Big|_{z+\Delta z} - C_A \Big|_z}{\Delta z} = D_e \frac{\left( \frac{dC_A}{dz} \right) \Big|_{z+\Delta z} - \left( \frac{dC_A}{dz} \right) \Big|_z}{\Delta z} - r_A \quad (3)$$

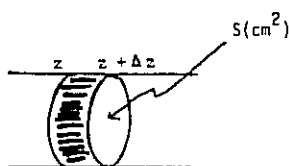


Figure 7.

The final result is obtained by letting  $\Delta z$  approach zero:

$$\bar{u} \frac{dC_A}{dz} = D_e \frac{d^2 C_A}{dz^2} + r_A \quad (4)$$

This is the axial dispersion model equation. Once two boundary conditions are specified and a rate law is substituted for  $r_A$ , the equation can be solved, analytically or numerically, for  $C_A(z)$ ; the result can in turn be used to determine the reactor length and hence the mean residence time  $\epsilon L/\bar{u}$  needed to achieve a specified conversion. Here  $\epsilon$  is the fraction of the reactor volume occupied by the flowing fluid, i.e.  $\epsilon = 1$  for empty tubes and  $\epsilon =$  bed porosity for packed bed reactors.

A number of complexities are associated with the choice of boundary conditions for Equation 4, which center about the question of whether or not diffusion of  $A$  across the reactor boundaries takes place. These problems will not be considered here, except to note that the closer the reactor is to ideal plug flow (i.e., the lower the value of  $D_e$ ) the less difference this question makes and the more reliable is the model. For a more complete discussion, see Reference (2).

### Dimensional Analysis of the Dispersion Model

It is often useful to write a model equation such as Equation 4 in terms of dimensionless variables. Let us define  $Z = z/L$  and  $C = C_A/C_{A0}$ . If one assumes an  $n$ th-order rate law,

$$-r_A = kC_A^n$$

and substitute  $LZ$  for  $z$  and  $C_{A0}C$  for  $C_A$  in Equation 4, the result may be written as

$$\frac{1}{N_{Pe}} \frac{d^2 C}{dZ^2} - \frac{dC}{dZ} - N_{Da} (C^n) = 0 \quad (5)$$

where the dimensionless group

$$N_{Pe} = \bar{u} L / D_e = \frac{(L^2 / D_e)}{(L / \bar{u})} \quad (6)$$

is the *Peclet number*, which represents the ratio of characteristic dispersion time to characteristic convection time (residence time).

$$N_{Da} = k C_{A0}^{n-1} L / \bar{u} \quad (7)$$

is the *Damkohler number*, which represents the ratio of the characteristic convection time (residence time) and characteristic process (reaction) time.

The proper boundary conditions discussed at length in Reference (2) for the reactor at steady state require continuity of flux at the entrance and exit:

$$Z=0 \quad C - \frac{1}{N_{Pe}} \frac{dC}{dZ} = 1 \quad (5a)$$

$$Z = 1 \quad \frac{dC}{dZ} = 0 \quad (5b)$$

Equations 5, 5a and 5b complete the statement of the problem.

The degree to which axial dispersion influences the performance of a chemical reactor is determined by the value of the Peclet number. A high value of  $N_{Pe}$  corresponds to a slightly dispersed reactor, with  $N_{Pe} \rightarrow \infty (D_e \rightarrow 0)$ , signifying ideal plug flow. Similarly, a low value of  $N_{Pe}$  represents a high degree of backmixing; in the limit as  $N_{Pe} = 0$ , backmixing is in effect complete—the concentration of  $A$  is uniform throughout the reaction volume, and the reactor functions as a perfect mixer. Although the validity of the dispersion model depends to a great extent on the process (for a reactor, on the value of the Damkohler number) it may be stated as a rule of thumb that the dispersion model may be used with confidence as long as  $N_{Pe}$  is greater than 20, and should be used with increasing caution as the Peclet number falls below this value.

This dispersion model has been found especially useful in modeling the behavior of packed bed reactors. A dimensionless group which frequently occurs in this context is the Bodenstein number

$$N_{Bo} = \frac{\bar{u}d_p}{\epsilon D'_e} \quad (8)$$

where  $d_p$  is the mean particle diameter of the packing and  $\epsilon$  is the void fraction (porosity) of the bed. The inverse of the Bodenstein number,  $\epsilon D'_e / \bar{u}d_p$ , is sometimes called the *intensity of dispersion*\*. Here  $D'_e$  is the dispersion coefficient based on actual cross sectional area available for fluid transport.

## ANALYSIS OF DISPERSED PLUG FLOW REACTORS

To predict the conversion which will be achieved in a dispersed plug flow reactor for a reaction with known kinetics, one must integrate Equation 4 or 5, substituting values of the superficial velocity  $\bar{u}$  and the effective axial dispersion coefficient  $D_e$ . The velocity can be easily determined as the volumetric flow rate of the reaction mixture divided by the cross-sectional area of the empty reactor; the problem is to determine  $D_e$ .

As will be shown in a later section, axial dispersion coefficients (or equivalently, Peclet numbers) can be determined from tracer response measurements. The results of many such measurements have been used to derive correlations which may be used to estimate dispersion coefficients from known reactor geometric

\*Unfortunately the terminology regarding these dimensionless groups is not universally accepted, and you should be aware that other conventions are commonly used. The term "Bodenstein number" is sometimes used to denote the Peclet number as defined by Equation 6, and what we have called the Bodenstein number is also called the "Peclet number based on particle diameter."

variables and reaction mixture properties. In the remainder of this section, two such correlations will be presented. The module will illustrate how to use them, and show how the performance of a dispersed plug flow reactor can be predicted once the value of  $D_e$  has been estimated.

## Correlations for Dispersion Coefficients

Wen and Fan [Reference (2), Figures 5-15 through 5-22.] summarize correlations for straight pipes, fixed and fluidized beds, and bubble towers. The correlations involve the following dimensionless groups:

$D_e / \bar{u}d$  or  $\epsilon D'_e / \bar{u}d_p$  Intensity of dispersion

$N_{Re} = d\bar{u}/\nu$  Reynolds number (empty tubes)

$= d_p \bar{u} / \nu$  Particle Reynolds number (packed beds)

$N_{Sc} = \nu / D_{mol}$  Schmidt number

where  $d$  (cm) is the flow channel diameter for an empty tube,  $d_p$  is the mean particle diameter for packed beds,  $\nu$  (cm<sup>2</sup>/s) is the kinematic viscosity of the fluid (viscosity/density), and  $D_{mol}$  is the molecular diffusivity of the reactant (or tracer) in the fluid ( $D_{mol} \approx 10^{-5}$  cm<sup>2</sup>/s for liquids, 1 cm<sup>2</sup>/s for gases). If the viscosity and density of the reaction mixture, the flow channel diameter, and void fraction of the bed, and the superficial fluid velocity are known, one can calculate the Reynolds number, estimate the intensity of dispersion from the appropriate correlation, and use the resulting value to estimate the effective dispersion coefficient  $D_e$  or  $D'_e$ .

Figures 8 and 9 presents two such correlations, the first for fluids flowing through empty pipes and the

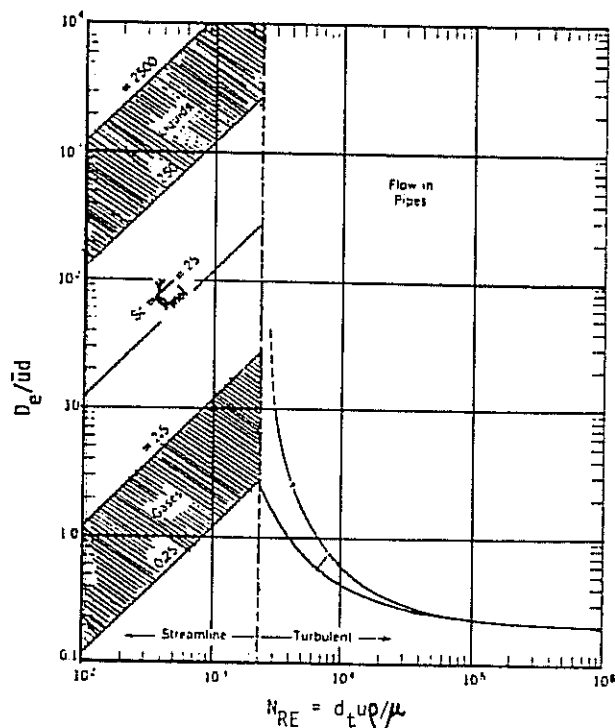


Figure 8. Dispersion intensity versus Reynolds number for flow of fluids in empty pipes (1).

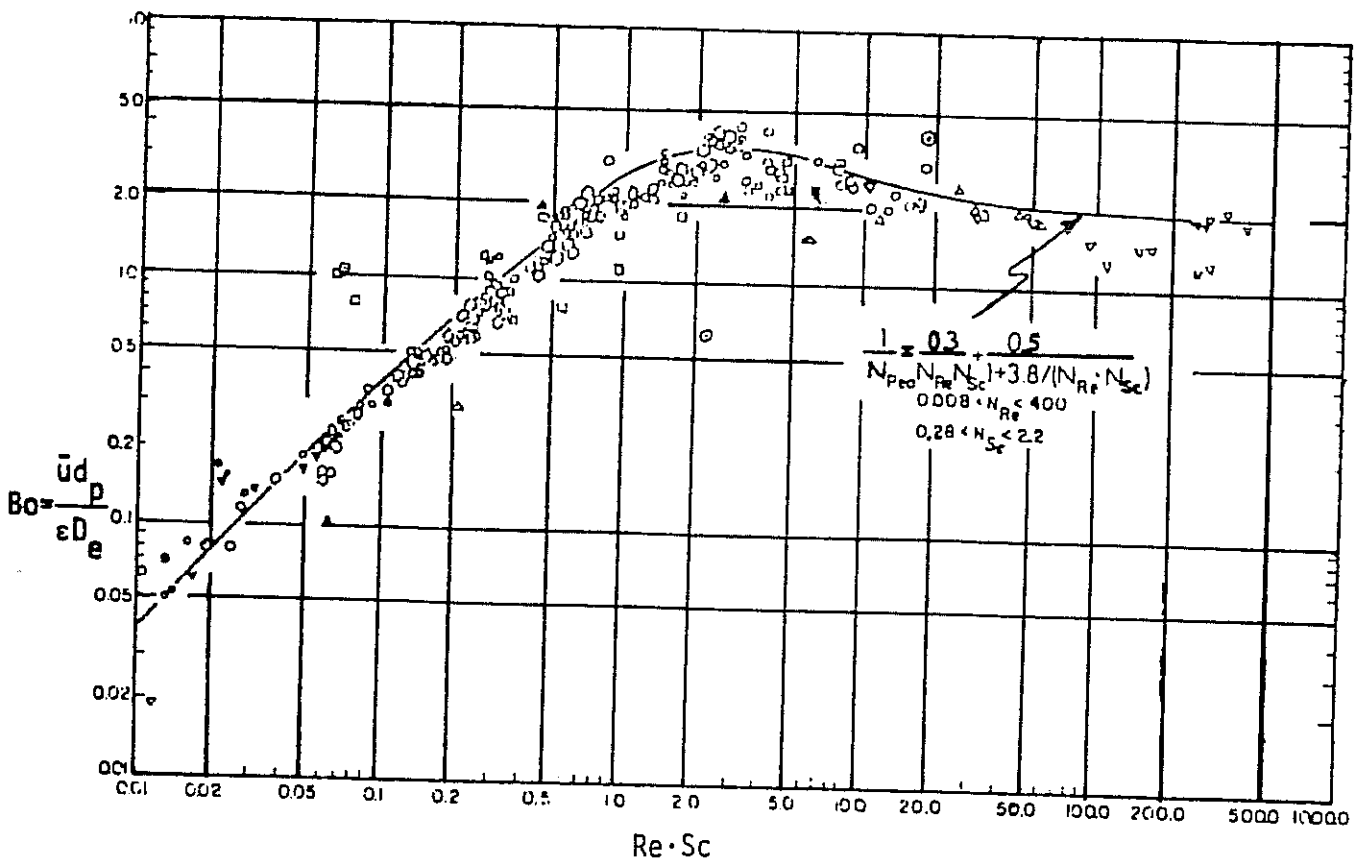


Figure 9. Correlation of Bodenstein number with Reynolds and Schmidt numbers for flow of gases through fixed beds (2).

second for flow in packed beds. Their use will be illustrated in the next section.

### Effect of Dispersion on Reactor Performance

The performance of an isothermal dispersed plug flow reactor can be analyzed by substituting a rate law into Equation 4 or 5 and integrating the resulting equation (analytically for a first-order reaction, otherwise numerically) to determine the reactant concentration (or fractional conversion) versus axial position.

The qualitative effect of dispersion can be inferred by noting that, as the dispersion coefficient  $D_e$  varies from 0 to  $\infty$ , the reactor behavior changes from ideal plug flow to perfect mixing. Recall that for a single  $n$ th-order reaction at constant temperature, the conversion obtained in a perfect mixer is always less than that obtained in an ideal PFR with the same space time. One might then guess that as the rate of dispersion increases (or equivalently, as  $D_e$  increases), conversion decreases. This is in fact the case.

Figure 10 shows the results of solving Equation 4 for a first-order reaction: the abscissa is  $(C_A)_{outlet}/(C_A)_{inlet}$ , or  $1 - x_A$ , and the ordinate is the ratio of the dispersed plug flow reactor volume to the volume of an ideal PFR which would be required to achieve the same conversion. A similar graph for a second-order reaction is given by Levenspiel in Reference (1), chapter 9, Figure 22.

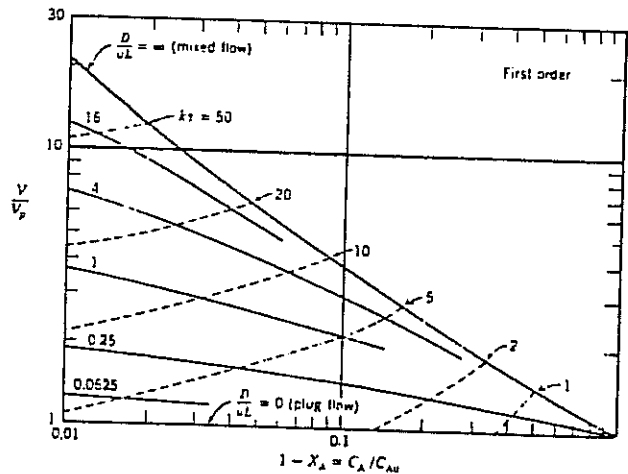


Figure 10. Ratio of dispersed plug flow reactor volume to ideal plug flow reactor volume versus 1-fractional conversion for first-order reaction  $A \rightarrow$  products, assuming negligible expansion (1).

The extent to which axial dispersion influences the reactor performance is determined by the value of a dimensionless group shown in Figure 8 as  $D_e/\bar{u}d$ , which is proportional to the inverse of the Peclet number. Figure 10 confirms the expected result that as the rate of dispersion increases, the reactor volume required to achieve a fixed conversion increases from a minimum

value for ideal plug flow ( $D_c=0$ ) to a maximum for a perfect mixer ( $D_c=\infty$ ).

Figure 10 can be used in several ways. Suppose a first-order reaction with a known rate constant  $k$ , is being carried out in a continuous isothermal tubular reactor. If the throughput  $q$  ( $m^3/s$ ) and desired conversion  $X_A$  are specified then:

1. Calculate the required ideal plug flow reactor volume as

$$V_p = -\frac{q}{k} \ln(1 - X_A) = \frac{q}{k} \ln\left(\frac{1}{1 - X_A}\right) \quad (9)$$

(Be sure you know where this formula comes from.)

2. Specify a flow channel (or packing particle) diameter, calculate  $S$ , the flow channel cross section, and determine the superficial velocity  $\bar{u} = q/S$  and the ideal plug flow reactor length  $L_p = V_p/S$ .
3. Calculate the Reynolds number  $N_{Re} = d\bar{u}/\nu$  (or  $d_p \bar{u}/\nu$  for a packed bed), then use the appropriate correlation (e.g. Figure 8 for an empty tube) to estimate the dispersion intensity  $D_c/\bar{u}d$ . (If the flow is laminar, one must also determine the Schmidt number to use the correlation.) Next, from the value of  $D_c/\bar{u}d$  and the known tube diameter, calculate the ratio  $\bar{u}/D_c$ , and finally calculate the inverse Peclet number  $D_c/\bar{u}L$ , using the value of  $L$  calculated assuming ideal plug flow.
4. Locate the specified conversion on the abscissa of Figure 10. Then
  - a) To estimate the reactor volume required to achieve the same conversion, move up vertically to the curve corresponding to the calculated inverse Peclet number, read  $V/V_p$  on the ordinate, and calculate  $V$  from the known value of  $V_p$ . (One can refine the calculation by recalculating  $D/\bar{u}L$  with the new value of  $V$ , and repeating until the initial and final values of  $V$  agree.)
  - b) If, instead, one wished to calculate the final conversion which will be achieved in the reactor of length  $L_p$ , move up the constant  $k\bar{t}$  line to the curve corresponding to the calculated value of  $D_c/\bar{u}L$ , and read the abscissa value (Question: why is  $k\bar{t}$  constant in this calculation?).

For a first-order reaction, an analytical solution of the axial dispersion equation is available (2). It is instructive to compare the results obtained using Figure 10 with this solution. However, graphical representations similar to Figure 10 are useful for reaction orders other than one for which analytical solutions are not available.

### Criteria for Neglecting Dispersion Effects

Although the dispersion model is a relatively simple approximation to the behavior of a real reactor, it is still much more cumbersome to use than the ideal plug flow model. It is therefore important for the design engineer to be able to predict whether or not dispersion effects must be taken into account in assessing reactor performance. Criteria can be developed by

applying perturbation theory to Equation 5. See, for instance, References (4) and (5). Only the pertinent results will be presented in this section.

Suppose one is carrying out an  $n$ th-order reaction,  $A \rightarrow$  products in a continuous reactor of length  $L$ . Several questions may be asked:

- a) Given rate law parameters ( $k$  and  $n$ ) and a desired fractional conversion  $x_A$ , what condition guarantees that the required volume of an ideal PFR and that which would be calculated (taking dispersion into account) will be within  $p\%$  of each other?

Conditions

$$N_{Pr} \geq \frac{100}{p} n \ln\left(\frac{1}{1 - x_A}\right) \quad (\text{any reactor}) \quad (10)$$

$$\frac{L}{d_p} \geq \frac{100}{p} \frac{n}{N_{Bo}} \ln\left(\frac{1}{1 - x_A}\right) \quad (\text{packed bed}) \quad (11)$$

Procedure:

Use a dimensionless correlation to estimate the value of  $N_{Pr}$  or  $N_{Bo}$  from the design variables; choose a value of  $p$  (5%, for example, or 1% if a closer tolerance is required), and see if the condition of Equation 10 or 11 is satisfied. If it is, use the ideal plug flow model as the basis of the design.

- b) Given a set of reactor parameters (including length), what condition guarantees that the fractional conversion predicted assuming ideal plug flow and that which would be predicted taking dispersion into account will be within  $p\%$  of each other?

Conditions:

$$N_{Pr} \geq \frac{100}{p} (N_{Da})^2 \quad \text{and} \quad n = 1 \quad (12)$$

$$\geq \frac{100}{p} \frac{n}{(n-1)} \frac{N_{Da}}{[1 + (n-1)N_{Da}]} \cdot \ln [1 + (n-1)N_{Da}], \quad n \neq 1 \quad (13)$$

and for packed beds

$$\frac{L}{d_p} \geq \frac{100}{p} \frac{(N_{Da})^2}{N_{Bo}} \quad \text{and} \quad n = 1 \quad (14)$$

$$\geq \frac{100}{p} \frac{n}{(n-1)} \frac{N_{Bo}}{N_{Bo} [1 + (n-1)N_{Da}]} \cdot \ln [1 + (n-1)N_{Da}], \quad n \neq 1 \quad (15)$$

Note in the case of packed bed reactor, the reaction rate constant in the above formulas is based per unit reactor volume.

### Example 1:

A second-order gas-phase reaction  $A \rightarrow B$  takes place in an isothermal packed bed reactor. The particle Reynolds number is greater than 50, and the length of the reactor

determined for desired conversion assuming ideal plug flow is 7.2 meters. The mean particle diameter of the packing is 1 cm. The Schmidt number of the gas is close to 1. The Damkohler number is evaluated and is found to equal 2.9. Would the conversion actually achieved be within 1% of the specified value?

**Solution:**

Use Equation 15.

$$L/d_p = (720 \text{ cm}) / (1 \text{ cm}) = 720$$

From Figure 9, for a Reynolds number of 50 and a Schmidt number of 1, set  $N_{Bo} = 2$ . The right-hand side of Equation 15 is then determined to be

$$\left(\frac{100}{1}\right) \left(\frac{2}{1}\right) \left[\frac{2.9}{2(1+2.9)}\right] \ln(1+2.9) = 101$$

Since  $720 > 101$ , according to Equation 15 one can use the ideal plug flow design calculation with confidence.

The next example illustrates the design of a reactor under conditions when dispersion cannot be neglected.

**Example 2:**

A liquid-phase reaction  $A \rightarrow B$  is to be carried out in an isothermal tubular reactor. The rate law for the reaction at the proposed operating temperature is

$$-r_A \text{ (mol/L} \cdot \text{s)} = 0.40 C_A$$

A pipe with an 8 cm inner diameter is to be used, and a 99% conversion is desired. The feed is pure  $A$ , and the throughput rate is 0.24 L/s. Calculate the conversion which will be achieved in the reactor, taking axial dispersion into account. The fluid properties of the reaction mixture may be taken to be those of pure water.

**Solution:**

If the reactor were in ideal plug flow, the required volume would be:

$$V_p = \frac{q}{k} \ln(1 - X_A) \\ = \frac{0.24 \text{ L/s}}{0.40 \text{ s}^{-1}} \ln(1 - 0.99) = 2.76 \text{ L}$$

and its length would be

$$L_p = \frac{(2.76 \times 10^3) \text{ cm}^3}{(\pi \times 4^2) \text{ cm}^2} = 54.9 \text{ cm} \approx 55 \text{ cm}$$

The mean velocity of the reaction mixture is

$$\bar{u} = q/S = \frac{(0.24 \times 10^3) \text{ cm}^3/\text{s}}{(\pi \times 4^2) \text{ cm}^2} \\ \approx 4.8 \left(\frac{\text{cm}}{\text{s}}\right)$$

The density of the fluid is 1.0 (g/cm<sup>3</sup>), and its viscosity is 0.010 (g/cm · s), so that its kinematic

viscosity is

$$\nu = \frac{0.010 \text{ (g/cm} \cdot \text{s)}}{1.0 \text{ (g/cm}^3\text{)}} = 0.010 \text{ (cm}^2/\text{s)}$$

The Reynolds number is

$$N_{Re} = \frac{d\bar{u}}{\nu} = \frac{(8 \text{ cm})(4.8 \text{ cm/s})}{0.01 \text{ cm}^2/\text{s}} = 3840$$

The flow is thus turbulent, and there is no need to calculate the Schmidt number. From Figure 8, for a Reynolds number of 3840

$$D_e/\bar{u}d \approx 2$$

$$\frac{D_e}{\bar{u}L} = \frac{D_e}{\bar{u}d} \times \frac{d}{L} \approx 2 \times \frac{8}{55} = 0.29$$

The Damkohler number for this reactor is

$$N_{Da} = \frac{kC_{A0}^{-1}L}{\bar{u}} = \frac{(0.40)(1)(55)}{4.8} = 4.58$$

Let us see if the conversion obtained in the reactor is within 1% of the ideal PFR value of 0.99. The right-hand side of Equation 12 is

$$\frac{100}{1} (4.58)^2 = 2098$$

while the Peclet number is  $1/0.29 = 3.4$ . The condition of Equation 12 is thus not satisfied, and dispersion should accordingly be taken into account in the design.

The point  $1 - X_A = 0.01$  is located on the abscissa of Figure 10 (it is the origin of the graph). A line of constant  $k\bar{t}$  is followed until the point corresponding to  $D_e/\bar{u}L \approx 0.29$  is reached, at which point,  $1 - X_A \approx 0.06$ . The effect of the dispersion is therefore to lower the achievable conversion from the design value of 99% to 94%.

One can also estimate the volume required to achieve the 99% conversion for the same throughput rate. Proceeding vertically from the 99% conversion point to the curve for  $D_e/\bar{u}L = 0.29$ , estimate  $V/V_p = L/L_p \approx 2.0$ , so that to a first approximation, a length of roughly (2.0) (55.9) = 110 cm is required to achieve the desired conversion, when dispersion is taken into account. (The estimate can be refined by recalculating  $D/\bar{u}L$  using the new value of  $L$ , reading  $V/V_p = L/L_p$  again from Figure 10, and iterating until two successive values of  $L$  agree.)

**MEASUREMENT OF AXIAL DISPERSION COEFFICIENTS**

Suppose a tracer impulse is injected at the inlet of a dispersed plug flow reactor, and the response is monitored at the outlet. The shape of the response depends on the relative magnitudes of the rates of convection and dispersion: if dispersion is much slower than convection, the reactor behaves as though it were in ideal plug flow, while if dispersion is very rapid compared to convection, the reactor approaches a perfect mixer in its behavior.

The Peclet number  $N_{Pe} = \bar{u}L/D_e$  (which can be thought of as a ratio of the rate of convection to the rate of dispersion) provides a measure of the extent of

deviation from ideal flow conditions:  $N_{pe} \rightarrow \infty$  corresponds to ideal plug flow, and  $N_{pe} = 0$  represents perfect mixing. Representative impulse responses corresponding to various degrees of dispersion, and several values of  $N_{pe}$ , are shown in Figure 11a, b, c and d.  $R(t)$  is a property of the outflow which is directly proportional to tracer concentration and which is monitored as the response of the system to an impulse tracer injection in the inflow.

There are several statistical techniques which can be used to extract the value of  $D_e$  from a tracer response. One such technique is the *method of moments*. Derivations of the formulas to be given, and discussions of alternative estimation methods, may be found in Reference (2).

If a tracer impulse is injected at a reactor inlet and  $R(t)$  is the measured response at the outlet, the first step in implementing the method of moments is to calculate the following quantities by numerical integration:

$$\mu = \frac{\int_0^{\infty} tR(t)dt}{\int_0^{\infty} R(t)dt} \quad (16)$$

is the mean or centroid of  $R(t)$ .

$$\sigma^2 = \frac{\int_0^{\infty} (t - \mu)^2 R(t)dt}{\int_0^{\infty} R(t)dt} \quad (17)$$

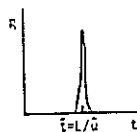


Figure 11a.  $N_{pe} = 200$ .

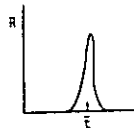


Figure 11b.  $N_{pe} = 20$ .

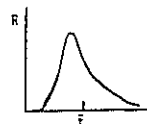


Figure 11c.  $N_{pe} = 5$ .

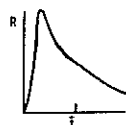


Figure 11d.  $N_{pe} = 0.1$ .

is the variance of  $R(t)$ . The mean  $\mu$  is the average value of the response time  $t$ , and the variance is a measure of the spread of the response peak about the mean; a low value of  $\sigma^2$  corresponds to a narrow peak, and conversely.

If the peak is symmetrical (like those in Figure 12), the mean  $\mu$  coincides with the time at which the response is a maximum, and in general, corresponds to the mean residence time in the system (see Module E4.4). The value of  $\sigma^2$  depends very strongly on the degree of dispersion in the system; the higher the degree of dispersion, the more the response curve spreads and hence, the greater the value of  $\sigma^2$ .

It can be shown (3) that if the degree of dispersion is not too great,

$$\frac{\sigma^2}{\mu^2} \approx \frac{2}{N_{pe}} = \frac{2D_e}{\bar{u}L} \quad (18)$$

The criterion for the validity of Equation 18 is  $N_{pe} \gg 1$ ; a rough rule of thumb is  $N_{pe} > 10$ . If this condition is not satisfied, the correct formula depends on the boundary conditions at the inlet and outlet, and the validity of the dispersion model itself becomes questionable [The formulas applicable for different boundary conditions are given by Reference (1) and (2).] A procedure for determining  $D_e$  is thus as follows:

1. Measure the outlet response  $R(t)$  to a tracer impulse injected at the inlet.
2. Calculate the mean,  $\mu$ , and the variance,  $\sigma^2$ , according to Equations 16 and 17 by numerical integration.
3. Estimate the Peclet number using Equation 18 as:

$$N_{pe} = 2\mu^2/\sigma^2 \quad (19)$$

If the value is 10 or greater, accept it; if not, either use a refinement of the theory which takes into account the boundary conditions at the outlet, or use a different model altogether.

4. Determine the mean (superficial) fluid velocity  $\bar{u}$  as the volumetric flow rate divided by the flow channel cross section, or if both are not known, as

$$\bar{u} = \epsilon L/\mu \quad (20)$$

5. Estimate  $D_e$  from the definition of the Peclet number as

$$D_e = \bar{u}L/N_{pe} \quad (21)$$

### Example 3:

An impulse response measurement is carried out on a tubular reactor 4 meters long. The pipe inner

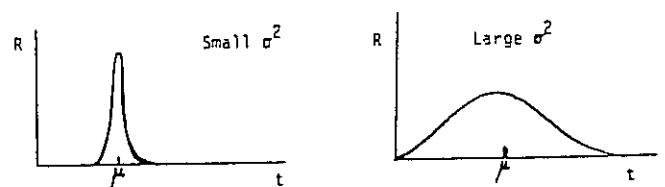


Figure 12.



diameter is 10 cm, and the volumetric flow rate is 0.63 L/s. The response appears in Figure 13, and is corrected by subtracting the constant background signal  $R_b$ ; the mean and variance of the corrected signal are calculated using Simpson's rule (using a computer program such as the one available for Module E4.4), with the following results:

$$\mu = \frac{\int_0^{\infty} t R_c(t) dt}{\int_0^{\infty} R_c(t) dt} = 50 \text{ s}$$

$$\sigma^2 = \frac{\int_0^{\infty} (t - \mu)^2 R_c(t) dt}{\int_0^{\infty} R_c(t) dt} = 62.5 \text{ s}^2$$

From Equation 19, the Peclet number is estimated to be

$$N_{Pe} = \frac{2\mu^2}{\sigma^2} = \frac{2(50)^2}{62.5} = 80$$

Since this is greater than 10, the dispersion model and the estimated value of the Peclet number can be used with a reasonable degree of confidence.

The mean velocity is calculated as

$$\bar{u} = \frac{q(\text{cm}^3/\text{s})}{S(\text{cm}^2)} = \frac{(0.63 \times 1000)}{(\pi)(5^2)} = 8.02 \text{ cm/s}$$

and from Equation 21

$$D_e = \frac{\bar{u}L}{N_{Pe}} = \frac{(8.02 \text{ cm/s})(400 \text{ cm})}{80} = \boxed{40.1 \text{ cm}^2/\text{s}}$$

### Determination of $D_e$ - Two Peak Method

It is not always possible to inject a tracer in a time period short enough to be considered instantaneous compared to the residence time of the fluid in the system under investigation (recall that this was the condition for the injection to be treated as a perfect impulse). Fortunately, the analysis outlined in the preceding section can still be performed with relatively few additional calculations, if a tracer pulse (not necessarily an impulse) is injected at a point upstream of the inlet of the system to be modeled, and the responses at the inlet and outlet are measured.

The dispersion coefficient can be calculated from the means and variances of the inlet and outlet response curves. In Figure 14, let  $t$  be the time from the

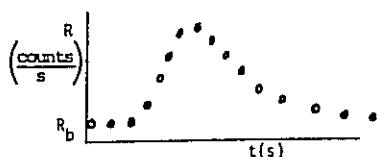


Figure 13.

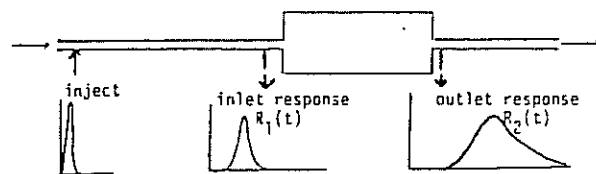


Figure 14.

beginning of the injection. First calculate:

$$\mu_1 = \frac{\int_0^{\infty} t R_1(t) dt}{\int_0^{\infty} R_1(t) dt} \quad \text{and} \quad \mu_2 = \frac{\int_0^{\infty} t R_2(t) dt}{\int_0^{\infty} R_2(t) dt}$$

$$\sigma_1^2 = \frac{\int_0^{\infty} (t - \mu_1)^2 R_1(t) dt}{\int_0^{\infty} R_1(t) dt}, \quad \sigma_2^2 = \frac{\int_0^{\infty} (t - \mu_2)^2 R_2(t) dt}{\int_0^{\infty} R_2(t) dt} \quad (22)$$

In terms of these moments, the mean and variance of the system impulse response are

$$\mu = \mu_2 - \mu_1 \quad (23)$$

$$\sigma^2 = \sigma_2^2 - \sigma_1^2 \quad (24)$$

Thus, one can calculate the desired impulse response moments while avoiding the need for a perfect impulse injection or anything close to it. Once  $\mu$  and  $\sigma^2$  are known,  $D_e$  may be calculated from Equation 18, as before.

### NOMENCLATURE

$C$	= dimensionless reactant concentration
$C_A$	= reactant concentration
$C_{A_0}$	= reactant concentration in the feed
$D_e$	= axial dispersion coefficient based on total cross-sectional area
$D_e'$	= axial dispersion coefficient based on cross-sectional area available for fluid flow
$D_{mol}$	= molecular diffusivity
$d$	= tube or vessel diameter
$d_p$	= particle diameter
$J_{tot}$	= total flux (convection + dispersion)
$k$	= reaction rate constant
$L$	= reactor length (calculated by the axial dispersion model)
$L_p$	= reactor length (calculated by the ideal plug flow model)
$N_{Bo} = \bar{u}d_p / \epsilon D_e'$	= Bodenstein number
$N_{Da} = kC_{A_0}^{-1}L/\bar{u}$	= Damkohler number
$N_{Pe} = \bar{u}L/D_e$	= Peclet number
$N_{Re} = d\bar{u}/\nu(d_p\bar{u}/\nu)$	= Reynolds number
$N_{Sc} = \nu/D_{mol}$	= Schmidt number
$n$	= reaction order
$p$	= percent deviation from ideal plug flow reactor solution
$q$	= volumetric flow rate

$R$	= system response to impulse injection
$-r_A$	= rate of reaction (disappearance) for reactant $A$
$S$	= cross-sectional area of the reactor
$t$	= time
$\bar{t}$	= mean residence time
$\bar{u}$	= mean velocity
$V$	= reactor volume
$V_p$	= volume of an ideal plug flow reactor
$x_A$	= fractional conversion of reactant $A$
$Z = z/L$	= dimensionless axial position in the reactor
$z$	= axial position in the reactor
$\epsilon$	= porosity (external voidage) of packed beds
$\epsilon_g$	= gas holdup (fraction of reactor volume occupied by gas)
$\mu$	= first moment of impulse response (or viscosity)
$\nu$	= kinematic viscosity
$\sigma^2$	= variance of impulse response

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## STUDY PROBLEMS

- What is meant by the term axial dispersion?
- How would the dispersion model equation, Equation 4, simplify for an ideal plug flow reactor?
- What assumptions underlie the dispersion model? Under what conditions is this model most likely to provide an accurate representation of a flow reactor?
- Suppose you have designed a tubular reactor. Outline how you would obtain an estimate of the value of the effective dispersion coefficient in the unit from the known flow rate of the reaction mixture, physical properties of the fluid, and the tube dimensions.
- Once you have gone through the exercise of the previous example and estimated  $D_e$ , how would you estimate the conversion for a first-order reaction which would be achieved if the reactor had been designed to achieve a 95% conversion, assuming ideal plug flow?
- A first-order reaction is carried out in a tubular reactor. By inspection of Figure 10, indicate whether the following statements are true or false:
  - As the Peclet number goes from 0 to  $\infty$ , the performance of a flow reactor varies from that of an ideal CSTR to that of an ideal PFR.
  - For a given flow rate, the assumption of ideal plug flow is more likely to be valid for a long reactor than a short one.
  - As the effective dispersion coefficient increases from 0 to infinity for a given flow rate and reactor length, the conversion in the reactor goes from its ideal plug flow value to 0.
- Would you use an ideal plug flow model, a perfect mixer model, or neither, to simulate a reactor for which  $N_{pe}$  is a)  $1.0 \times 10^{-3}$ , b)  $1.0 \times 10^0$ ; c)  $1.0 \times 10^5$ ?
- Sketch impulse responses corresponding to a) slightly dispersed plug flow; b) moderately dispersed plug flow; c) highly dispersed plug flow.
- What are the physical significances of the mean and the variance of an impulse response?
- How would you calculate the Peclet number for a flow unit from a measured impulse response?
- How would you calculate the Peclet number for a flow unit from measured tracer response peaks at the inlet and outlet of the unit?
- What is the advantage of the two-peak method?

## HOMEWORK PROBLEMS

- A reaction mixture flows through a 4 cm inner diameter tubular reactor at a rate of 25 cm<sup>3</sup>/s. The concentration of a reactant varies with axial position in the reactor according to the formula
 
$$C_A \text{ (mol/cm}^3\text{)} = 3.00 \exp(-0.200z)$$
 where  $z$  (cm) is the distance from the reactor inlet. The axial dispersion coefficient of the reactant is 0.02 cm<sup>2</sup>/s.
  - Calculate the flux of the reactant,  $J$ (mol/s), through the cross section at  $z = 10$  cm.
  - What is the predominant mode of transport—axial convection or dispersion?
- An 8 cm ID tubular reactor has been designed to achieve a 98% conversion of the reactant in a first-order reaction. The specified reactor length is 110 cm. In a batch run at the specified reaction temperature, the reactant half-life was found to be 4.6 seconds. The kinematic viscosity of the reaction mixture is 0.012 cm<sup>2</sup>/s.
  - What throughput rate (cm<sup>3</sup>/s) is the reactor designed to accommodate?
  - Use Figures 8 and 10 to estimate the percentage

difference between the design conversion and the conversion which will actually be achieved.

(c) Comment on the applicability of the dispersion model for this reactor.

3. An impulse response test is performed on an empty tubular reactor. The flow rate through the reactor is 8 L/s, and the reactor inner diameter is 10 cm. The response at the outlet can be approximated as in Figure 15.

a) Estimate the reactor volume and the Peclet number. You may find it helpful to know that for the response shown in the figure

$$\int_0^{\infty} (t-5)^2 R(t) dt = 3.65 \text{ s}^3$$

b) Is the dispersion model appropriate to simulate the reactor? Explain.

c) Suppose a first-order reaction is to be carried out in the reactor and a 95% conversion is specified. Is an ideal plug flow model suitable for the design calculation? Justify your answer.

4. In Figure 16 sulfur dioxide is to be absorbed in an aqueous KOH solution in a packed column. The packed section is 1 meter in diameter. The volumetric flow rate of the gas stream in the absorber is approximately constant at 0.016 m<sup>3</sup>/s. A pulse of radioactive argon (<sup>41</sup>Ar) is injected into the gas feed

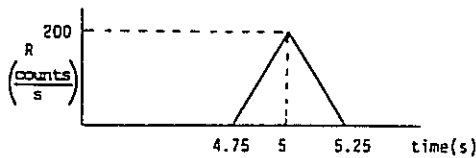


Figure 15.

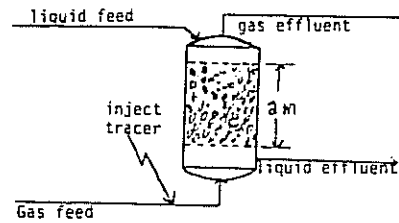


Figure 16.

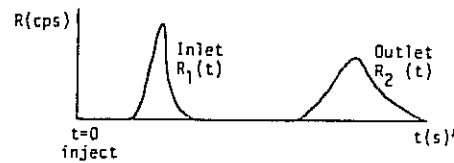


Figure 17.

line, and the responses close to both ends of the packed bed are monitored with externally mounted scintillation detectors 4 meters apart from each other. The responses corrected for background and decay appear as shown in Figure 17. The means and variances of these signals are calculated by numerical integration, with the following results:

$$\mu_1 = 1.8 \text{ s}, \mu_2 = 73.8 \text{ s}$$


$$\sigma_1^2 = 0.4 \text{ s}^2, \sigma_2^2 = 15.3 \text{ s}^2$$

Use these results to estimate the mean residence time of gas in the packed bed (more precisely, in the portion between the detectors) the gas holdup (*ie* fraction of reactor volume occupied by gas),  $\epsilon_g$  (m<sup>3</sup> gas space/m<sup>3</sup> total volume), and the effective gas-phase dispersion coefficient  $D_e$  (cm<sup>2</sup>/s). Comment on the applicability of the dispersion model.

## SOLUTIONS TO THE STUDY PROBLEMS

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1. The combined action of all phenomena--molecular and turbulent diffusion, and a nonuniform velocity profile-- that give rise to a distribution of residence times in a reactor.
2. The second derivative term is deleted. ( $D_e=0$ ).
3. All radial nonuniformities and axial mixing phenomena can be represented as plug flow with axial diffusion. The model is most reliable under conditions close to ideal plug flow (slight degree of dispersion).
4. Calculate the Reynolds number, calculate the Schmidt number for laminar flow, look up the Peclet number or the dispersion intensity on a graphical correlation (e.g. Figure 8), calculate  $D_e$  from known  $\bar{u}$  and  $d$ .
5. Calculate  $D_e/\bar{u}L$ . Find 0.05 on abscissa of Figure 3, move up line of constant  $kt^e$  to value of  $D_e/\bar{u}L$ , read corresponding value of  $1-x_A$ , calculate  $x_A$ .
6. (a) true; (b) true; (c) false
7. (a) perfect mixer; (b) neither; (c) ideal PFR
8.
 


9. The mean is approximately equal to the mean residence time in the flow unit. The variance is a measure of the degree to which individual residence times are spread about the mean.
10. Calculate  $\mu$  and  $\sigma^2$  by numerical integration; calculate  $Pe = 2\mu^2/\sigma^2$
11. Calculate the means and variances of both peaks by numerical integration, then  $\mu = \mu_{out} - \mu_{in}$ ,  $\sigma^2 = \sigma_{out}^2 - \sigma_{in}^2$  then  $Pe = 2\mu^2/\sigma^2$ .
12. It does not require a perfect impulse injection.