

Chapter 12

Compartment Models

Flow models can be of different levels of sophistication and the compartment models of this chapter are the next stage beyond the very simplest, those that assume the extremes of plug flow and mixed flow. In the compartment models we consider the vessel and the flow through it as follows:

$$\text{Total volume } \cdot \cdot \cdot \left\{ \begin{array}{l} V_p \text{—plug flow region} \\ V_m \text{—mixed flow region} \\ V_d \text{—dead or stagnant region within the vessel} \end{array} \right\} V_a \text{—active volume}$$

V

$$\text{Total throughflow } \cdot \cdot \cdot \left\{ \begin{array}{l} v_a \text{—active flow, that through the plug and mixed flow regions} \\ v_b \text{—bypass flow} \\ v_r \text{—recycle flow} \end{array} \right.$$

v

By comparing the **E** curve for the real vessel with the theoretical curves for various combinations of compartments and throughflow, we can find which model best fits the real vessel. Of course, the fit will not be perfect; however, models of this kind are often a reasonable approximation to the real vessel.

Figure 12.1, on the next few pages, shows what the **E** curves look like for various combinations of the above elements—certainly not all combinations.

Hints, Suggestions, and Possible Applications

- (a) If we know M (kilograms of tracer introduced in the pulse) we can make a material balance check. Remember that $M = v$ (area of curve). However, if we only measure the output C on an arbitrary scale, we cannot find M or make this material balance check.

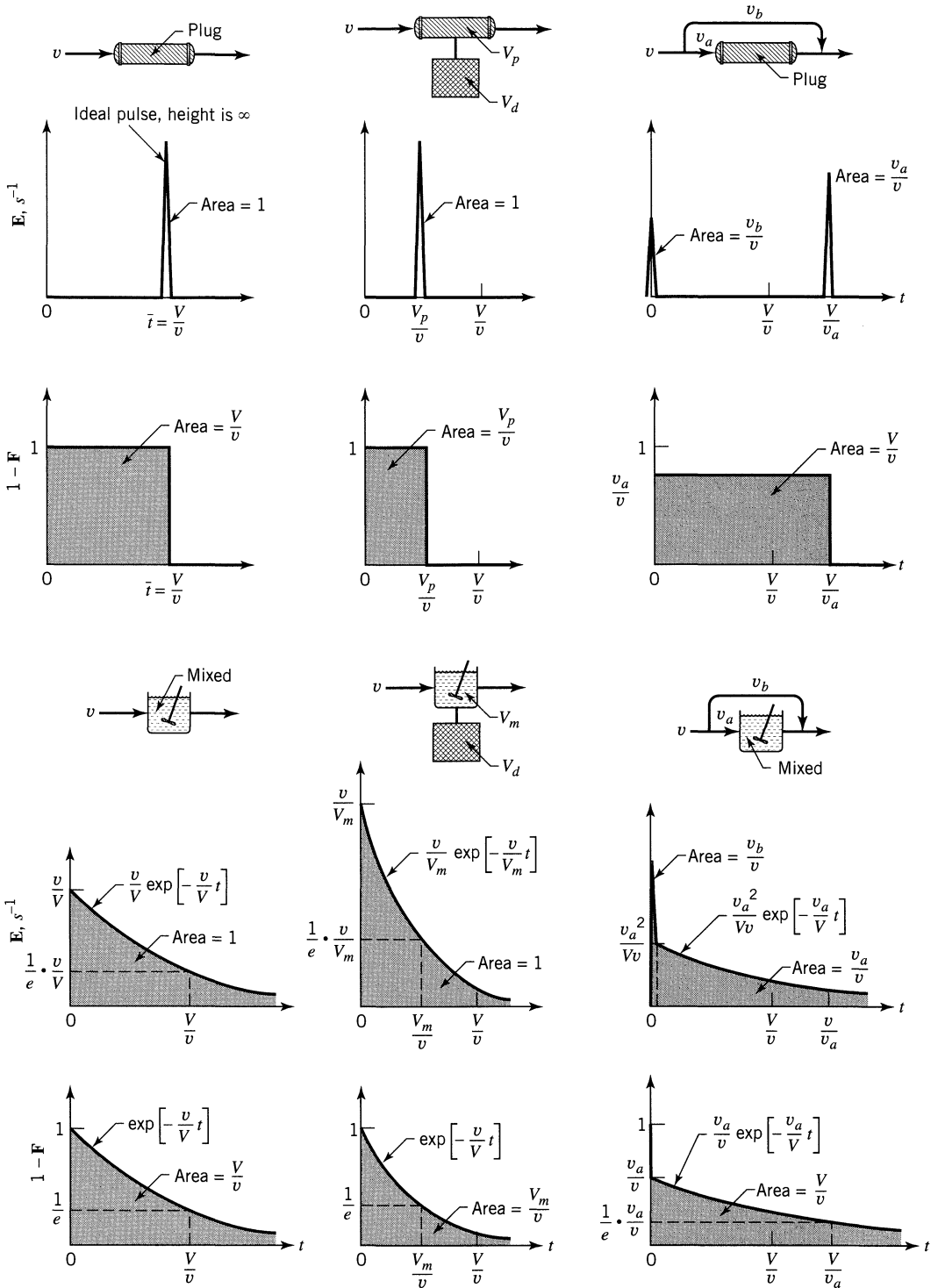


Figure 12.1 Various compartment flow models.

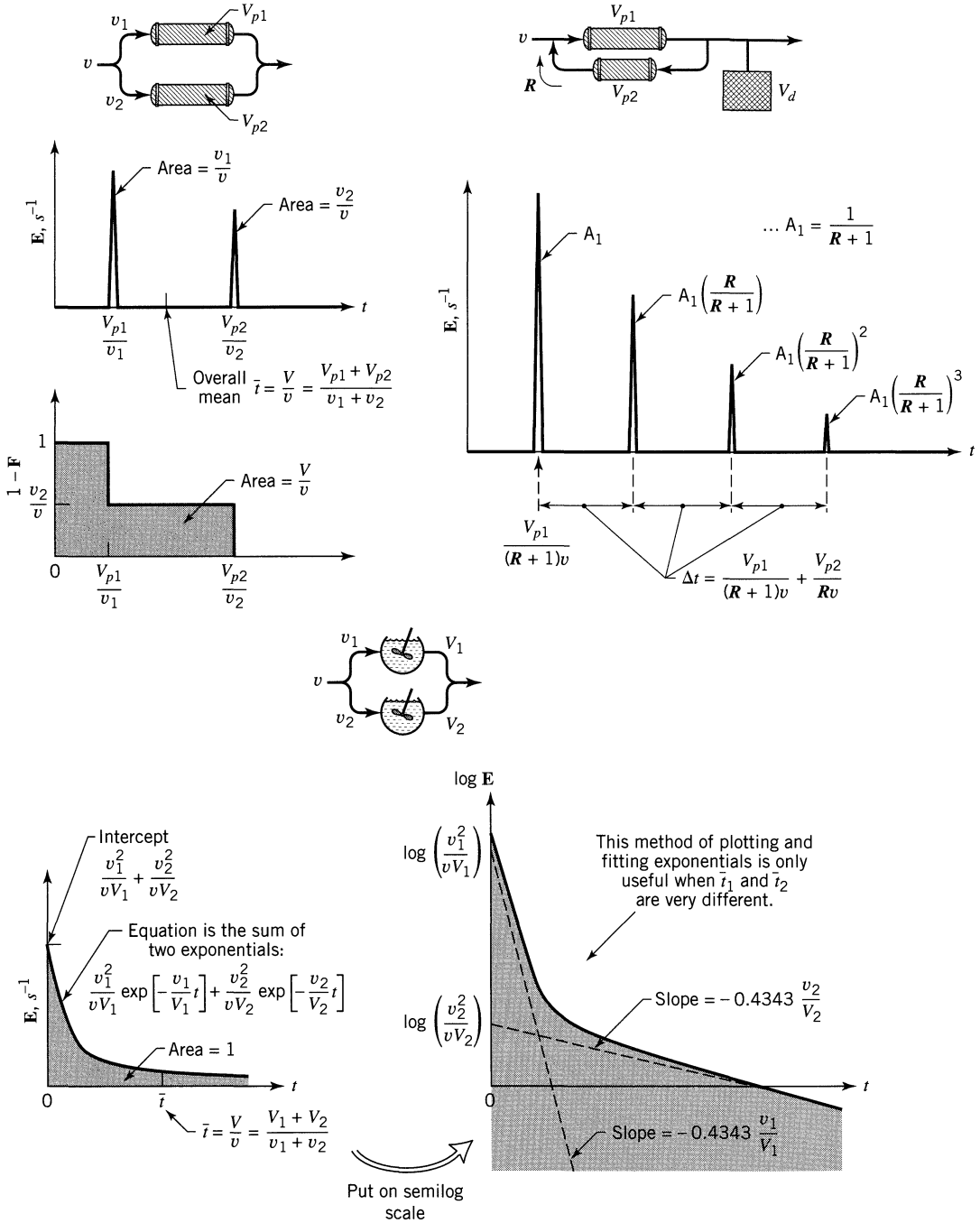


Figure 12.1 (Continued)

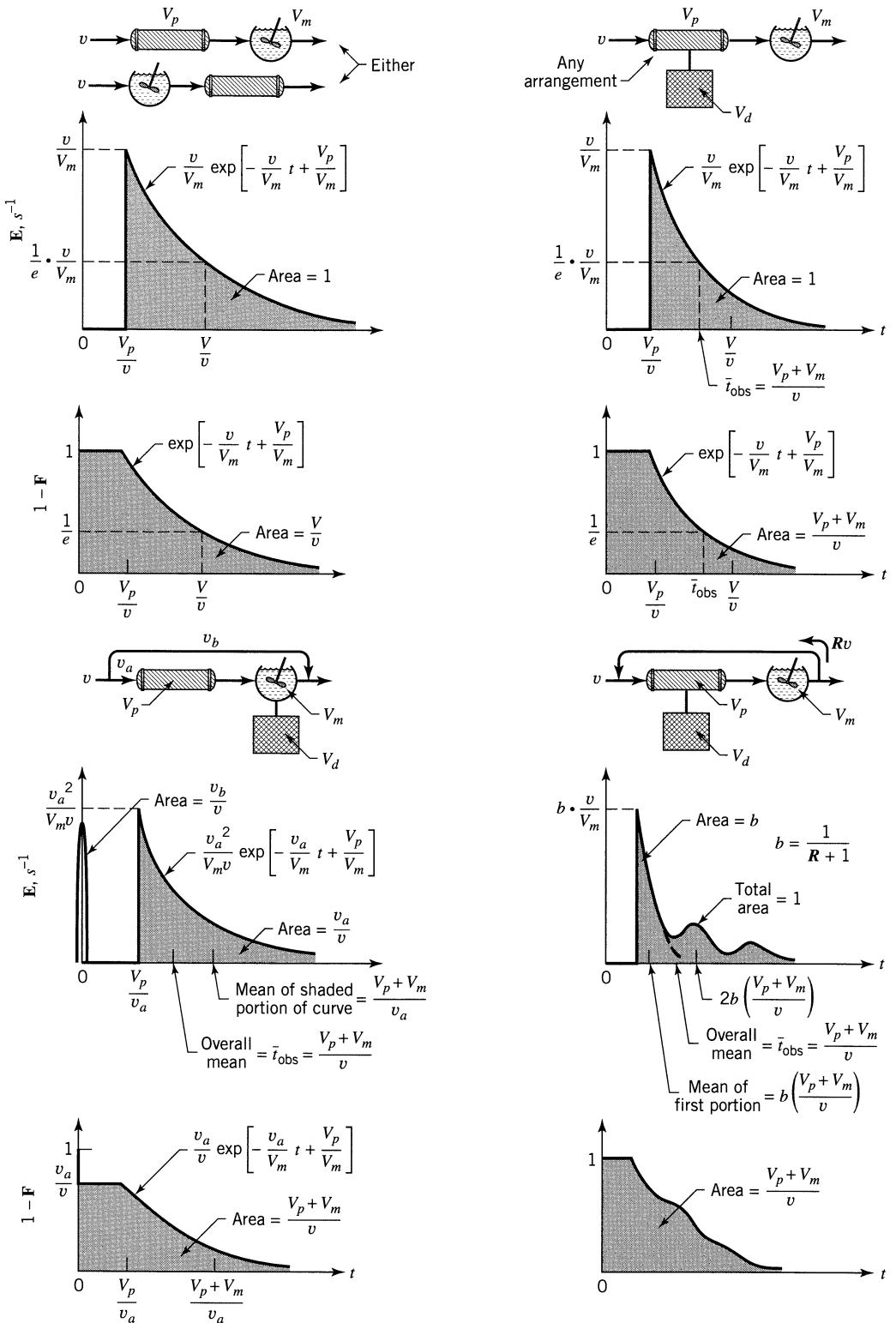


Figure 12.1 (Continued)

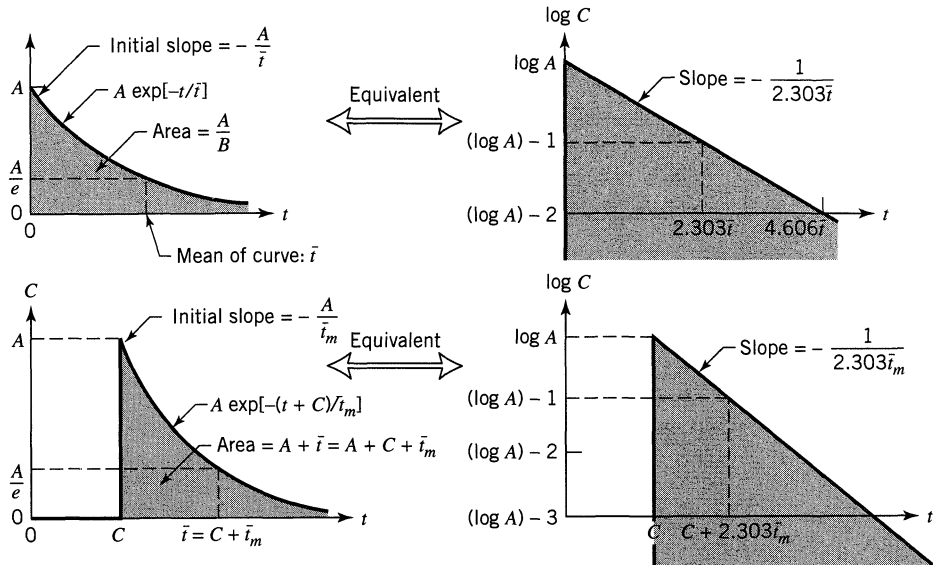


Figure 12.2 Properties of exponential decay tracer curves.

- (b) We must know both V and v if we want to properly evaluate all the elements of a model, including dead spaces. If we only measure \bar{t}_{obs} , we cannot find the size of these stagnant regions and must ignore them in our model building. Thus

If the real vessel has dead spaces:	$\bar{t}_{\text{obs}} < \bar{t}$	}	where	$\bar{t} = \frac{V}{v}$
If the real vessel has no dead spaces:	$\bar{t}_{\text{obs}} = \bar{t}$			$\bar{t}_{\text{obs}} = \frac{V_{\text{active}}}{v}$

- (c) The semilog plot is a convenient tool for evaluating the flow parameters of a mixed flow compartment. Just draw the tracer response curve on this plot, find the slope and intercept and this gives the quantities A , B , and C , as shown in Fig. 12.2.

Diagnosing Reactor Ills

These combined models are useful for diagnostic purposes, to pinpoint faulty flow and suggest causes. For example, if you expect plug flow and you know $\bar{t} = V/v$, Fig. 12.3 shows what you could find.

If you expect mixed flow, Fig. 12.4 shows what you may find.

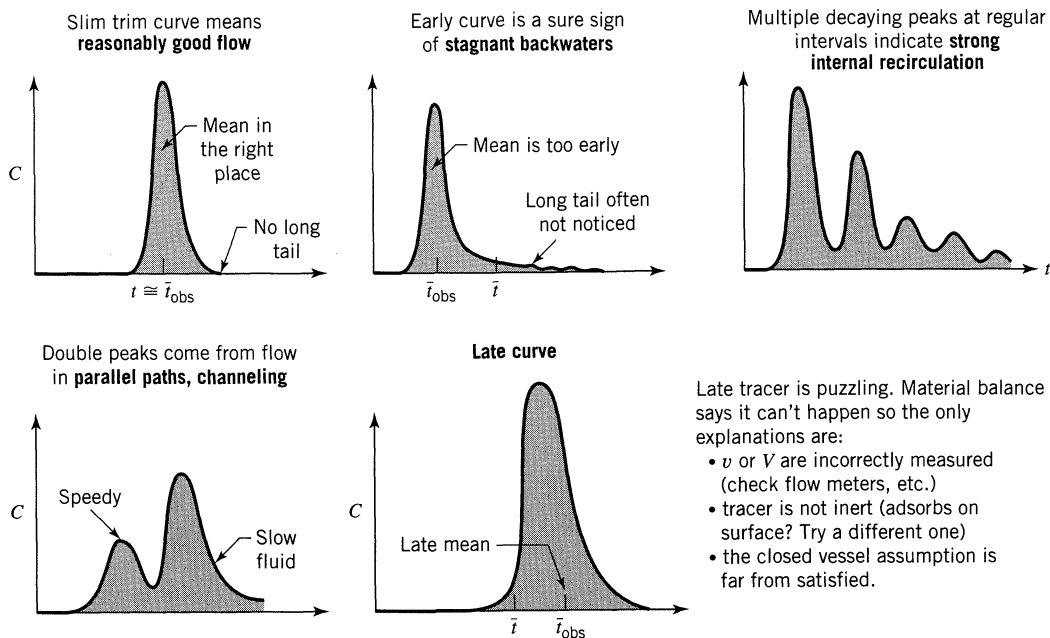


Figure 12.3 Misbehaving plug flow reactors.

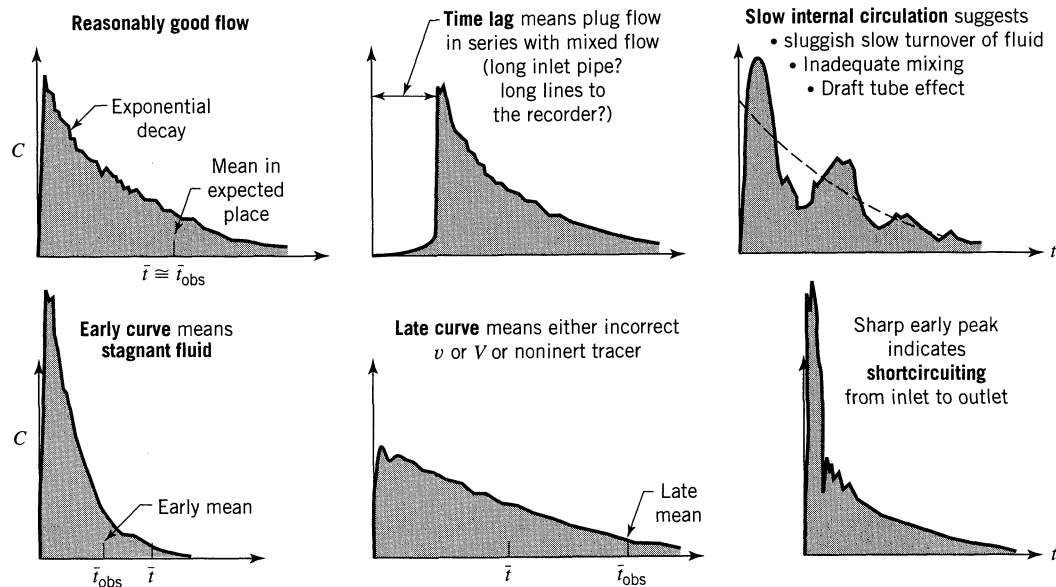


Figure 12.4 Misbehaving mixed flow reactors.

EXAMPLE 12.1 BEHAVIOR OF A G/L CONTACTOR

From the measured pulse tracer response curves (see figure), find the fraction of gas, of flowing liquid, and of stagnant liquid in the gas-liquid contactor shown in Fig. E12.1.

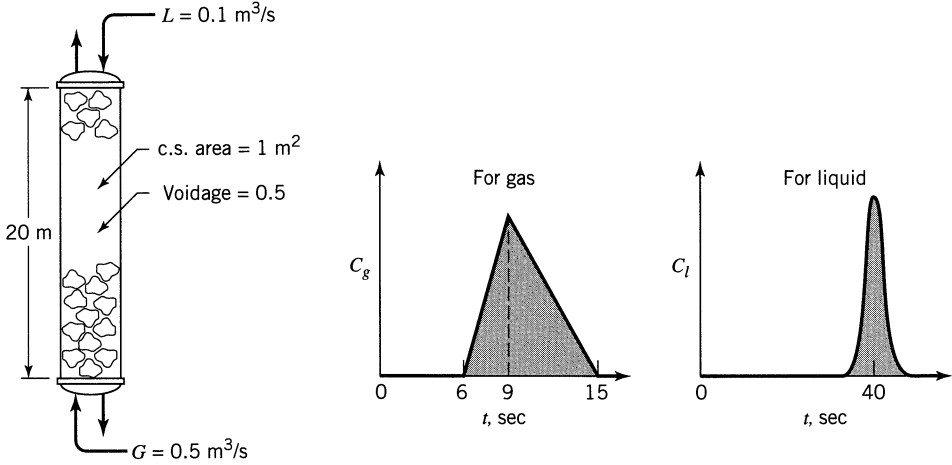


Figure E12.1

SOLUTION

To find V_g , V_l , and V_{stag} , first calculate \bar{t}_g and \bar{t}_l from the tracer curves. Thus from Fig. E12.1

$$\bar{t}_g = \frac{\sum tC}{\sum C} = \frac{8(9-6)(h/2) + 11(15-9)(h/2)}{(15-6)(h/2)} = 10 \text{ s}$$

and

$$\bar{t}_l = 40 \text{ s.}$$

Therefore

$$V_g = \bar{t}_g v_g = (10)(0.5) = 5 \text{ m}^3$$

$$V_l = \bar{t}_l v_l = 40(0.1) = 4 \text{ m}^3$$

In terms of void volume

$$\left. \begin{array}{l} \% G = 50\% \\ \% L = 40\% \\ \% \text{ stagnant} = 10\% \end{array} \right\} \leftarrow$$

EXAMPLE 12.2 CURING A MISBEHAVING REACTOR

At present our 6-m³ tank reactor gives 75% conversion for the first order reaction $A \rightarrow R$. However, since the reactor is stirred with an underpowered paddle turbine, we suspect incomplete mixing and poor flow patterns in the vessel. A pulse tracer shows that this is so and gives the flow model sketched in Fig. E12.2. What conversion can we expect if we replace the stirrer with one powerful enough to ensure mixed flow?

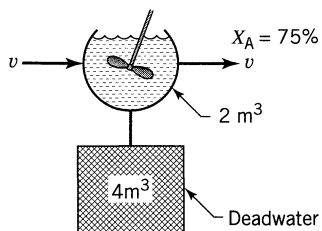


Figure E12.2

SOLUTION

Let subscript 1 represent today's reactor and subscript 2 represent the cured reactor. At present, from Chapter 5 for the MFR, we have

$$k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{C_{A0}}{C_A} - 1 = \frac{1}{0.25} - 1 = 3$$

$$\text{But } k\tau_2 = 3 \quad k\tau_1 = 3 \times 3 = 9$$

Therefore

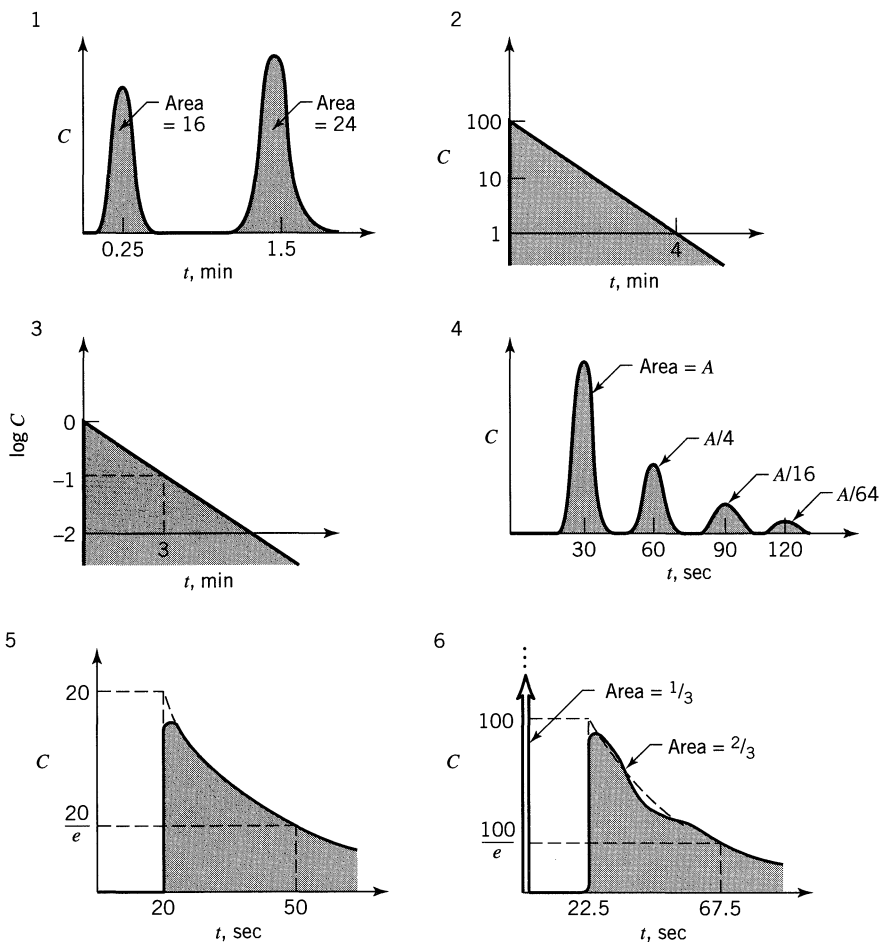
$$\frac{C_{A2}}{C_{A0}} = \frac{1}{k\tau_2 + 1} = \frac{1}{9 + 1} = 0.1$$

or

$$\underline{\underline{X_{A2} = 90\%}}$$

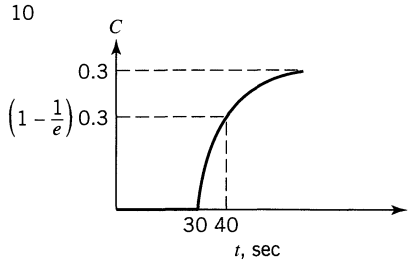
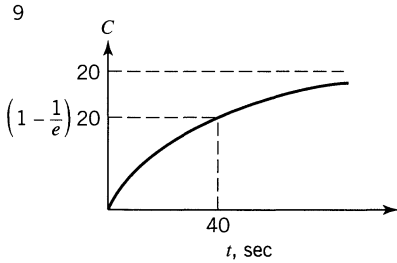
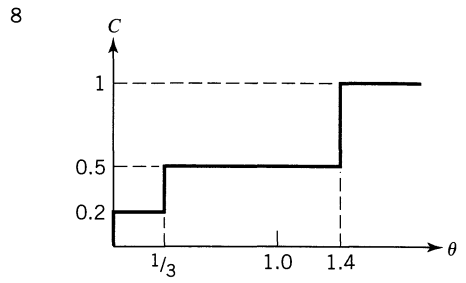
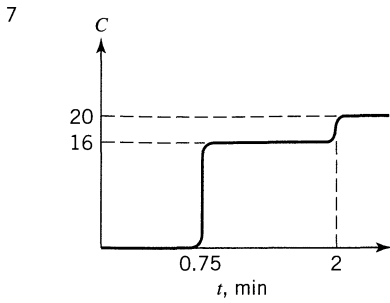
PROBLEMS

12.1. to 12.6. A pulse of concentrated NaCl solution is introduced as tracer into the fluid entering a vessel ($V = 1 \text{ m}^3, v = 1 \text{ m}^3/\text{min}$) and the concentration of tracer is measured in the fluid leaving the vessel. Develop a flow model to represent the vessel from the tracer output data sketched in Figs. P12.1 to P12.6.



Figures P12.1 through P12.6

12.7. to 12.10. A step input tracer test (switching from tap water to salt water, measuring the conductivity of fluid leaving the vessel) is used to explore the flow pattern of fluid through the vessel ($V = 1 \text{ m}^3, v = 1 \text{ m}^3/\text{min}$). Devise a flow model to represent the vessel from the data of Figs. P12.7 to P12.10.



Figures P12.7 through P12.10

12.11. The second order aqueous reaction $A + B \rightarrow R + S$ is run in a large tank reactor ($V = 6 \text{ m}^3$) and for an equimolar feed stream ($C_{A0} = C_{B0}$) conversion of reactants is 60%. Unfortunately, agitation in our reactor is rather inadequate and tracer tests of the flow within the reactor give the flow model sketched in Fig. P12.11. What size of mixed flow reactor will equal the performance of our present unit?

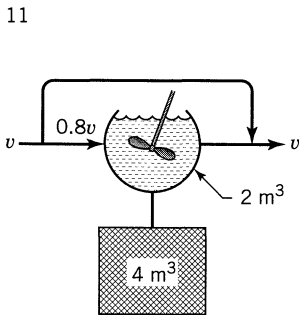


Figure P12.11

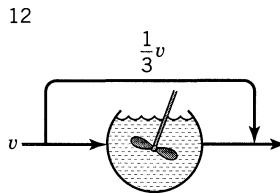


Figure P12.12

12.12. Repeat Example 12.2 with one change: The model for the present flow is as shown in Fig. P12.12.

Chapter 13

The Dispersion Model

Choice of Models

Models are useful for representing flow in real vessels, for scale up, and for diagnosing poor flow. We have different kinds of models depending on whether flow is close to plug, mixed, or somewhere in between.

Chapters 13 and 14 deal primarily with small deviations from plug flow. There are two models for this: the **dispersion model** and the **tanks-in-series** model. Use the one that is comfortable for you. They are roughly equivalent. These models apply to turbulent flow in pipes, laminar flow in very long tubes, flow in packed beds, shaft kilns, long channels, screw conveyers, etc.

For laminar flow in short tubes or laminar flow of viscous materials these models may not apply, and it may be that the parabolic velocity profile is the main cause of deviation from plug flow. We treat this situation, called the **pure convection model**, in Chapter 15.

If you are unsure which model to use go to the chart at the beginning of Chapter 15. It will tell you which model should be used to represent your setup.

13.1 AXIAL DISPERSION

Suppose an ideal pulse of tracer is introduced into the fluid entering a vessel. The pulse spreads as it passes through the vessel, and to characterize the spreading according to this model (see Fig. 13.1), we assume a diffusion-like process superimposed on plug flow. We call this **dispersion** or longitudinal dispersion to distinguish it from molecular diffusion. The dispersion coefficient **D** (m^2/s) represents this spreading process. Thus

- large **D** means rapid spreading of the tracer curve
- small **D** means slow spreading
- **D** = 0 means no spreading, hence plug flow

Also

$\left(\frac{\mathbf{D}}{uL}\right)$ is the dimensionless group characterizing the spread in the whole vessel.

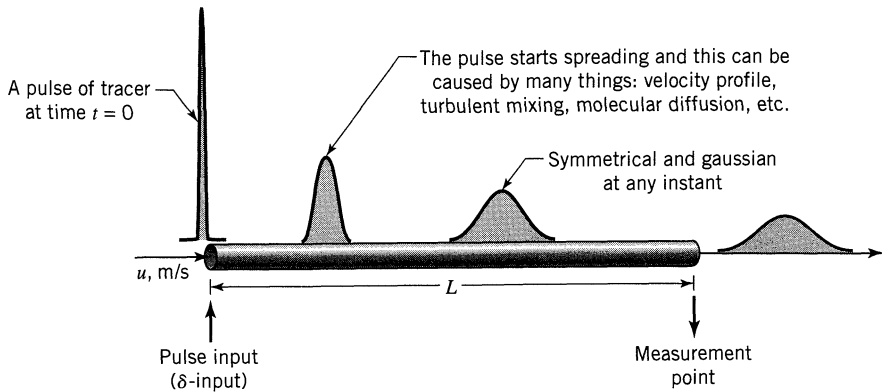


Figure 13.1 The spreading of tracer according to the dispersion model.

We evaluate \mathbf{D} or \mathbf{D}/uL by recording the shape of the tracer curve as it passes the exit of the vessel. In particular, we measure

\bar{t} = mean time of passage, or when the curve passes by the exit

σ^2 = variance, or a measure of the spread of the curve

These measures, \bar{t} and σ^2 , are directly linked by theory to \mathbf{D} and \mathbf{D}/uL . The mean, for continuous or discrete data, is defined as

$$\bar{t} = \frac{\int_0^{\infty} t C dt}{\int_0^{\infty} C dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad (1)$$

The variance is defined as

$$\sigma^2 = \frac{\int_0^{\infty} (t - \bar{t})^2 C dt}{\int_0^{\infty} C dt} = \frac{\int_0^{\infty} t^2 C dt}{\int_0^{\infty} C dt} - \bar{t}^2 \quad (2)$$

or in discrete form

$$\sigma^2 \cong \frac{\sum (t_i - \bar{t})^2 C_i \Delta t_i}{\sum C_i \Delta t_i} = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2 \quad (3)$$

The variance represents the square of the spread of the distribution as it passes the vessel exit and has units of $(\text{time})^2$. It is particularly useful for matching experimental curves to one of a family of theoretical curves. Figure 13.2 illustrates these terms.

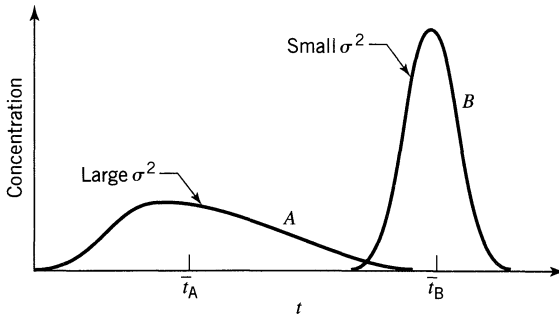


Figure 13.2

Consider plug flow of a fluid, on top of which is superimposed some degree of backmixing, the magnitude of which is independent of position within the vessel. This condition implies that there exist no stagnant pockets and no gross bypassing or short-circuiting of fluid in the vessel. This is called the dispersed plug flow model, or simply the **dispersion model**. Figure 13.3 shows the conditions visualized. Note that with varying intensities of turbulence or intermixing the predictions of this model should range from plug flow at one extreme to mixed flow at the other. As a result the reactor volume for this model will lie between those calculated for plug and mixed flow.

Since the mixing process involves a shuffling or redistribution of material either by slippage or eddies, and since this is repeated many, many times during the flow of fluid through the vessel we can consider these disturbances to be statistical in nature, somewhat as in molecular diffusion. For molecular diffusion in the x -direction the governing differential equation is given by Fick's law:

$$\frac{\partial C}{\partial t} = \mathcal{D} \frac{\partial^2 C}{\partial x^2} \quad (4)$$

where \mathcal{D} , the coefficient of molecular diffusion, is a parameter which uniquely characterizes the process. In an analogous manner we may consider all the contributions to intermixing of fluid flowing in the x -direction to be described

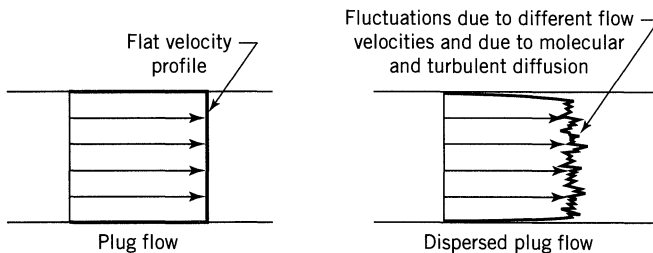


Figure 13.3 Representation of the dispersion (dispersed plug flow) model.

by a similar form of expression, or

$$\frac{\partial C}{\partial t} = \mathbf{D} \frac{\partial^2 C}{\partial x^2} \quad (5)$$

where the parameter \mathbf{D} , which we call the *longitudinal* or *axial dispersion coefficient*, uniquely characterizes the degree of backmixing during flow. We use the terms *longitudinal* and *axial* because we wish to distinguish mixing in the direction of flow from mixing in the lateral or radial direction, which is not our primary concern. These two quantities may be quite different in magnitude. For example, in streamline flow of fluids through pipes, axial mixing is mainly due to fluid velocity gradients, whereas radial mixing is due to molecular diffusion alone.

In dimensionless form where $z = (ut + x)/L$ and $\theta = t/\bar{t} = tu/L$, the basic differential equation representing this dispersion model becomes

$$\frac{\partial C}{\partial \theta} = \left(\frac{\mathbf{D}}{uL} \right) \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \quad (6)$$

where the dimensionless group $\left(\frac{\mathbf{D}}{uL} \right)$, called the vessel dispersion number, is the parameter that measures the extent of axial dispersion. Thus

$$\begin{aligned} \frac{\mathbf{D}}{uL} \rightarrow 0 & \quad \text{negligible dispersion, hence plug flow} \\ \frac{\mathbf{D}}{uL} \rightarrow \infty & \quad \text{large dispersion, hence mixed flow} \end{aligned}$$

This model usually represents quite satisfactorily flow that deviates not too greatly from plug flow, thus real packed beds and tubes (long ones if flow is streamline).

Fitting the Dispersion Model for Small Extents of Dispersion, $\mathbf{D}/uL < 0.01$

If we impose an idealized pulse onto the flowing fluid then dispersion modifies this pulse as shown in Fig. 13.1. For small extents of dispersion (if \mathbf{D}/uL is small) the spreading tracer curve does not significantly change in shape as it passes the measuring point (during the time it is being measured). Under these conditions the solution to Eq. 6 is not difficult and gives the symmetrical curve of Eq. 7 shown in Figs. 13.1 and 13.4.

$$C = \frac{1}{2\sqrt{\pi(\mathbf{D}/uL)}} \exp \left[-\frac{(1-\theta)^2}{4(\mathbf{D}/uL)} \right] \quad (7)$$

This represents a family of gaussian curves, also called error or Normal curves.

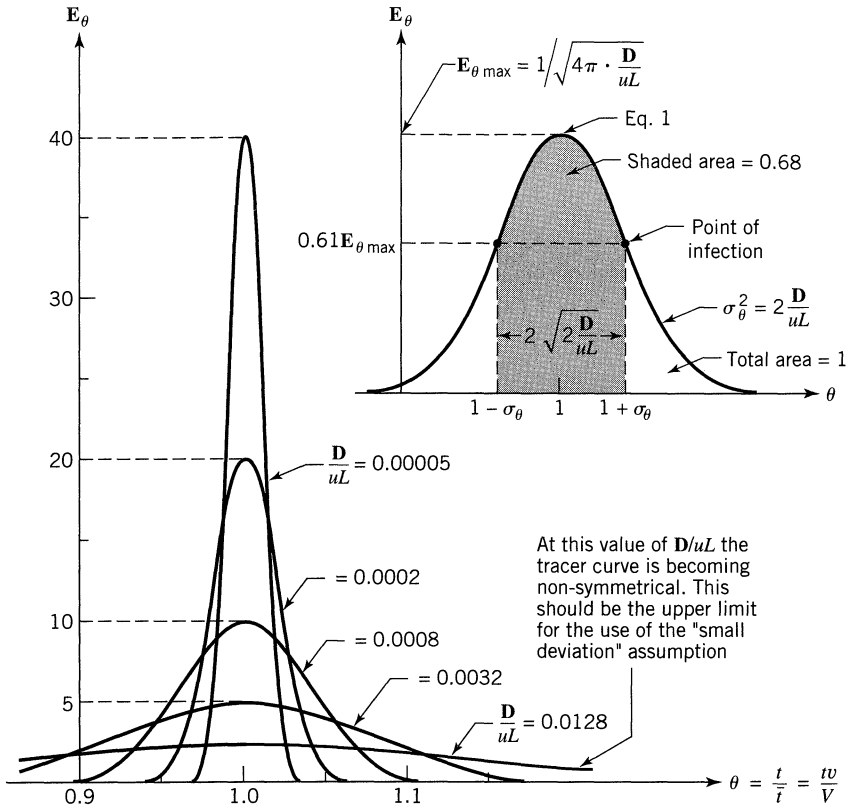


Figure 13.4 Relationship between D/uL and the dimensionless E_θ curve for small extents of dispersion, Eq. 7.

The equations representing this family are

$$\begin{aligned}
 E_\theta &= \bar{t} \cdot E = \frac{1}{\sqrt{4\pi(D/uL)}} \exp \left[-\frac{(1-\theta)^2}{4(D/uL)} \right] \\
 E &= \sqrt{\frac{u^3}{4\pi DL}} \exp \left[-\frac{(L-ut)^2}{4DLu} \right] \\
 \bar{t}_E &= \frac{V}{v} = \frac{L}{u} \quad \text{or} \quad \bar{\theta}_E = 1 \quad \text{mean of } E \text{ curve} \\
 \sigma_\theta^2 &= \frac{\sigma_t^2}{\bar{t}^2} = 2 \left(\frac{D}{uL} \right) \quad \text{or} \quad \sigma^2 = 2 \left(\frac{DL}{u^3} \right)
 \end{aligned} \tag{8}$$

Note that D/uL is the one parameter of this curve. Figure 13.4 shows a number of ways to evaluate this parameter from an experimental curve: by calculating its variance, by measuring its maximum height or its width at the point of inflection, or by finding that width which includes 68% of the area.

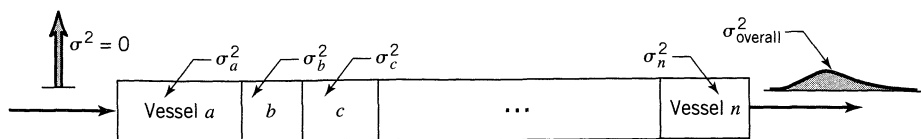


Figure 13.5 Illustration of additivity of means and of variances of the \mathbf{E} curves of vessels a, b, \dots, n .

Also note how the tracer spreads as it moves down the vessel. From the variance expression of Eq. 8 we find that

$$\sigma^2 \propto L \quad \text{or} \quad \left(\frac{\text{width of tracer}}{\text{curve}} \right)^2 \propto L$$

Fortunately, for small extents of dispersion numerous simplifications and approximations in the analysis of tracer curves are possible. First, the shape of the tracer curve is insensitive to the boundary condition imposed on the vessel, whether closed or open (see above Eq. 11.1). So for both closed and open vessels $C_{\text{pulse}} = \mathbf{E}$ and $C_{\text{step}} = \mathbf{F}$.

For a series of vessels the \bar{t} and σ^2 of the individual vessels are additive, thus, referring to Fig. 13.5 we have

$$\bar{t}_{\text{overall}} = \bar{t}_a + \bar{t}_b + \dots = \frac{V_a}{v} + \frac{V_b}{v} + \dots = \left(\frac{L}{u} \right)_a + \left(\frac{L}{u} \right)_b + \dots \quad (9)$$

and

$$\sigma_{\text{overall}}^2 = \sigma_a^2 + \sigma_b^2 + \dots = 2 \left(\frac{DL}{u^3} \right)_a + 2 \left(\frac{DL}{u^3} \right)_b + \dots \quad (10)$$

The additivity of times is expected, but the additivity of variance is not generally expected. This is a useful property since it allows us to subtract for the distortion of the measured curve caused by input lines, long measuring leads, etc.

This additivity property of variances also allows us to treat any one-shot tracer input, no matter what its shape, and to extract from it the variance of the \mathbf{E} curve of the vessel. So, on referring to Fig. 13.6, if we write for a one-shot input

$$\Delta\sigma^2 = \sigma_{\text{out}}^2 - \sigma_{\text{in}}^2 \quad (11)$$

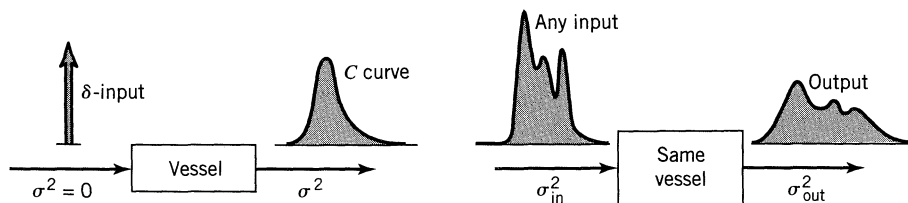


Figure 13.6 Increase in variance is the same in both cases, or $\sigma^2 = \sigma_{\text{out}}^2 - \sigma_{\text{in}}^2 = \Delta\sigma^2$.

Aris (1959) has shown, for small extents of dispersion, that

$$\frac{\sigma_{\text{out}}^2 - \sigma_{\text{in}}^2}{(\bar{t}_{\text{out}} - \bar{t}_{\text{in}})^2} = \frac{\Delta\sigma^2}{(\Delta\bar{t})^2} = \Delta\sigma_{\theta}^2 = 2\left(\frac{\mathbf{D}}{uL}\right) \quad (12)$$

Thus no matter what the shape of the input curve, the \mathbf{D}/uL value for the vessel can be found.

The goodness of fit for this simple treatment can only be evaluated by comparison with the more exact but much more complex solutions. From such a comparison we find that the maximum error in estimate of \mathbf{D}/uL is given by

$$\text{error} < 5\% \text{ when } \frac{\mathbf{D}}{uL} < 0.01$$

Large Deviation from Plug Flow, $\frac{\mathbf{D}}{uL} > 0.01$

Here the pulse response is broad and it passes the measurement point slowly enough that it changes shape—it spreads—as it is being measured. This gives a nonsymmetrical \mathbf{E} curve.

An additional complication enters the picture for large \mathbf{D}/uL : What happens right at the entrance and exit of the vessel strongly affects the shape of the tracer curve as well as the relationship between the parameters of the curve and \mathbf{D}/uL .

Let us consider two types of boundary conditions: either the flow is undisturbed as it passes the entrance and exit boundaries (we call this the open b.c.), or you have plug flow outside the vessel up to the boundaries (we call this the closed b.c.). This leads to four combinations of boundary conditions, closed-closed, open-open, and mixed. Figure 13.7 illustrates the closed and open extremes, whose RTD curves are designated as \mathbf{E}_{cc} and \mathbf{E}_{oo} .

Now only one boundary condition gives a tracer curve which is identical to the \mathbf{E} function and which fits all the mathematics of Chapter 11, and that is the closed vessel. For all other boundary conditions you do not get a proper RTD.

In all cases you can evaluate \mathbf{D}/uL from the parameters of the tracer curves; however, each curve has its own mathematics. Let us look at the tracer curves for closed and for the open boundary conditions.

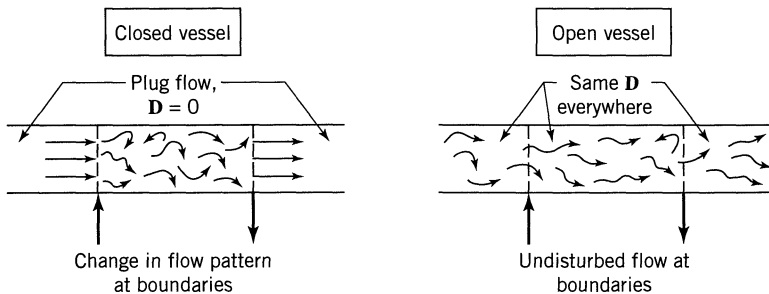


Figure 13.7 Various boundary conditions used with the dispersion model.

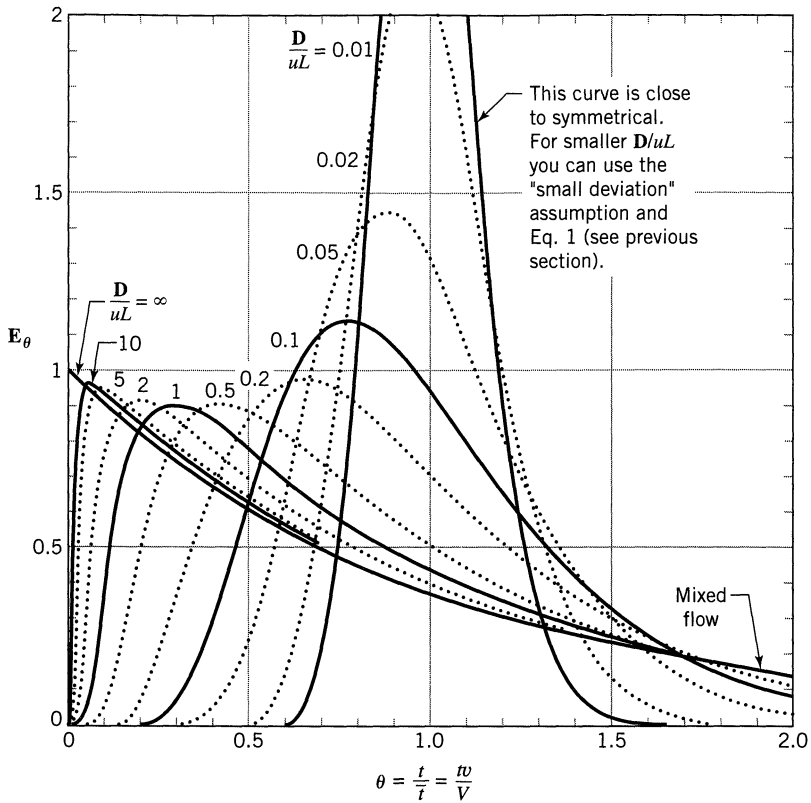


Figure 13.8 Tracer response curves for closed vessels and large deviations from plug flow.

Closed Vessel. Here an analytic expression for the **E** curve is not available. However, we can construct the curve by numerical methods, see Fig. 13.8, or evaluate its mean and variance exactly, as was first done by van der Laan (1958). Thus

$$\begin{aligned}
 \bar{t}_E = \bar{t} = \frac{V}{v} \quad \dots \text{ or } \dots \quad \bar{\theta}_E = \frac{\bar{t}_E}{\bar{t}} = \frac{\bar{t}_E v}{V} = 1 \\
 \sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = 2\left(\frac{D}{uL}\right) - 2\left(\frac{D}{uL}\right)^2 [1 - e^{-uL/D}]
 \end{aligned}
 \tag{13}$$

Open Vessel. This represents a convenient and commonly used experimental device, a section of long pipe (see Fig. 13.9). It also happens to be the only physical situation (besides small D/uL) where the analytical expression for the **E** curve is not too complex. The results are given by the response curves shown

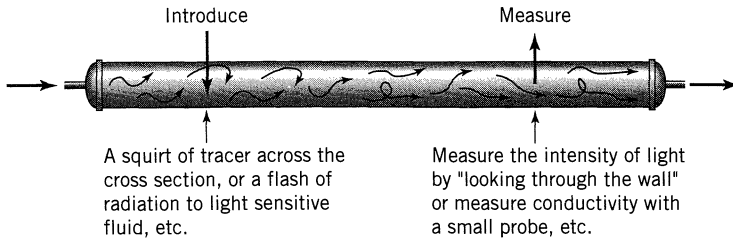


Figure 13.9 The open-open vessel boundary condition.

in Fig. 13.10, and by the following equations, first derived by Levenspiel and Smith (1957).

$$E_{\theta,oo} = \frac{1}{\sqrt{4\pi(D/uL)}} \exp\left[-\frac{(1-\theta)^2}{4\theta(D/uL)}\right] \quad (14)$$

$$E_{t,oo} = \frac{u}{\sqrt{4\pi Dt}} \exp\left[-\frac{(L-ut)^2}{4Dt}\right]$$

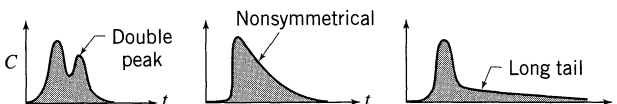
$$\bar{\theta}_{E,oo} = \frac{\bar{t}_{E,oo}}{\bar{t}} = 1 + 2\left(\frac{D}{uL}\right) \quad \dots \text{or} \dots \quad t_{E,oo} = \frac{V}{v} \left[1 + 2\frac{D}{uL}\right] \quad (15)$$

open-open vessel

$$\sigma_{\theta,oo}^2 = \frac{\sigma_{t,oo}^2}{\bar{t}^2} = 2\frac{D}{uL} + 8\left(\frac{D}{uL}\right)^2$$

Comments

- For small D/uL the curves for the different boundary conditions all approach the “small deviation” curve of Eq. 8. At larger D/uL the curves differ more and more from each other.
- To evaluate D/uL either match the measured tracer curve or the measured σ^2 to theory. Matching σ^2 is simplest, though not necessarily best; however, it is often used. But be sure to use the right boundary conditions.
- If the flow deviates greatly from plug (D/uL large) chances are that the real vessel doesn't meet the assumption of the model (a lot of independent random fluctuations). Here it becomes questionable whether the model should even be used. I hesitate when $D/uL > 1$.
- You must always ask whether the model should be used. You can always match σ^2 values, but if the shape looks wrong, as shown in the accompanying sketches, don't use this model, use some other model.



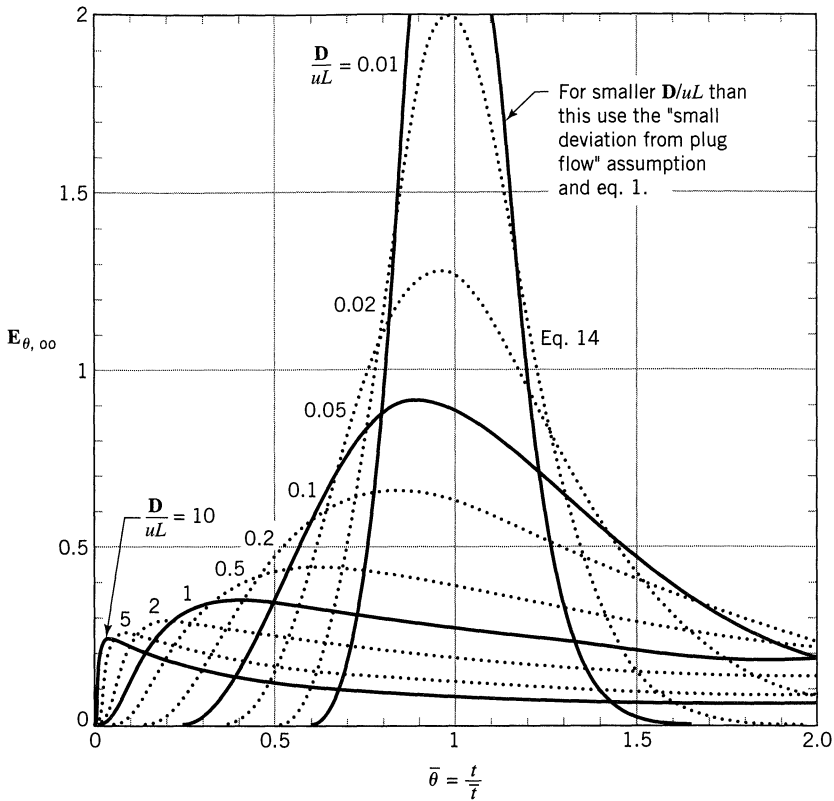


Figure 13.10 Tracer response curves for “open” vessels having large deviations from plug flow.

- (e) For large D/uL the literature is profuse and conflicting, primarily because of the unstated and unclear assumptions about what is happening at the vessel boundaries. The treatment of end conditions is full of mathematical subtleties as noted above, and the additivity of variances is questionable. Because of all this we should be very careful in using the dispersion model where backmixing is large, particularly if the system is not closed.
- (f) We will not discuss the equations and curves for the open-closed or closed-open boundary conditions. These can be found in Levenspiel (1996).

Step Input of Tracer

Here the output F curve is S-shaped and is obtained by integrating the corresponding E curve. Thus at any time t or θ

$$F = \int_0^{\theta} E_{\theta} d\theta = \int_0^t E dt \quad (16)$$

The shape of the F curve depends on D/uL and the boundary conditions for the vessel. Analytical expressions are not available for any of the F curves;

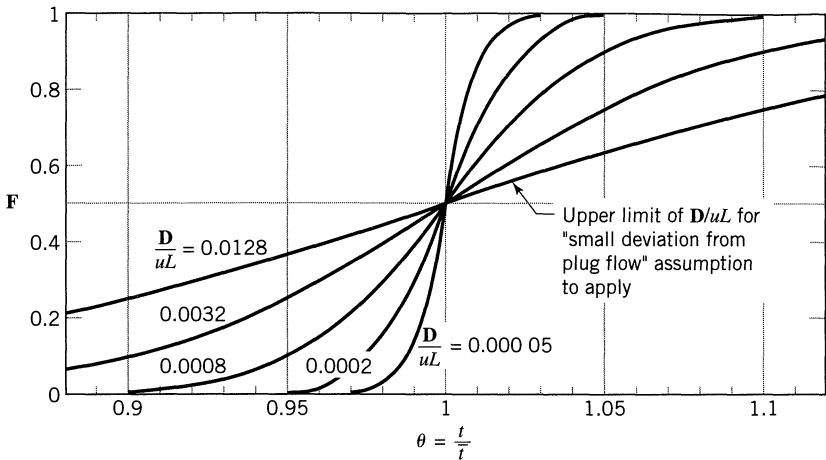


Figure 13.11 Step response curves for small deviations from plug flow.

however, their graphs can be constructed. Two typical cases are displayed below, in Figs. 13.11 and 13.13.

Small Deviation from Plug Flow, $D/uL < 0.01$ From Eqs. 8 and 16 we can find the curves of Fig. 13.11, as shown. For these small deviations from plug flow we can find D/uL directly by plotting the experimental data on probability graph paper as indicated in Fig. 13.12. Example 13.2 shows in detail how this is done.

Step Response for Large Dispersion, $D/uL > 0.01$. For large deviations from plug flow, the problem of boundary conditions must be considered, the resulting S-shaped response curves are not symmetrical, their equations are not available, and they are best analyzed by first differentiating them to give the corresponding C_{pulse} curve. Figure 13.13 shows an example of this family of curves.

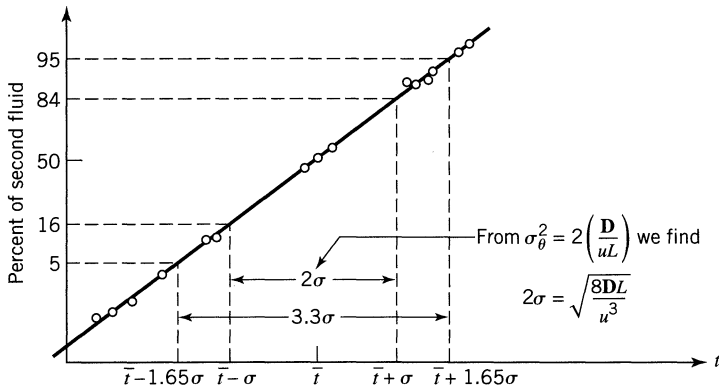


Figure 13.12 Probability plot of a step response signal. From this we find D/uL directly.

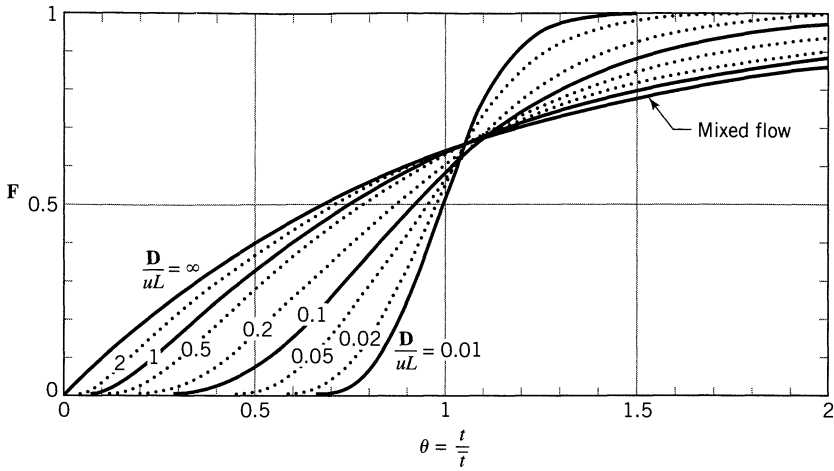


Figure 13.13 Step response curves for large deviations from plug flow in closed vessels.

Comments

- (a) One direct commercial application of the step experiment is to find the zone of intermixing—the contaminated width—between two fluids of somewhat similar properties flowing one after the other in a long pipeline. Given D/uL we find this from the probability plot of Fig. 13.12. Design charts to ease the calculation are given by Levenspiel (1958a).
- (b) Should you use a pulse or step injection experiment? Sometimes one type of experiment is naturally more convenient for one of many reasons. In such a situation this question does not arise. But when you do have a choice, then the pulse experiment is preferred because it gives a more “honest” result. The reason is that the F curve integrates effects; it gives a smooth good-looking curve which could well hide real effects. For example, Fig. 13.14 shows the corresponding E and F curves for a given vessel.

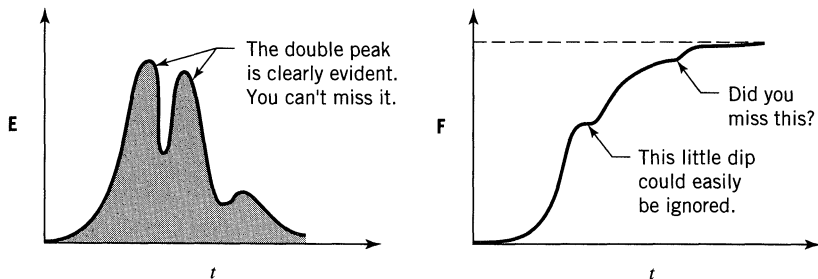


Figure 13.14 Sensitivity of the E and F curves for the same flow.

EXAMPLE 13.1 *D_uL FROM A C_{pulse} CURVE*

On the assumption that the closed vessel of Example 11.1, Chapter 11, is well represented by the dispersion model, calculate the vessel dispersion number D_{uL} . The C versus t tracer response of this vessel is

$t, \text{ min}$	0	5	10	15	20	25	30	35
$C_{\text{pulse}}, \text{ gm/liter}$	0	3	5	5	4	2	1	0

SOLUTION

Since the C curve for this vessel is broad and unsymmetrical, see Fig. 11.E1, let us guess that dispersion is too large to allow use of the simplification leading to Fig. 13.4. We thus start with the variance matching procedure of Eq. 18. The mean and variance of a continuous distribution measured at a finite number of equidistant locations is given by Eqs. 3 and 4 as

$$\bar{t} = \frac{\sum t_i C_i}{\sum C_i}$$

and

$$\sigma^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \bar{t}^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \left[\frac{\sum t_i C_i}{\sum C_i} \right]^2$$

Using the original tracer concentration-time data, we find

$$\sum C_i = 3 + 5 + 5 + 4 + 2 + 1 = 20$$

$$\sum t_i C_i = (5 \times 3) + (10 \times 5) + \dots + (30 \times 1) = 300 \text{ min}$$

$$\sum t_i^2 C_i = (25 \times 3) + (100 \times 5) + \dots + (900 \times 1) = 5450 \text{ min}^2$$

Therefore

$$\bar{t} = \frac{300}{20} = 15 \text{ min}$$

$$\sigma^2 = \frac{5450}{20} - \left(\frac{300}{20} \right)^2 = 47.5 \text{ min}^2$$

and

$$\sigma_{\theta}^2 = \frac{\sigma^2}{\bar{t}^2} = \frac{47.5}{(15)^2} = 0.211$$

Now for a closed vessel Eq. 13 relates the variance to \mathbf{D}/uL . Thus

$$\sigma_{\theta}^2 = 0.211 = 2 \frac{\mathbf{D}}{uL} - 2 \left(\frac{\mathbf{D}}{uL} \right)^2 (1 - e^{-uL/\mathbf{D}})$$

Ignoring the second term on the right, we have as a first approximation

$$\frac{\mathbf{D}}{uL} \cong 0.106$$

Correcting for the term ignored we find by trial and error that

$$\frac{\mathbf{D}}{uL} = \underline{\underline{0.120}}$$

Our original guess was correct: This value of \mathbf{D}/uL is much beyond the limit where the simple gaussian approximation should be used. ■

EXAMPLE 13.2 \mathbf{D}/uL FROM AN F CURVE

von Rosenberg (1956) studied the displacement of benzene by *n*-butyrate in a 38 mm diameter packed column 1219 mm long, measuring the fraction of *n*-butyrate in the exit stream by refractive index methods. When graphed, the fraction of *n*-butyrate versus time was found to be S-shaped. This is the **F** curve, and it is shown in Fig. E13.2a for von Rosenberg's run at the lowest flow rate, where $u = 0.0067$ mm/s, which is about 0.5 m/day.

Find the vessel dispersion number of this system.

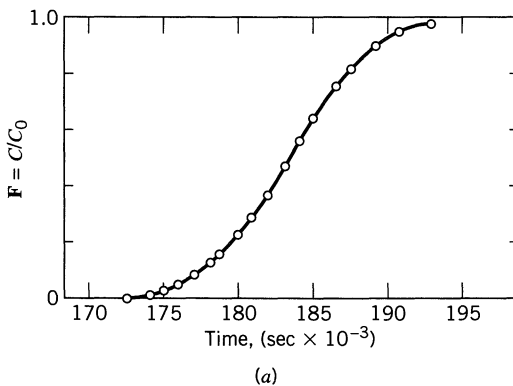
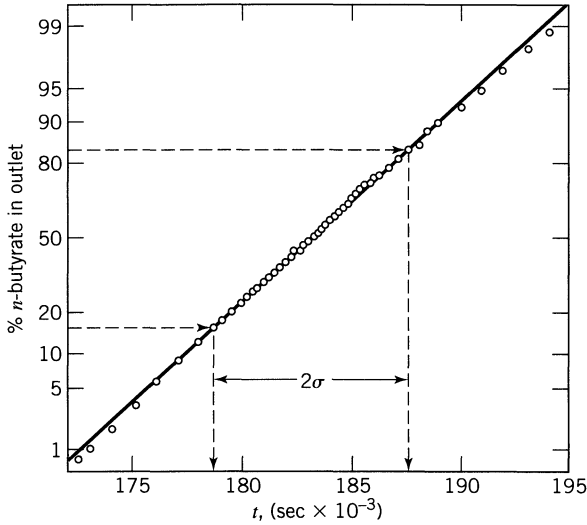


Figure E13.2a From von Rosenberg (1956).

SOLUTION

Instead of taking slopes of the **F** curve to give the **E** curve and then determining the spread of this curve, let us use the probability paper method. So, plotting the data on this paper does actually give close to a straight line, as shown in Fig. E13.2b.



(b)

Figure E13.2b From Levenspiel and Smith (1957).

To find the variance and \mathbf{D}/uL from a probability graph is a simple matter. Just follow the procedure illustrated in Fig. 13.12. Thus Fig. E13.2b shows that

the 16th percentile point falls at $t = 178\,550$ s

the 84th percentile point falls at $t = 187\,750$ s

and this time interval represents 2σ . Therefore the standard deviation is

$$\sigma = \frac{187\,750 - 178\,500}{2} = 4600 \text{ s}$$

We need this standard deviation in dimensionless time units if we are to find **D**. Therefore

$$\sigma_\theta = \frac{\sigma}{\bar{t}} = (4600 \text{ s}) \left(\frac{0.0067 \text{ mm/s}}{1219 \text{ mm}} \right) = 0.0252$$

Hence the variance

$$\sigma_{\theta}^2 = (0.0252)^2 = 0.00064$$

and from Eq. 8

$$\frac{D}{uL} = \frac{\sigma_{\theta}^2}{2} = \underline{\underline{0.00032}}$$

Note that the value of D/uL is well below 0.01, justifying the use of the gaussian approximation to the tracer curve and this whole procedure.

EXAMPLE 13.3 D/uL FROM A ONE-SHOT INPUT

Find the vessel dispersion number in a fixed-bed reactor packed with 0.625-cm catalyst pellets. For this purpose tracer experiments are run in equipment shown in Fig. E13.3.

The catalyst is laid down in a haphazard manner above a screen to a height of 120 cm, and fluid flows downward through this packing. A sloppy pulse of

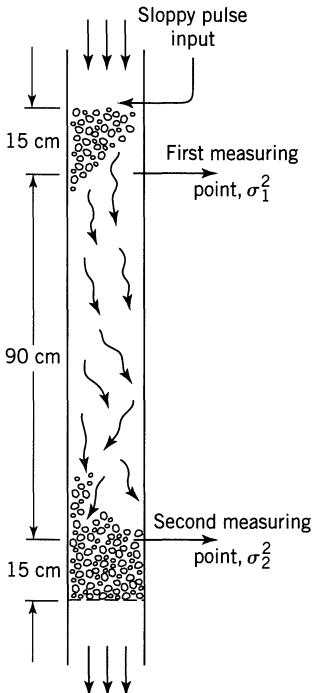


Figure E13.3

radioactive tracer is injected directly above the bed, and output signals are recorded by Geiger counters at two levels in the bed 90 cm apart.

The following data apply to a specific experimental run. Bed voidage = 0.4, superficial velocity of fluid (based on an empty tube) = 1.2 cm/sec, and variances of output signals are found to be $\sigma_1^2 = 39 \text{ sec}^2$ and $\sigma_2^2 = 64 \text{ sec}^2$. Find \mathbf{D}/uL .

SOLUTION

Bischoff and Levenspiel (1962) have shown that as long as the measurements are taken at least two or three particle diameters into the bed, then the open vessel boundary conditions hold closely. This is the case here because the measurements are made 15 cm into the bed. As a result this experiment corresponds to a one-shot input to an open vessel for which Eq. 12 holds. Thus

$$\Delta\sigma^2 = \sigma_2^2 - \sigma_1^2 = 64 - 39 = 25 \text{ sec}^2$$

or in dimensionless form

$$\Delta\sigma_\theta^2 = \Delta\sigma^2 \left(\frac{v}{V}\right)^2 = (25 \text{ sec}^2) \left[\frac{1.2 \text{ cm/sec}}{(90 \text{ cm})(0.4)}\right]^2 = \frac{1}{36}$$

from which the dispersion number is

$$\frac{\mathbf{D}}{uL} = \frac{\Delta\sigma_\theta^2}{2} = \underline{\underline{\frac{1}{72}}}$$

13.2 CORRELATIONS FOR AXIAL DISPERSION

The vessel dispersion number \mathbf{D}/uL is a product of two terms

$$\frac{\mathbf{D}}{uL} = \left(\begin{array}{c} \text{intensity of} \\ \text{dispersion} \end{array}\right) \left(\begin{array}{c} \text{geometric} \\ \text{factor} \end{array}\right) = \left(\frac{\mathbf{D}}{ud}\right) \left(\frac{d}{L}\right)$$

where

$$\frac{\mathbf{D}}{ud} = f \left(\begin{array}{c} \text{fluid} \\ \text{properties} \end{array}\right) \left(\begin{array}{c} \text{flow} \\ \text{dynamics} \end{array}\right) = f \left[\left(\begin{array}{c} \text{Schmidt} \\ \text{no.} \end{array}\right) \left(\begin{array}{c} \text{Reynolds} \\ \text{no.} \end{array}\right) \right]$$

and where

$$d \text{ is a characteristic length} = d_{\text{tube}} \text{ or } d_p$$

Experiments show that the dispersion model well represents flow in packed beds and in pipes. Thus theory and experiment give \mathbf{D}/ud for these vessels. We summarize them in the next three charts.

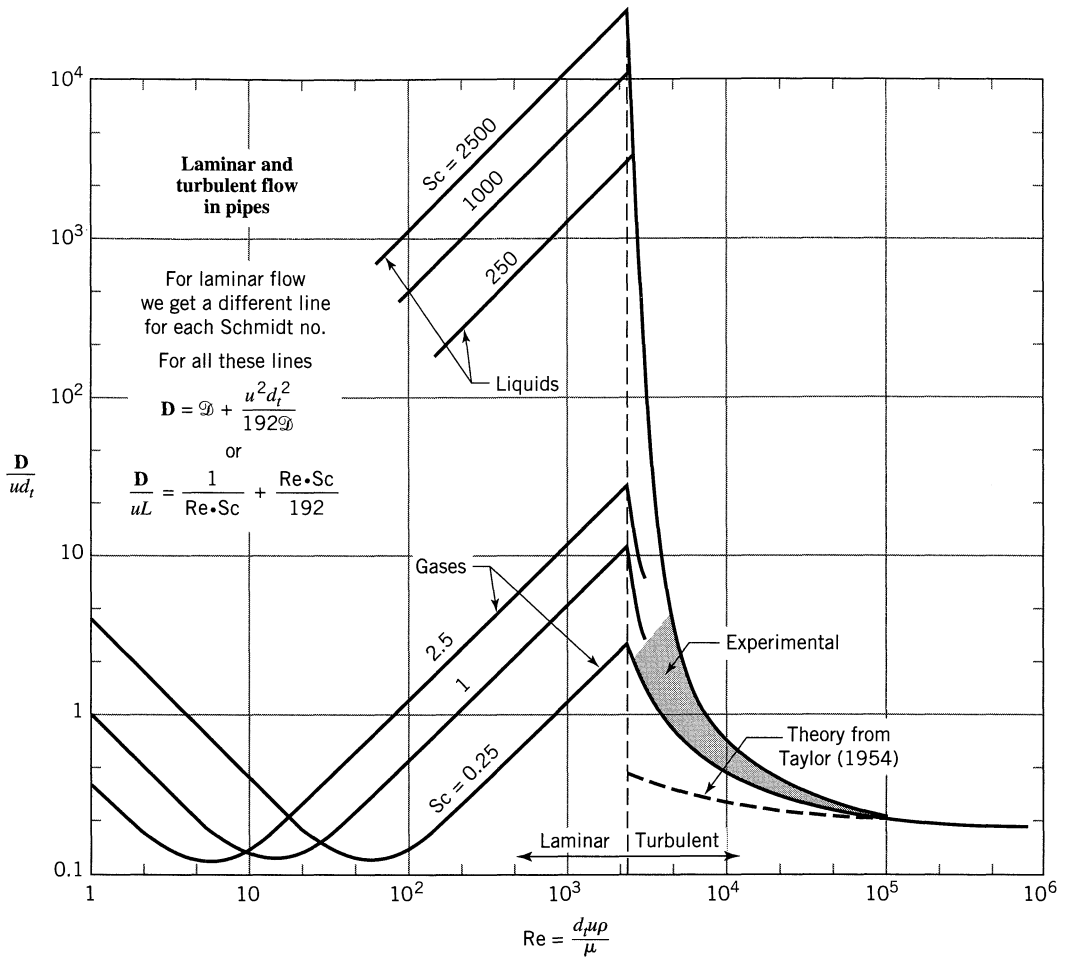


Figure 13.15 Correlation for the dispersion of fluids flowing in pipes, adapted from Levenspiel (1958b).

Figures 13.15 and 13.16 show the findings for flow in pipes. This model represents turbulent flow, but only represents streamline flow in pipes when the pipe is long enough to achieve radial uniformity of a pulse of tracer. For liquids this may require a rather long pipe, and Fig. 13.16 shows these results. Note that molecular diffusion strongly affects the rate of dispersion in laminar flow. At low flow rate it promotes dispersion; at higher flow rate it has the opposite effect.

Correlations similar to these are available or can be obtained for flow in beds of porous and/or adsorbing solids, in coiled tubes, in flexible channels, for pulsating flow, for non-Newtonians, and so on. These are given in Chapter 64 of Levenspiel (1996).

Figure 13.17 shows the findings for packed beds.

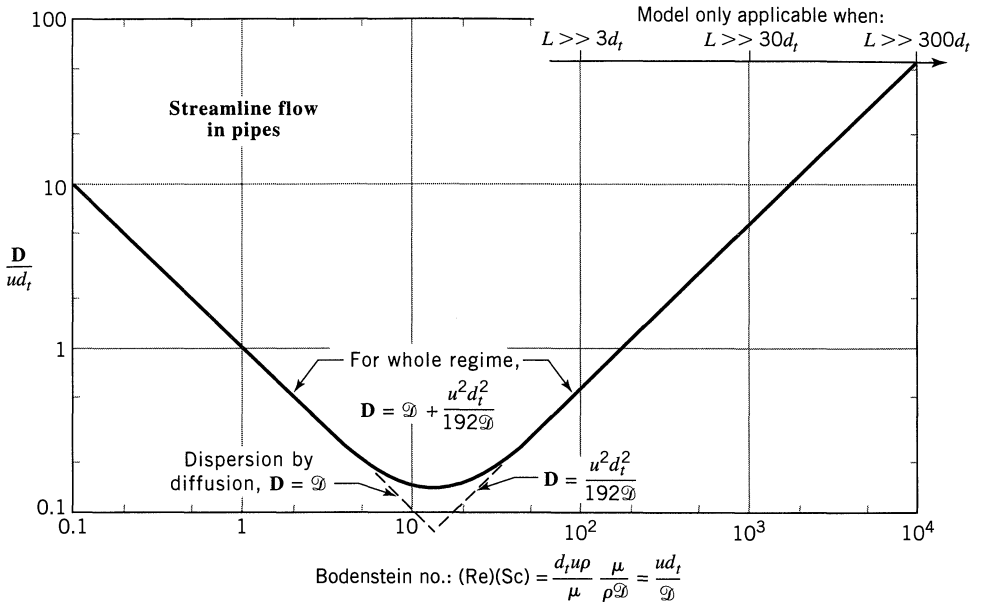


Figure 13.16 Correlation for dispersion for streamline flow in pipes; prepared from Taylor (1953, 1954a) and Aris (1956).

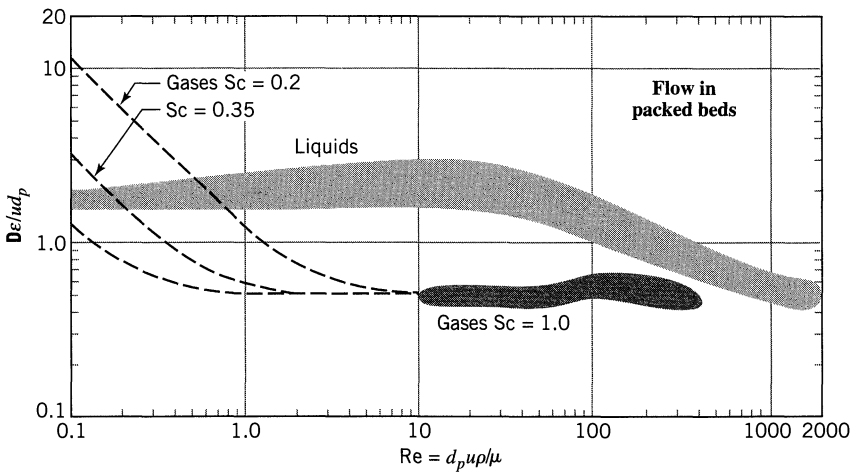
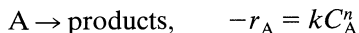


Figure 13.17 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds; prepared in part from Bischoff (1961).

13.3 CHEMICAL REACTION AND DISPERSION

Our discussion has led to the measure of dispersion by a dimensionless group D/ul . Let us now see how this affects conversion in reactors.

Consider a steady-flow chemical reactor of length L through which fluid is flowing at a constant velocity u , and in which material is mixing axially with a dispersion coefficient D . Let an n th-order reaction be occurring.



By referring to an elementary section of reactor as shown in Fig. 13.18, the basic material balance for any reaction component

$$\text{input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} \quad (4.1)$$

becomes for component A, at steady state,

$$(\text{out-in})_{\text{bulk flow}} + (\text{out-in})_{\text{axial dispersion}} + \frac{\text{disappearance}}{\text{by reaction}} + \text{accumulation} = 0 \quad (17)$$

The individual terms (in moles A/time) are as follows:

$$\begin{aligned} \text{entering by bulk flow} &= \left(\frac{\text{moles A}}{\text{volume}} \right) \left(\frac{\text{flow}}{\text{velocity}} \right) \left(\frac{\text{cross-sectional}}{\text{area}} \right) \\ &= C_{A,l} u S, \quad [\text{mol/s}] \end{aligned}$$

$$\text{leaving by bulk flow} = C_{A,l+\Delta l} u S$$

$$\text{entering by axial dispersion} = \frac{dN_A}{dt} = - \left(DS \frac{dC_A}{dl} \right)_{l+\Delta l}$$

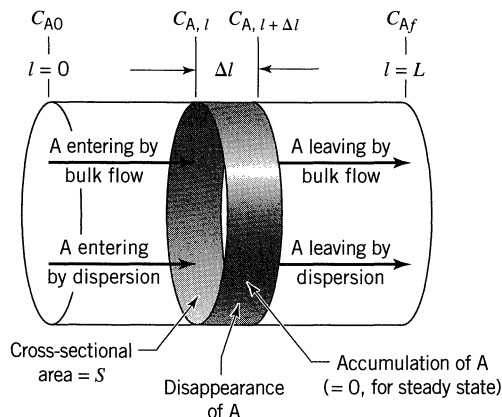


Figure 13.18 Variables for a closed vessel in which reaction and dispersion are occurring.

$$\text{leaving by axial dispersion} = \frac{dN_A}{dt} = - \left(\mathbf{D} S \frac{dC_A}{dl} \right)_{l+\Delta l}$$

$$\text{disappearance by reaction} = (-r_A) V = (-r_A) S \Delta l, \quad [\text{mol/s}]$$

Note that the difference between this material balance and that for the ideal plug flow reactors of Chapter 5 is the inclusion of the two dispersion terms, because material enters and leaves the differential section not only by bulk flow but by dispersion as well. Entering all these terms into Eq. 17 and dividing by $S \Delta l$ gives

$$u \frac{(C_{A,l+\Delta l} - C_{A,l})}{\Delta l} - \mathbf{D} \frac{\left[\left(\frac{dC_A}{dl} \right)_{l+\Delta l} - \left(\frac{dC_A}{dl} \right)_l \right]}{\Delta l} + (-r_A) = 0$$

Now the basic limiting process of calculus states that for any quantity Q which is a smooth continuous function of l

$$\lim_{l_2 \rightarrow l_1} \frac{Q_2 - Q_1}{l_2 - l_1} = \lim_{\Delta l \rightarrow 0} \frac{\Delta Q}{\Delta l} = \frac{dQ}{dl}$$

So taking limits as $\Delta l \rightarrow 0$ we obtain

$$u \frac{dC_A}{dl} - \mathbf{D} \frac{d^2 C_A}{dl^2} + k C_A^n = 0 \quad (18a)$$

In dimensionless form where $z = l/L$ and $\tau = \bar{t} = L/u = V/v$, this expression becomes

$$\frac{\mathbf{D}}{uL} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} - k\tau C_A^n = 0 \quad (18b)$$

or in terms of fractional conversion

$$\frac{\mathbf{D}}{uL} \frac{d^2 X_A}{dz^2} - \frac{dX_A}{dz} + k\tau C_{A0}^{n-1} (1 - X_A)^n = 0 \quad (18c)$$

This expression shows that the fractional conversion of reactant A in its passage through the reactor is governed by three dimensionless groups: a reaction rate group $k\tau C_{A0}^{n-1}$, the dispersion group \mathbf{D}/uL , and the reaction order n .

First-Order Reaction. Equation 18 has been solved analytically by Wehner and Wilhelm (1956) for first-order reactions. For vessels with any kind of entrance

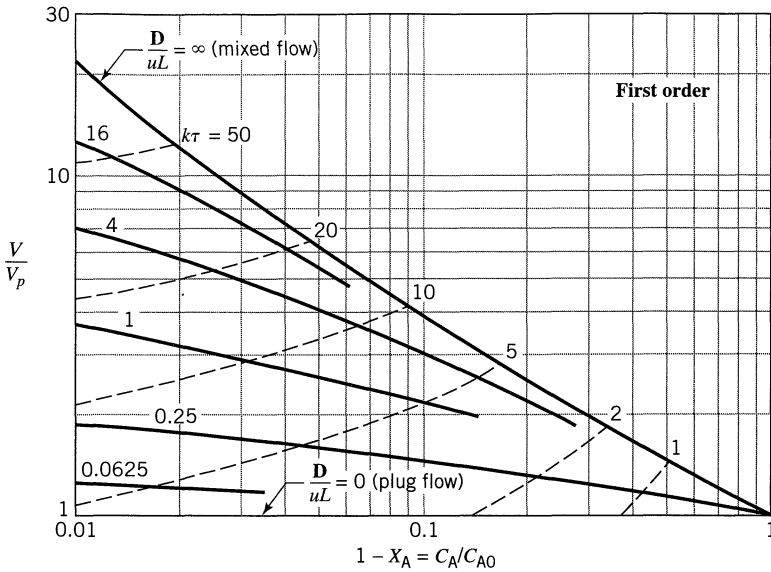


Figure 13.19 Comparison of real and plug flow reactors for the first-order $A \rightarrow$ products, assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

and exit conditions the solution is

$$\frac{C_A}{C_{A0}} = 1 - X_A = \frac{4a \exp\left(\frac{1}{2} \frac{uL}{D}\right)}{(1+a)^2 \exp\left(\frac{a}{2} \frac{uL}{D}\right) - (1-a)^2 \exp\left(-\frac{a}{2} \frac{uL}{D}\right)} \quad (19)$$

where

$$a = \sqrt{1 + 4k\tau(D/uL)}$$

Figure 13.19 is a graphical representation of these results in useful form, prepared by combining Eq. 19 and Eq. 5.17, and allows comparison of reactor sizes for plug and dispersed plug flow.

For *small deviations from plug flow* D/uL becomes small, the E curve approaches gaussian; hence, on expanding the exponentials and dropping higher order terms Eq. 19 reduces to

$$\frac{C_A}{C_{A0}} = \exp\left[-k\tau + (k\tau)^2 \frac{D}{uL}\right] \quad (20)$$

$$= \exp\left[-k\tau + \frac{k^2 \sigma^2}{2}\right] \quad (21)^*$$

* It should be noted that Eq. 21 applies to any gaussian RTD with variance σ^2 .

Equation 20 with Eq. 5.17 compares the performance of real reactors which are close to plug flow with plug flow reactors. Thus the size ratio needed for identical conversion is given by

$$\frac{L}{L_p} = \frac{V}{V_p} = 1 + (k\tau) \frac{D}{uL} \quad \text{for same } C_{A \text{ out}} \quad (22)$$

while the exit concentration ratio for identical reactor size is given by

$$\frac{C_A}{C_{Ap}} = 1 + (k\tau)^2 \frac{D}{uL} \quad \text{for same } V \text{ or } \tau \quad (23)$$

***n*th-Order Reactions.** Figure 13.20 is the graphical representation of the solution of Eq. 18 for second-order reactions in closed vessels. It is used in a manner similar to the chart for first-order reactions. To estimate reactor performance for reactions of order different from one and two we may extrapolate or interpolate between Figs. 13.19 and 13.20.

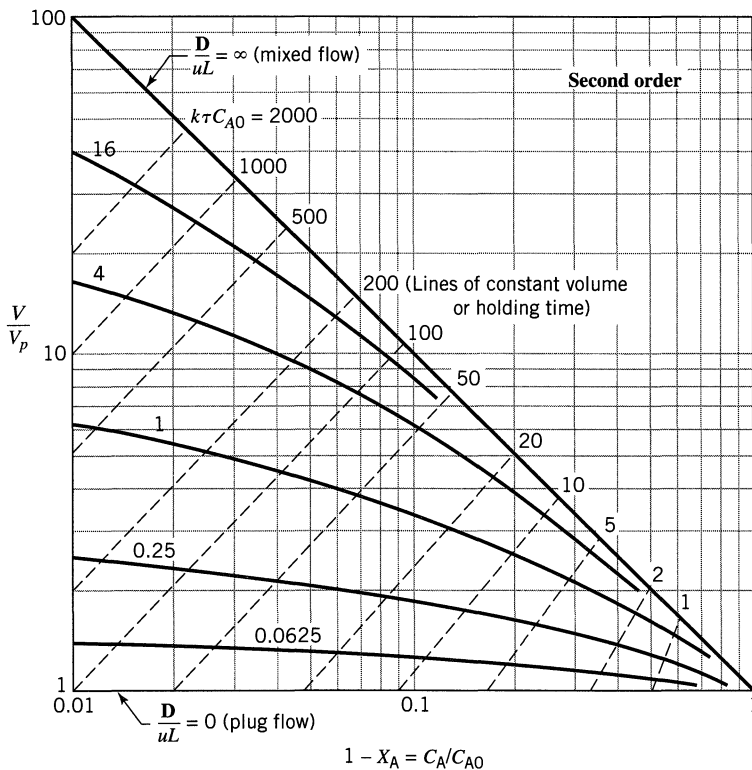
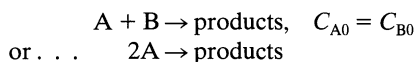


Figure 13.20 Comparison of real and plug flow reactors for the second-order reactions



assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

EXAMPLE 13.4 CONVERSION FROM THE DISPERSION MODEL

Redo Example 11.3 of Chapter 11 assuming that the dispersion model is a good representation of flow in the reactor. Compare the calculated conversion by the two methods and comment.

SOLUTION

Matching the experimentally found variance with that of the dispersion model, we find from Example 13.1

$$\frac{D}{uL} = 0.12$$

Conversion in the real reactor is found from Fig. 13.19. Thus moving along the $k\tau = (0.307)(15) = 4.6$ line from $C/C_0 = 0.01$ to $D/uL = 0.12$, we find that the fraction of reactant unconverted is approximately

$$\frac{C}{C_0} = 0.035, \quad \text{or} \quad \underline{\underline{3.5\%}}$$

Comments. Figure E13.4 shows that except for a long tail the dispersion model curve has for the most part a greater central tendency than the actual curve. On the other hand, the actual curve has more short-lived material leaving the vessel.

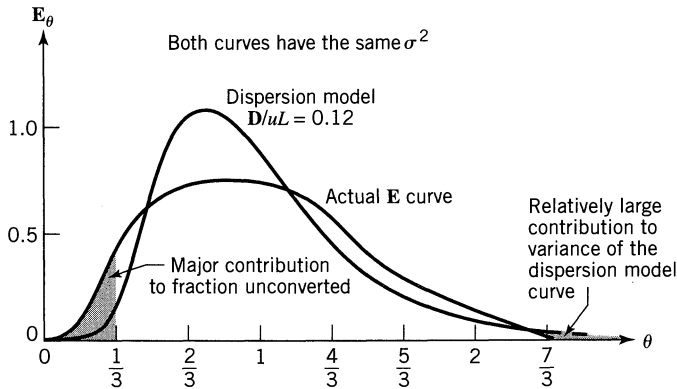


Figure E13.4

Because this contributes most to the reactant remaining unconverted, the finding

$$\left(\frac{C}{C_0}\right)_{\text{actual}} = 4.7\% > \left(\frac{C}{C_0}\right)_{\text{dispersion model}} = 3.5\%$$

is expected.

Extensions

Levenspiel (1996) Chapter 64 discusses and presents performance equations for various extensions to this treatment. A much more detailed exposition of this subject is given by Westerterp et al. (1984) Chapter 4.

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PROBLEMS

13.1. The flow pattern of gas through blast furnaces was studied by VDEh (Veren Deutscher Eisenhüttenleute Betriebsforschungsinstitut) by injecting Kr-85 into the air stream entering the tuyeres of the 688 m³ furnace. A sketch and listing of pertinent quantities for run 10.5 of 9.12.1969 is shown in Fig. P13.1. Assuming that the axial dispersion model applies to the flow of gas

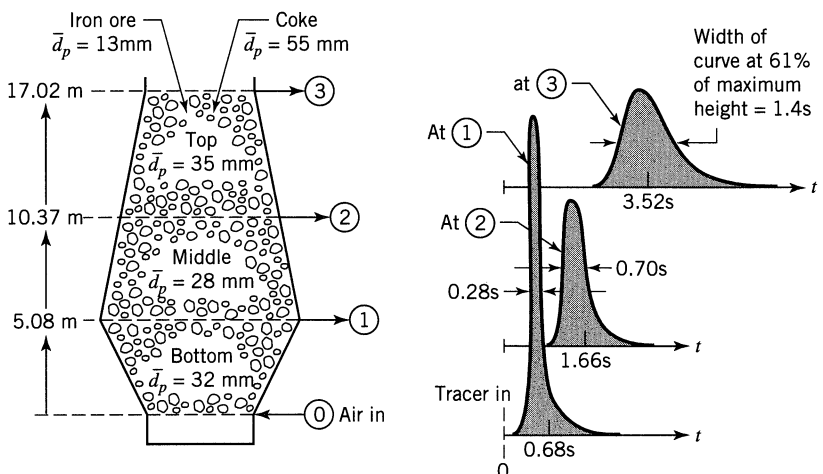


Figure P13.1

in the blast furnace, compare D/ud for the middle section of the blast furnace with that expected in an ordinary packed bed.

From Standish and Polthier, *Blast Furnace Aerodynamics*, p. 99, N. Standish, ed., Australian I. M. M. Symp., Wollongong, 1975.

- 13.2.** Denmark's longest and greatest river, the Gudena, certainly deserves study, so pulse tracer tests were run on various stretches of the river using radioactive Br-82. Find the axial dispersion coefficient in the upper stretch of the river, between Tørring and Udum, 8.7 km apart, from the following reported measurements.

t , hr	C , arbitrary	t , hr	C , arbitrary
3.5	0	5.75	440
3.75	3	6	250
4	25	6.25	122
4.25	102	6.5	51
4.5	281	6.75	20
4.75	535	7	9
5	740	7.25	3
5.25	780	7.5	0
5.5	650		

Data from Danish Isotope Center, report of November 1976.

- 13.3.** RTD studies were carried out by Jagadeesh and Satyanarayana (IEC/PDD **11** 520, 1972) in a tubular reactor ($L = 1.21$ m, 35 mm ID). A squirt of NaCl solution (5 N) was rapidly injected at the reactor entrance, and mixing cup measurements were taken at the exit. From the following results calculate the vessel dispersion number; also the fraction of reactor volume taken up by the baffles.

t , sec	NaCl in sample	
0–20	0	
20–25	60	
25–30	210	
30–35	170	
35–40	75	$(v = 1300 \text{ ml/min})$
40–45	35	
45–50	10	
50–55	5	
55–70	0	

- 13.4.** A pulse of radioactive Ba-140 was injected into a 10-in. pipeline (25.5 cm ID) 293 km long used for pumping petroleum products ($u = 81.7$ cm/s, $Re = 24\,000$) from Rangely, Colorado to Salt Lake City, Utah. Estimate the time of passage of fluid having more than $1/2 C_{\max}$ of tracer and compare the value you calculate with the reported time of passage of 895 sec averaged over five runs. From the table of values for the gaussian distribution $C > C_{\max}/2$ occurs between $\bar{\theta} \pm 1.18 \sigma_{\theta}$. This may be helpful information. Data from Hull and Kent, *Ind. Eng. Chem.*, **44**, 2745 (1952).

- 13.5.** An injected slug of tracer material flows with its carrier fluid down a long, straight pipe in dispersed plug flow. At point *A* in the pipe the spread of tracer is 16 m. At point *B*, 1 kilometer downstream from *A*, its spread is 32 m. What do you estimate its spread to be at a point *C*, which is 2 kilometers downstream from point *A*?
- 13.6.** A refinery pumps products *A* and *B* successively to receiving stations up to 100 km away through a 10-cm ID pipeline. The average properties of *A* and *B* are $\rho = 850 \text{ kg/m}^3$, $\mu = 1.7 \times 10^{-3} \text{ kg/m}\cdot\text{s}$, $\mathcal{D} = 10^{-9} \text{ m}^2/\text{s}$, the fluid flows at $u = 20 \text{ cm/s}$, and there are no reservoirs, holding tanks or pipe loops in the line; just a few bends. Estimate the 16%–84% contaminated width 100 km downstream. Adapted from *Petroleum Refiner*, **37**, 191 (March 1958); *Pipe Line Industry*, pg. 51 (May 1958).
- 13.7.** Kerosene and gasoline are pumped successively at 1.1 m/s through a 25.5-cm ID pipeline 1000 km long. Calculate the 5/95%–95/5% contaminated width at the exit of the pipe given that the kinematic viscosity for the 50/50% mixture is

$$\mu/\rho = 0.9 \times 10^{-6} \text{ m}^2/\text{s}$$

(Data and problem from Sjenitzer, *Pipeline Engineer*, December 1958).

- 13.8.** Water is drawn from a lake, flows through a pump and passes down a long pipe in turbulent flow. A slug of tracer (not an ideal pulse input) enters the intake line at the lake, and is recorded downstream at two locations in the pipe L meters apart. The mean residence time of fluid between recording points is 100 sec, and variance of the two recorded signals is

$$\sigma_1^2 = 800 \text{ sec}^2$$

$$\sigma_2^2 = 900 \text{ sec}^2$$

What would be the spread of an ideal pulse response for a section of this pipe, free from end effects and of length $L/5$?

- 13.9.** Last autumn our office received complaints of a large fish kill along the Ohio River, indicating that someone had discharged highly toxic material into the river. Our water monitoring stations at Cincinnati and Portsmouth, Ohio (119 miles apart) report that a large slug of phenol is moving down the river and we strongly suspect that this is the cause of the pollution. The slug took 9 hours to pass the Portsmouth monitoring station, and its concentration peaked at 8:00 A.M. Monday. About 24 hours later the slug peaked at Cincinnati, taking 12 hours to pass this monitoring station.

Phenol is used at a number of locations on the Ohio River, and their distance upriver from Cincinnati are as follows:

Ashland, KY—150 miles upstream	Marietta, OH—303
Huntington, WV—168	Wheeling, WV—385
Pomeroy, OH—222	Steubenville, OH—425
Parkersburg, WV—290	Pittsburgh, PA—500

What can you say about the probable pollution source?

- 13.10.** A 12-m length of pipe is packed with 1 m of 2-mm material, 9 m of 1-cm material, and 2 m of 4-mm material. Estimate the variance in the output C curve for a pulse input into this packed bed if the fluid takes 2 min to flow through the bed. Assume a constant bed voidage and a constant intensity of dispersion given by $\mathbf{D}/ud_p = 2$.
- 13.11.** The kinetics of a homogeneous liquid reaction are studied in a flow reactor, and to approximate plug flow the 48-cm long reactor is packed with 5-mm nonporous pellets. If the conversion is 99% for a mean residence time of 1 sec, calculate the rate constant for the first-order reaction
- assuming that the liquid passes in plug flow through the reactor
 - accounting for the deviation of the actual flow from plug flow
 - What is the error in calculated k if deviation from plug flow is not considered?

Data: Bed voidage $\varepsilon = 0.4$

Particle Reynolds number $Re_p = 200$

- 13.12.** Tubular reactors for thermal cracking are designed on the assumption of plug flow. On the suspicion that nonideal flow may be an important factor now being ignored, let us make a rough estimate of its role. For this assume isothermal operations in a 2.5-cm ID tubular reactor, using a Reynolds number of 10 000 for flowing fluid. The cracking reaction is approximately first order. If calculations show that 99% decomposition can be obtained in a plug flow reactor 3 m long, how much longer must the real reactor be if nonideal flow is taken into account?
- 13.13.** Calculations show that a plug flow reactor would give 99.9% conversion of reactant which is in aqueous solution. However, our reactor has an RTD somewhat as shown in Fig. P13.13. If $C_{A0} = 1000$, what outlet concentration can we expect in our reactor if reaction is first order? From mechanics $\sigma^2 = a^2/24$ for a symmetrical triangular distribution with base a , rotating about its center of gravity.

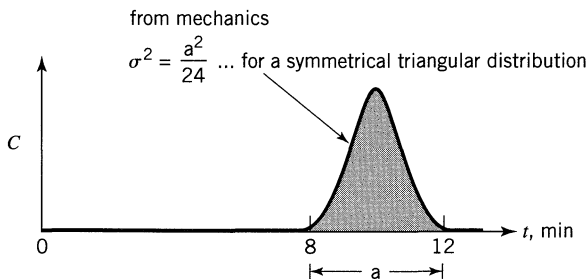


Figure P13.13

Chapter 14

The Tanks-In-Series Model

This model can be used whenever the dispersion model is used; and for not too large a deviation from plug flow both models give identical results, for all practical purposes. Which model you use depends on your mood and taste.

The dispersion model has the advantage in that all correlations for flow in real reactors invariably use that model. On the other hand the tanks-in-series model is simple, can be used with any kinetics, and it can be extended without too much difficulty to any arrangement of compartments, with or without recycle.

14.1 PULSE RESPONSE EXPERIMENTS AND THE RTD

Figure 14.1 shows the system we are considering. We also define

$$\theta_i = \frac{t}{\bar{t}_i} = \text{dimensionless time based on the mean residence time per tank } \bar{t}_i$$

$$\theta = \frac{t}{\bar{t}} = \text{dimensionless time based on the mean residence time in all } N \text{ tanks, } \bar{t}.$$

Then

$$\theta_i = N\theta \quad \dots \quad \text{and} \quad \dots \quad \bar{\theta}_i = 1, \quad \bar{\theta} = 1$$

and at any particular time, from Eq. 11 in Chapter 11

$$\mathbf{E}_\theta = \bar{t}\mathbf{E}$$

For the first tank. Consider a steady flow v m³/s of fluid into and out of the first of these ideal mixed flow units of volume V_1 . At time $t = 0$ inject a pulse of tracer into the vessel which when evenly distributed in the vessel (and it is) has a concentration C_0 .

At any time t after the tracer is introduced make a material balance, thus

$$\left(\begin{array}{c} \text{rate of disappearance} \\ \text{of tracer} \end{array} \right) = \left(\begin{array}{c} \text{input} \\ \text{rate} \end{array} \right) - \left(\begin{array}{c} \text{output} \\ \text{rate} \end{array} \right)$$

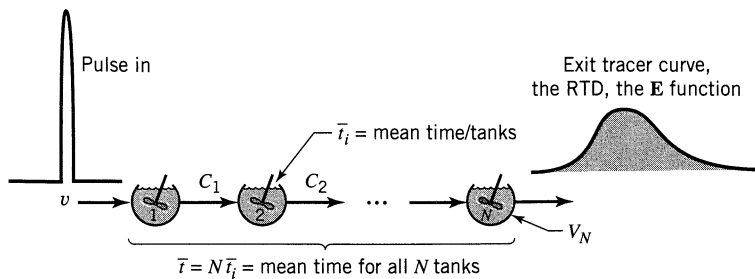


Figure 14.1 The tanks-in-series model.

In symbols this expression becomes

$$V_1 \frac{dC_1}{dt} = 0 - vC_1 \quad \left[\frac{\text{mol tracer}}{\text{s}} \right]$$

where C_1 is the concentration of tracer in tank “1.” Separating and integrating then gives

$$\int_{C_0}^{C_1} \frac{dC_1}{C_1} = -\frac{1}{t_1} \int_0^t dt$$

or

$$\frac{C_1}{C_0} = e^{-t/t_1}$$

Since the area under this C/C_0 versus t curve is t_1 (check this if you wish) it allows you to find the **E** curve; so one may write

$$t_1 \mathbf{E}_1 = e^{-t/t_1} \quad [-] \quad N = 1 \tag{1}$$

For the second tank where C_1 enters, C_2 leaves, a material balance gives

$$V_2 \frac{dC_2}{dt} = v \cdot \underbrace{\frac{C_0}{t_1}}_{C_1} e^{-t/t_1} - vC_2 \quad \left[\frac{\text{mol tracer}}{\text{s}} \right]$$

Separating gives a first-order differential equation, which when integrated gives

$$t_2 \mathbf{E}_2 = \frac{t}{t_2} e^{-t/t_2} \quad [-] \quad N = 2 \tag{2}$$

For the Nth tank. Integration for the 3rd, 4th, . . . , Nth tank becomes more complicated so it is simpler to do all of this by Laplace transforms.

The RTD's, means and variances, both in time and dimensionless time were first derived by MacMullin and Weber (1935) and are summarized by Eq. 3.

$$\begin{aligned}
 \bar{t} \mathbf{E} &= \left(\frac{t}{\bar{t}}\right)^{N-1} \frac{N^N}{(N-1)!} e^{-Nt/\bar{t}} \quad \dots \bar{t} = N\bar{t}_i \dots \sigma^2 = \frac{\bar{t}^2}{N} \\
 \bar{t}_i \mathbf{E} &= \left(\frac{t}{\bar{t}_i}\right)^{N-1} \frac{1}{(N-1)!} e^{-t/\bar{t}_i} \quad \dots \bar{t}_i = \frac{\bar{t}}{N} \dots \sigma^2 = N\bar{t}_i^2 \\
 \mathbf{E}_{\theta_i} &= \bar{t}_i \mathbf{E} = \frac{\theta_i^{N-1}}{(N-1)!} e^{-\theta_i} \quad \dots \sigma_{\theta_i}^2 = N \\
 \mathbf{E}_\theta &= (N\bar{t}_i) \mathbf{E} = N \frac{(N\theta)^{N-1}}{(N-1)!} e^{-N\theta} \dots \sigma_\theta^2 = \frac{1}{N}
 \end{aligned} \tag{3}$$

Graphically these equations are shown in Fig. 14.2. The properties of the RTD curves are sketched in Fig. 14.3.

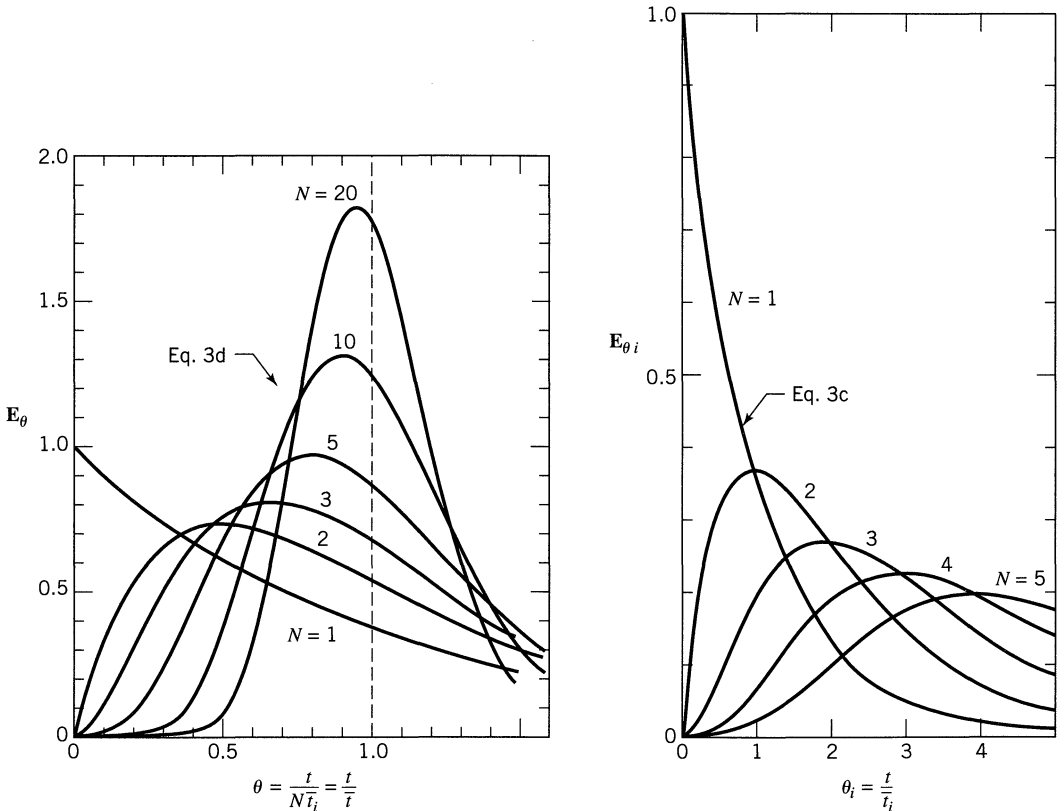


Figure 14.2 RTD curves for the tanks-in-series model, Eq. 3.

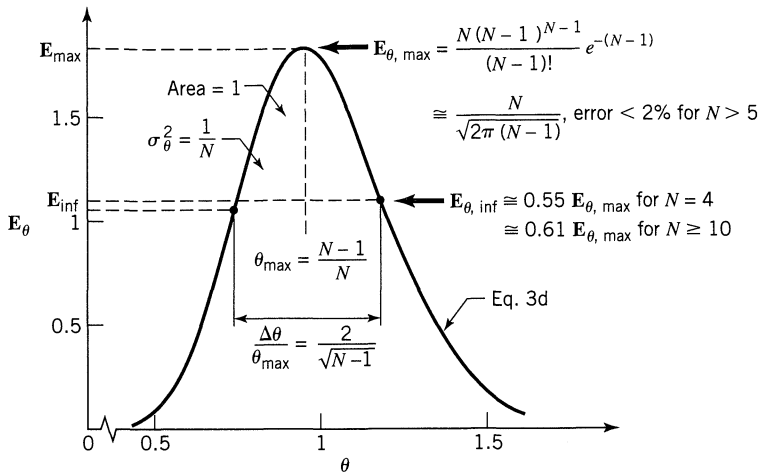


Figure 14.3 Properties of the RTD curve for the tanks-in-series model.

Comments and Extensions

Independence.¹ If M tanks are connected to N more tanks (all of the same size) then the individual means and variances (in ordinary time units) are additive, or

$$\bar{t}_{M+N} = \bar{t}_M + \bar{t}_N \dots \quad \text{and} \quad \dots \sigma_{M+N}^2 = \sigma_M^2 + \sigma_N^2 \quad (4)$$

Because of this property we can join incoming streams with recycle streams. Thus this model becomes useful for treating recirculating systems.

One-shot Tracer Input. If we introduce any one-shot tracer input into N tanks, as shown in Fig. 14.4, then from Eqs. 3 and 4 we can write

$$\Delta\sigma^2 = \sigma_{\text{out}}^2 - \sigma_{\text{in}}^2 = \frac{(\Delta\bar{t})^2}{N} \quad (5)$$

Because of the independence of stages it is easy to evaluate what happens to the C curve when tanks are added or subtracted. Thus this model becomes useful in treating recycle flow and closed recirculation systems. Let us briefly look at these applications.

¹ By independence we mean that the fluid loses its memory as it passes from vessel to vessel. Thus a faster moving fluid element in one vessel does not remember this fact in the next vessel and doesn't preferentially flow faster (or slower) there. Laminar flow often does not satisfy this requirement of independence; however, complete (or lateral) mixing of fluid between units satisfies this condition.

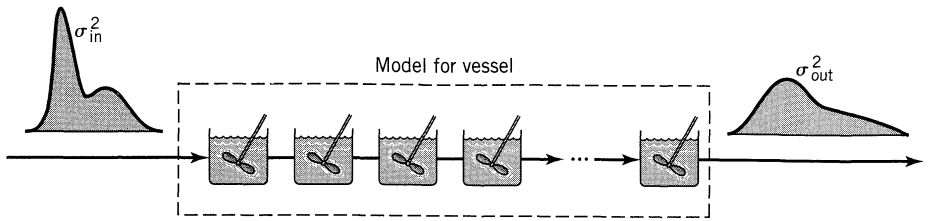


Figure 14.4 For any one-shot tracer input Eq. 4 relates input, output, and number of tanks.

Closed Recirculation System. If we introduce a δ signal into an N stage system, as shown in Fig. 14.5, the recorder will measure tracer as it flows by the first time, the second time, and so on. In other words it measures tracer which has passed through N tanks, $2N$ tanks, and so on. In fact it measures the superposition of all these signals.

To obtain the output signal for these systems simply sum up the contributions from the first, second, and succeeding passes. If m is the number of passes, we then have from Eq. 3

$$\bar{t}_i C_{\text{pulse}} = e^{-t/\bar{t}_i} \sum_{m=1}^{\infty} \frac{(t/\bar{t}_i)^{mN-1}}{(mN-1)!} \quad (6a)$$

$$C_{\theta_i, \text{pulse}} = e^{-\theta_i} \sum_{m=1}^{\infty} \frac{\theta_i^{mN-1}}{(mN-1)!} \quad (6b)$$

$$C_{\theta, \text{pulse}} = N e^{-N\theta} \sum_{m=1}^{\infty} \frac{(N\theta)^{mN-1}}{(mN-1)!} \quad (6c)$$

Figure 14.5 shows the resulting C curve. As an example of the expanded form of Eq. 5 we have for five tanks in series

$$C_{\text{pulse}} = \frac{5}{t} e^{-5t/\bar{t}_i} \left[\frac{(5t/\bar{t}_i)^4}{4!} + \frac{(5t/\bar{t}_i)^9}{9!} + \dots \right] \quad (7a)$$

$$C_{\theta_i, \text{pulse}} = e^{-\theta_i} \left[\frac{\theta_i^4}{4!} + \frac{\theta_i^9}{9!} + \frac{\theta_i^{14}}{14!} + \dots \right] \quad (7b)$$

$$C_{\theta, \text{pulse}} = 5e^{-5\theta} \left[\frac{(5\theta)^4}{4!} + \frac{(5\theta)^9}{9!} + \dots \right] \quad (7c)$$

where the terms in brackets represent the tracer signal from the first, second, and successive passes.

Recirculation systems can be represented equally well by the dispersion model [see van der Vusse (1962), Voncken et al. (1964), and Harrell and Perona (1968)]. Which approach one takes simply is a matter of taste, style, and mood.

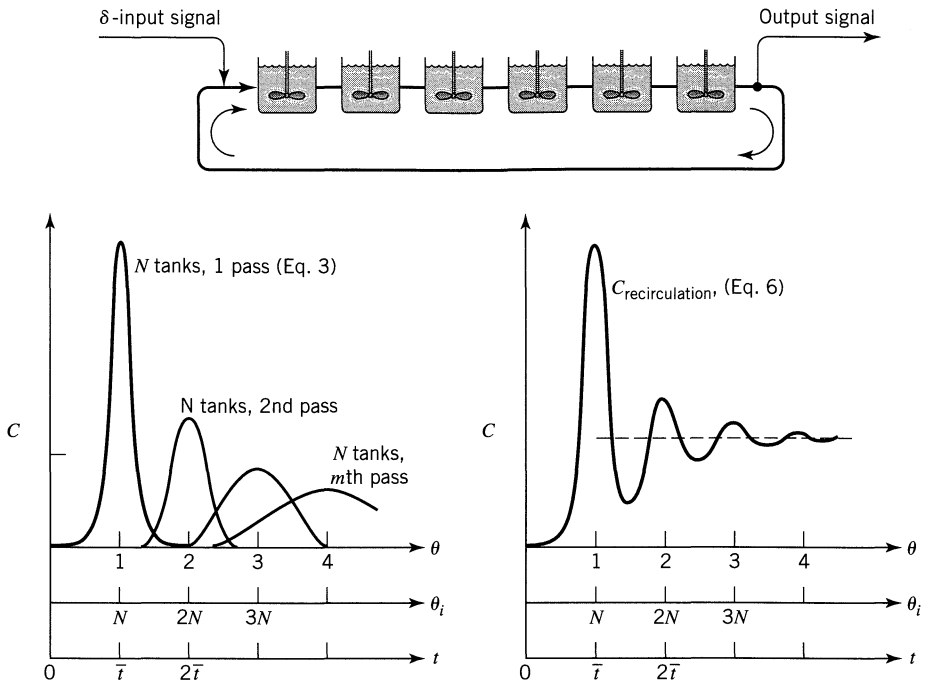


Figure 14.5 Tracer signal in a recirculating system.

Recirculation with Throughflow. For relatively rapid recirculation compared to throughflow, the system as a whole acts as one large stirred tank; hence, the observed tracer signal is simply the superposition of the recirculation pattern and the exponential decay of an ideal stirred tank. This is shown in Fig. 14.6 where C_0 is the concentration of tracer if it is evenly distributed in the system.

This form of curve is encountered in closed recirculation systems in which tracer is broken down and removed by a first-order process, or in systems using

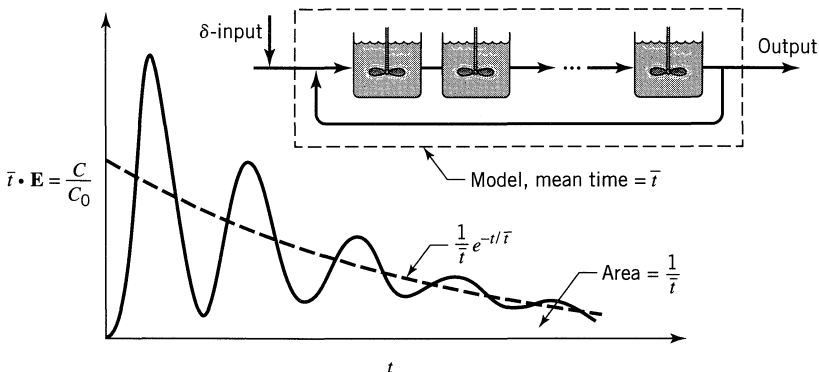


Figure 14.6 Recirculation with slow throughflow.

radioactive tracer. Drug injection on living organisms give this sort of superposition because the drug is constantly being eliminated by the organism.

Step Response Experiments and the F Curve The output **F** curve from a series of N ideal stirred tanks is, in its various forms, given by Eq. 8.

$$\begin{aligned}
 \mathbf{F} &= 1 - e^{-N\theta} \left[1 + N\theta + \frac{(N\theta)^2}{2!} + \dots + \frac{(N\theta)^{N-1}}{(N-1)!} + \dots \right] \\
 \mathbf{F} &= 1 - e^{-\theta_i} \left[1 + \theta_i + \frac{\theta_i^2}{2!} + \dots + \frac{\theta_i^{N-1}}{(N-1)!} + \dots \right]
 \end{aligned}
 \tag{8}$$

Number of tanks

{

→ For one tank use the first term

→ For $N = 2$

→ For $N = 3$

→ For N tanks

This is shown in graphical form in Fig. 14.7.

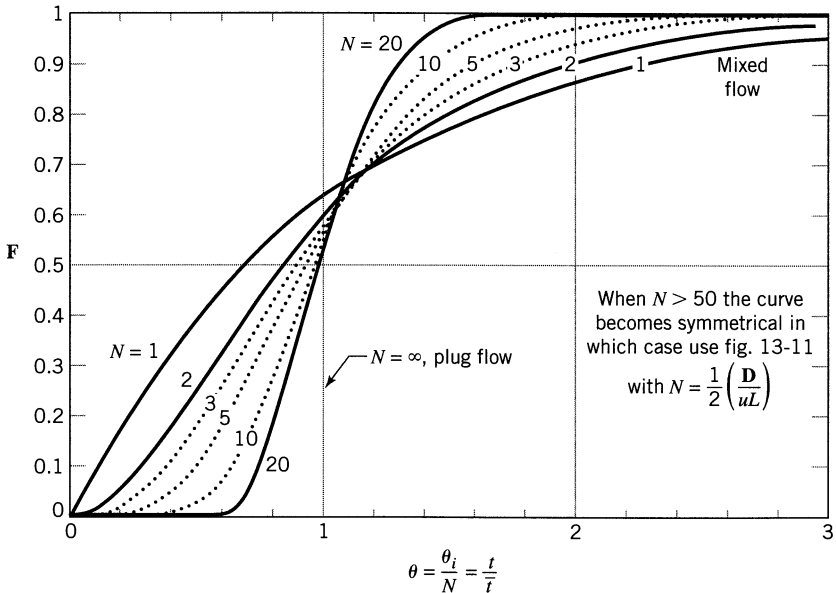


Figure 14.7 The **F** curve for the tanks-in-series model, from MacMullin and Weber (1935).

14.2 CHEMICAL CONVERSION

First-Order Reaction

Chapter 6 develops the conversion equation. Thus for first-order reactions in one tank

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k\bar{t}_i} = \frac{1}{1 + k\bar{t}}$$

for N tanks in series

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k\bar{t}_i)^N} = \frac{1}{\left(1 + \frac{k\bar{t}}{N}\right)^N} \quad (9)$$

A comparison with plug flow performance is given in Fig. 6.5.

For small deviations from plug flow (large N) comparison with plug flow gives

$$\text{for same } C_{A \text{ final}}: \quad \frac{V_{N \text{ tanks}}}{V_p} = 1 + k\bar{t}_i = 1 + \frac{k\bar{t}}{2N}$$

$$\text{for same volume } V: \quad \frac{C_{A, N \text{ tanks}}}{C_{Ap}} = 1 + \frac{(k\bar{t})^2}{2N}$$

These equations apply to both micro- and macrofluids.

Second-Order Reaction of a Microfluid, $A \rightarrow R$ or $A + B \rightarrow R$ with $C_{A0} = C_{B0}$

For a microfluid flowing through N tanks in series Eq. 6.8 gives

$$C_N = \frac{1}{4k\tau_i} \left(-2 + 2 \sqrt{-1 \cdots + 2 \sqrt{-1 + 2 \sqrt{1 + 4C_0 k \tau_i}}} \right)^N \quad (10)$$

and Fig. 6.6 compares the performance to that for plug flow.

All Other Reaction Kinetics of Microfluids

Either solve the mixed flow equation for tank after tank

$$\bar{t}_i = \frac{C_{Ai-1} - C_{Ai}}{-r_i}$$

a rather tedious process, but no problem today with our handy slave, the computer. Or else we could use the graphical procedure shown in Fig. 14.8.

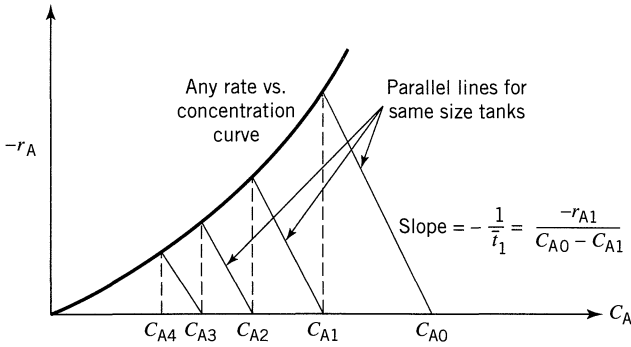


Figure 14.8 Graphical method of evaluating the performance of N tanks in series for any kinetics.

Chemical Conversion of Macrofluids

There is rare use for macrofluid equations for homogeneous reactions. However, if you do need them combine Eq. 11.3 with Eq. 3 for N tanks in series, to give

$$\frac{C_A}{C_{A0}} = \frac{N^N}{(N-1)! \cdot \bar{t}_N} \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} \cdot t^{N-1} e^{-tN/\bar{t}} dt \quad (11)$$

These equations may not be of practical use for homogeneous systems; however, they are of primary importance for heterogeneous systems, especially for G/S systems.

EXAMPLE 14.1 MODIFICATIONS TO A WINERY

A small diameter pipe 32 m long runs from the fermentation room of a winery to the bottle filling cellar. Sometimes red wine is pumped through the pipe, sometimes white, and whenever the switch is made from one to the other a small amount of “house blend” rosé is produced (8 bottles). Because of some construction in the winery the pipeline length will have to be increased to 50 m. For the same flow rate of wine, how many bottles of rosé may we now expect to get each time we switch the flow?

SOLUTION

Figure E14.1 sketches the problem. Let the number of bottles, the spread, be related to σ .

Original:	$L_1 = 32 \text{ m}$	$\sigma_1 = 8$	$\sigma_1^2 = 64$
Longer pipe:	$L_2 = 50 \text{ m}$	$\sigma_2 = ?$	$\sigma_2^2 = ?$

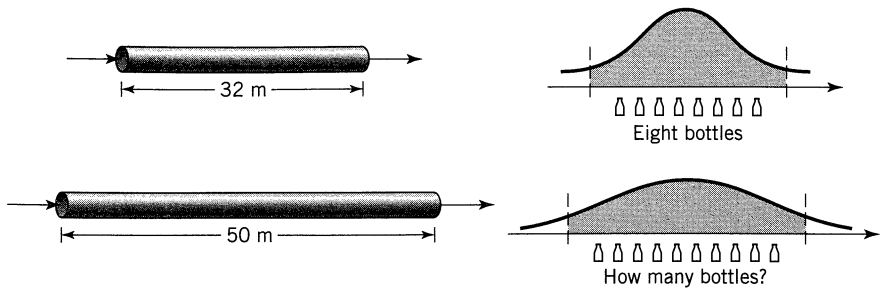


Figure E14.1

But for small deviations from plug flow, from Eq. 3 $\sigma^2 \propto N$ or $\sigma^2 \propto L$.

$$\therefore \frac{\sigma_2^2}{\sigma_1^2} = \frac{L_2}{L_1} = \frac{50}{32}$$

$$\therefore \sigma_2^2 = \frac{50}{32} (64) = 100$$

$$\therefore \sigma_2 = 10 \dots \text{or we can expect } \underline{\underline{10 \text{ bottles of vin rosé}}}$$

EXAMPLE 14.2 A FABLE ON RIVER POLLUTION

Last spring our office received complaints of a large fish kill along the Ohio River, indicating that someone had discharged highly toxic material into the river. Our water monitoring stations at Cincinnati and Portsmouth, Ohio (119 miles apart), report that a large slug of phenol is moving down the river, and we strongly suspect that this is the cause of the pollution. The slug took about 10.5 hours to pass the Portsmouth monitoring station, and its concentration peaked at 8:00 A.M. Monday. About 26 hours later the slug peaked at Cincinnati, taking 14 hours to pass this monitoring station.

Phenol is used at a number of locations on the Ohio River, and their distance upriver from Cincinnati are as follows:

Ashland, KY—150 miles upstream	Marietta, OH—303
Huntington, WV—168	Wheeling, WV—385
Pomeroy, OH—222	Steubenville, OH—425
Parkersburg, WV—290	Pittsburgh, PA—500

What can you say about the probable pollution source?

SOLUTION

Let us first sketch what is known, as shown in Fig. E14.2. To start, assume that a perfect pulse is injected. Then according to any reasonable flow model, either

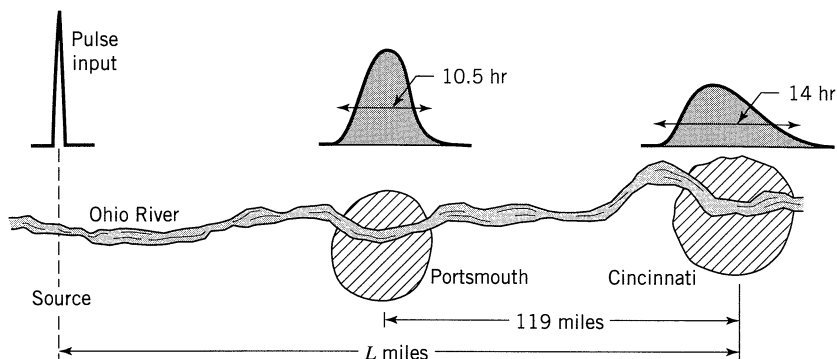


Figure E14.2

dispersion or tanks-in-series, we have

$$\sigma_{\text{tracer curve}}^2 \propto \left(\begin{array}{l} \text{distance from} \\ \text{point of origin} \end{array} \right)$$

or

$$\left(\begin{array}{l} \text{spread of} \\ \text{curve} \end{array} \right) \propto \sqrt{\begin{array}{l} \text{distance from} \\ \text{origin} \end{array}}$$

$$\left. \begin{array}{l} \therefore \text{from Cincinnati: } 14 = k L^{1/2} \\ \therefore \text{from Portsmouth: } 10.5 = k(L - 119)^{1/2} \end{array} \right\}$$

Dividing one by the other gives

$$\frac{14}{10.5} = \sqrt{\frac{L}{L - 119}} \quad \dots \text{from which } \underline{\underline{L = 272 \text{ miles}}}$$

Comment. Since the dumping of the toxic phenol may not have occurred instantaneously, any location where $L \leq 272$ miles is suspect, or

$$\left. \begin{array}{l} \underline{\text{Ashland}} \\ \underline{\text{Huntington}} \\ \underline{\text{Pomeroy}} \end{array} \right\} \leftarrow$$

This solution assumes that different stretches of the Ohio River have the same flow and dispersion characteristics (reasonable), and that no suspect tributary joins the Ohio within 272 miles of Cincinnati. This is a poor assumption . . . check a map for the location of Charleston, WV, on the Kanawah River.

EXAMPLE 14.3 FLOW MODELS FROM RTD CURVES

Let us develop a tanks-in-series model to fit the RTD shown in Fig. E14.3a.

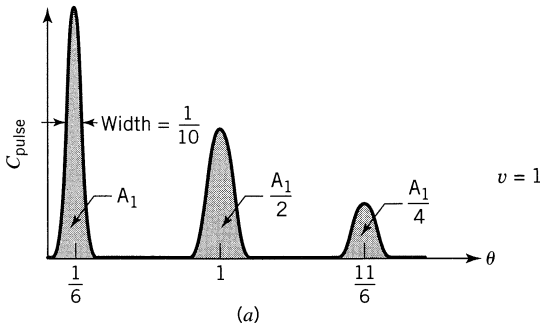


Figure E14.3a

SOLUTION

As a first approximation, assume that all the tracer curves are ideal pulses. We will later relax this assumption. Next notice that the first pulse appears early. This suggests a model as shown in Fig. E14.3b, where $v = 1$ and $V_1 + V_2 + V_d = 1$. In Chapter 12 we see the characteristics of this model, so let us fit it. Also it should be mentioned that we have a number of approaches. Here is one:

- Look at the ratio of areas of the first two peaks

$$\frac{A_2}{A_1} = \frac{1}{2} = \frac{R}{R+1} \quad \dots \cdot \underline{\underline{R=1}}$$

- From the location of the first peak

$$\frac{V_1}{(R+1)v} = \frac{V_1}{(1+1)} = \frac{1}{6} \quad \dots \cdot \underline{\underline{V_1 = \frac{1}{3}}}$$

- From the time between peaks

$$\Delta t = \frac{5}{6} = \frac{(1/3)}{(1+1)1} + \frac{V_2}{1(1)} \quad \dots \cdot \underline{\underline{V_2 = \frac{2}{3}}}$$

Since $V_1 + V_2$ add up to 1, there is no dead volume, so at this point our model reduces to Fig. E14.3c. Now relax the plug flow assumption and adopt the tanks-in-series model. From Fig. 14.3

$$\frac{\Delta\theta}{\theta_{\max}} = \frac{1/10}{1/6} = \frac{2}{\sqrt{N-1}} \quad \dots \cdot \underline{\underline{N=12}}$$

So our model finally is shown in Fig. E14.3d.

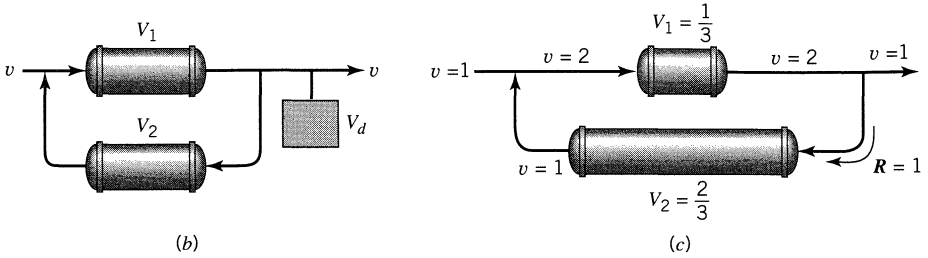


Figure E14.3b and c

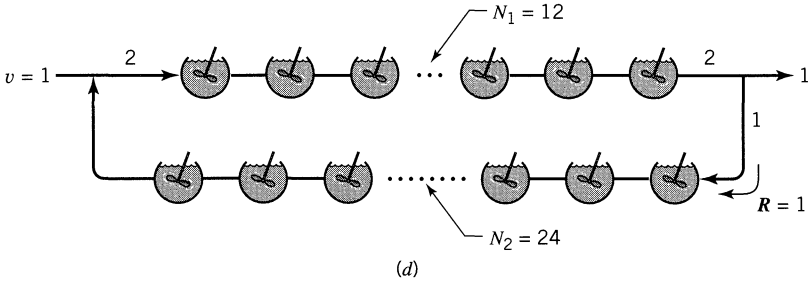


Figure E14.3d

Bypassing the Complex Process of Deconvolution

Suppose we measure the sloppy input and output tracer curves for a process vessel for the purpose of studying the flow through the vessel, thus to find the **E** curve for the vessel. In general this requires deconvolution (see Chapter 11); however, if we have a flow model in mind whose parameter has a one-to-one relationship with its variance, then we can use a very simple shortcut to find the **E** curve for the vessel.

Example 14.4 illustrates this method.

EXAMPLE 14.4 FINDING THE VESSEL **E** CURVE USING A SLOPPY TRACER INPUT

Given C_{in} and C_{out} as well as the location and spread of these tracer curves, as shown in Fig. E14.4a estimate the vessel **E** curve. We suspect that the tanks-in-series model reasonably represents the flow in the vessel.

SOLUTION

From Fig. E14.4a we have, for the vessel,

$$\Delta \bar{t} = 280 - 220 = 60 \text{ s}$$

$$\Delta(\sigma^2) = 1000 - 100 = 900 \text{ s}$$

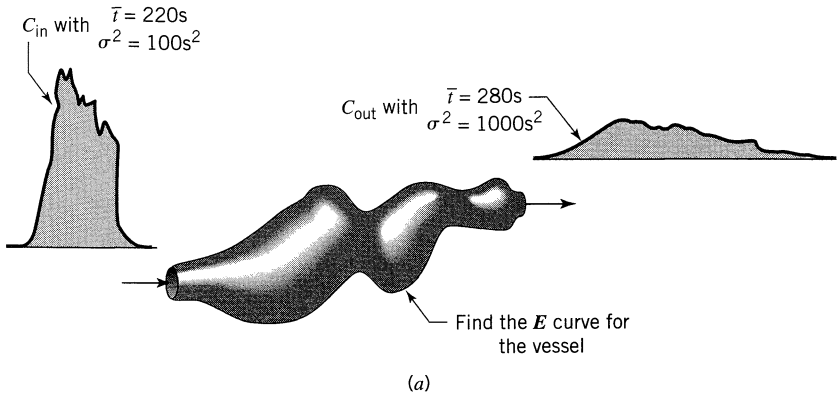


Figure E14.4a

Equation 3 represents the tanks-in-series model and gives

$$N = \frac{(\Delta\bar{t})^2}{\Delta(\sigma^2)} = \frac{60^2}{900} = 4 \text{ tanks}$$

So from Eq. 3a, for N tanks-in-series we have

$$E = \frac{t^{N-1}}{\bar{t}^N} \cdot \frac{N^N}{(N-1)!} e^{-tN/\bar{t}}$$

and for $N = 4$

$$E = \frac{t^3}{60^4} \cdot \frac{4^4}{3 \times 2} e^{-4t/60}$$

$$\underline{\underline{E = 3.2922 \times 10^{-6} t^3 e^{-0.0667t}}}$$

Figure E14.4b shows the shape of this E curve.

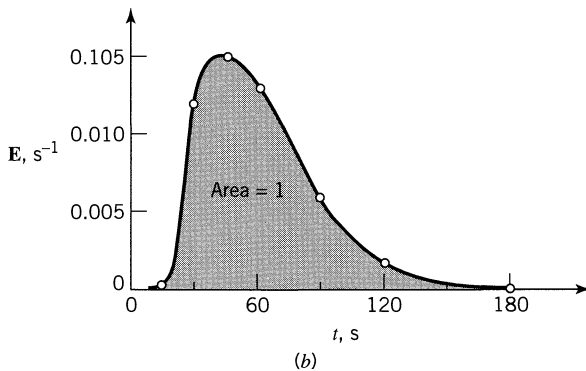


Figure E14.4b

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PROBLEMS

- 14.1.** Fit the tanks-in-series model to the following mixing cup output data to a pulse input.

t	0-2	2-4	4-6	6-8	8-10	10-12
C	2	10	8	4	2	0

- 14.2.** Fluid flows at a steady rate through ten well-behaved tanks in series. A pulse of tracer is introduced into the first tank, and at the time this tracer leaves the system

$$\text{maximum concentration} = 100 \text{ mmol}$$

$$\text{tracer spread} = 1 \text{ min}$$

If ten more tanks are connected in series with the original ten tanks, what would be

- (a) the maximum concentration of leaving tracer?
 - (b) the tracer spread?
 - (c) How does the relative spread change with number of tanks?
- 14.3.** From the *New York Times Magazine*, December 25, 1955, we read: "The United States Treasury reported that it costs eight-tenths of a cent to print dollar bills, and that of the billion and a quarter now in circulation, a billion have to be replaced annually." Assume that the bills are put into circulation at a constant rate and continuously, and that they are withdrawn from circulation without regard to their condition, in a random manner.
- Suppose that a new series of dollar bills is put in circulation at a given instant in place of the original bills.
- (a) How many new bills will be in circulation at any time?
 - (b) 21 years later, how many old bills will still be in circulation?
- 14.4.** Referring to the previous problem, suppose that during a working day a gang of counterfeiters put into circulation one million dollars in fake one-dollar bills.
- (a) If not detected, what will be the number in circulation as a function of time?
 - (b) After 10 years, how many of these bills would still be in circulation?

- 14.5. Repeat Problem 13.13, but solve it using the tanks-in-series model instead of the dispersion model.
- 14.6. A stream of fully suspended fine solids ($v = 1 \text{ m}^3/\text{min}$) passes through two mixed flow reactors in series, each containing 1 m^3 of slurry. As soon as a particle enters the reactors, conversion to product begins and is complete after two minutes in the reactors. When a particle leaves the reactors, reaction stops. What fraction of particles is completely converted to product in this system?
- 14.7. Fit the RTD of Fig. P14.7 with the tanks-in-series model.

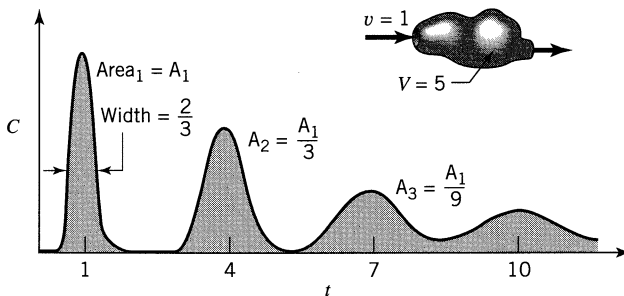


Figure P14.7

- 14.8. From a pulse input into a vessel we obtain the following output signal

Time, min	1	3	5	7	9	11	13	15
Concentration (arbitrary)	0	0	10	10	10	10	0	0

We want to represent the flow through the vessel with the tanks-in-series model. Determine the number of tanks to use.

- 14.9. Strongly radioactive waste fluids are stored in “safe-tanks” which are simply long, small-diameter (e.g., 20 m by 10 cm) slightly sloping pipes. To avoid sedimentation and development of “hot spots,” and also to insure uniformity before sampling the contents, fluid is recirculated in these pipes.

To model the flow in these tanks, a pulse of tracer is introduced and the curve of Fig. P14.9 is recorded. Develop a suitable model for this system and evaluate the parameters.

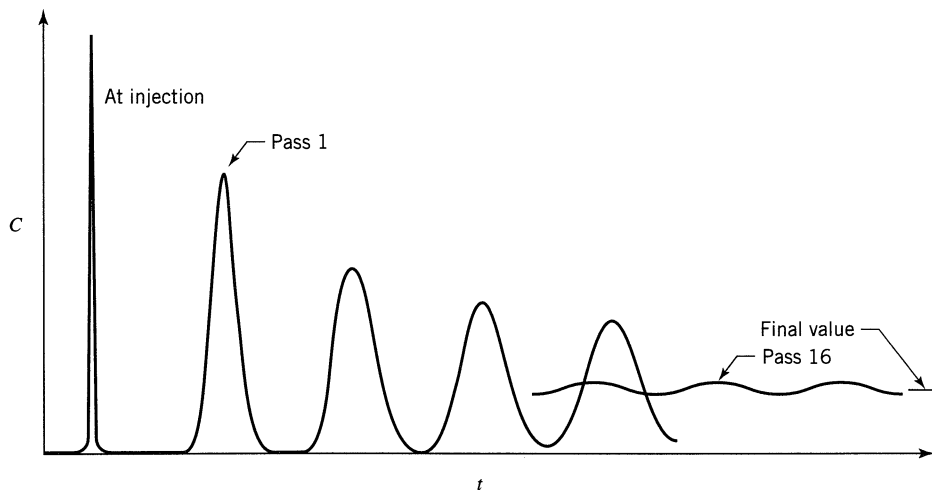
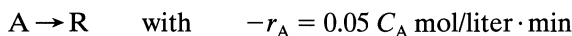


Figure P14.9 RTD for a closed recirculating system.

- 14.10.** A reactor with a number of dividing baffles is to be used to run the reaction



A pulse tracer test gives the following output curve:

Time, min	0	10	20	30	40	50	60	70
Concentration reading	35	38	40	40	39	37	36	35

- Find the area under the C versus t curve.
 - Find the E versus t curve.
 - Calculate the variance of the E curve.
 - How many tanks in series is this vessel equivalent to?
 - Calculate X_A assuming plug flow.
 - Calculate X_A assuming mixed flow.
 - Calculate X_A assuming the tanks-in-series model.
 - Calculate X_A directly from the data.
- 14.11.** A reactor has flow characteristics given by the nonnormalized C curve in Table P14.11, and by the shape of this curve we feel that the dispersion or tanks-in-series models should satisfactorily represent flow in the reactor.
- Find the conversion expected in this reactor, assuming that the dispersion model holds.
 - Find the number of tanks in series which will represent the reactor and the conversion expected, assuming that the tanks-in-series model holds.

Table P14.11.

Time	Tracer Concentration	Time	Tracer Concentration
0	0	10	67
1	9	15	47
2	57	20	32
3	81	30	15
4	90	41	7
5	90	52	3
6	86	67	1
8	77	70	0

- (c) Find the conversion by direct use of the tracer curve.
 (d) Comment on the difference in these results, and state which one you think is the most reliable.

Data. The elementary liquid-phase reaction taking place is $A + B \rightarrow$ products, with a large enough excess of B so that the reaction is essentially first order. In addition, if plug flow existed, conversion would be 99% in the reactor.