

Part II

Flow Pattern, Contacting, and Non-Ideal Flow

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Chapter 11

Basics of Non-Ideal Flow

So far we have treated two flow patterns, plug flow and mixed flow. These can give very different behavior (size of reactor, distribution of products). We like these flow patterns and in most cases we try to design equipment to approach one or the other because

- one or the other often is optimum no matter what we are designing for.
- these two patterns are simple to treat.

But real equipment always deviates from these ideals. How to account for this? That is what this and the following chapters are about.

Overall three somewhat interrelated factors make up the contacting or flow pattern:

1. the **RTD** or residence time distribution of material which is flowing through the vessel
2. the **state of aggregation** of the flowing material, its tendency to clump and for a group of molecules to move about together
3. the **earliness and lateness of mixing** of material in the vessel.

Let us discuss these three factors in a qualitative way at first. Then, this and the next few chapters treat these factors and show how they affect reactor behavior.

The Residence Time Distribution, RTD

Deviation from the two ideal flow patterns can be caused by channeling of fluid, by recycling of fluid, or by creation of stagnant regions in the vessel. Figure 11.1 shows this behavior. In all types of process equipment, such as heat exchangers, packed columns, and reactors, this type of flow should be avoided since it always lowers the performance of the unit.

If we know precisely what is happening within the vessel, thus if we have a complete velocity distribution map for the fluid in the vessel, then we should, in principle, be able to predict the behavior of a vessel as a reactor. Unfortunately, this approach is impractical, even in today's computer age.

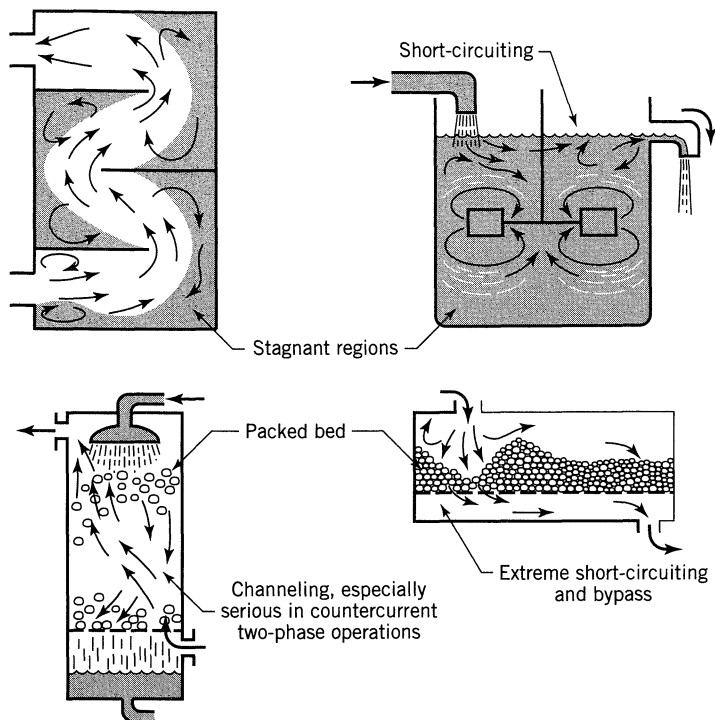


Figure 11.1 Nonideal flow patterns which may exist in process equipment.

Setting aside this goal of complete knowledge about the flow, let us be less ambitious and see what it is that we actually need to know. In many cases we really do not need to know very much, simply how long the individual molecules stay in the vessel, or more precisely, the distribution of residence times of the flowing fluid. This information can be determined easily and directly by a widely used method of inquiry, the stimulus-response experiment.

This chapter deals in large part with the residence time distribution (or RTD) approach to nonideal flow. We show when it may legitimately be used, how to use it, and when it is not applicable what alternatives to turn to.

In developing the “language” for this treatment of nonideal flow (see Danckwerts, 1953), we will only consider the steady-state flow, without reaction and without density change, of a single fluid through a vessel.

State of Aggregation of the Flowing Stream

Flowing material is in some particular state of aggregation, depending on its nature. In the extremes these states can be called *microfluids* and *macrofluids*, as sketched in Fig. 11.2.

Single-Phase Systems. These lie somewhere between the extremes of macro- and microfluids.

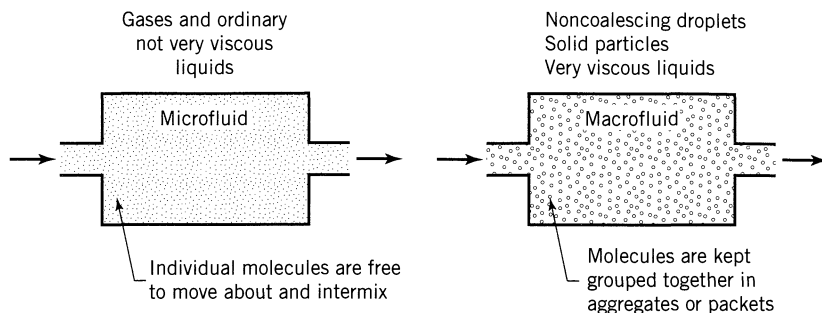


Figure 11.2 Two extremes of aggregation of fluid.

Two-Phase Systems. A stream of solids always behaves as a macrofluid, but for gas reacting with liquid, either phase can be a macro- or microfluid depending on the contacting scheme being used. The sketches of Fig. 11.3 show completely opposite behavior. We treat these two phase reactors in later chapters.

Earliness of Mixing

The fluid elements of a single flowing stream can mix with each other either early or late in their flow through the vessel. For example, see Fig. 11.4.

Usually this factor has little effect on overall behavior for a single flowing fluid. However, for a system with two entering reactant streams it can be very important. For example, see Fig. 11.5.

Role of RTD, State of Aggregation, and Earliness of Mixing in Determining Reactor Behavior

In some situations one of these three factors can be ignored; in others it can become crucial. Often, much depends on the time for reaction, \bar{t}_{rx} , the time for

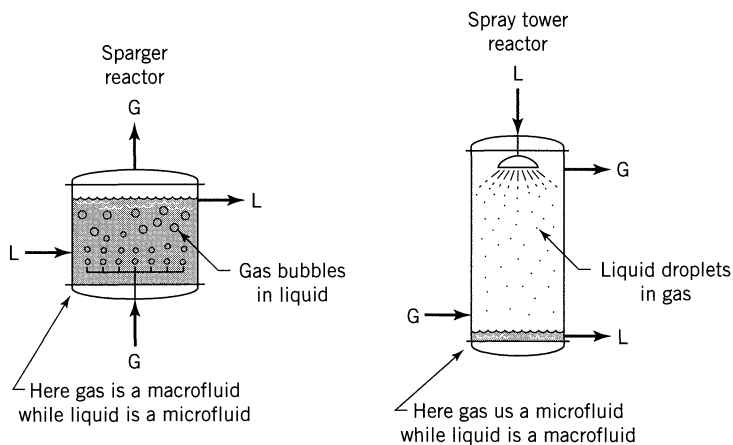


Figure 11.3 Examples of macro- and microfluid behavior.

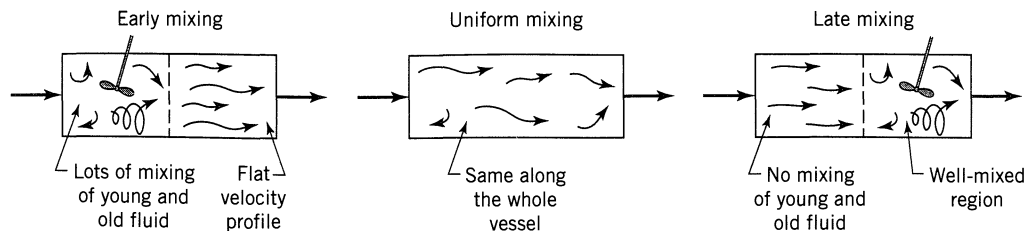


Figure 11.4 Examples of early and of late mixing of fluid.

mixing \bar{t}_{mix} , and the time for stay in the vessel \bar{t}_{stay} . In many cases \bar{t}_{stay} has a meaning somewhat like \bar{t}_{mix} but somewhat broader.

11.1 E, THE AGE DISTRIBUTION OF FLUID, THE RTD

It is evident that elements of fluid taking different routes through the reactor may take different lengths of time to pass through the vessel. The distribution of these times for the stream of fluid leaving the vessel is called the exit age distribution **E**, or the residence time distribution RTD of fluid. **E** has the units of time^{-1} .

We find it convenient to represent the RTD in such a way that the area under the curve is unity, or

$$\int_0^{\infty} \mathbf{E} \, dt = 1 \quad [-]$$

This procedure is called normalizing the distribution, and Fig. 11.6 shows this.

We should note one restriction on the **E** curve—that the fluid only enters and only leaves the vessel one time. This means that there should be no flow or diffusion or upflow eddies at the entrance or at the vessel exit. We call this the *closed* vessel boundary condition. Where elements of fluid can cross the vessel boundary more than one time we call this the *open* vessel boundary condition.

With this representation the fraction of exit stream of age* between t and $t + dt$ is

$$\mathbf{E} \, dt \quad [-]$$

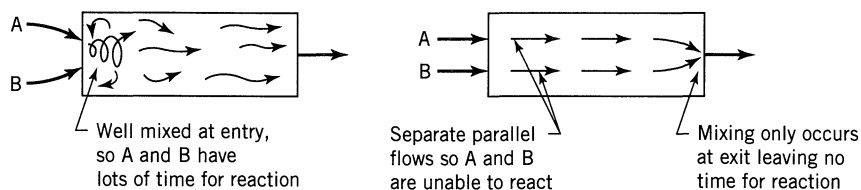


Figure 11.5 Early or late mixing affects reactor behavior.

* The term “age” for an element of the exit stream refers to the time spent by that element in the vessel.

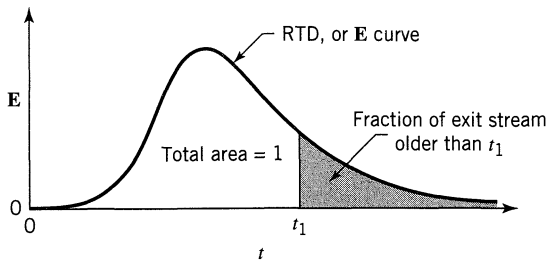


Figure 11.6 The exit age distribution curve **E** for fluid flowing through a vessel; also called the residence time distribution, or RTD.

the fraction younger than age t_1 is

$$\int_0^{t_1} E \, dt \quad [-] \quad (1)$$

whereas the fraction of material older than t_1 , shown as the shaded area in Fig. 11.6, is

$$\int_{t_1}^{\infty} E \, dt = 1 - \int_0^{t_1} E \, dt \quad [-] \quad (2)$$

The **E** curve is the distribution needed to account for nonideal flow.

Experimental Methods (Nonchemical) for Finding **E**

The simplest and most direct way of finding the **E** curve uses a physical or nonreactive tracer. For special purposes, however, we may want to use a reactive tracer. This chapter deals in detail with the nonreactive tracer, and for this all sorts of experiments can be used. Figure 11.7 shows some of these. Because the pulse and the step experiments are easier to interpret, the periodic and random harder, here we only consider the pulse and the step experiment.

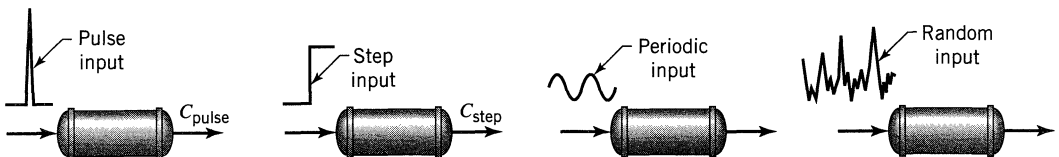


Figure 11.7 Various ways of studying the flow pattern in vessels.

We next discuss these two experimental methods for finding the **E** curve. We then show how to find reactor behavior knowing the **E** curve for the reactor.

The Pulse Experiment

Let us find the **E** curve for a vessel of volume $V \text{ m}^3$ through which flows $v \text{ m}^3/\text{s}$ of fluid. For this instantaneously introduce M units of tracer (kg or moles) into the fluid entering the vessel, and record the concentration-time of tracer leaving the vessel. This is the C_{pulse} curve. From the material balance for the vessel we find

$$\left(\begin{array}{l} \text{Area under the} \\ C_{\text{pulse}} \text{ curve} \end{array} \right): A = \int_0^\infty C dt \cong \sum_i C_i \Delta t_i = \frac{M}{v} \quad \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right] \quad (3)$$

$$\left(\begin{array}{l} \text{Mean of the} \\ C_{\text{pulse}} \text{ curve} \end{array} \right): \bar{t} = \frac{\int_0^\infty tC dt}{\int_0^\infty C dt} \cong \frac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i} = \frac{V}{v} \quad [\text{s}] \quad (4)$$

All this is shown in Fig. 11.8.

To find the **E** curve from the C_{pulse} curve simply change the concentration scale such that the area under the curve is unity. Thus, simply divide the concentration readings by M/v , as shown in Fig. 11.9.

$$\mathbf{E} = \frac{C_{\text{pulse}}}{M/v} \quad (5a)$$

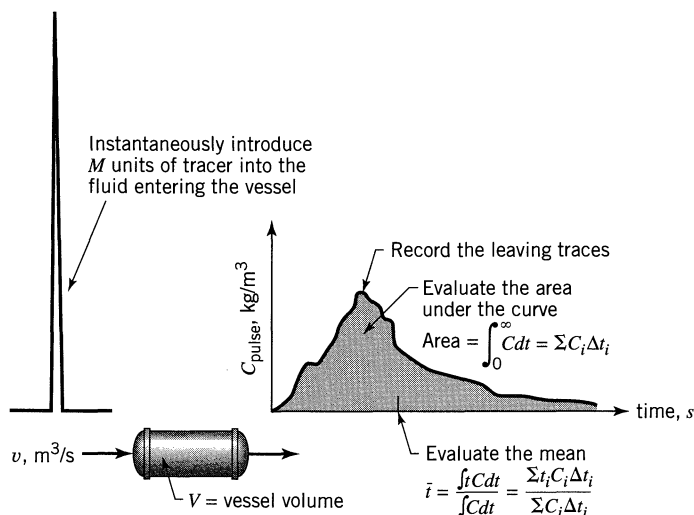


Figure 11.8 The useful information obtainable from the pulse trace experiment.

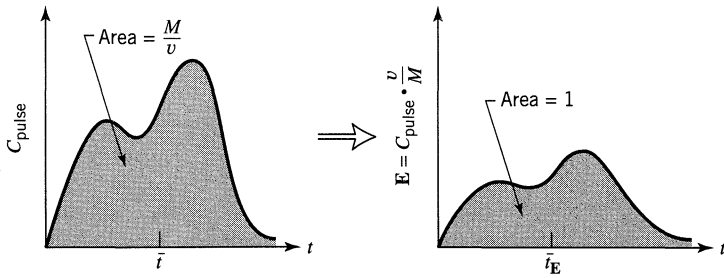


Figure 11.9 Transforming an experimental C_{pulse} curve into an \mathbf{E} curve.

We have another RTD function \mathbf{E}_θ . Here time is measured in terms of mean residence time $\theta = t/\bar{t}$. Thus

$$\mathbf{E}_\theta = \bar{t}\mathbf{E} = \frac{V}{v} \cdot \frac{C_{\text{pulse}}}{M/v} = \frac{V}{M} C_{\text{pulse}} \quad (5b)$$

\mathbf{E}_θ is a useful measure when dealing with flow models which come up in Chapters 13, 14, and 15. Figure 11.10 shows how to transform \mathbf{E} into \mathbf{E}_θ .

One final reminder, the relationship between C_{pulse} and the \mathbf{E} curves only holds exactly for vessels with *closed* boundary conditions.

The Step Experiment

Consider $v \text{ m}^3/\text{s}$ of fluid flowing through a vessel of volume V . Now at time $t = 0$ switch from ordinary fluid to fluid with tracer of concentration $C_{\text{max}} = \left[\frac{\text{kg or mol}}{\text{m}^3} \right]$, and measure the outlet tracer concentration C_{step} versus t , as shown in Fig. 11.11.

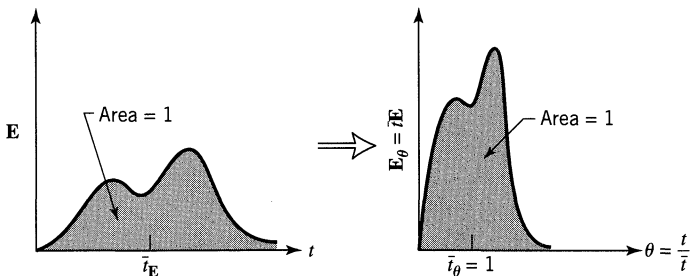


Figure 11.10 Transforming an \mathbf{E} curve into an \mathbf{E}_θ curve.

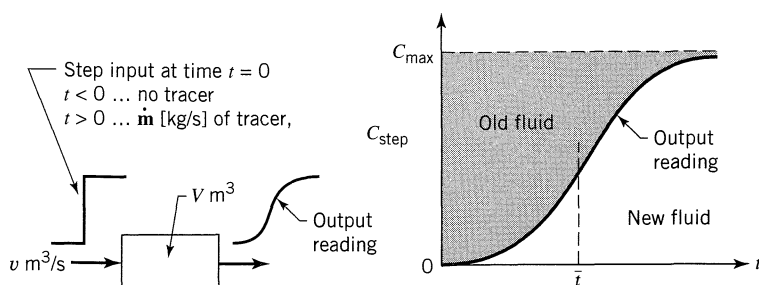


Figure 11.11 Information obtainable from a step tracer experiment.

A material balance relates the different measured quantities of the output curve of a step input

$$C_{\max} = \frac{\dot{m}}{v} \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right]$$

and

$$\left(\text{shaded area of Fig. 11.11} \right) = C_{\max} \bar{t} = \frac{\dot{m} V}{v^2} \left[\frac{\text{kg} \cdot \text{s}^2}{\text{m}^3} \right] \quad (6)$$

$$\bar{t} = \frac{\int_0^{C_{\max}} t dC_{\text{step}}}{\int_0^{C_{\max}} dC_{\text{step}}} = \frac{1}{C_{\max}} \int_0^{C_{\max}} t dC_{\text{step}}$$

where \dot{m} [kg/s] is the flow rate of tracer in the entering fluid.

The dimensionless form of the C_{step} curve is called the **F** curve. It is found by having the tracer concentration rise from zero to unity, as shown in Fig. 11.12.

Relationship between the F and E Curves

To relate **E** with **F** imagine a steady flow of white fluid. Then at time $t = 0$ switch to red and record the rising concentration of red fluid in the exit stream, the **F**

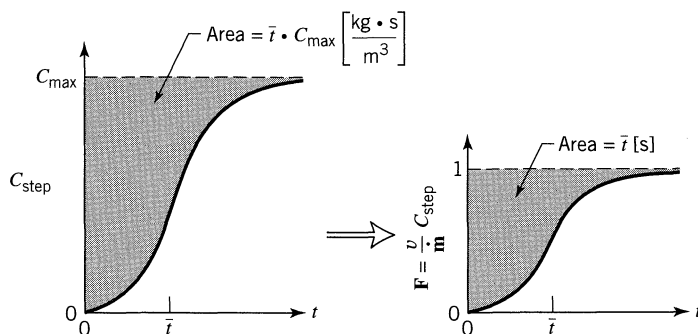


Figure 11.12 Transforming an experimental C_{step} curve to an **F** curve.

curve. At any time $t > 0$ red fluid and only red fluid in the exit stream is younger than age t . Thus we have

$$\left(\begin{array}{c} \text{fraction of red fluid} \\ \text{in the exit stream} \end{array} \right) = \left(\begin{array}{c} \text{fraction of exit stream} \\ \text{younger than age } t \end{array} \right)$$

But the first term is simply the \mathbf{F} value, while the second is given by Eq. 1. So we have, at time t ,

$$\mathbf{F} = \int_0^t \mathbf{E} \, dt \quad (7)$$

and on differentiating

$$\frac{d\mathbf{F}}{dt} = \mathbf{E} \quad (8)$$

In graphical form this relationship is shown in Fig. 11.13.

These relationships show how stimulus-response experiments, using either step or pulse inputs can conveniently give the RTD and mean flow rate of fluid in the vessel. We should remember that these relationships only hold for closed vessels. When this boundary condition is not met, then the C_{pulse} and \mathbf{E} curves differ. The C_{pulse} curves of the convection model (see Chap. 15) clearly show this.

Figure 11.14 shows the shapes of these curves for various types of flow.

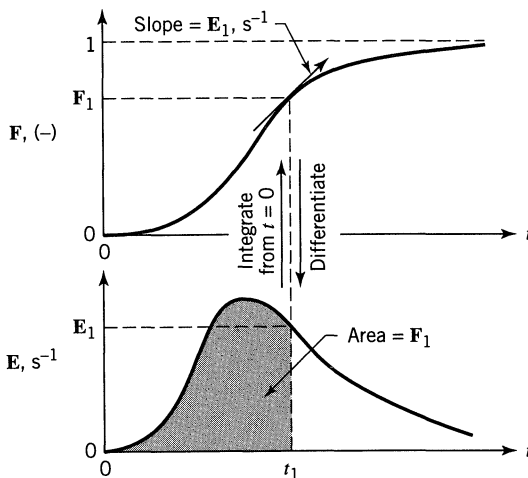


Figure 11.13 Relationship between the \mathbf{E} and \mathbf{F} curves.

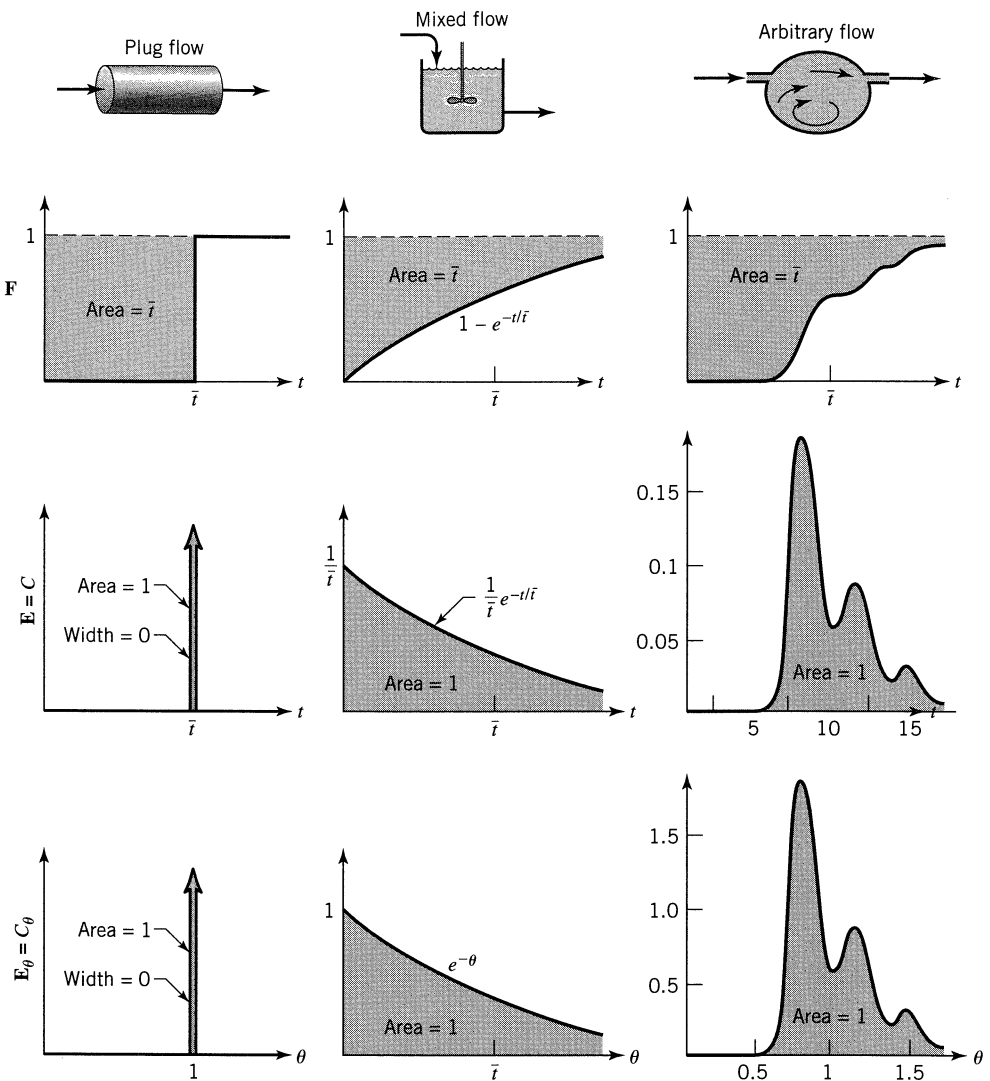


Figure 11.14 Properties of the E and F curves for various flows. Curves are drawn in terms of ordinary and dimensionless time units. Relationship between curves is given by Eqs. 7 and 8.

At any time these curves are related as follows:

$$\begin{aligned} \mathbf{E} &= \frac{v}{\dot{\mathbf{m}}} \cdot C_{\text{pulse}}, & \mathbf{F} &= \frac{v}{\dot{\mathbf{m}}} \cdot C_{\text{step}}, & \mathbf{E} &= \frac{d\mathbf{F}}{dt}, \\ \bar{t} &= \frac{V}{v}, & \theta &= \frac{t}{\bar{t}}, & \bar{\theta}_{\mathbf{E}} &= 1, & \mathbf{E}_{\theta} &= \bar{t}\mathbf{E} \\ \theta, \mathbf{E}_{\theta}, \mathbf{F} \dots &\text{all dimensionless, } \mathbf{E} &= [\text{time}^{-1}] \end{aligned}$$

(9)

EXAMPLE 11.1 FINDING THE RTD BY EXPERIMENT

The concentration readings in Table E11.1 represent a continuous response to a pulse input into a closed vessel which is to be used as a chemical reactor. Calculate the mean residence time of fluid in the vessel t , and tabulate and plot the exit age distribution E .

Table E11.1

Time t , min	Tracer Output Concentration, C_{pulse} gm/liter fluid
0	0
5	3
10	5
15	5
20	4
25	2
30	1
35	0

SOLUTION

The mean residence time, from Eq. 4, is

$$\bar{t} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \xrightarrow{\Delta t = \text{constant}} \frac{\sum t_i C_i}{\sum C_i}$$

$$= \frac{5 \times 3 + 10 \times 5 + 15 \times 5 + 20 \times 4 + 25 \times 2 + 30 \times 1}{3 + 5 + 5 + 4 + 2 + 1} = 15 \text{ min}$$

The area under the concentration-time curve,

$$\text{Area} = \sum C \Delta t = (3 + 5 + 5 + 4 + 2 + 1)5 = 100 \text{ gm} \cdot \text{min/liter}$$

gives the total amount of tracer introduced. To find E , the area under this curve must be unity; hence, the concentration readings must each be divided by the total area, giving

$$E = \frac{C}{\text{area}}$$

Thus we have

$E = \frac{C}{\text{area}}, \text{min}^{-1}$	t, min	0	5	10	15	20	25	30
		0	0.03	0.05	0.05	0.04	0.02	0.01

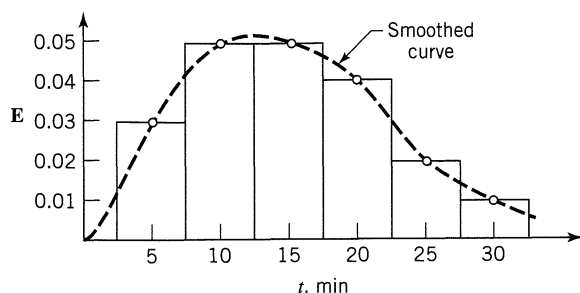


Figure E11.1

Figure E11.1 is a plot of this distribution.

EXAMPLE 11.2 FINDING THE E CURVE FOR LIQUID FLOWING THROUGH A VESSEL

A large tank (860 liters) is used as a gas-liquid contactor. Gas bubbles up through the vessel and out the top, liquid flows in at one part and out the other at 5 liters/s. To get an idea of the flow pattern of liquid in this tank a pulse of tracer ($M = 150$ gm) is injected at the liquid inlet and measured at the outlet, as shown in Fig. E11.2a.

- Is this a properly done experiment?
- If so, find the liquid fraction in the vessel.
- Determine the E curve for the liquid.
- Qualitatively what do you think is happening in the vessel?

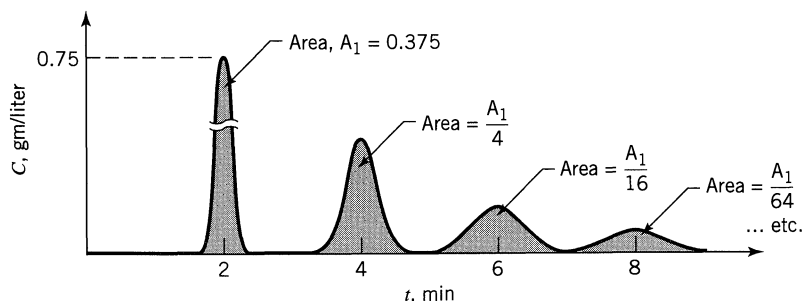


Figure E11.2a

SOLUTION

- Check the material balance against the tracer curve. From the material balance, Eq. 3, we should have

$$\text{Area} = \frac{M}{v} = \frac{150 \text{ gm}}{5 \text{ liters/s}} = 30 \frac{\text{gm} \cdot \text{s}}{\text{liter}} = 0.5 \frac{\text{gm} \cdot \text{min}}{\text{liter}}$$

From the tracer curve

$$\text{Area} = A_1 \left(1 + \frac{1}{4} + \frac{1}{16} + \dots \right) = 0.375 \left(\frac{4}{3} \right) = 0.5 \frac{\text{gm} \cdot \text{min}}{\text{liter}}$$

These values agree. The results are consistent.

(a)

(b) For the liquid, Eq. 4 gives

$$\bar{t}_l = \frac{\int tC dt}{\int C dt} = \frac{1}{0.5} \left[2A_1 + 4 \times \frac{A_1}{4} + 6 \times \frac{A_1}{16} + 8 \times \frac{A_1}{64} + \dots \right] = 2.67 \text{ min}$$

Thus the liquid volume in the vessel is

$$V_l = \bar{t}_l v_l = 2.67(5 \times 60) = 800 \text{ liters}$$

and the volume fraction of phases is

$$\left. \begin{array}{l} \text{Fraction of liquid} = \frac{800}{860} = 93\% \\ \text{Fraction of gas} = 7\% \end{array} \right\} \quad \text{(b)}$$

(c) Finally, from Eq. 5 we find the **E** curve, or

$$\mathbf{E} = \frac{C_{\text{pulse}}}{M/v} = \frac{0.75}{0.5} C = 1.5 C$$

Thus the **E** curve for the liquid is as shown in Fig. E11.2b.

(c)

(d) The vessel has a strong recirculation of liquid, probably induced by the rising bubbles.

(d)

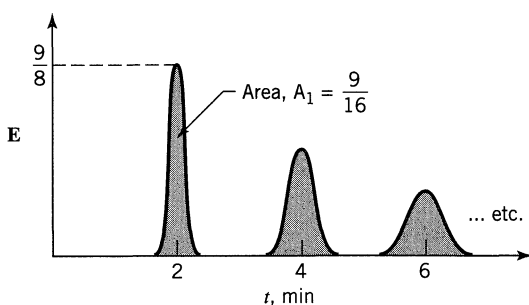


Figure E11.2b

The Convolution Integral

Suppose we introduce into a vessel a one-shot tracer signal C_{in} versus t as shown in Fig. 11.15. In passing through the vessel the signal will be modified to give an output signal C_{out} versus t . Since the flow with its particular RTD is responsible for this modification let us relate C_{in} , \mathbf{E} , and C_{out} .

Focus attention on tracer leaving at time about t . This is shown as the narrow rectangle B in Fig. 11.15. We may then write

$$\left(\begin{array}{c} \text{tracer leaving} \\ \text{in rectangle } B \end{array} \right) = \left(\begin{array}{c} \text{all the tracer entering } t' \text{ seconds earlier than } t, \\ \text{and staying for time } t' \text{ in the vessel} \end{array} \right)$$

We show the tracer which enters t' seconds earlier than t as the narrow rectangle A . In terms of this rectangle the above equation may be written

$$\left(\begin{array}{c} \text{tracer leaving} \\ \text{in rectangle } B \end{array} \right) = \sum_{\substack{\text{all rectangles} \\ A \text{ which enter} \\ \text{earlier then} \\ \text{time } t}} \left(\begin{array}{c} \text{tracer in} \\ \text{rectangle} \\ A \end{array} \right) \left(\begin{array}{c} \text{fraction of tracer in } A \\ \text{which stays for about} \\ t' \text{ seconds in the vessel} \end{array} \right)$$

In symbols and taking limits (shrinking the rectangles) we obtain the desired relationship, which is called the convolution integral

$$C_{out}(t) = \int_0^t C_{in}(t-t')\mathbf{E}(t')dt' \quad (10a)$$

In what can be shown to be equivalent form we also have

$$C_{out}(t) = \int_0^t C_{in}(t')\mathbf{E}(t-t')dt' \quad (10b)$$

We say that C_{out} is the *convolution* of \mathbf{E} with C_{in} and we write concisely

$$C_{out} = \mathbf{E} * C_{in} \quad \text{or} \quad C_{out} = C_{in} * \mathbf{E} \quad (10c)$$

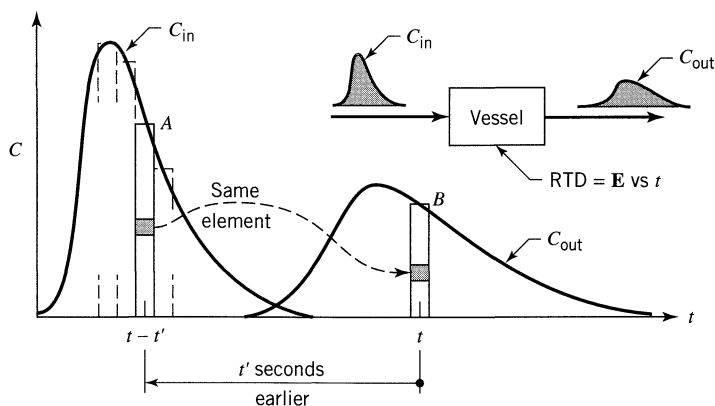


Figure 11.15 Sketch showing derivation of the convolution integral.

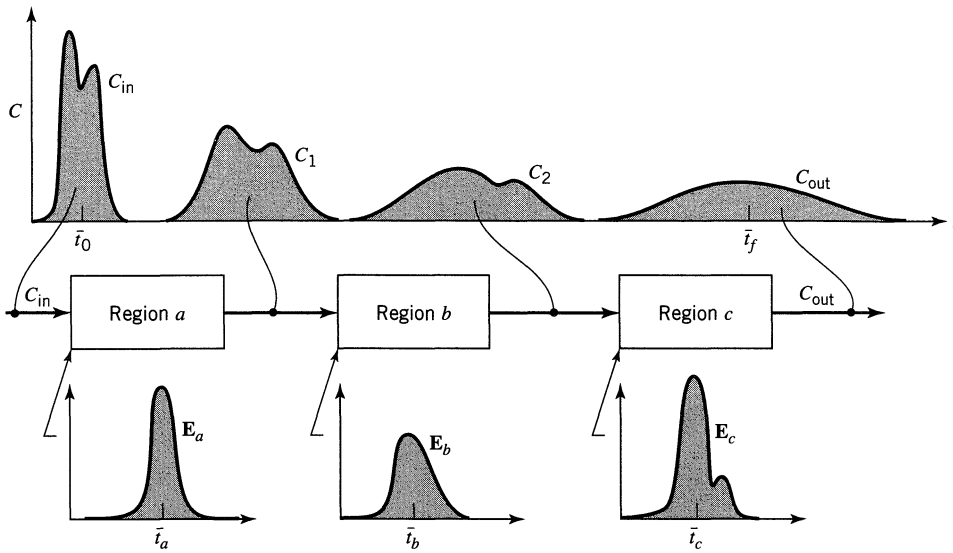


Figure 11.16 Modification of an input tracer signal C_{in} on passing through three successive regions.

Application of These Tools. To illustrate the uses of these mathematical tools consider three independent* flow units a , b , and c , which are closed and connected in series (see Fig. 11.16).

Problem 1. If the input signal C_{in} is measured and the exit age distribution functions E_a , E_b , and E_c are known, then C_1 is the convolution of E_a with C_{in} and so on, thus

$$C_1 = C_{in} * E_a, \quad C_2 = C_1 * E_b, \quad C_{out} = C_2 * E_c$$

and on combining

$$C_{out} = C_{in} * E_a * E_b * E_c \quad (11)$$

Thus we can determine the output from a multiregion flow unit.

Problem 2. If we measure C_{in} and C_{out} and know E_a and E_c we can then extract the unknown E_b . This type of problem is of particular importance in experimentation where the entrance region and collection region for tracer are both large compared with the experimental section.

It is a straightforward matter to convolute; however, to *deconvolute*, to find one of the distribution functions under the integral, is difficult. Thus Problem 2 is harder to treat than Problem 1 and requires using a computer.

* 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.

In some cases, however, we can in essence deconvolute. This special situation is considered at the end of Chapter 14 and is illustrated with an example there.

Example 11.3 illustrates convolution; Example 14.4 illustrates deconvolution.

EXAMPLE 11.3 CONVOLUTION

Let us illustrate the use of the convolution equation, Eq. 10, with a very simple example in which we want to find C_{out} given C_{in} and the E curve for the vessel, as shown in Fig. E11.3a.

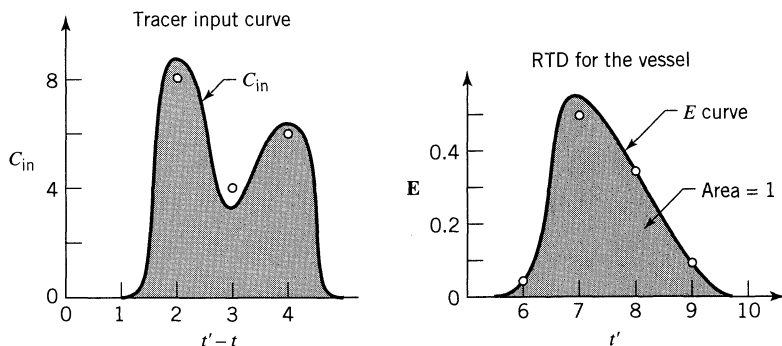


Figure E11.3a

SOLUTION

First of all, take 1 min time slices. The given data are then

$t' - t$	C_{in}	t'	E
0	0	5	0
1	0	6	0.05
2	8	7	0.50
3	4	8	0.35
4	6	9	0.10
5	0	10	0

Note: The area under the E curve is unity.

Now the first bit of tracer leaves at 8 min, the last bit at 13 min. Thus, applying the convolution integral, in discrete form, we have

t	C_{out}	
7	0	= 0
8	8×0.05	= 0.4
9	$8 \times 0.5 + 4 \times 0.05$	= 4.2
10	$8 \times 0.35 + 4 \times 0.5 + 6 \times 0.05$	= 5.1
11	$8 \times 0.10 + 4 \times 0.35 + 6 \times 0.5$	= 5.2
12	$4 \times 0.10 + 6 \times 0.35$	= 2.5
13	6×0.10	= 0.6
14		= 0

The C_{in} , E , and C_{out} curves, in discrete and in continuous form, are shown in Fig. E11.3b. Note that the area under the C_{out} curve equals the area under the C_{in} curve.

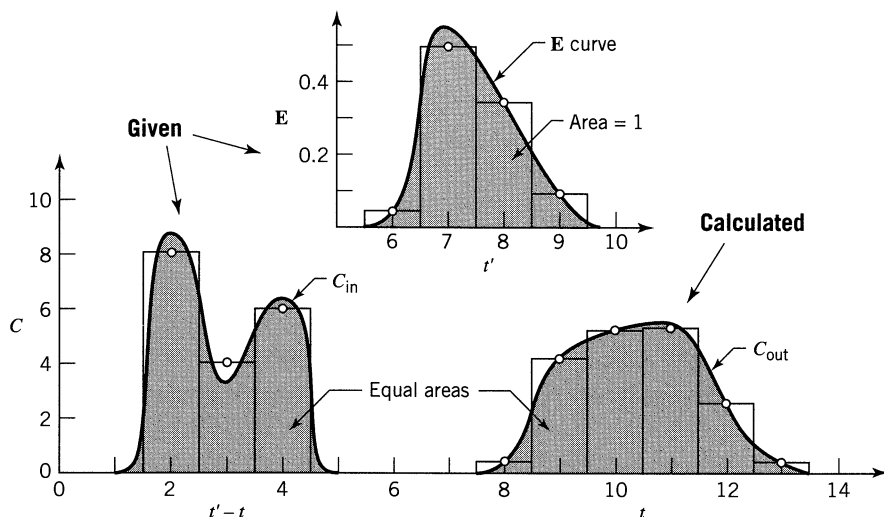


Figure E11.3b

11.2 CONVERSION IN NON-IDEAL FLOW REACTORS

To evaluate reactor behavior in general we have to know four factors:

1. the kinetics of the reaction
2. the RTD of fluid in the reactor
3. the earliness or lateness of fluid mixing in the reactor
4. whether the fluid is a micro or macro fluid

For *microfluids* in plug or mixed flow we have developed the equations in the earlier chapters. For intermediate flow we will develop appropriate models in Chapters 12, 13, and 14.

To consider the *early and late mixing of a microfluid*, consider the two flow patterns shown in Fig. 11.17 for a reactor processing a second-order reaction. In (a) the reactant starts at high concentration and reacts away rapidly because $n > 1$. In (b) the fluid drops immediately to a low concentration. Since the rate of reaction drops more rapidly than does the concentration you will end up with a lower conversion. Thus, for microfluids

Late mixing favors reactions where $n > 1$
Early mixing favors reactions where $n < 1$

(12)

For *macrofluids*, imagine little clumps of fluid staying for different lengths of time in the reactor (given by the E function). Each clump reacts away as a little

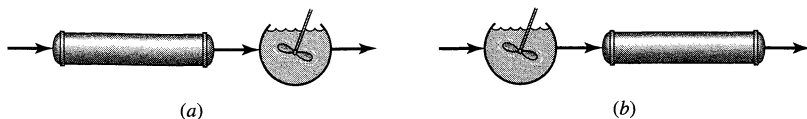


Figure 11.17 This shows the latest and the earliest mixing we can have for a given RTD.

batch reactor, thus fluid elements will have different compositions. So the mean composition in the exit stream will have to account for these two factors, the kinetics and the RTD. In words, then

$$\left(\begin{array}{c} \text{mean concentration} \\ \text{of reactant} \\ \text{in exit stream} \end{array} \right) = \sum_{\text{all elements of exit stream}} \left(\begin{array}{c} \text{concentration of} \\ \text{reactant remaining} \\ \text{in an element of} \\ \text{age between } t \\ \text{and } t + dt \end{array} \right) \left(\begin{array}{c} \text{fraction of exit} \\ \text{stream which is} \\ \text{of age between } t \\ \text{and } t + dt \end{array} \right)$$

In symbols this becomes

$$\left(\frac{\bar{C}_A}{C_{A0}} \right)_{\text{at exit}} = \int_0^{\infty} \left(\frac{C_A}{C_{A0}} \right)_{\text{for an element or little batch of fluid of age } t} \cdot E \, dt$$

or in terms of conversions

$$\bar{X}_A = \int_0^{\infty} (X_A)_{\text{element}} \cdot E \, dt \quad (13)$$

or in a form suitable for numerical integration

$$\frac{\bar{C}_A}{C_{A0}} = \sum_{\text{all age intervals}} \left(\frac{C_A}{C_{A0}} \right)_{\text{element}} \cdot E \, \Delta t$$

From Chapter 3 on batch reactors we have

- for first-order reactions $\left(\frac{C_A}{C_{A0}} \right)_{\text{element}} = e^{-kt} \quad (14)$

- for second-order reactions $\left(\frac{C_A}{C_{A0}} \right)_{\text{element}} = \frac{1}{1 + kC_{A0}t} \quad (15)$

- for an n th-order reaction $\left(\frac{C_A}{C_{A0}} \right)_{\text{element}} = [1 + (n-1)C_{A0}^{n-1}kt]^{1/1-n} \quad (16)$

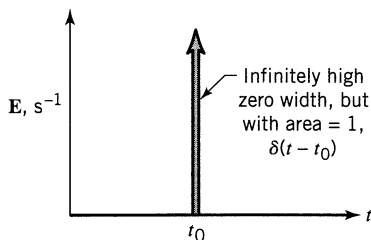


Figure 11.18 The E function for plug flow.

These are terms to be introduced into the performance equation, Eq. 13. Also, further on in this chapter we will show that for first-order reactions, the macrofluid equation is identical to the batch or to the microfluid equation.

We continue this discussion in Chapter 16.

The Dirac Delta Function, $\delta(t - t_0)$. One E curve which may puzzle us is the one which represents plug flow. We call this the Dirac δ function, and in symbols we show it as

$$\delta(t - t_0) \quad (17)$$

which says that the pulse occurs at $t = t_0$, as seen in Fig. 11.18.

The two properties of this function which we need to know are

$$\text{Area under the curve: } \int_0^\infty \delta(t - t_0) dt = 1 \quad (18)$$

$$\text{Any integration with a } \delta \text{ function: } \int_0^\infty \delta(t - t_0) f(t) dt = f(t_0) \quad (19)$$

Once we understand what this means we will see that it is easier to integrate with a δ function than with any other. For example,

$$\int_0^\infty \delta(t - 5) t^6 dt = 5^6 \quad (\text{just replace } t_0 \text{ by } 5)$$

$$\int_0^3 \delta(t - 5) t^6 dt = 0$$

EXAMPLE 11.4

CONVERSION IN REACTORS HAVING NON-IDEAL FLOW

The vessel of Example 11.1 is to be used as a reactor for a liquid decomposing with rate

$$-r_A = kC_A, \quad k = 0.307 \text{ min}^{-1}$$

Find the fraction of reactant unconverted in the real reactor and compare this with the fraction unconverted in a plug flow reactor of the same size.

SOLUTION

For the *plug flow reactor* with negligible density change we have

$$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = -\frac{1}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \frac{1}{k} \ln \frac{C_{A0}}{C_A}$$

and with τ from Example 11.1

$$\frac{C_A}{C_{A0}} = e^{-k\tau} = e^{-(0.307)(15)} = e^{-4.6} = \underline{\underline{0.01}}$$

Thus the fraction of reactant unconverted in a plug flow reactor equals 1.0%.

For the *real reactor* the fraction unconverted, given by Eq. 13 for macrofluids, is found in Table E11.4. Hence the fraction of reactant unconverted in the real reactor

$$\frac{C_A}{C_{A0}} = \underline{\underline{0.047}}$$

Table E11.4

t	E	kt	e^{-kt}	$e^{-kt}E \Delta t$
5	0.03	1.53	0.2154	$(0.2154)(0.03)(5) = 0.0323$
10	0.05	3.07	0.0464	0.0116
15	0.05	4.60	0.0100	0.0025
20	0.04	6.14	0.0021	0.0004
25	0.02	7.68	0.0005	0.0001
30	0.01	9.21	0.0001	0
<div style="display: flex; align-items: center;"> } given </div>				$\frac{C_A}{C_{A0}} = \sum e^{-kt}E \Delta t = \underline{\underline{0.0469}}$

From the table we see that the unconverted material comes mostly from the early portion of the E curve. This suggests that channeling and short-circuiting can seriously hinder attempts to achieve high conversion in reactors.

Note that since this is a first-order reaction we can treat it as a microfluid, or a macrofluid, whatever we wish. In this problem we solved the plug flow case as a microfluid, and we solved the nonideal case as a macrofluid.

EXAMPLE 11.5 REACTION OF A MACROFLUID

Dispersed noncoalescing droplets ($C_{A0} = 2$ mol/liter) react ($A \rightarrow R$, $-r_A = kC_A^2$, $k = 0.5$ liter/mol \cdot min) as they pass through a contactor. Find the average concentration of A remaining in the droplets leaving the contactor if their RTD is given by the curve in Fig. E11.5.

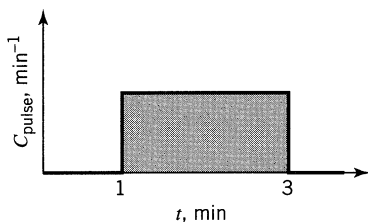


Figure E11.5

SOLUTION

Equation 13 is the pertinent performance equation. Evaluate terms in this expression. For

$$-r_A = kC_A^2, \quad k = 0.5 \text{ liter/mol} \cdot \text{min}$$

The batch equation from Chapter 3 is

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + kC_{A0}t} = \frac{1}{1 + 0.5(2)t} = \frac{1}{1 + t}$$

With $E = 0.5$ for $1 < t < 3$, Eq. 13 becomes

$$\frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} E dt = \int_1^3 \frac{1}{1+t} \cdot (0.5) dt = 0.5 \ln 2 = 0.347$$

So

$$\bar{X}_A = 1 - 0.347 = 0.653, \quad \text{or} \quad \underline{\underline{65\%}}$$

REFERENCE

Danckwerts, P. V., *Chem. Eng. Sci.*, **2**, 1 (1953).

PROBLEMS

- 11.1. A pulse input to a vessel gives the results shown in Fig. P11.1.
- (a) Check the material balance with the tracer curve to see whether the results are consistent.
 - (b) If the result is consistent, determine \bar{t} , V and sketch the E curve.

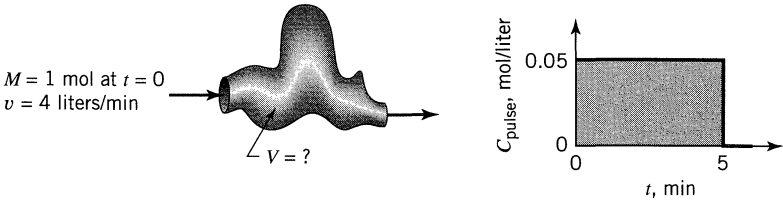


Figure P11.1

- 11.2. Repeat Problem P11.1 with one change: The tracer curve is now as shown in Fig. P11.2.

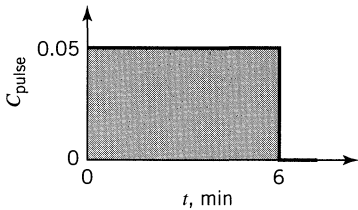


Figure P11.2

- 11.3. A pulse input to a vessel gives the results shown in Fig. P11.3.
- (a) Are the results consistent? (Check the material balance with the experimental tracer curve.)
 - (b) If the results are consistent, determine the amount of tracer introduced M , and the E curve.

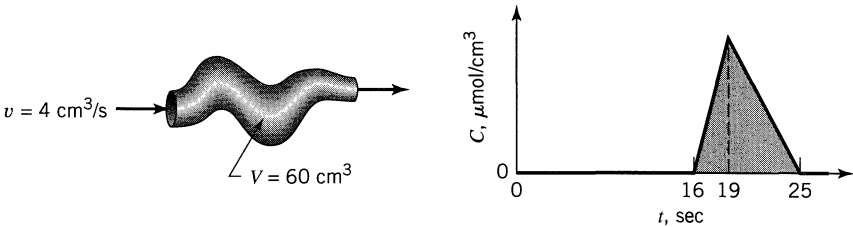


Figure P11.3

- 11.4. A step experiment is made on a reactor. The results are shown in Fig. P11.4.
- (a) Is the material balance consistent with the tracer curve?
 - (b) If so, determine the vessel volume V , \bar{t} , the F curve, and the E curve.

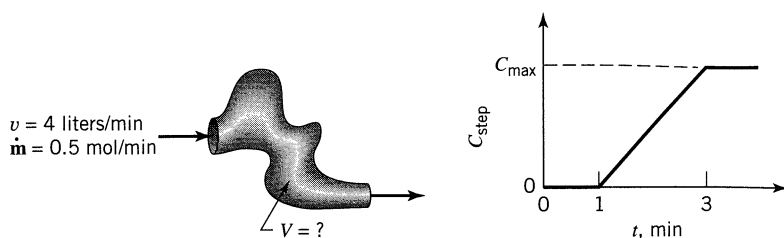


Figure P11.4

- 11.5.** A batch of radioactive material is dumped into the Columbia River at Hanford, Washington. At Bonneville Dam, about 400 km downstream the flowing waters ($6000 \text{ m}^3/\text{s}$) are monitored for a particular radioisotope ($t_{1/2} > 10 \text{ yr}$) and the data of Fig. P11.5 are obtained.
- (a) How many units of this tracer were introduced into the river?
- (b) What is the volume of Columbia River waters between Bonneville Dam and the point of introduction of tracer?

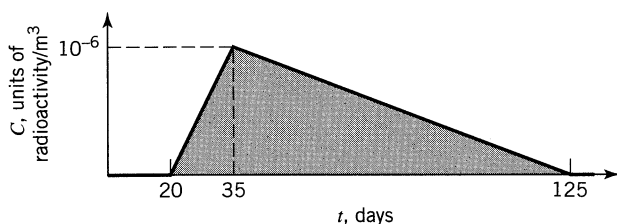


Figure P11.5

- 11.6.** A pipeline (10 cm I.D., 19.1 m long) simultaneously transports gas and liquid from here to there. The volumetric flow rate of gas and liquid are $60\,000 \text{ cm}^3/\text{s}$ and $300 \text{ cm}^3/\text{s}$, respectively. Pulse tracer tests on the fluids flowing through the pipe give results as shown in Fig. P11.6. What fraction of the pipe is occupied by gas and what fraction by liquid?

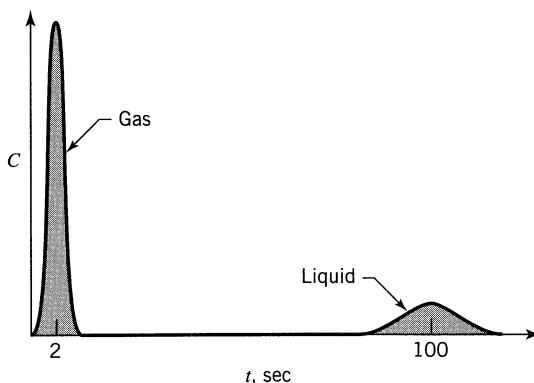
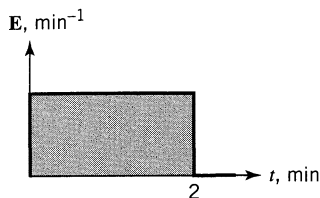


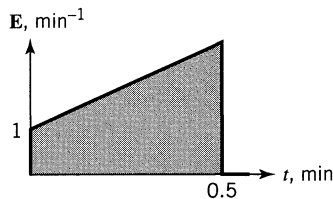
Figure P11.6

A liquid macrofluid reacts according to $A \rightarrow R$ as it flows through a vessel. Find the conversion of A for the flow patterns of Figs. P11.7 to P11.11 and kinetics as shown.

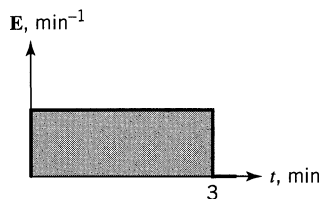
- 11.7.** $C_{A0} = 1 \text{ mol/liter}$
 $-r_A = kC_A^{0.5}$
 $k = 2 \text{ mol}^{0.5}/\text{liter}^{0.5} \cdot \text{min}$



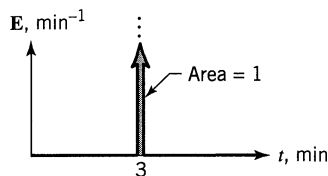
- 11.8.** $C_{A0} = 2 \text{ mol/liter}$
 $-r_A = kC_A^2$
 $k = 2 \text{ liter/mol} \cdot \text{min}$



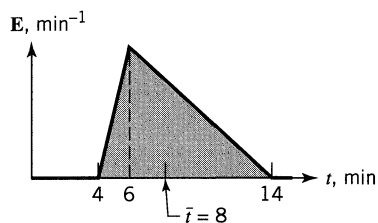
- 11.9.** $C_{A0} = 6 \text{ mol/liter}$
 $-r_A = k$
 $k = 3 \text{ mol/liter} \cdot \text{min}$



- 11.10.** $C_{A0} = 4 \text{ mol/liter}$
 $-r_A = k$
 $k = 1 \text{ mol/liter} \cdot \text{min}$

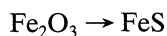


- 11.11.** $C_{A0} = 0.1 \text{ mol/liter}$
 $-r_A = k$
 $k = 0.03 \text{ mol/liter} \cdot \text{min}$



Figures P11.7, P11.8, P11.9, P11.10, P11.11

11.12–11.14. Hydrogen sulfide is removed from coal gas by contact with a moving bed of iron oxide particles which convert to the sulfide as follows:



In our reactor the fraction of oxide converted in any particle is determined by its residence time t and the time needed for complete conversion of

the particle τ , and this is given by

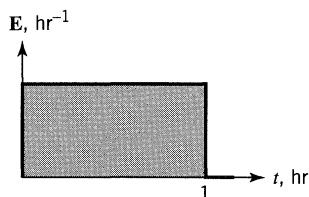
$$1 - X = \left(1 - \frac{t}{\tau}\right)^3 \quad \text{when } t < 1 \text{ hr, and with } \tau = 1 \text{ hr}$$

and

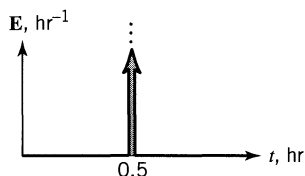
$$X = 1 \quad \text{when } t \geq 1 \text{ hr}$$

Find the conversion of iron oxide to sulfide if the RTD of solids in the contactor is approximated by the curve of Fig. P11.12, P11.13, or P11.14.

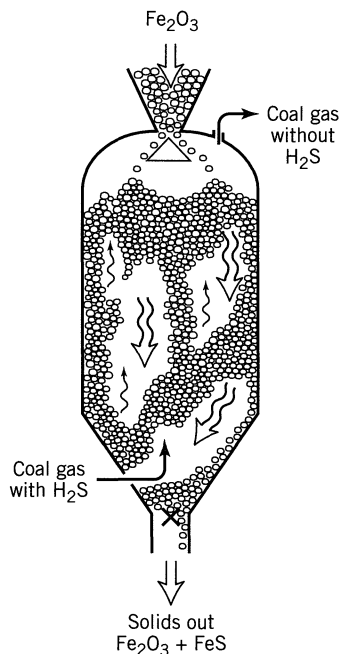
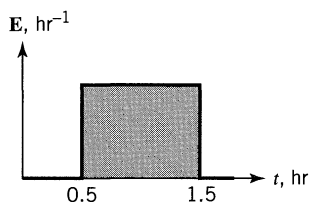
11.12.



11.13.



11.14.



Figures P11.12, P11.13, P11.14

11.15. Cold solids flow continuously into a fluidized bed where they disperse rapidly enough so that they can be taken as well mixed. They then heat up, they devolatilize slowly, and they leave. Devolatilization releases gaseous A which then decomposes by first-order kinetics as it passes through the bed. When the gas leaves the bed decomposition of gaseous A stops. From the following information determine the fraction of gaseous A which has decomposed.

Data: Since this is a large-particle fluidized bed containing cloudless bubbles, assume plug flow of gas through the unit. Also assume that the volume of gases released by the solids is small compared to the volume of carrier gas passing through the bed.

Mean residence time in the bed:

$$\bar{t}_s = 15 \text{ min}, \bar{t}_g = 2 \text{ s for carrier gas}$$

For the reaction: $A \rightarrow \text{products}$, $-r_A = kC_A$, $k = 1 \text{ s}^{-1}$

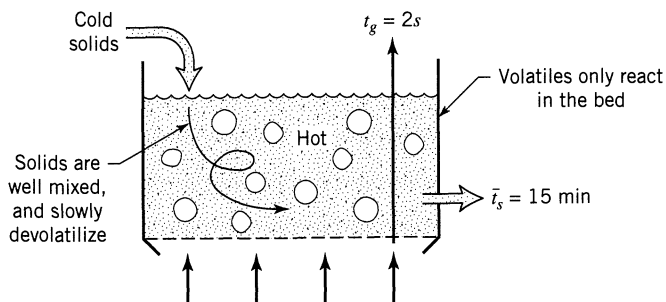
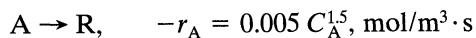


Figure P11.15

11.16. Reactant A ($C_{A0} = 64 \text{ mol/m}^3$) flows through a plug flow reactor ($\tau = 50 \text{ s}$), and reacts away as follows:



Determine the conversion of A if the stream is:

- (a) a microfluid,
- (b) a macrofluid.

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:

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

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

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.

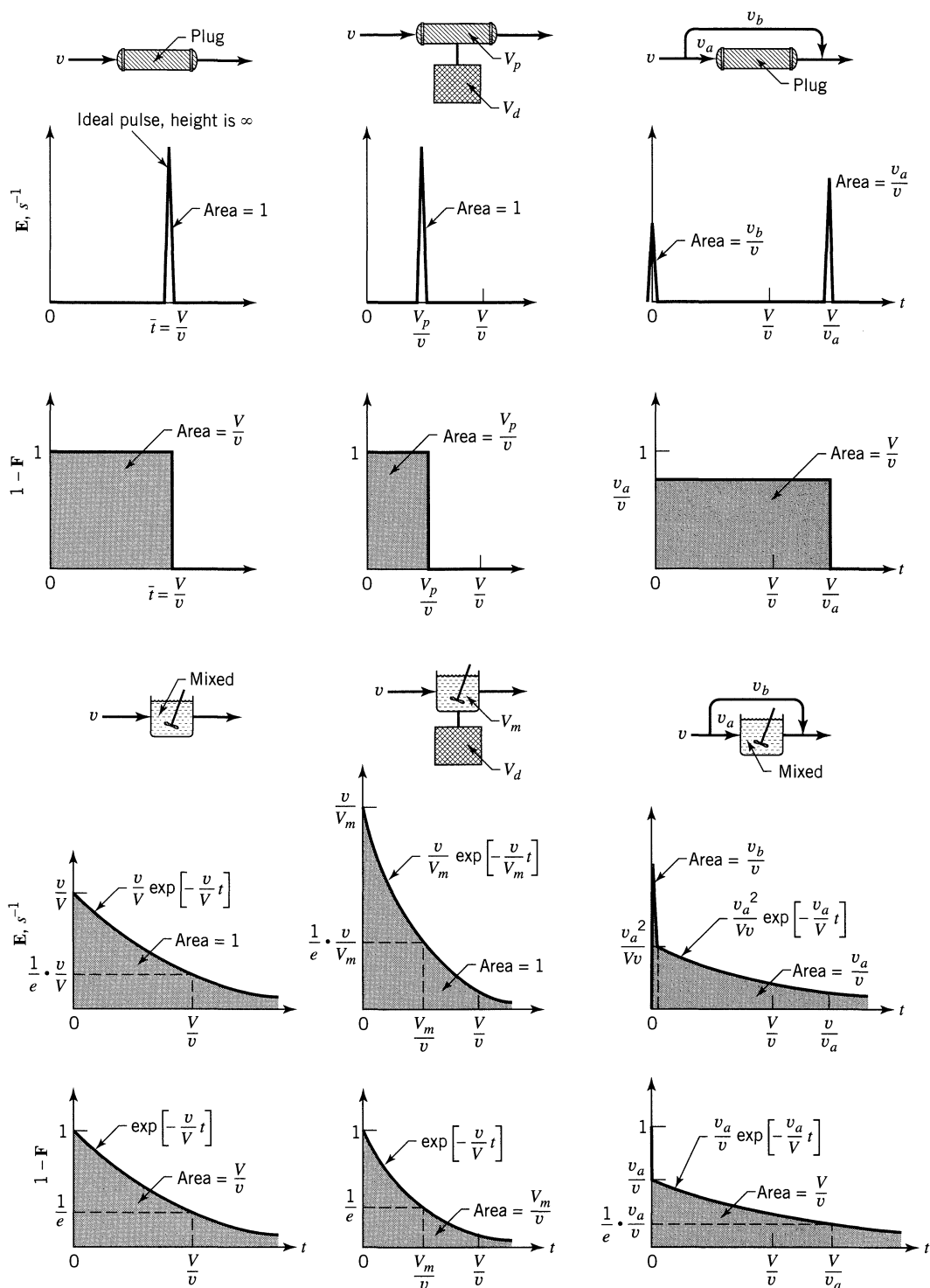


Figure 12.1 Various compartment flow models.

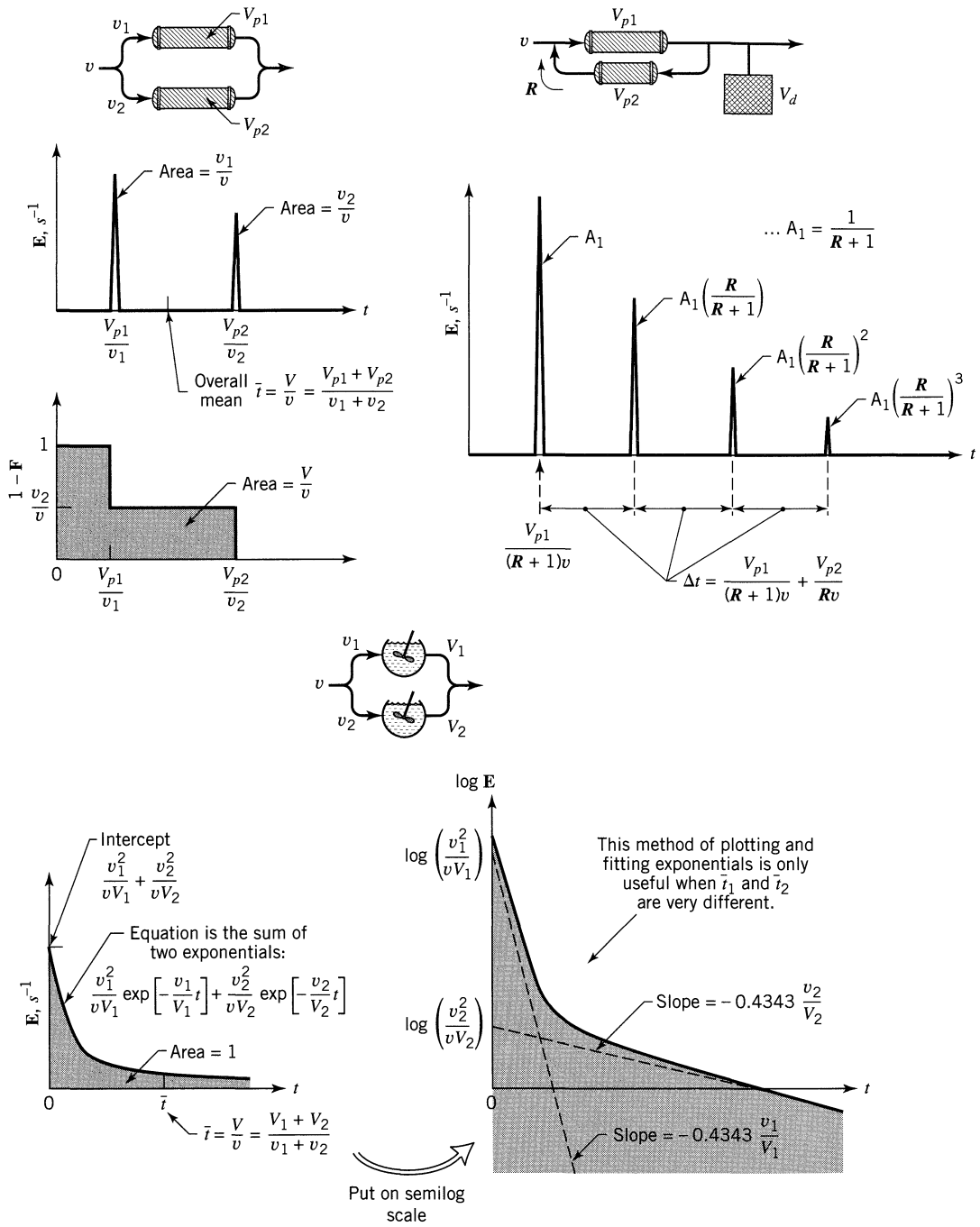


Figure 12.1 (Continued)

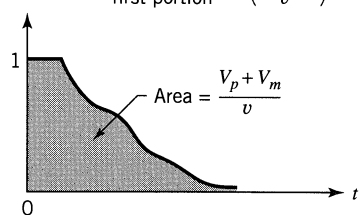
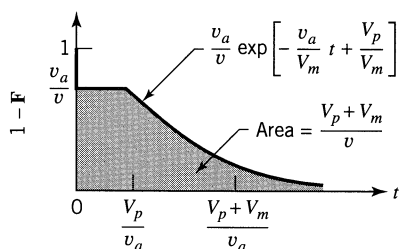
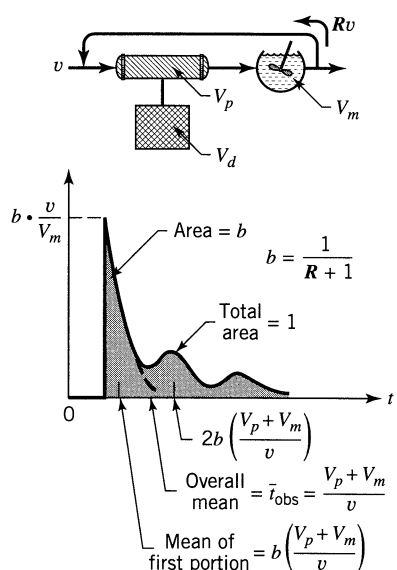
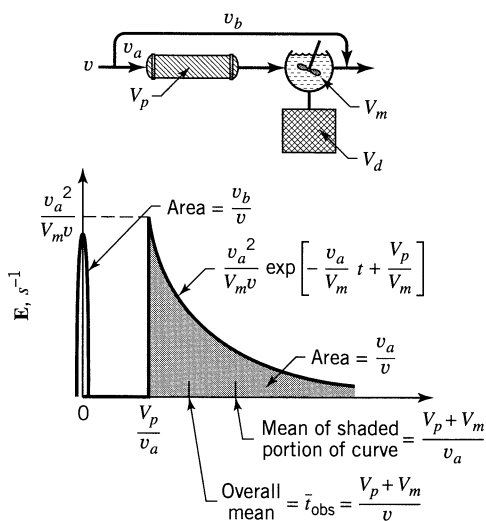
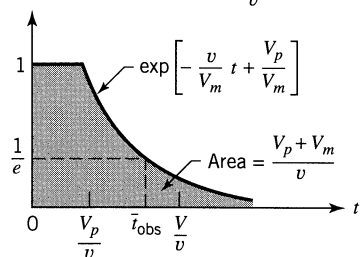
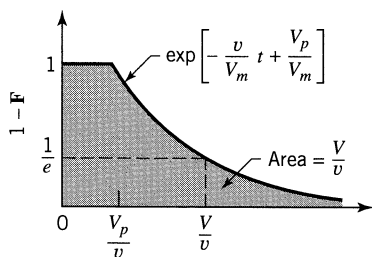
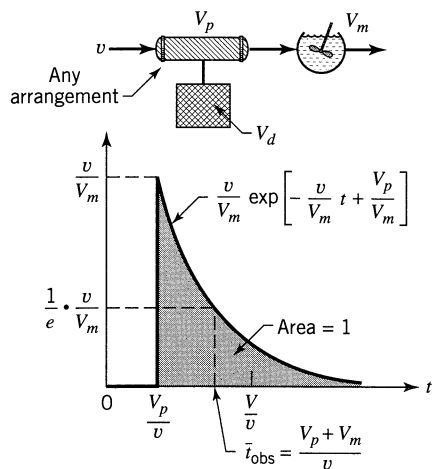
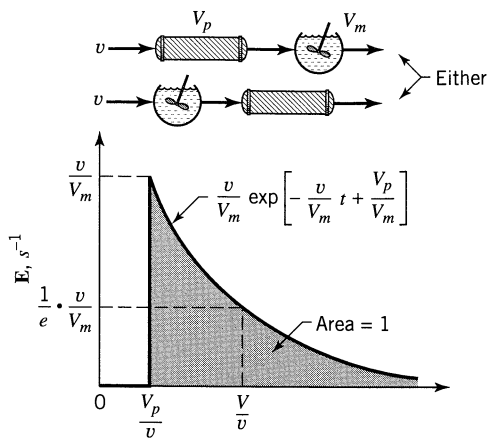


Figure 12.1 (Continued)

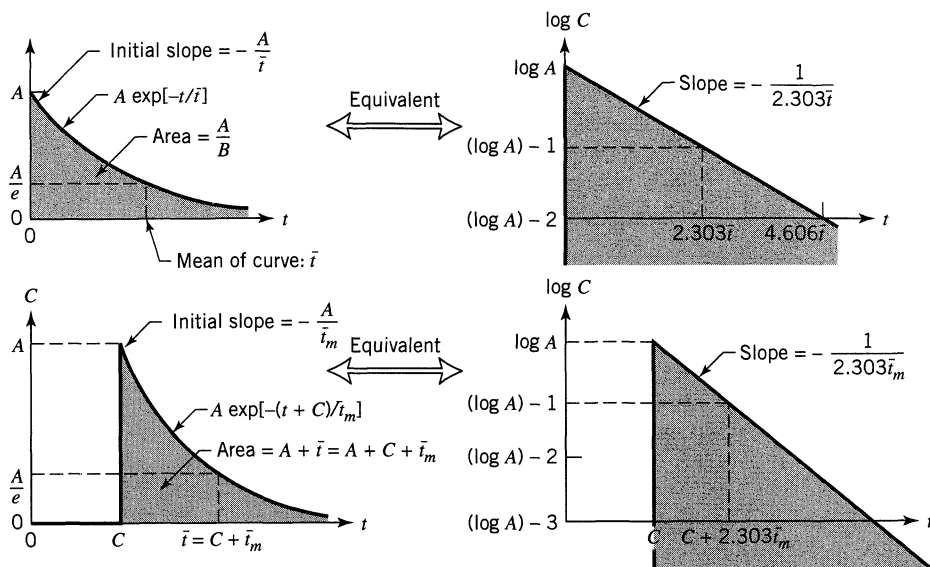


Figure 12.2 Properties of exponential decay tracer curves.

- (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

$$\begin{array}{ll} \text{If the real vessel} & \bar{t}_{\text{obs}} < \bar{t} \\ \text{has dead spaces:} & \cdots \text{ where } \begin{cases} \bar{t} = \frac{V}{v} \\ \bar{t}_{\text{obs}} = \frac{V_{\text{active}}}{v} \end{cases} \\ \text{If the real vessel} & \bar{t}_{\text{obs}} = \bar{t} \\ \text{has no dead spaces:} & \end{array}$$

- (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.

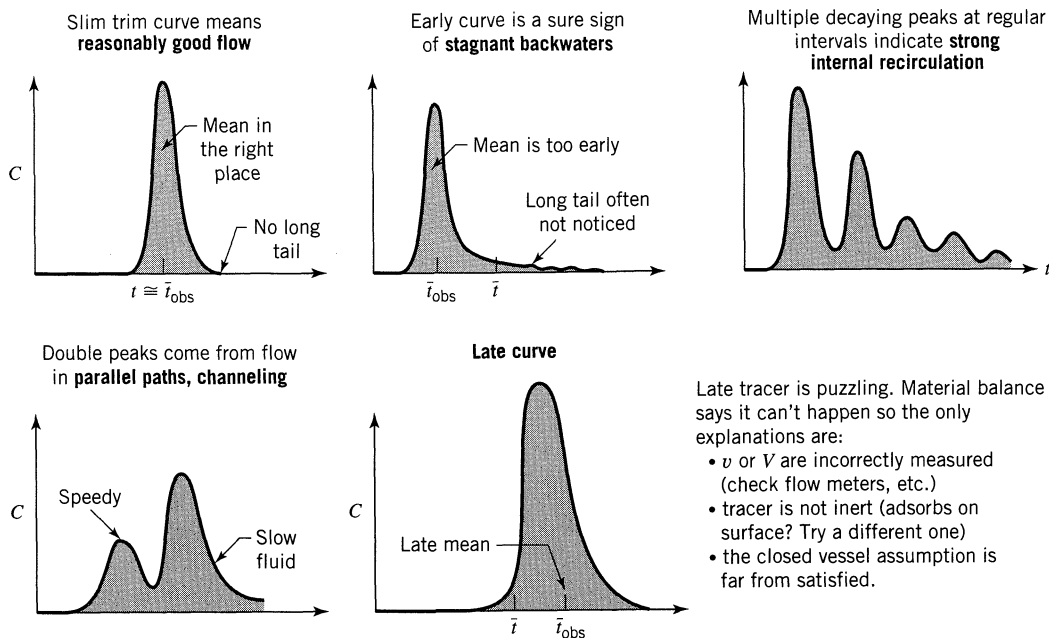


Figure 12.3 Misbehaving plug flow reactors.

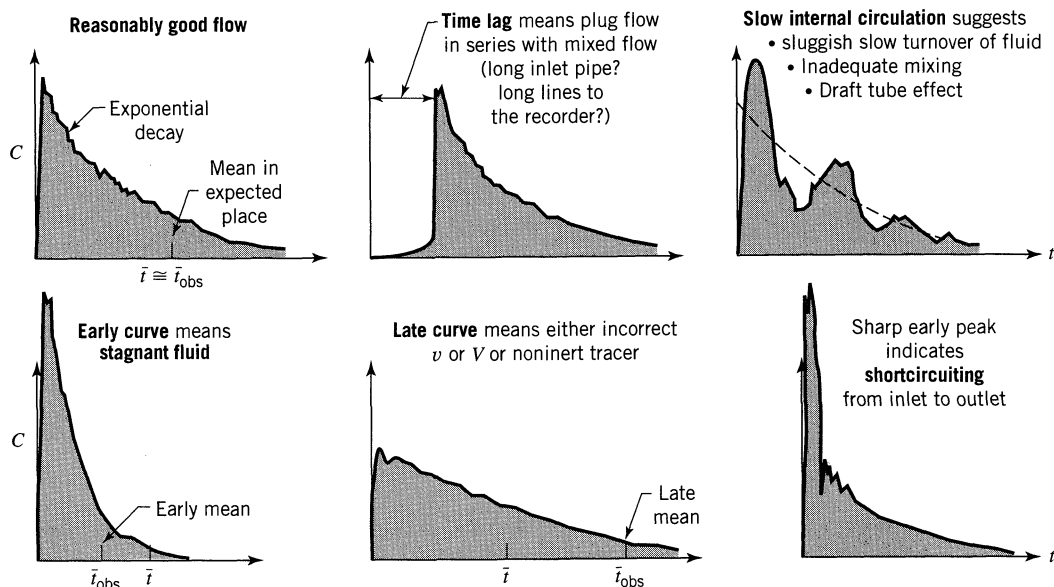


Figure 12.4 Misbehaving mixed flow reactors.

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.

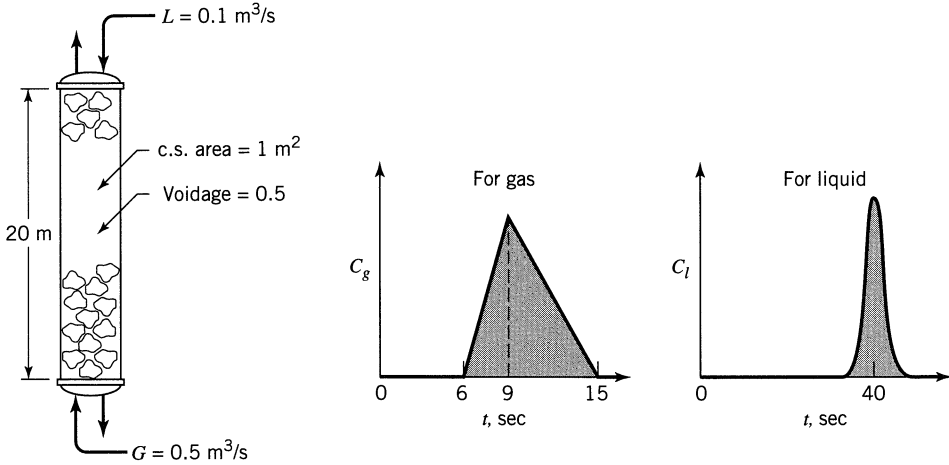


Figure E12.1

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?

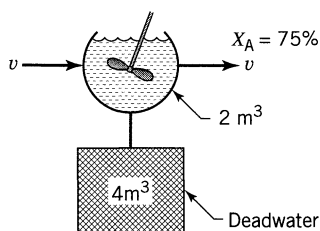


Figure E12.2

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

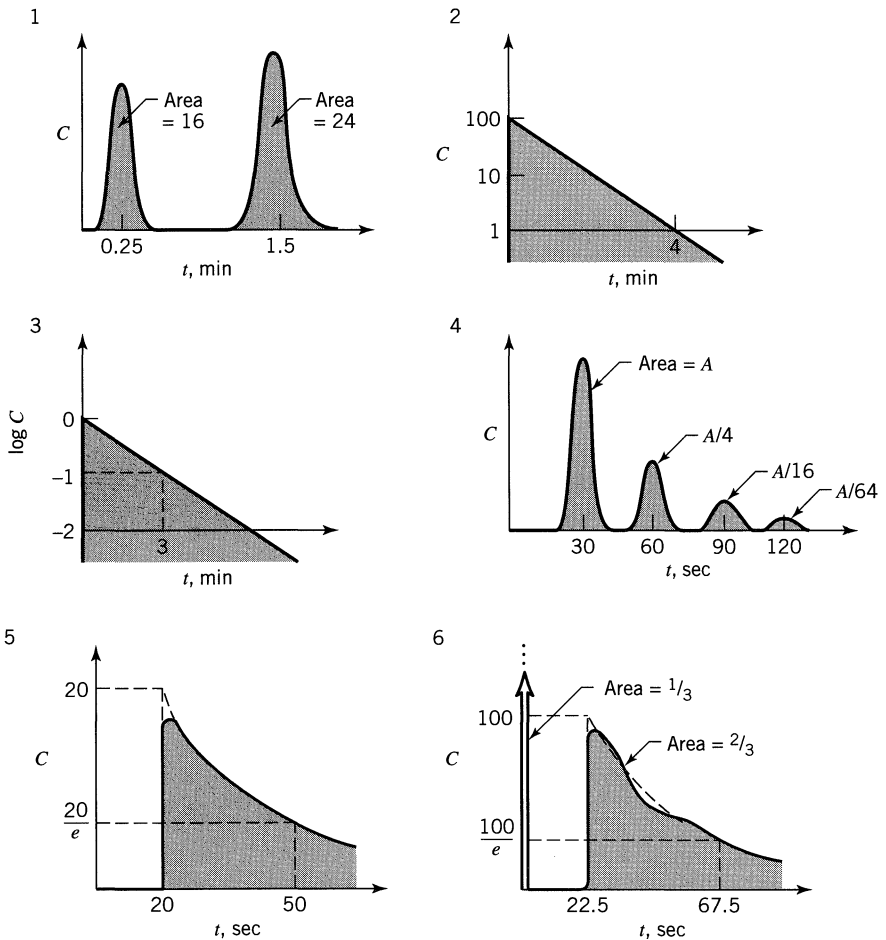
$$\frac{C_{A2}}{C_{A0}} = \frac{1}{k\tau_2 + 1} = \frac{1}{9 + 1} = 0.1$$

or

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

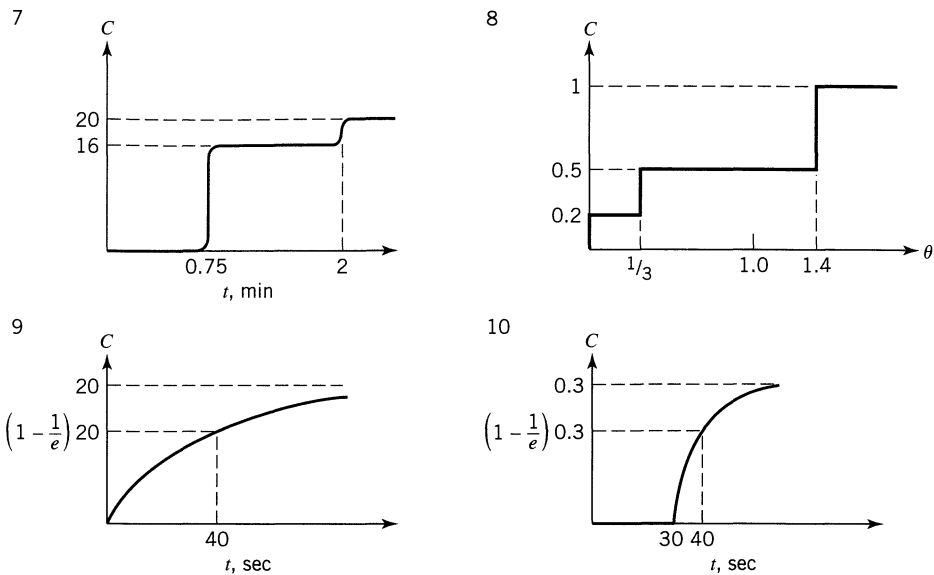
PROBLEMS

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?

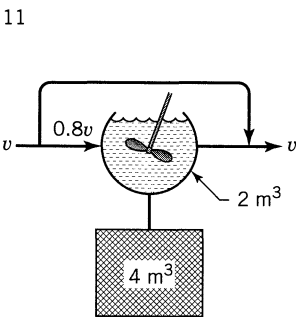


Figure P12.11

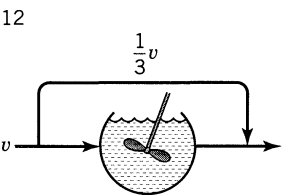


Figure P12.12

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** (m²/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

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

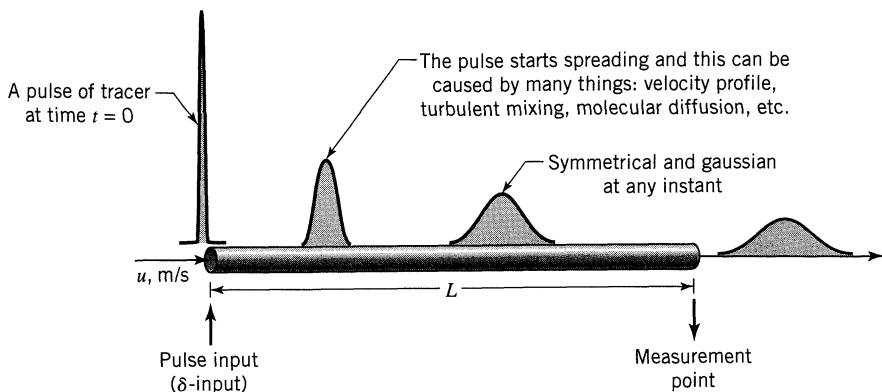


Figure 13.1 The spreading of tracer according to the dispersion model.

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 (time)². It is particularly useful for matching experimental curves to one of a family of theoretical curves. Figure 13.2 illustrates these terms.

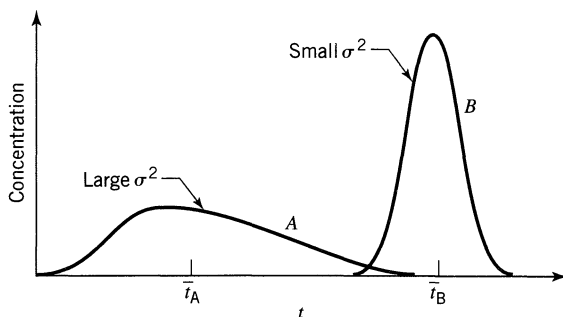


Figure 13.2

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

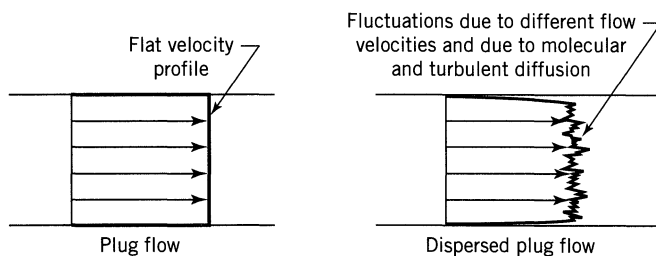


Figure 13.3 Representation of the dispersion (dispersed plug flow) model.

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

$$\frac{\mathbf{D}}{uL} \rightarrow 0 \quad \text{negligible dispersion, hence plug flow}$$

$$\frac{\mathbf{D}}{uL} \rightarrow \infty \quad \text{large dispersion, hence mixed flow}$$

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.

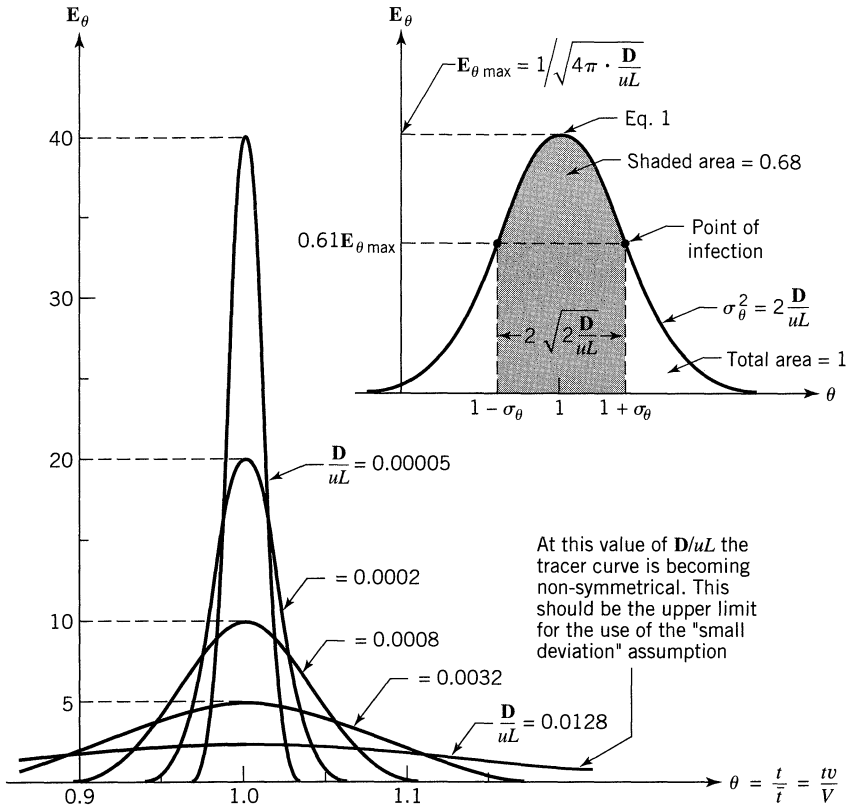


Figure 13.4 Relationship between D/uL and the dimensionless E_θ curve for small extents of dispersion, Eq. 7.

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.

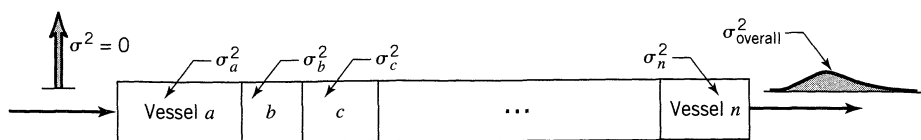


Figure 13.5 Illustration of additivity of means and of variances of the **E** curves of vessels a, b, \dots, n .

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 **E** curve of the vessel. So, on referring to Fig. 13.6, if we write for a one-shot input

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

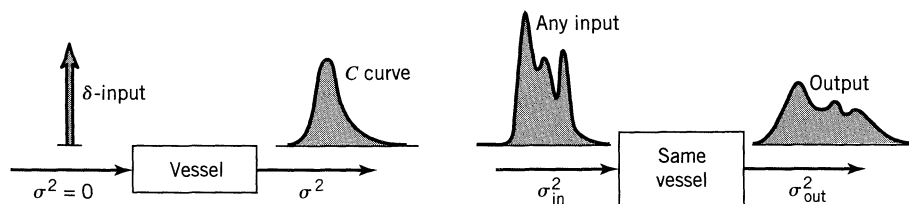


Figure 13.6 Increase in variance is the same in both cases, or $\sigma^2 = \sigma_{\text{out}}^2 - \sigma_{\text{in}}^2 = \Delta\sigma^2$.

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.

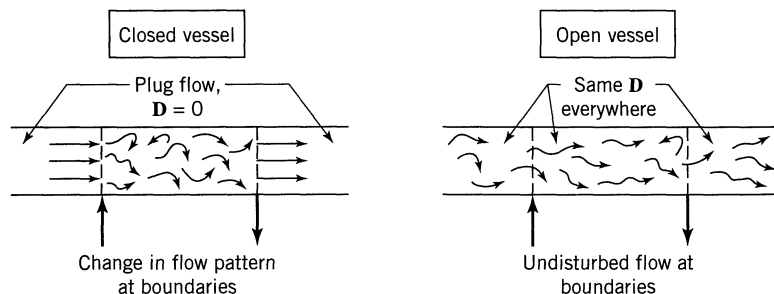


Figure 13.7 Various boundary conditions used with the dispersion model.

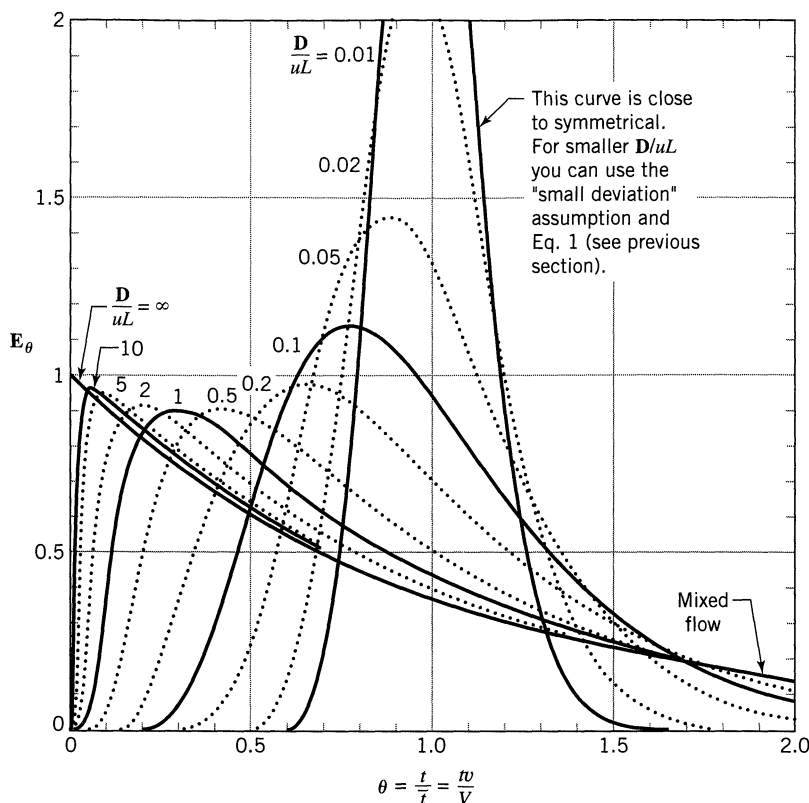


Figure 13.8 Tracer response curves for closed vessels and large deviations from plug flow.

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

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

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

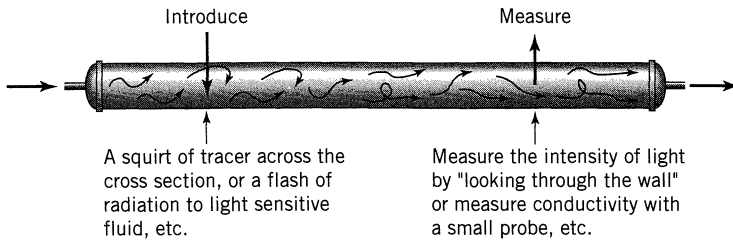


Figure 13.9 The open-open vessel boundary condition.

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

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

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

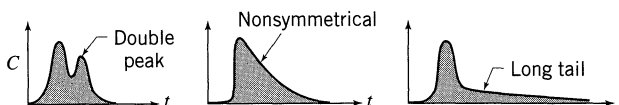
$$\bar{\theta}_{E,oo} = \frac{t_{E,oo}}{\bar{t}} = 1 + 2\left(\frac{D}{uL}\right) \quad \dots \text{or} \dots \quad t_{E,oo} = \frac{V}{v} \left[1 + 2\frac{D}{uL} \right] \quad (15)$$

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.



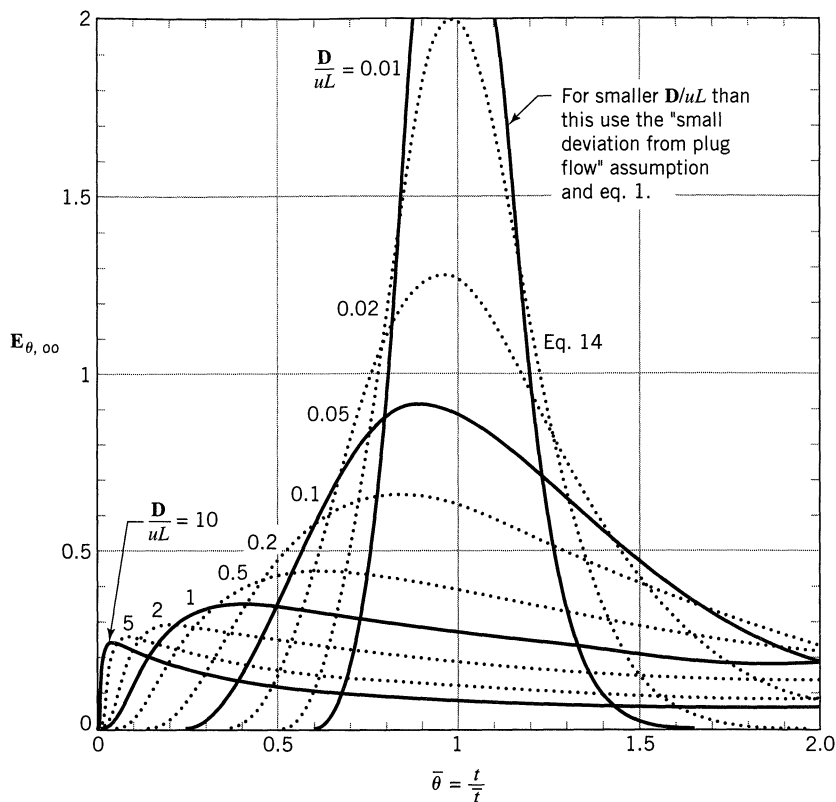


Figure 13.10 Tracer response curves for “open” vessels having large deviations from plug flow.

- (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;

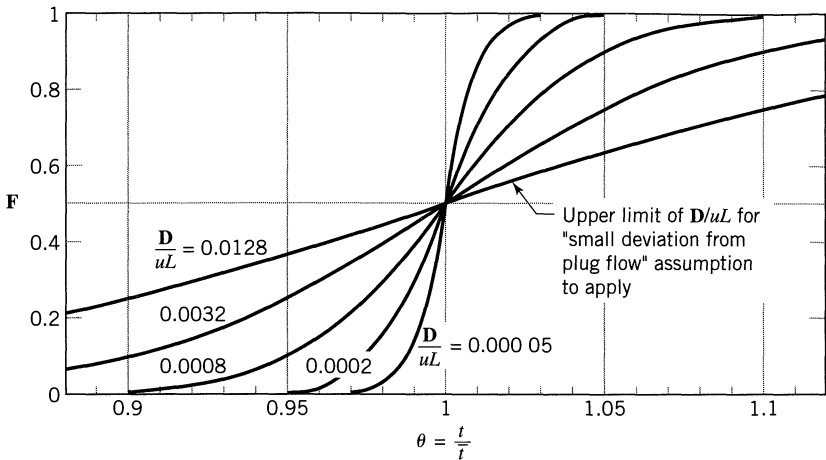


Figure 13.11 Step response curves for small deviations from plug flow.

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.

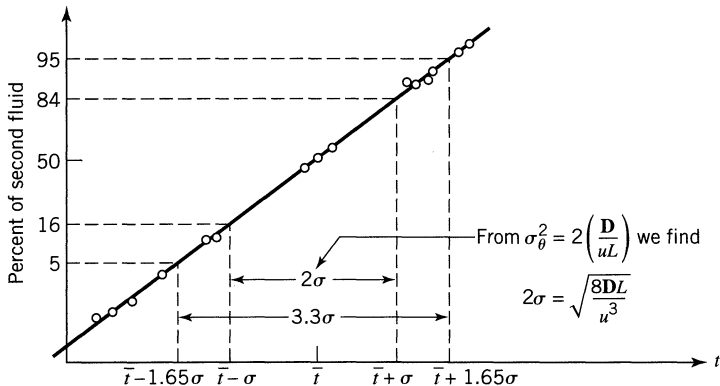


Figure 13.12 Probability plot of a step response signal. From this we find D/uL directly.

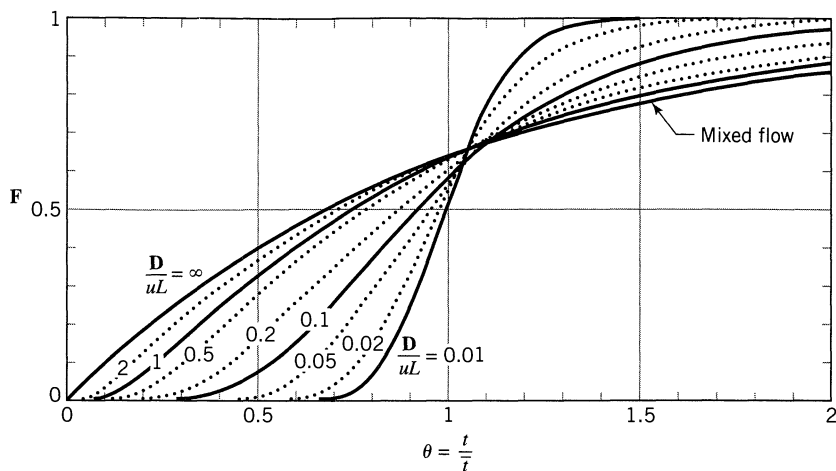


Figure 13.13 Step response curves for large deviations from plug flow in closed vessels.

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.

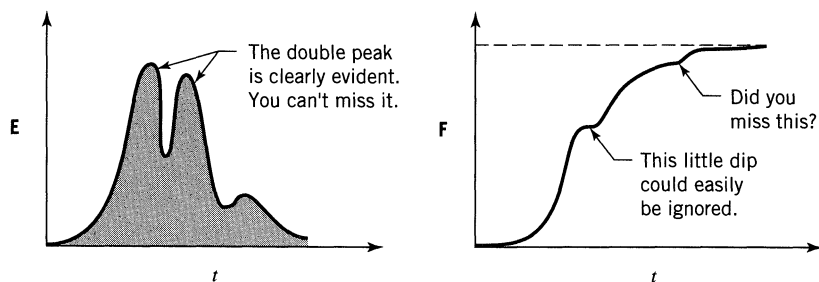


Figure 13.14 Sensitivity of the E and F curves for the same flow.

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

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

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

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

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.

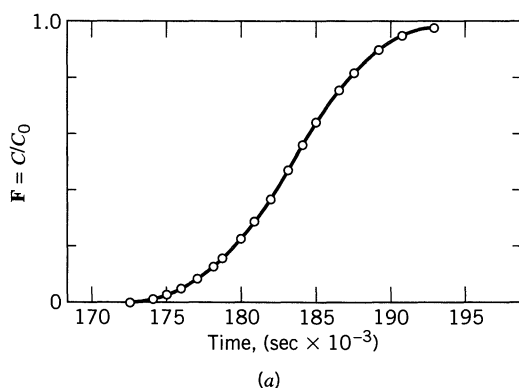


Figure E13.2a From von Rosenberg (1956).

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.

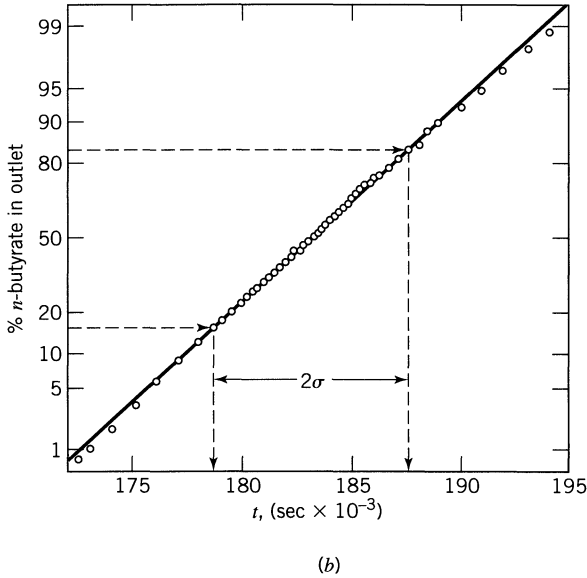


Figure E13.2b From Levenspiel and Smith (1957).

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

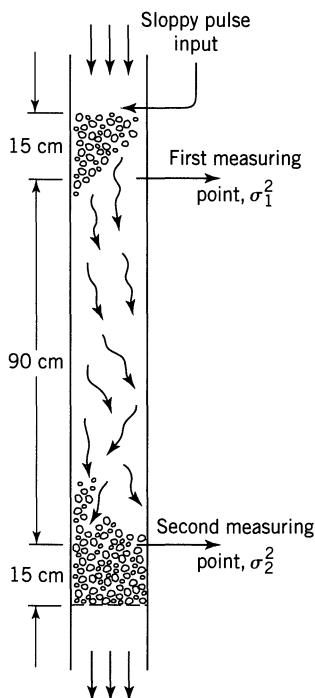


Figure E13.3

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.

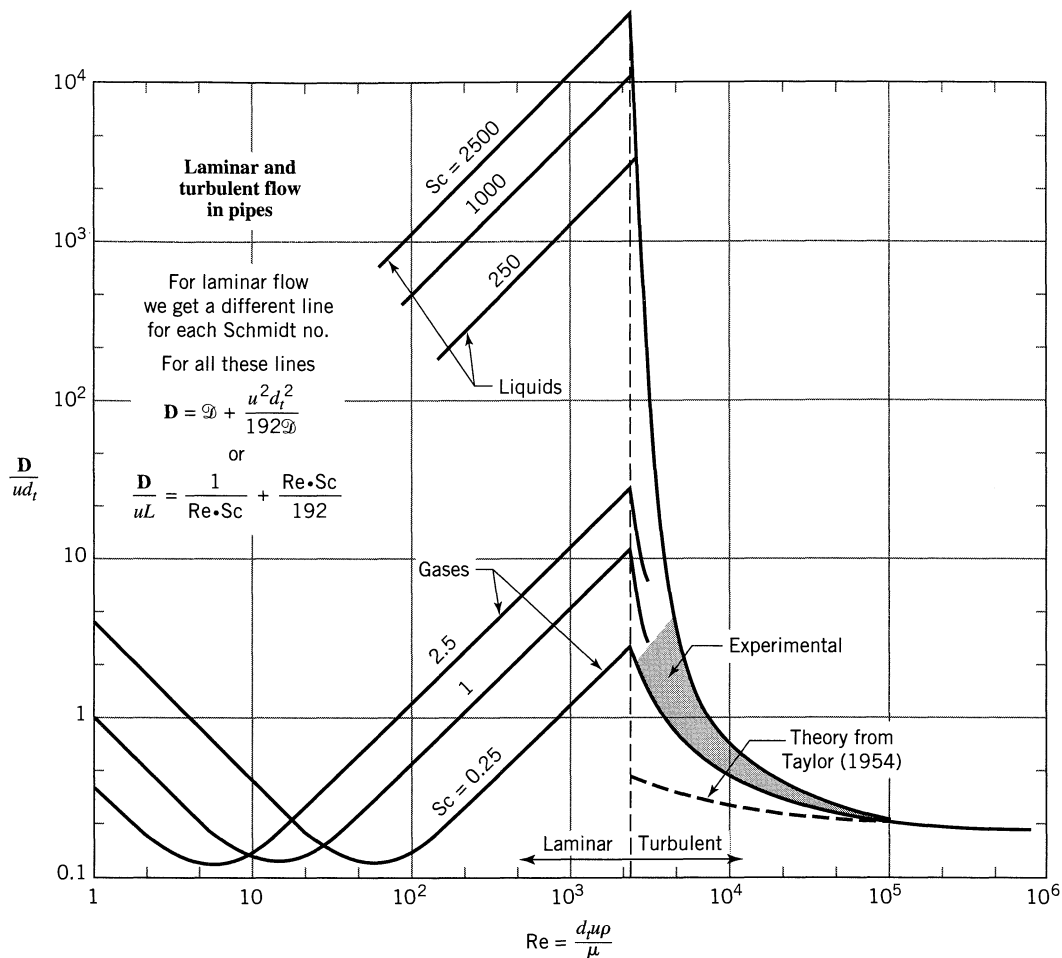


Figure 13.15 Correlation for the dispersion of fluids flowing in pipes, adapted from Levenspiel (1958b).

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.

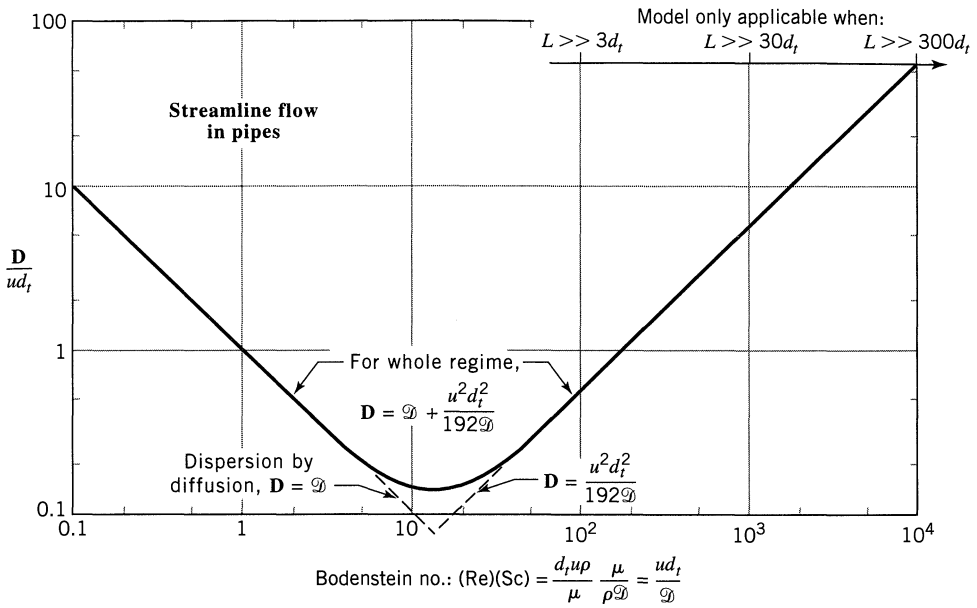


Figure 13.16 Correlation for dispersion for streamline flow in pipes; prepared from Taylor (1953, 1954a) and Aris (1956).

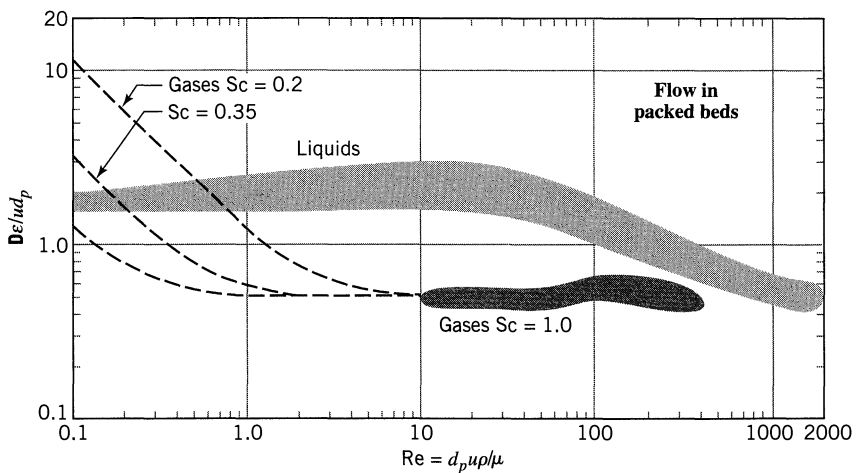
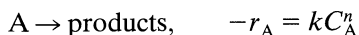


Figure 13.17 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds; prepared in part from Bischoff (1961).

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:

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

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

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

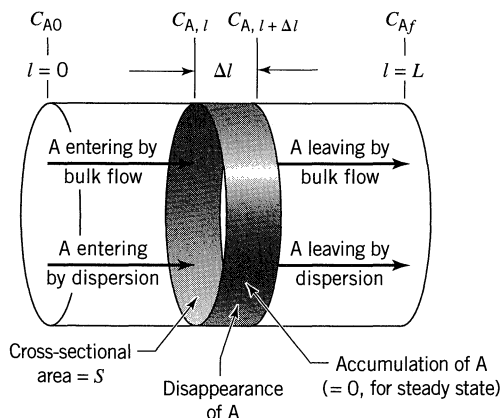


Figure 13.18 Variables for a closed vessel in which reaction and dispersion are occurring.

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

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

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

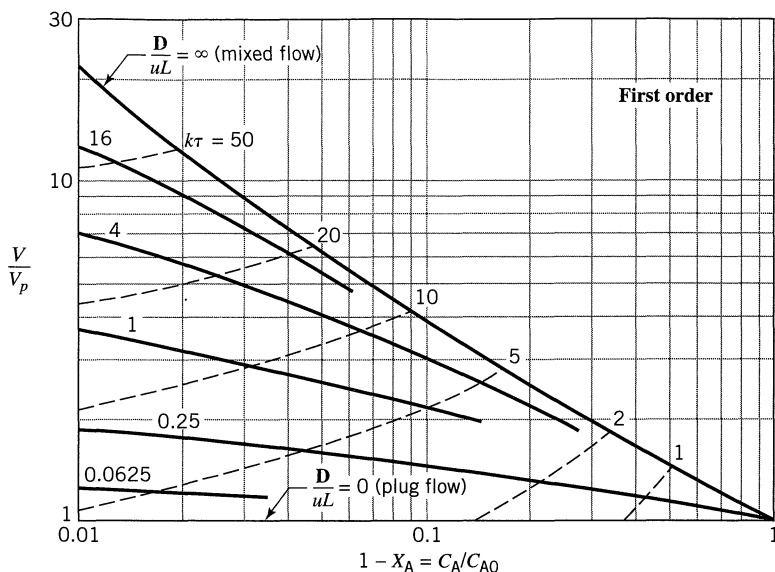


Figure 13.19 Comparison of real and plug flow reactors for the first-order $A \rightarrow$ products, assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

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.

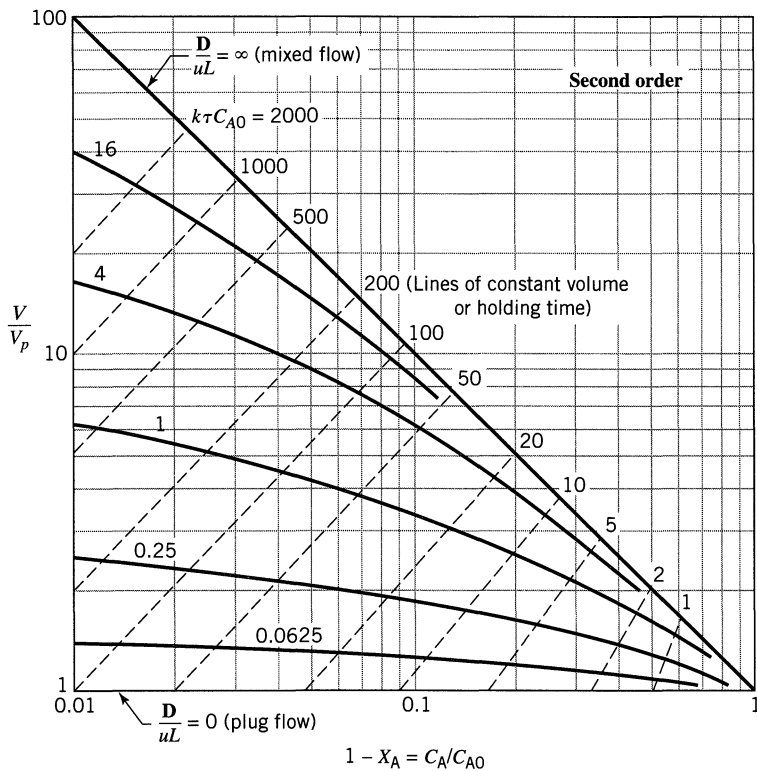
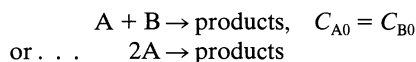


Figure 13.20 Comparison of real and plug flow reactors for the second-order reactions



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.

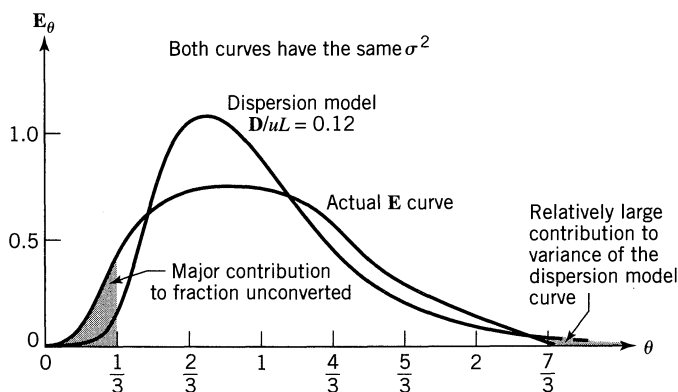


Figure E13.4

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

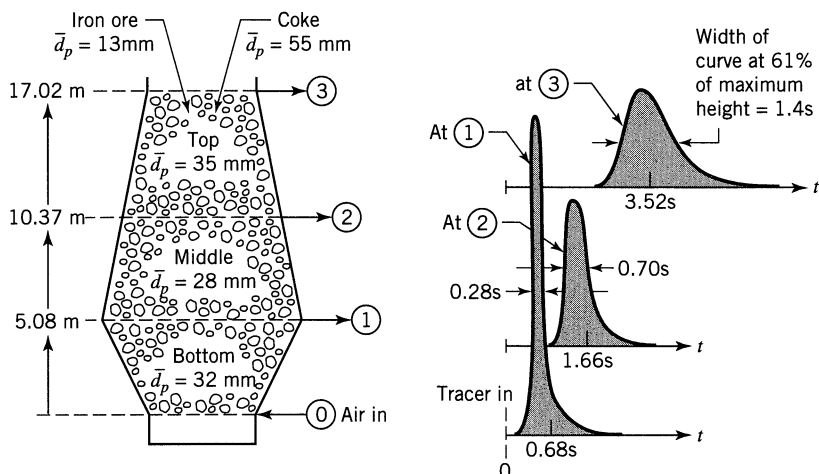


Figure P13.1

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 Gudenaa, 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 Udlum, 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.

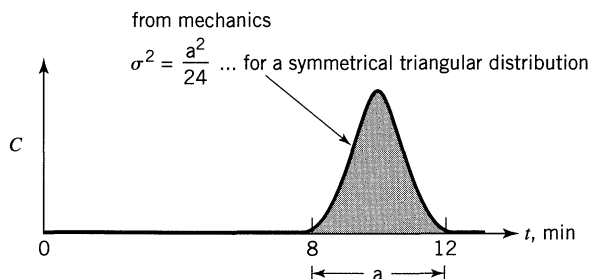


Figure P13.13

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

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

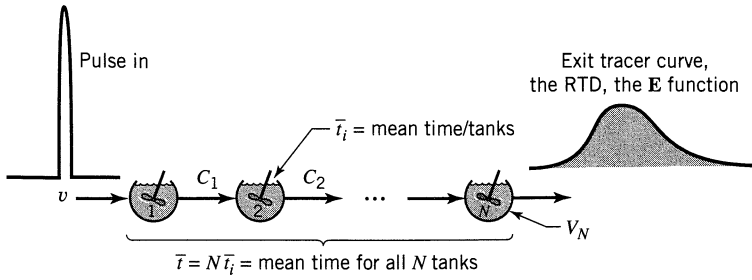


Figure 14.1 The tanks-in-series model.

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

$$\int_{C_0}^{C_1} \frac{dC_1}{C_1} = -\frac{1}{\bar{t}_1} \int_0^t dt$$

or

$$\frac{C_1}{C_0} = e^{-t/\bar{t}_1}$$

Since the area under this C/C_0 versus t curve is \bar{t}_1 (check this if you wish) it allows you to find the E curve; so one may write

$$\bar{t}_1 E_1 = e^{-t/\bar{t}_1} \quad [-] \quad N = 1 \quad (1)$$

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

$$V_2 \frac{dC_2}{dt} = v \cdot \underbrace{\frac{C_0}{\bar{t}_1} e^{-t/\bar{t}_1}}_{C_1} - vC_2 \quad \left[\frac{\text{mol tracer}}{\text{s}} \right]$$

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

$$\bar{t}_2 E_2 = \frac{t}{\bar{t}_2} e^{-t/\bar{t}_2} \quad [-] \quad N = 2 \quad (2)$$

For the N th tank. Integration for the 3rd, 4th, . . . , N th 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.

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

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

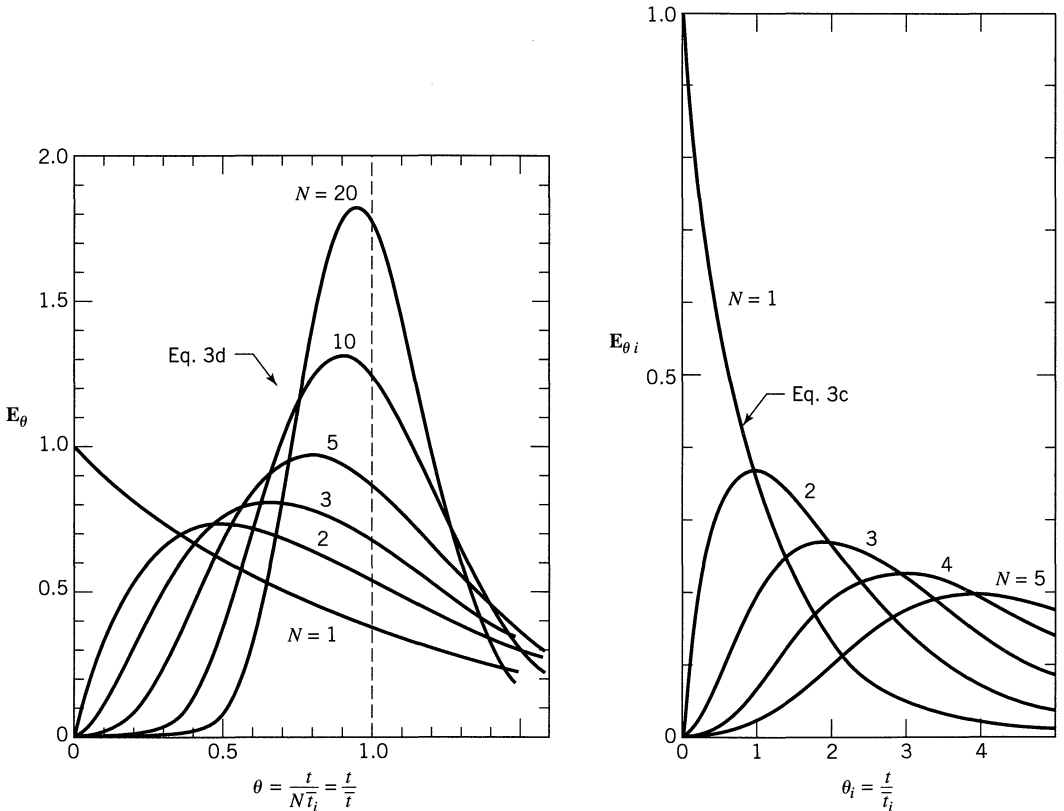


Figure 14.2 RTD curves for the tanks-in-series model, Eq. 3.

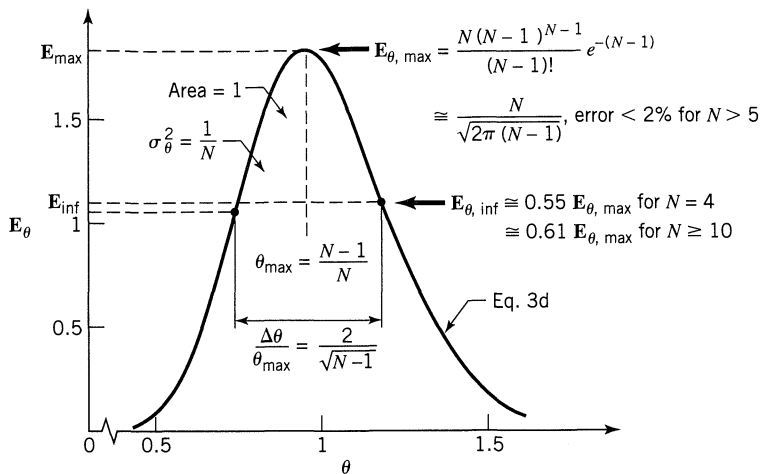


Figure 14.3 Properties of the RTD curve for the tanks-in-series model.

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.

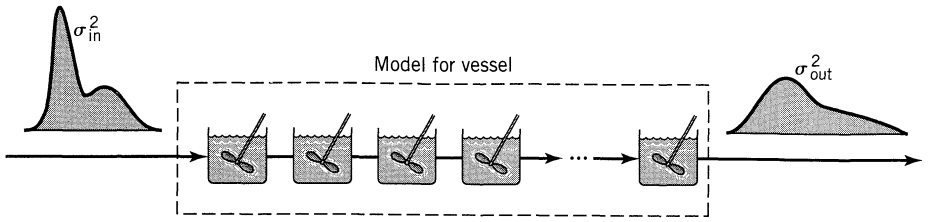


Figure 14.4 For any one-shot tracer input Eq. 4 relates input, output, and number of tanks.

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

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

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

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

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.

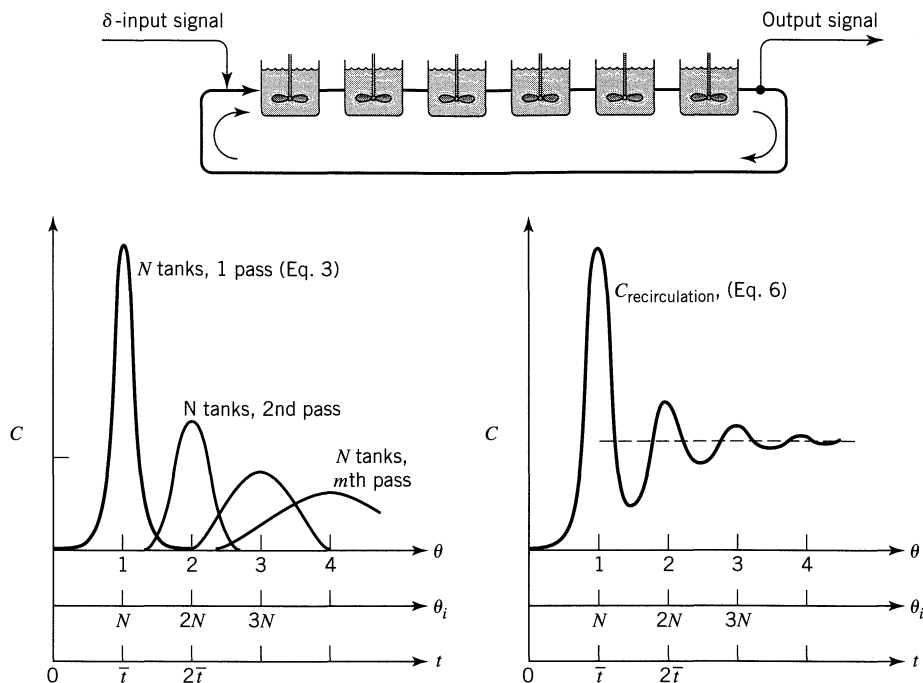


Figure 14.5 Tracer signal in a recirculating system.

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

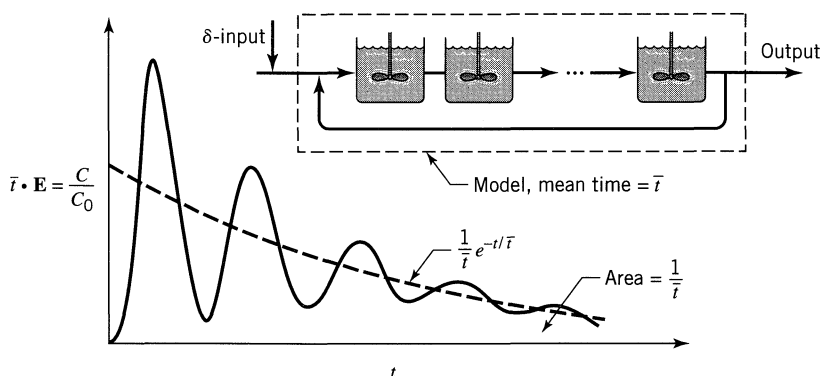


Figure 14.6 Recirculation with slow throughflow.

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.

$$\mathbf{F} = 1 - e^{-N\theta} \left[1 + N\theta + \frac{(N\theta)^2}{2!} + \cdots + \frac{(N\theta)^{N-1}}{(N-1)!} + \cdots \right] \quad (8)$$

$$\mathbf{F} = 1 - e^{-\theta_i} \left[1 + \theta_i + \frac{\theta_i^2}{2!} + \cdots + \frac{\theta_i^{N-1}}{(N-1)!} + \cdots \right]$$

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.

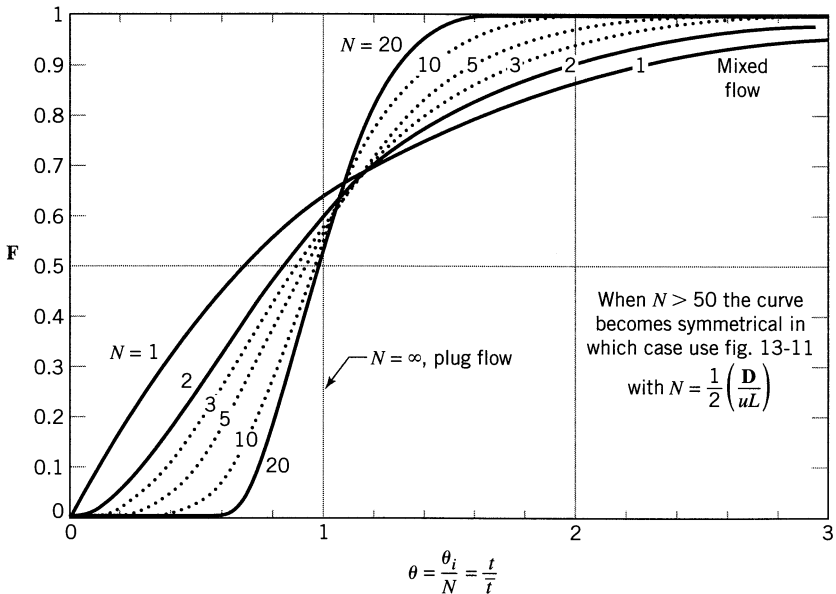


Figure 14.7 The F curve for the tanks-in-series model, from MacMullin and Weber (1935).

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.

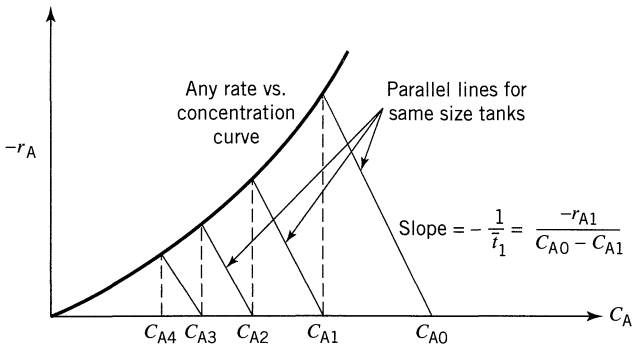


Figure 14.8 Graphical method of evaluating the performance of N tanks in series for any kinetics.

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

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

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:	$L_2 = 50 \text{ m}$	$\sigma_2 = ?$	$\sigma_2^2 = ?$

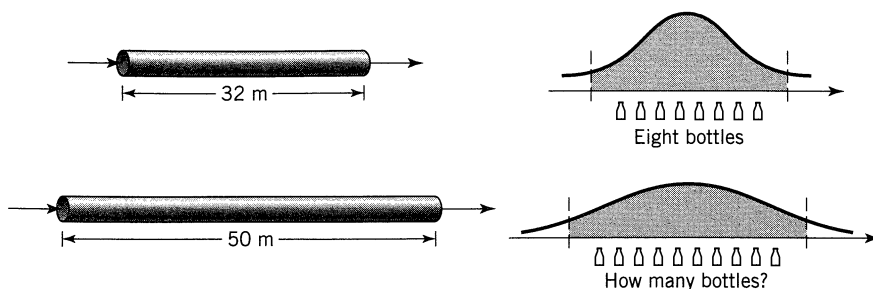


Figure E14.1

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

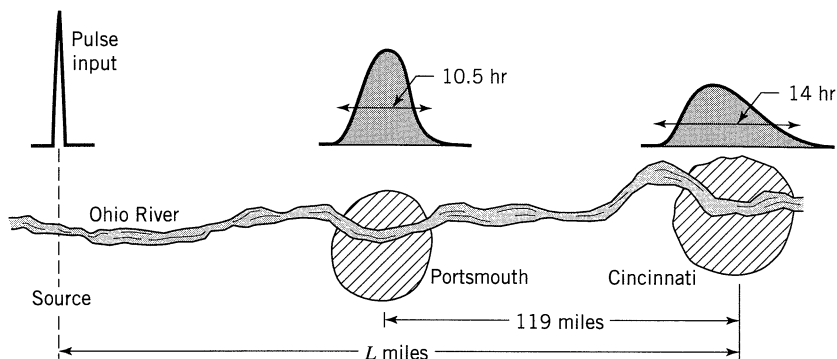


Figure E14.2

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.

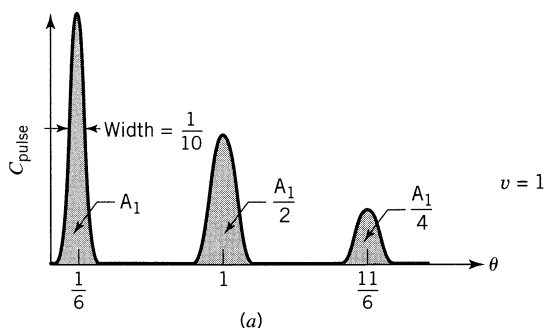


Figure E14.3a

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.

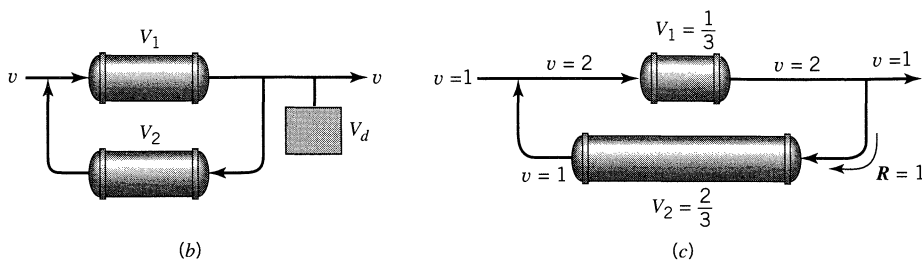


Figure E14.3b and c

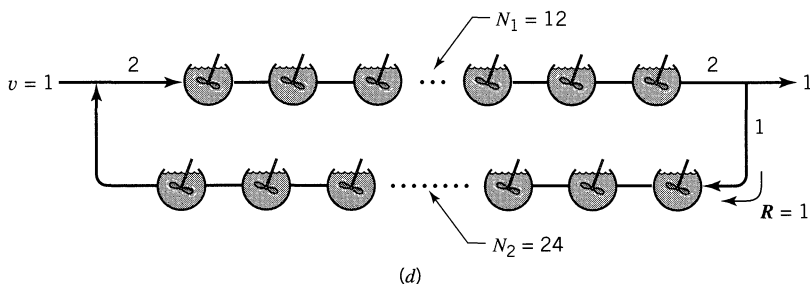


Figure E14.3d

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

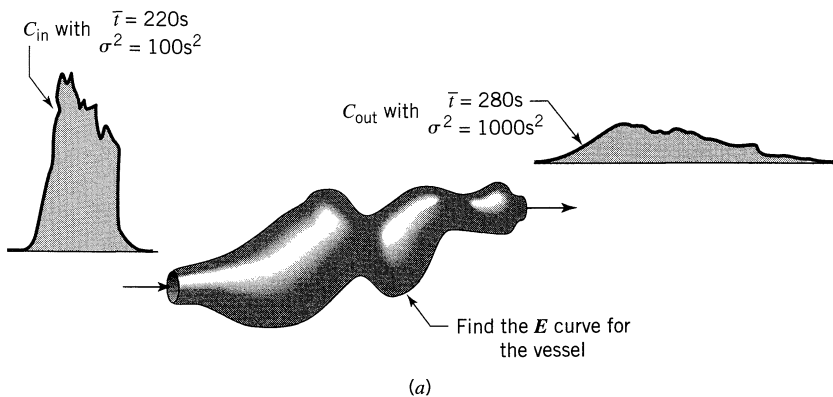
Given C_{in} and C_{out} as well as the location and spread of these tracer curves, as shown in Fig. E14.4a estimate the vessel **E** curve. We suspect that the tanks-in-series model reasonably represents the flow in the vessel.

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

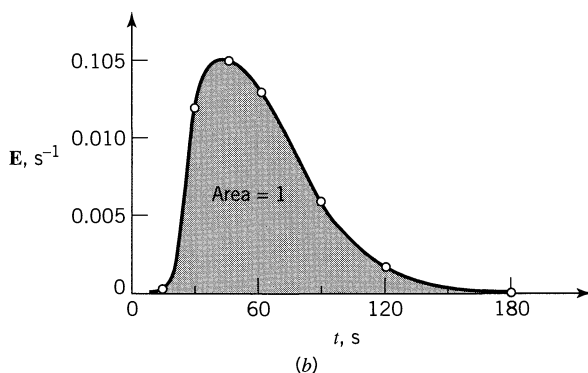
$$E = \frac{t^{N-1}}{\bar{t}^N} \cdot \frac{N^N}{(N-1)!} e^{-tN/\bar{t}}$$

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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- Harrell, J. E., Jr., and Perona, J. J., *Ind. Eng. Chem. Process Design Develop.*, **7**, 464 (1968).
 MacMullin, R. B., and Weber, M., Jr., *Trans. AIChE*, **31**, 409 (1935).
 van der Vusse, J. G., *Chem. Eng. Sci.*, **17**, 507 (1962).
 Vonken, R. M., Holmes, D. B., and den Hartog, H. W., *Chem. Eng. Sci.*, **19**, 209 (1964).

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

maximum concentration = 100 mmol

tracer spread = 1 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.

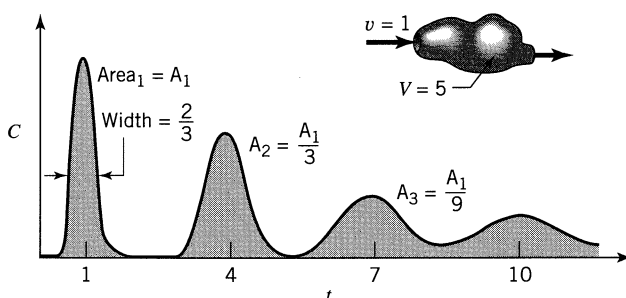


Figure P14.7

- 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.

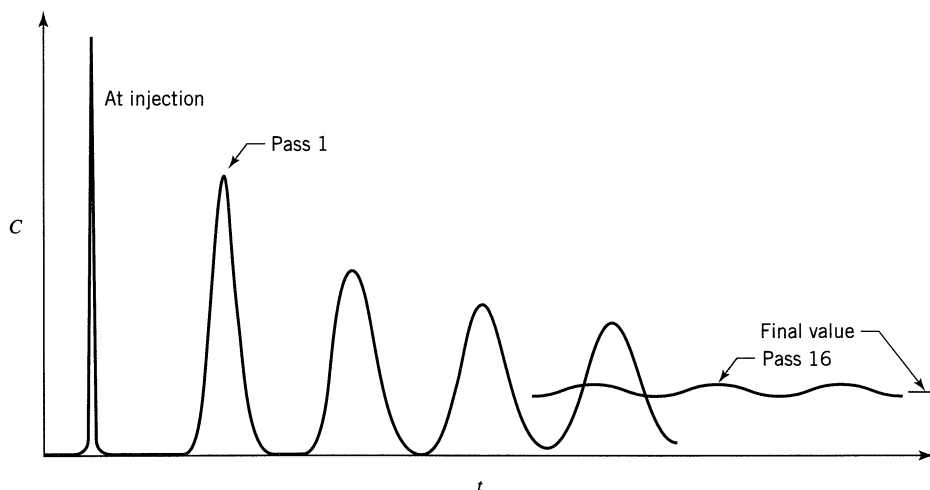
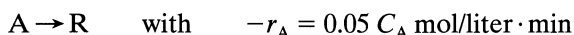


Figure P14.9 RTD for a closed recirculating system.

- 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.

Chapter 15

The Convection Model for Laminar Flow

When a tube or pipe is long enough and the fluid is not very viscous, then the dispersion or tanks-in-series model can be used to represent the flow in these vessels. For a viscous fluid, one has laminar flow with its characteristic parabolic velocity profile. Also, because of the high viscosity there is but slight radial diffusion between faster and slower fluid elements. In the extreme we have the *pure convection model*. This assumes that each element of fluid slides past its neighbor with no interaction by molecular diffusion. Thus the spread in residence times is caused only by velocity variations. This flow is shown in Fig. 15.1. This chapter deals with this model.

15.1 THE CONVECTION MODEL AND ITS RTD

How to Tell from Theory Which Model to Use

The first question to ask is, “Which model should be used in a given situation?” The following chart, adapted from Ananthakrishnan et al. (1965), tells what regime you are in and which model to use. Just locate the point on Fig. 15.2 which corresponds to the fluid being used (Schmidt number), the flow conditions (Reynolds number), and vessel geometry (L/d_i). But be sure to check that your system is not in turbulent flow. Remember that this chart only has meaning if you have laminar flow. In this chart \mathcal{D}/ud_i is the reciprocal of the Bodenstein number. It measures the flow contribution made by molecular diffusion. It is NOT the axial dispersion number, D/ud_i except in the pure diffusion regime. The pure diffusion regime is not a very interesting regime because it represents very very slow flow.

Gases are likely to be in the dispersion regime, not the pure convection regime. Liquids can well be in one regime or another. Very viscous liquids such as polymers are likely to be in the pure convection regime. If your system falls in the no-man’s-land between regimes, calculate the reactor behavior based on

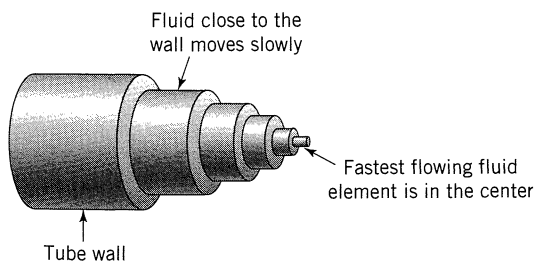


Figure 15.1 Flow of fluid according to the convection model.

the two bounding regimes and then try averaging. The numerical solution is impractically complex to use.

Finally, it is very important to use the correct type of model because the RTD curves are completely different for the different regimes. As an illustration, Fig. 15.3 shows RTD curves typical of these regimes.

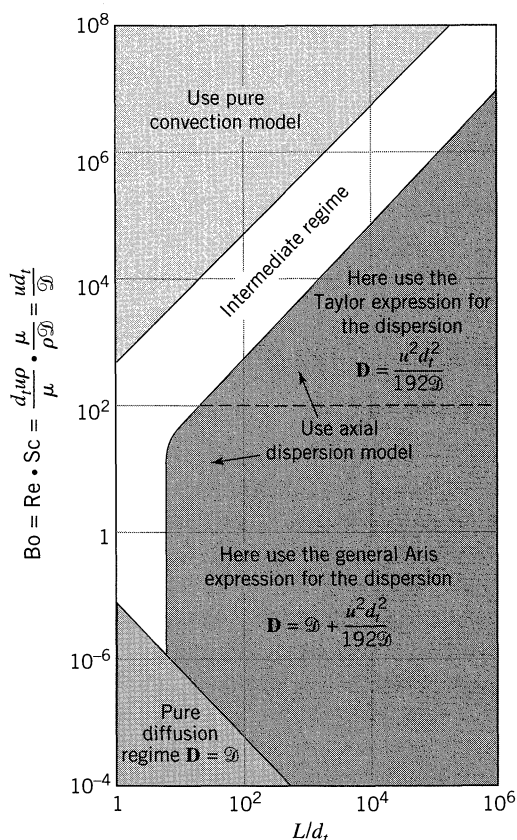


Figure 15.2 Map showing which flow models should be used in any situation.

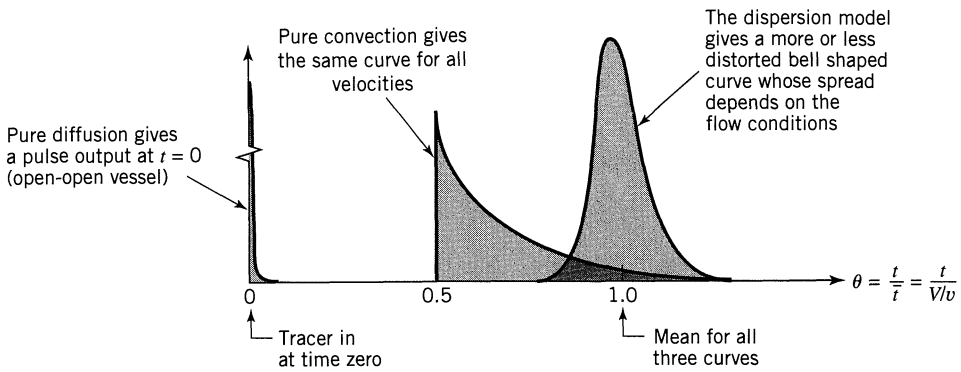


Figure 15.3 Comparison of the RTD of the three models.

How to Tell from Experiment Which Model to Use

The sharpest way of experimentally distinguishing between models comes by noting how a pulse or sloppy input pulse of tracer spreads as it moves downstream in a flow channel. For example, consider the flow, as shown in Fig. 15.4. The dispersion or tanks-in-series models are both stochastic models; thus, from Eq. 13.8 or Eq. 14.3 we see that the *variance grows linearly with distance* or

$$\sigma^2 \propto L \quad (1)$$

The convective model is a deterministic model; thus, the *spread of tracer grows linearly with distance*, or

$$\sigma \propto L \quad (2)$$

Whenever you have measurements of σ at 3 points use this test to tell which model to use. Just see if, in Fig. 15.4,

$$\frac{\Delta\sigma_{12}^2}{\Delta L_{12}} = \frac{\Delta\sigma_{23}^2}{\Delta L_{23}} \quad \text{or if} \quad \frac{\Delta\sigma_{12}}{\Delta L_{12}} = \frac{\Delta\sigma_{23}}{\Delta L_{12}} \quad (3)$$

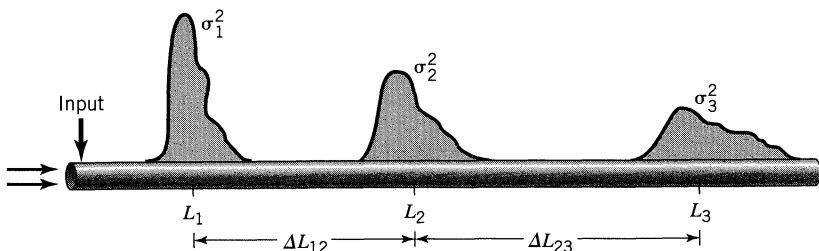


Figure 15.4 The changing spread of a tracer curve tells which model is the right one to use.

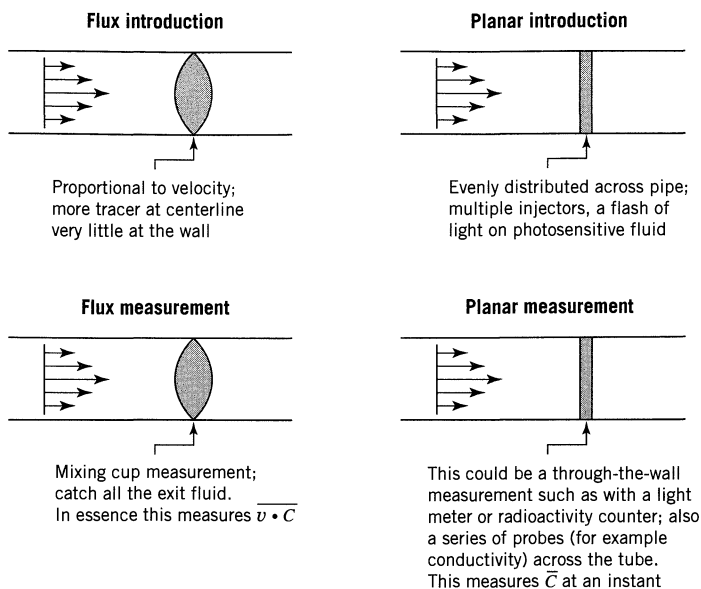


Figure 15.5 Various ways of introducing and measuring tracer.

Pulse Response Experiment and the E Curve for Laminar Flow in Pipes

The shape of the response curve is strongly influenced by the way tracer is introduced into the flowing fluid, and how it is measured. You may inject or measure the tracer in two main ways, as shown in Fig. 15.5. We therefore have four combinations of boundary conditions, as shown in Fig. 15.6, each with its own particular **E** curve. These **E** curves are shown in Fig. 15.7.

As may be seen in Fig. 15.7, the **E**, **E***, and **E**** curves are quite different, one from the other.

- **E** is the proper response curve for reactor purposes; it is the curve treated in Chapter 11, and it represents the RTD in the vessel.
- **E*** and ***E** are identical always, so we will call them **E*** from now on. One correction for the planar boundary condition will transform this curve to the proper RTD.
- **E**** requires two corrections—one for entrance, one for exit—to transform it to a proper RTD.

It may be simpler to determine **E*** or **E**** rather than **E**. This is perfectly all right. However, remember to transform these measured tracer curves to the **E** curve before calling it the RTD. Let us see how to make this transformation.

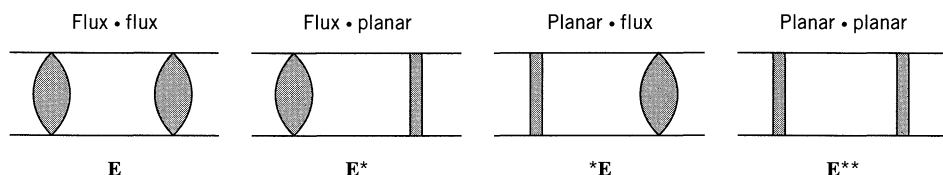


Figure 15.6 Various combinations of input-output methods.

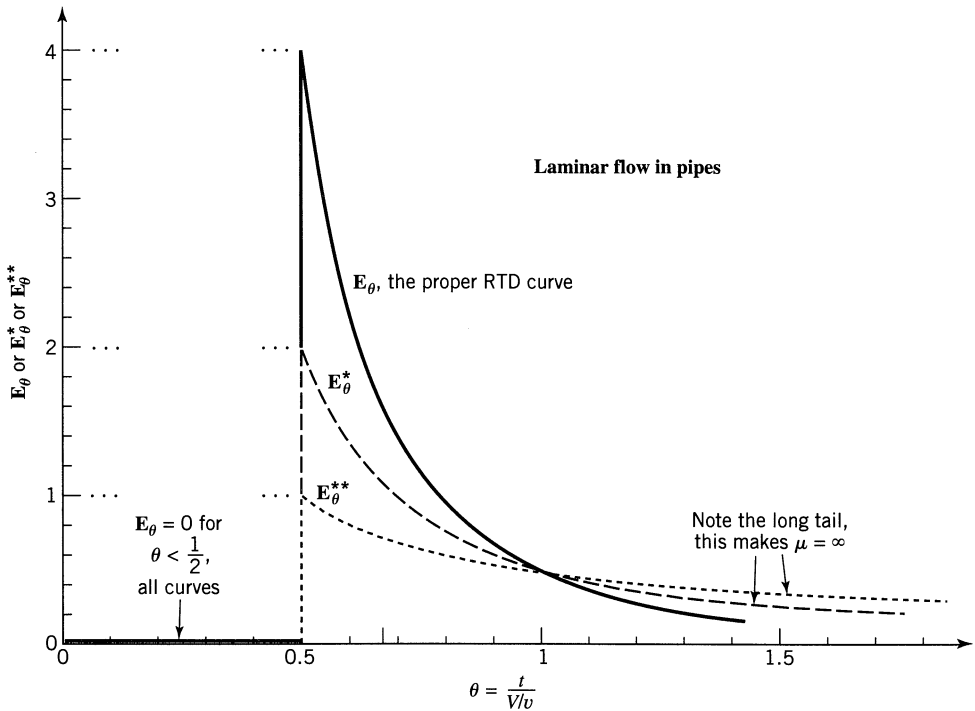


Figure 15.7 Note how different are the output curves depending on how you introduce and measure tracer.

For pipes and tubes with their parabolic velocity profile the various pulse response curves are found to be as follows:

$$\left. \begin{aligned}
 E &= \frac{\bar{t}^2}{2t^3} \quad \text{for } t \geq \frac{\bar{t}}{2} & \mu_t = \bar{t} = \frac{V}{v} \\
 E_\theta &= \frac{1}{2\theta^3} \quad \text{for } \theta \geq \frac{1}{2} & \mu_\theta = 1
 \end{aligned} \right\} \text{and} \quad \left. \begin{aligned}
 E^* &= \frac{\bar{t}}{2t^2} \quad \text{for } t \geq \frac{\bar{t}}{2} & \mu^* = \infty \\
 E_\theta^* &= \frac{1}{2\theta^2} \quad \text{for } \theta \geq \frac{1}{2} & \bar{t} = \frac{V}{v} \\
 & & \theta = t / \left(\frac{V}{v} \right)
 \end{aligned} \right\} \quad (4)$$

$$\left. \begin{aligned}
 E^{**} &= \frac{1}{2t} \quad \text{for } t \geq \frac{\bar{t}}{2} & \mu^{**} = \infty \\
 E_\theta^{**} &= \frac{1}{2\theta} \quad \text{for } \theta \geq \frac{1}{2} & \bar{t} = \frac{V}{v} \\
 & & \theta = t / \left(\frac{V}{v} \right)
 \end{aligned} \right\} \text{and} \quad \left. \begin{aligned}
 & & \bar{t} = \frac{V}{v} \\
 & & \theta = t / \left(\frac{V}{v} \right)
 \end{aligned} \right\}$$

where μ , μ^* , and μ^{**} are the mean values of the measured curves.

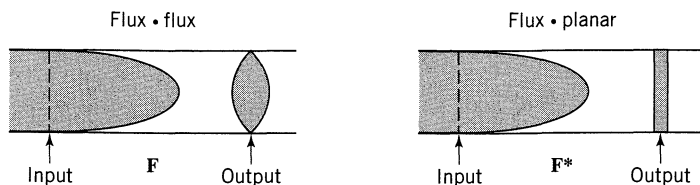


Figure 15.8 Two different ways of measuring the output curves.

Note the simple relationship between \mathbf{E} , \mathbf{E}^* , and \mathbf{E}^{**} . Thus at any time we can write

$$\text{or} \quad \left. \begin{aligned} \mathbf{E}^{**} &= \theta \mathbf{E}^* = \theta^2 \mathbf{E} \\ \mathbf{E}^{**} &= \frac{t}{\bar{t}} \mathbf{E}^* = \frac{t^2}{\bar{t}^2} \mathbf{E} \end{aligned} \right\} \quad \text{where} \quad \bar{t} = \frac{V}{v} \quad (5)$$

Step Response Experiments and the F Curve for Laminar Flow in Pipes

When we do the step experiment by switching from one fluid to the other we obtain the C_{step} curve (see Chapter 11), from which we should be able to find the \mathbf{F} curve. However, this input always represents the flux input, while the output can be either planar or flux. Thus we only have two combinations, as shown in Fig. 15.8. With these two combinations of boundary conditions their equations and graphs are given in Eq. 6 and Fig. 15.9.

$$\left. \begin{aligned} \mathbf{F} &= 1 - \frac{1}{4\theta^2} \quad \text{for} \quad \theta \geq \frac{1}{2} \\ \mathbf{F}^* &= 1 - \frac{1}{2\theta} \quad \text{for} \quad \theta \geq \frac{1}{2} \end{aligned} \right\} \quad \text{where} \quad \theta = t / \bar{t} = \frac{t}{V/v} \quad (6)$$

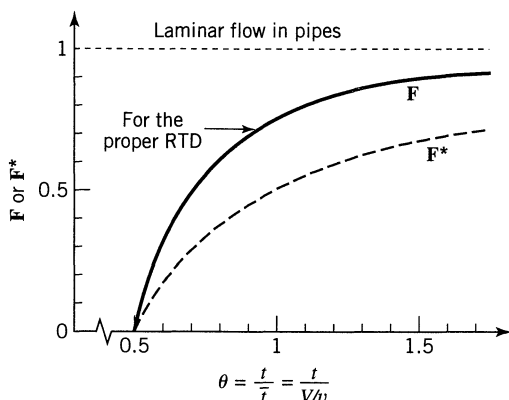


Figure 15.9 Different ways of measuring the output gives different \mathbf{F} curves.

Also each **F** curve is related to its corresponding **E** curve. Thus at any time t_1 or θ_1

$$\mathbf{F}^* = \int_0^{t_1} \mathbf{E}_t^* dt = \int_0^{\theta_1} \mathbf{E}_\theta^* d\theta \quad \text{and} \quad \mathbf{E}_t^* = \left. \frac{d\mathbf{F}^*}{dt} \right|_{t_1} \quad \text{or} \quad \mathbf{E}_\theta^* = \left. \frac{d\mathbf{F}^*}{d\theta} \right|_{\theta_1} \quad (7)$$

The relationship is similar between **E** and **F**.

E Curves for Non-newtonians and for Non-circular Channels

Since plastics and nonnewtonians are often very viscous they usually should be treated by the convective model of this chapter. The **E**, **E***, and **E**** curves for various situations besides newtonian fluids in circular pipes have been developed, for example,

- for power law fluids
- for Bingham plastics

E curves have also been developed

- for falling films
- for flow between parallel plates
- where line measurements are made rather than across the whole vessel cross section.

These **E** equations and corresponding charts plus sources to various other analyses can be found in Levenspiel, (1996).

15.2 CHEMICAL CONVERSION IN LAMINAR FLOW REACTORS

Single n -th Order Reactions

In the pure convection regime (negligible molecular diffusion) each element of fluid follows its own streamline with no intermixing with neighboring elements. In essence this gives macrofluid behavior. From Chapter 11 the conversion expression is then

$$\frac{C_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{element of fluid}} \cdot \mathbf{E} dt$$

{

for zero reaction order

for first order reaction

for second order reaction

$\frac{C_A}{C_{A0}} = 1 - \frac{kt}{C_{A0}} \text{ for } t \leq \frac{C_{A0}}{k}$

$\frac{C_A}{C_{A0}} = e^{-kt}$

$\frac{C_A}{C_{A0}} = \frac{1}{1 + kC_{A0}t}$

For *zero-order reaction* of a newtonian in laminar flow in a pipe, integration of Eq. 8 gives

$$\frac{C_A}{C_{A0}} = \left(1 - \frac{k\bar{t}}{2C_{A0}}\right)^2 \quad (9)$$

For *first-order reaction* of a newtonian in laminar flow in a pipe,

$$\frac{C_A}{C_{A0}} = \frac{\bar{t}^2}{2} \int_{\bar{t}/2}^{\infty} \frac{e^{-kt}}{t^3} dt = y^2 \text{ei}(y) + (1 - y)e^{-y}, \quad y = \frac{k\bar{t}}{2} \quad (10)$$

where $\text{ei}(y)$ is the exponential integral, see Chapter 16.

For *second-order reaction* of a newtonian in laminar flow in a pipe:

$$\frac{C_A}{C_{A0}} = 1 - kC_{A0}\bar{t} \left[1 - \frac{kC_{A0}\bar{t}}{2} \ln \left(1 + \frac{2}{kC_{A0}\bar{t}} \right) \right] \quad (11)$$

These performance expressions were first developed by Bosworth (1948) for zero order, by Denbigh (1951) for second order, and by Cleland and Wilhelm (1956) for first order reactions. For other kinetics, channel shapes, or types of fluids insert the proper terms in the general performance expression and integrate.

Comments

- (a) *Test for the RTD curve.* Proper RTD curves must satisfy the material balance checks (calculated zero and first moments should agree with measured values)

$$\int_0^{\infty} \mathbf{E}_{\theta} d\theta = 1 \quad \text{and} \quad \int_0^{\infty} \theta \mathbf{E}_{\theta} d\theta = 1 \quad (12)$$

The \mathbf{E} curves of this chapter, for non-newtonians and all shapes of channels, all meet this requirement. All the \mathbf{E}^* and \mathbf{E}^{**} curves of this chapter do not; however, their transforms to \mathbf{E} do.

- (b) *The variance and other RTD descriptors.* The variance of all the \mathbf{E} curves of this chapter is finite; but it is infinite for all the \mathbf{E}^* and \mathbf{E}^{**} curves. So be sure you know which curve you are dealing with.

In general the convection model \mathbf{E} curve has a long tail. This makes the measurement of its variance unreliable. Thus σ^2 is not a useful parameter for convection models and is not presented here.

The breakthrough time θ_0 is probably the most reliably measured and most useful descriptive parameter for convection models, so it is widely used.

- (c) Comparison with plug flow for n th-order reaction is shown in Fig. 15.10.

This graph shows that even at high X_A convective flow does not drastically lower reactor performance. This result differs from the dispersion and tanks-in-series models (see Chapters 13 and 14).

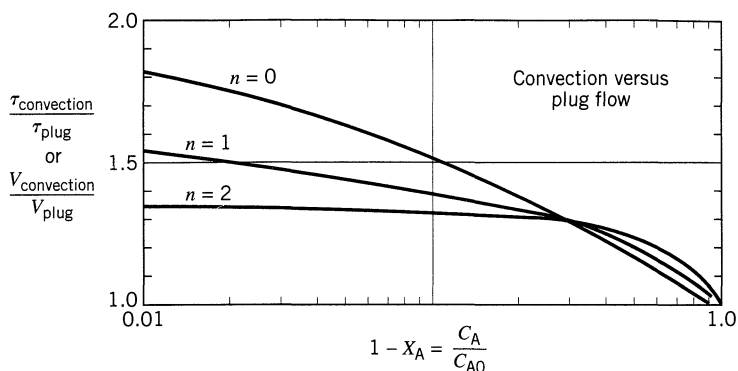
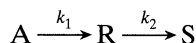


Figure 15.10 Convective flow lowers conversion compared to plug flow.

Multiple Reaction in Laminar Flow

Consider a two-step first-order irreversible reactions in series



Because laminar flow represents a deviation from plug flow, the amount of intermediate formed will be somewhat less than for plug flow. Let us examine this situation.

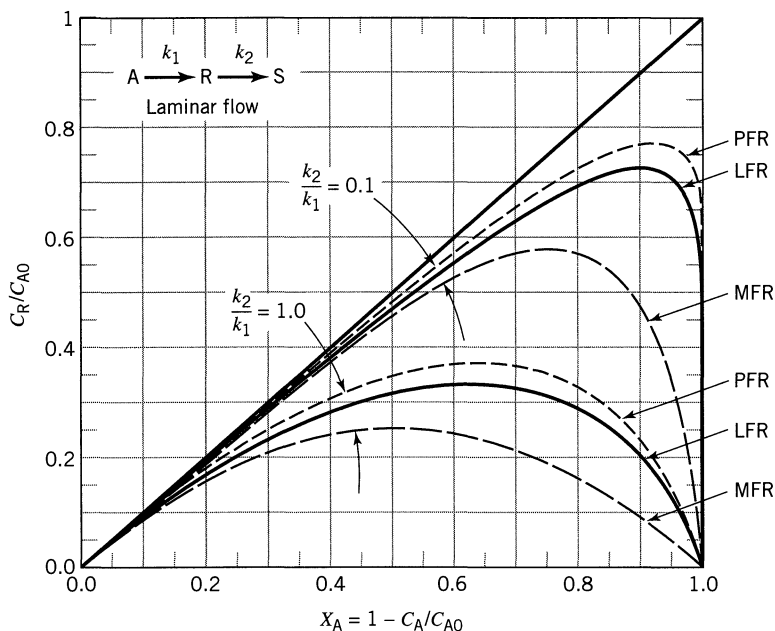


Figure 15.11 Typical product distribution curves for laminar flow compared with the curves for plug flow (Fig. 8.13) and mixed flow (Fig. 8.14).

The disappearance of A is given by the complicated Eq. 10, and the formation and disappearance of R is given by an even more complicated equation. Developing the product distribution relationship, solving numerically, and comparing the results with those for plug flow and for mixed flow gives Fig. 15.11; see Johnson (1970) and Levien and Levenspiel (1998).

This graph shows that the LFR gives a little less intermediate than does the PFR, about 20% of the way from the PFR to the MFR.

We should be able to generalize these findings to other more complex reaction systems, such as for two component multistep reactions; to polymerizations; and to non-Newtonian power law fluids.

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PROBLEMS

A viscous liquid is to react while passing through a tubular reactor in which flow is expected to follow the convection model. What conversion can we expect in this reactor if plug flow in the reactor will give 80% conversion?

15.1. Reaction follows zero-order kinetics.

15.2. Reaction is second order.

15.3. Assuming plug flow we calculate that a tubular reactor 12 m long would give 96% conversion of A for the second-order reaction $A \rightarrow R$. However, the fluid is very viscous, and flow will be strongly laminar, thus we expect the convection model, not the plug flow model, to closely represent the flow. How long should we make the reactor to insure 96% conversion of A?

15.4. Aqueous A ($C_{A0} = 1$ mol/liter) with physical properties close to water ($\rho = 1000$ kg/m³, $\mathcal{D} = 10^{-9}$ m²/s) reacts by a first-order homogeneous reaction ($A \rightarrow R$, $k = 0.2$ s⁻¹) as it flows at 100 mm/s through a tubular reactor ($d_t = 50$ mm, $L = 5$ m). Find the conversion of A in the fluid leaving this reactor.

- 15.5.** Aqueous A ($C_{A0} = 50 \text{ mol/m}^3$) with physical properties close to water ($\rho = 1000 \text{ kg/m}^3$, $\mathcal{D} = 10^{-9} \text{ m}^2/\text{s}$) reacts by a second-order reaction ($k = 10^{-3} \text{ m}^3/\text{mol} \cdot \text{s}$) as it flows at 10 mm/s through a tubular reactor ($d_t = 10 \text{ mm}$, $L = 20 \text{ m}$). Find the conversion of reactant A from this reactor.
- 15.6.** We want to model the flow of fluid in a flow channel. For this we locate three measuring points *A*, *B*, and *C*, 100 m apart along the flow channel. We inject tracer upstream of point *A*, fluid flows past points *A*, *B*, and *C* with the following results:
- At *A* the tracer width is 2 m
 - At *B* the tracer width is 10 m
 - At *C* the tracer width is 14 m
- What type of flow model would you try to use to represent this flow: dispersion, convective, tanks-in-series, or none of these? Give a reason for your answer.

Chapter 16

Earliness of Mixing, Segregation, and RTD

The problem associated with the mixing of fluids during reaction is important for extremely fast reactions in homogeneous systems, as well as for all heterogeneous systems. This problem has two overlapping aspects: first, the *degree of segregation* of the fluid, or whether mixing occurs on the microscopic level (mixing of individual molecules) or the macroscopic level (mixing of clumps, groups, or aggregates of molecules); and second, the *earliness of mixing*, or whether fluid mixes early or late as it flows through the vessel.

These two concepts are intertwined with the concept of RTD, so it becomes rather difficult to understand their interaction. Please reread the first few pages of Chapter 11 where these concepts are introduced and discussed.

In this chapter we first treat systems in which a single fluid is reacting. Then we treat systems in which two fluids are contacted and reacted.

16.1 SELF-MIXING OF A SINGLE FLUID

Degree of Segregation

The normally accepted state of a liquid or gas is that of a microfluid, and all previous discussions on homogeneous reactions have been based on the assumption. Let us now consider a single reacting macrofluid being processed in turn in batch, plug flow, and mixed flow reactors, and let us see how this state of aggregation can result in behavior different from that of a microfluid.

Batch Reactor. Let the batch reactor be filled with a macrofluid containing reactant A. Since each aggregate or packet of macrofluid acts as its own little batch reactor, conversion is the same in all aggregates and is in fact identical to what would be obtained with a microfluid. Thus for batch operations the degree of segregation does not affect conversion or product distribution.

Plug Flow Reactor. Since plug flow can be visualized as a flow of small batch reactors passing in succession through the vessel, macro- and microfluids act

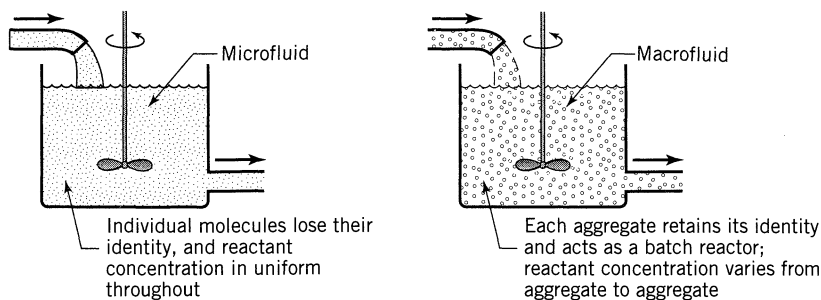


Figure 16.1 Difference in behavior of microfluids and macrofluids in mixed flow reactors.

alike. Consequently the degree of segregation does not influence conversion or product distribution.

Mixed Flow Reactor–Microfluid. When a microfluid containing reactant A is treated as in Fig. 16.1, the reactant concentration everywhere drops to the low value prevailing in the reactor. No clump of molecules retains its high initial concentration of A. We may characterize this by saying that each molecule loses its identity and has no determinable past history. In other words, by examining its neighbors we cannot tell whether a molecule is a newcomer or an old-timer in the reactor.

For this system the conversion of reactant is found by the usual methods for homogeneous reactions, or

$$X_A = \frac{(-r_A)V}{F_{A0}} \quad (5.11)$$

or, with no density changes,

$$\frac{C_A}{C_{A0}} = 1 - \frac{(-r_A)\bar{t}}{C_{A0}} \quad (1)$$

where \bar{t} is the mean residence time of fluid in the reactor.

Mixed Flow Reactor–Macrofluid. When a macrofluid enters a mixed flow reactor, the reactant concentration in an aggregate does not drop immediately to a low value but decreases in the same way as it would in a batch reactor. Thus a molecule in a macrofluid does not lose its identity, its past history is not unknown, and its age can be estimated by examining its neighboring molecules.

The performance equation for a macrofluid in a mixed flow reactor is given by Eq. 11.13 as

$$1 - \bar{X}_A = \frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} \mathbf{E} \, dt \quad (11.13) \text{ or } (2)$$

where

$$\mathbf{E} dt = \frac{v}{V} e^{-vt/V} dt = \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (3)$$

Replacing Eq. 3 in Eq. 2 gives

$$1 - \bar{X}_A = \frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (4)$$

This is the general equation for determining conversion of macrofluids in mixed flow reactors, and it may be solved once the kinetics of the reaction is given. Consider various reaction orders.

For a *zero-order reaction* in a batch reactor, Chapter 3 gives

$$\left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} = 1 - \frac{kt}{C_{A0}} \quad (3.31)$$

Inserting into Eq. 4 and integrating gives

$$\boxed{\frac{\bar{C}_A}{C_{A0}} = 1 - \frac{kt}{C_{A0}} (1 - e^{-C_{A0}/kt})} \quad (5)$$

For a *first-order reaction* in a batch, reactor Chapter 3 gives

$$\left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} = e^{-kt} \quad (3.11)$$

On replacing into Eq. 4 we obtain

$$\frac{\bar{C}_A}{C_{A0}} = \frac{1}{\bar{t}} \int_0^\infty e^{-kt} e^{-t/\bar{t}} dt$$

which on integration gives the expression for conversion of a macrofluid in a mixed flow reactor

$$\boxed{\frac{\bar{C}_A}{C_{A0}} = \frac{1}{1 + k\bar{t}}} \quad (6)$$

This equation is identical to that obtained for a microfluid; for example, see Eq. 5.14a. Thus we conclude that the degree of segregation has no effect on conversion for first-order reactions.

For a *second-order reaction* of a single reactant in a batch reactor Eq. 3.16 gives

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{batch}} = \frac{1}{1 + C_{A0}kt} \quad (7)$$

On replacing into Eq. 4 we find

$$\frac{\bar{C}_A}{C_{A0}} = \frac{1}{\bar{t}} \int_0^\infty \frac{e^{-t/\bar{t}}}{1 + C_{A0}kt} dt$$

and by letting $\alpha = 1/C_{A0}k\bar{t}$ and converting into reduced time units $\theta = t/\bar{t}$, this expression becomes

$$\frac{\bar{C}_A}{C_{A0}} = \alpha e^\alpha \int_\alpha^\infty \frac{e^{-(\alpha+\theta)}}{\alpha + \theta} d(\alpha + \theta) = \alpha e^\alpha \text{ei}(\alpha) \quad (8)$$

This is the conversion expression for second-order reaction of a macrofluid in a mixed flow reactor. The integral, represented by $\text{ei}(\alpha)$ is called an *exponential integral*. It is a function alone of α , and its value is tabulated in a number of tables of integrals. Table 16.1 presents a very abbreviated set of values for both $\text{ei}(x)$ and $\text{Ei}(x)$. We will refer to this table later in the book.

Table 16.1 Two of the Family of Exponential Integrals

Here are two useful exponential integrals			$\left\{ \begin{array}{l} \text{Ei}(x) = \int_{-\infty}^x \frac{e^u}{u} du = 0.577\,21 + \ln x + x + \frac{x^2}{2 \cdot 2!} + \frac{x^3}{3 \cdot 3} + \cdots \\ \text{ei}(x) = \int_x^\infty \frac{e^{-u}}{u} du = -0.577\,21 - \ln x + x - \frac{x^2}{2 \cdot 2!} + \frac{x^3}{3 \cdot 3!} - \cdots \end{array} \right.$					
x	$\text{Ei}(x)$	$\text{ei}(x)$	x	$\text{Ei}(x)$	$\text{ei}(x)$	x	$\text{Ei}(x)$	$\text{ei}(x)$
0	$-\infty$	$+\infty$	0.2	-0.8218	1.2227	2.0	4.9542	0.048 90
0.01	-4.0179	4.0379	0.3	-0.3027	0.9057	2.5	7.0738	0.024 91
0.02	-3.3147	3.3547	0.5	0.4542	0.5598	3.0	9.9338	0.013 05
0.05	-2.3679	2.4679	1.0	1.8951	0.2194	5.0	40.185	0.001 15
0.1	-1.6228	1.8229	1.4	3.0072	0.1162	7.0	191.50	0.000 12

$$\text{for } x \geq 10 \left\{ \begin{array}{l} \text{Ei}(x) = e^x \left[\frac{1}{x} + \frac{1}{x^2} + \frac{2!}{x^3} + \frac{3!}{x^4} + \cdots \right] \\ \text{ei}(x) = e^{-x} \left[\frac{1}{x} - \frac{1}{x^2} + \frac{2!}{x^3} - \frac{3!}{x^4} + \cdots \right] \end{array} \right.$$

Equation 8 may be compared with the corresponding expression for microfluids, Eq. 5.14

$$\frac{C_A}{C_{A0}} = \frac{-1 + \sqrt{1 + 4C_{A0}k\bar{t}}}{2C_{A0}k\bar{t}} \quad (9)$$

For an n th-order reaction the conversion in a batch reactor can be found by the methods of Chapter 3 to be

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{batch}} = [1 - (n-1)C_{A0}^{n-1}kt]^{1/(1-n)} \quad (10)$$

Insertion into Eq. 4 gives the conversion for an n th-order reaction of a macrofluid.

Difference in Performance: Early or Late Mixing, Macro- or Microfluids, PFR or MFR

Figure 16.2 illustrates the difference in performance of macrofluids and microfluids in mixed flow reactors, and they show clearly that a rise in segregation improves reactor performance for reaction orders greater than unity but lowers performance for reaction orders smaller than unity. Table 16.2 was used in preparing these charts.

Early and Late Mixing of Fluids

Each flow pattern of fluid through a vessel has associated with it a definite clearly defined residence time distribution (RTD), or exit age distribution function **E**. The converse is not true, however. Each RTD does not define a specific flow pattern; hence, a number of flow patterns—some with earlier mixing, others with later mixing of fluids—may be able to give the same RTD.

Idealized Pulse RTD. Reflection shows that the only pattern of flow consistent with this RTD is one with no intermixing of fluid of different ages, hence, that of plug flow. Consequently it is immaterial whether we have a micro- or macrofluid. In addition the question of early or late mixing of fluid is of no concern since there is no mixing of fluid of different ages.

Exponential Decay RTD. The mixed flow reactor can give this RTD. However, other flow patterns can also give this RTD, for example, a set of parallel plug flow reactors of proper length, a plug flow reactor with sidestreams, or a combination of these. Figure 16.3 shows a number of these patterns. Note that in patterns *a* and *b* entering fluid elements mix immediately with material of different ages, while in patterns *c* and *d* no such mixing occurs. Thus patterns *a* and *b* represent the microfluid, while patterns *c* and *d* represent the macrofluid.

Table 16.2 Conversion Equations for Macrofluids and Microfluids with $\varepsilon = 0$ in Ideal Reactors

	Plug Flow		Mixed Flow	
	Microfluid or Macrofluid		Microfluid	Macrofluid
General kinetics	$\tau = \int_{C_0-r}^C \frac{dC}{C_0-r}$		$\tau = \frac{C_0 - C}{-r}$	$\frac{\bar{C}}{C_0} = \frac{1}{\tau} \int_0^\infty \left(\frac{C}{C_0} \right)_{\text{batch}} e^{-l/\tau} dt$
n th-order reaction	$\frac{C}{C_0} = [1 + (n-1)R]^{1/(1-n)}$		$\left(\frac{C}{C_0} \right)^n R + \frac{C}{C_0} - 1 = 0$	$\frac{\bar{C}}{C_0} = \frac{1}{\tau} \int_0^\infty [1 + (n-1)C_0^{n-1}kt]^{1/(1-n)} e^{-l/\tau} dt$
$(R = C_0^{n-1}k\tau)$	$R = \frac{1}{n-1} \left[\left(\frac{C}{C_0} \right)^{1-n} - 1 \right]$		$R = \left(1 - \frac{C}{C_0} \right) \left(\frac{C_0}{C} \right)^n$	
Zero-order reaction	$\frac{C}{C_0} = 1 - R, \quad R \leq 1$		$\frac{C}{C_0} = 1 - R, \quad R \leq 1$	$\frac{\bar{C}}{C_0} = 1 - R + R e^{-1/R}$
$\left(R = \frac{k\tau}{C_0} \right)$	$C = 0, \quad R \geq 1$		$C = 0, \quad R \geq 1$	
First-order reaction	$\frac{C}{C_0} = e^{-R}$		$\frac{C}{C_0} = \frac{1}{1+R}$	$\frac{\bar{C}}{C_0} = \frac{1}{1+R}$
$(R = k\tau)$	$R = \ln \frac{C_0}{C}$		$R = \frac{C_0}{C} - 1$	$R = \frac{C_0}{C} - 1$
Second-order reaction	$\frac{C}{C_0} = \frac{1}{1+R}$		$\frac{C}{C_0} = \frac{-1 + \sqrt{1+4R}}{2R}$	$\frac{\bar{C}}{C_0} = \frac{e^{1/R}}{R} \text{ei} \left(\frac{1}{R} \right)$
$(R = C_0 k\tau)$	$R = \frac{C_0}{C} - 1$		$R = \left(\frac{C_0}{C} - 1 \right) \frac{C_0}{C}$	

$R = C_0^{n-1}k\tau$, reaction rate group for n th-order reaction, a time or capacity factor. $\tau = \bar{t}$ since $\varepsilon = 0$ throughout.

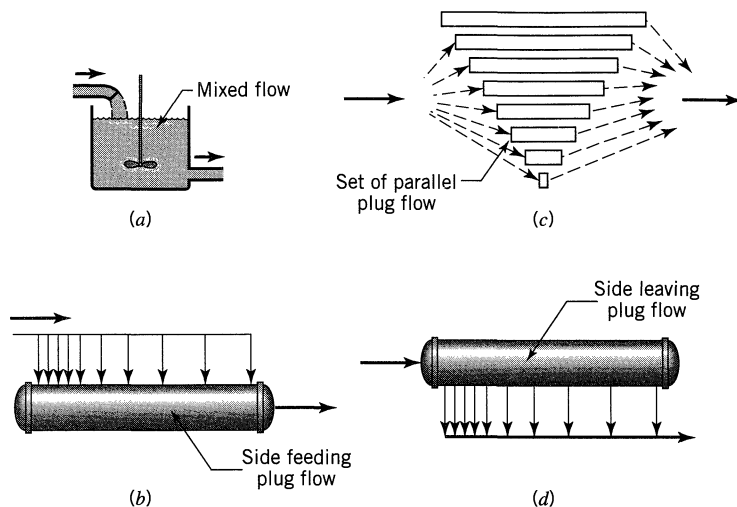


Figure 16.3 Four contacting patterns which can all give the same exponential decay RTD. Cases *a* and *b* represent the earliest possible mixing while cases *c* and *d* represent the latest possible mixing of fluid elements of different ages.

Summary of Findings for a Single Fluid

1. *Factors affecting the performance of a reactor.* In general we may write

$$\text{Performance: } X_A \text{ or } \varphi\left(\frac{R}{A}\right) = f\left(\begin{array}{c} \text{kinetics, RTD, degree of segregation,} \\ \text{earliness of mixing} \end{array}\right) \quad (11)$$

2. *Effect of kinetics, or reaction order.* Segregation and earliness of mixing affect the conversion of reactant as follows

$$\text{For } n > 1 \dots X_{\text{macro}} \text{ and } X_{\text{micro, late}} > X_{\text{micro, early}}$$

For $n < 1$ the inequality is reversed, and for $n = 1$ conversion is unaffected by these factors. This result shows that segregation and late mixing improves conversion for $n > 1$, and decreases conversion for $n < 1$.

3. *Effect of mixing factors for nonfirst-order reactions.* Segregation plays no role in plug flow; however, it increasingly affects the reactor performance as the RTD shifts from plug to mixed flow.
4. *Effect of conversion level.* At low conversion levels X_A is insensitive to RTD, earliness of mixing, and segregation. At intermediate conversion levels, the RTD begins to influence X_A ; however, earliness and segregation still have little effect. This is the case of Example 16.1. Finally, at high conversion levels all these factors may play important roles.
5. *Effect on product distribution.* Although segregation and earliness of mixing can usually be ignored when treating single reactions, this often is not so with multiple reactions where the effect of these factors on product distribution can be of dominating importance, even at low conversion levels.

As an example consider free-radical polymerization. When an occasional free radical is formed here and there in the reactor it triggers an extremely rapid chain of reactions, often thousands of steps in a fraction of a second. The local reaction rate and conversion can thus be very high. In this situation the immediate surroundings of the reacting and growing molecules—and hence the state of segregation of the fluid—can greatly affect the type of polymer formed.

EXAMPLE 16.1 EFFECT OF SEGREGATION AND EARLINESS OF MIXING ON CONVERSION

A second-order reaction occurs in a reactor whose RTD is given in Fig. E16.1. Calculate the conversion for the flow schemes shown in this figure. For simplicity take $C_0 = 1$, $k = 1$, and $\tau = 1$ for each unit.

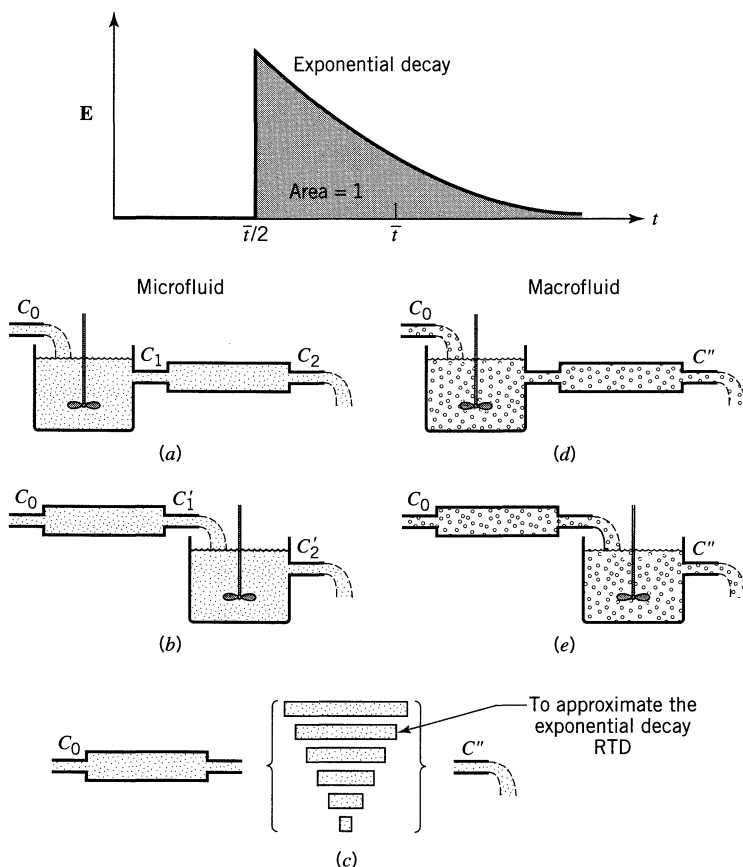


Figure E16.1 (a) Microfluid, early mixing at molecular level; (b) Microfluid, fairly late mixing at molecular level; (c) Microfluid, late mixing at molecular level; (d) Macrofluid, early mixing of elements; (e) Macrofluid, late mixing of elements.

SOLUTION

Scheme A. Referring to Fig. E16.1a we have for the mixed flow reactor

$$\tau = 1 = \frac{C_0 - C_1}{kC_1^2} = \frac{1 - C_1}{C_1^2}$$

or

$$C_1 = \frac{-1 + \sqrt{1 + 4}}{2} = 0.618$$

For the plug flow reactor

$$\tau = 1 = -\int_{C_1}^{C_2} \frac{dC}{kC^2} = \frac{1}{k} \left(\frac{1}{C_2} - \frac{1}{C_1} \right)$$

or

$$\underline{\underline{\text{Micro-early: } C_2 = \frac{C_1}{C_1 + 1} = \frac{0.618}{1.168} = 0.382}}$$

Scheme B. Referring to Fig. E16.1b, we have for the plug flow reactor

$$\tau = 1 = -\int_{C_0}^{C_1'} \frac{dC}{kC^2} = \frac{1}{C_1'} - 1$$

or

$$C_1' = 0.5$$

For the mixed reactor

$$\tau = 1 = \frac{C_1' - C_2'}{kC_2'^2} = \frac{0.5 - C_2'}{C_2'^2}$$

or

$$\underline{\underline{\text{Micro-fairly late: } C_2' = 0.366}}$$

Scheme C, D, and E. From Fig. 12.1 the exit age distribution function for the two equal-size plug-mixed flow reactor system is

$$\begin{aligned} \mathbf{E} &= \frac{2}{t} e^{1-2/t}, & \text{when } \frac{t}{\bar{t}} > \frac{1}{2} \\ &= 0, & \text{when } \frac{t}{\bar{t}} < \frac{1}{2} \end{aligned}$$

Thus Eq. 3 becomes

$$C'' = \int_{\bar{t}/2}^{\infty} \frac{1}{1 + C_0 k t} \cdot \frac{2}{\bar{t}} e^{1-2t/\bar{t}} dt$$

With the mean residence time in the two-vessel system $\bar{t} = 2$ min, this becomes

$$C'' = \int_1^{\infty} \frac{e^{1-t}}{1+t} dt$$

and replacing $1 + t$ by x we obtain the exponential integral

$$C'' = \int_2^{\infty} \frac{e^{2-x}}{x} dx = e^2 \int_2^{\infty} \frac{e^{-x}}{x} dx = e^2 \text{ei}(2)$$

From the table of integrals in Table 16.1 we find $\text{ei}(2) = 0.048\ 90$ from which

$$\underline{\underline{\text{Micro-late, and macro-late or early: } C'' = 0.362}}$$

The results of this example confirm the statements made above: that macrofluids and late mixing microfluids give higher conversions than early mixing microfluids for reaction orders greater than unity. The difference is small here because the conversion levels are low; however, this difference becomes more important as conversion approaches unity.

Extensions for a Single Fluid

Partial Segregation. There are various ways of treating intermediate extents of segregation, for example,

Intensity of segregation model—Danckwerts (1958)

Coalescence model—Curl (1963), Spielman and Levenspiel (1965)

Two environment and melting ice cube models—Ng and Rippin (1965) and Suzuki (1970)

These approaches are discussed in Levenspiel (1972).

The Life of an Element of Fluid. Let us estimate how long a fluid element retains its identity. First, all large elements are broken into smaller elements by stretching or folding (laminar behavior) or by turbulence generated by baffles, stirrers, etc., and mixing theory estimates the time needed for this breakup.

Small elements lose their identity by the action of molecular diffusion, and the Einstein random walk analysis estimates this time as

$$t = \frac{(\text{size of element})^2}{\left(\begin{array}{c} \text{diffusion} \\ \text{coefficient} \end{array} \right)} = \frac{d_{\text{element}}^2}{\mathcal{D}} \quad (12)$$

Thus an element of water 1 micron in size would lose its identity in a very short time, approximately

$$t = \frac{(10^{-4} \text{ cm})^2}{10^{-5} \text{ cm}^2/\text{sec}} = 10^{-3} \text{ sec} \quad (13a)$$

while an element of viscous polymer 1.0 mm in size and 100 times as viscous as water (10–30 W motor oil at room temperature) would retain its identity for a long time, roughly

$$t = \frac{(10^{-1} \text{ cm})^2}{10^{-7} \text{ cm}^2/\text{sec}} = 10^5 \text{ sec} \approx 30 \text{ hr} \quad (13b)$$

In general, then, ordinary fluids behave as microfluids except for very viscous materials and for systems in which very fast reactions are taking place.

The concept of micro- and macrofluids is of particular importance in heterogeneous systems because one of the two phases of such systems usually approximates a macrofluid. For example, the solid phase of fluid-solid systems can be treated exactly as a macrofluid because each particle of solid is a distinct aggregate of molecules. For such systems, then, Eq. 2 with the appropriate kinetic expression is the starting point for design.

In the chapters to follow we apply these concepts of micro- and macrofluids to heterogeneous systems of various kinds.

16.2 MIXING OF TWO MISCIBLE FLUIDS

Here we consider one topic, the role of the mixing process when two completely miscible reactant fluids A and B are brought together. When two miscible fluids A and B are mixed, we normally assume that they first form a homogeneous mixture which then reacts. However, when the time required for A and B to become homogeneous is not short with respect to the time for reaction to take place, reaction occurs during the mixing process, and the problem of mixing becomes important. Such is the case for very fast reactions or with very viscous reacting fluids.

To help understand what occurs, imagine that we have A and B available, each first as a microfluid, and then as a macrofluid. In one beaker mix micro A with micro B, and in another beaker mix macro A with macro B and let them react. What do we find? Micro A and B behave in the expected manner, and reaction occurs. However, on mixing the macrofluids no reaction takes place because molecules of A cannot contact molecules of B. These two situations are illustrated in Fig. 16.4. So much for the treatment of the two extremes in behavior.

Now a real system acts as shown in Fig. 16.5 with regions of A-rich fluid and regions of B-rich fluid.

Though partial segregation requires an increase in reactor size, this is not the only consequence. For example, when reactants are viscous fluids, their mixing in a stirred tank or batch reactor often places layers or “streaks” of one fluid next to the other. As a result reaction occurs at different rates from point to

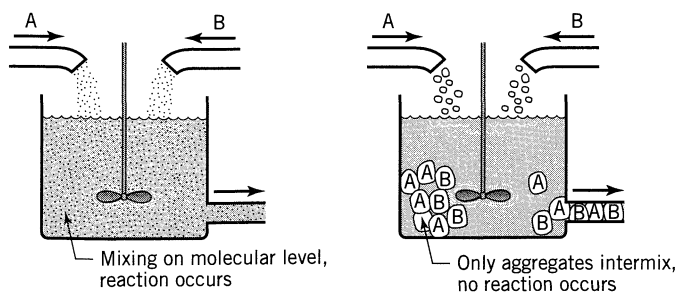


Figure 16.4 Difference in behavior of microfluids and macrofluids in the reaction of A and B.

point in the reactor, giving a nonuniform product which may be commercially unacceptable. Such is the case in polymerization reactions in which monomer must be intimately mixed with a catalyst. For reactions such as this, proper mixing is of primary importance and often the rate of reaction and product uniformity correlate well with the mixing energy input to the fluid.

For fast reactions the increase in reactor size needed because of segregation is of secondary importance while other effects become important. For example, if the product of reaction is a solid precipitate, the size of the precipitate particles may be influenced by the rate of intermixing of reactants, a fact that is well known from the analytical laboratory. As another example, hot gaseous reaction mixtures may contain appreciable quantities of a desirable compound because of favorable thermodynamic equilibrium at such temperatures. To reclaim this component the gas may have to be cooled. But, as is often the case, a drop in temperature causes an unfavorable shift in equilibrium with essentially complete disappearance of desired material. To avoid this and to “freeze” the composition of hot gases, cooling must be very rapid. When the method of quenching used involves mixing the hot gases with an inert cold gas, the success of such a procedure is primarily dependent on the rate at which segregation can be destroyed. Finally the length, type, and temperature of a burning flame, the combustion products obtained, the noise levels of jet engines, and the physical properties of polymers as they are affected by the molecular weight distribution of the

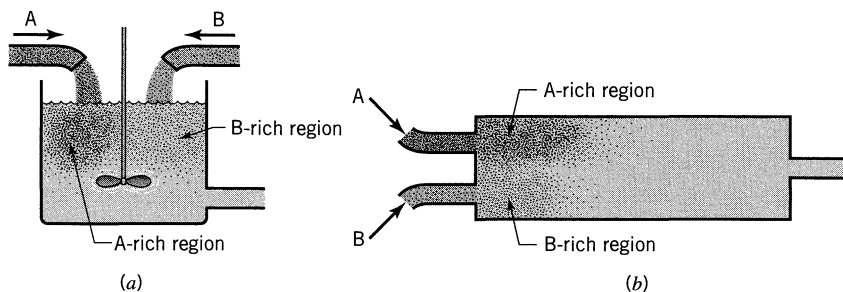


Figure 16.5 Partial segregation in the mixing of two miscible fluids in a reactor.

material are some of the many phenomena that are closely influenced by the rate and intimacy of fluid mixing.

Product Distribution in Multiple Reactions

When multiple reactions take place on mixing two reactant fluids and when these reactions proceed to an appreciable extent before homogeneity is attained, segregation is important and can affect product distribution.

Consider the homogeneous-phase competitive consecutive reactions



occurring when A and B are poured into a batch reactor. If the reactions are slow enough so that the contents of the vessel are uniform before reaction takes place, the maximum amount of R formed is governed by the k_2/k_1 ratio. This situation, treated in Chapter 8, is one in which we may assume microfluid behavior. If, however, the fluids are very viscous or if the reactions are fast enough, they will occur in the narrow zones between regions of high A concentration and high B concentration. This is shown in Fig. 16.6. The zone of high reaction rate will contain a higher concentration of R than the surrounding fluid. But from the qualitative treatment of this reaction in Chapter 8 we know that any nonhomogeneity in A and R will depress formation of R. Thus partial segregation of reactants will depress the formation of intermediate.

For increased reaction rate, the zone of reaction narrows, and in the limit, for an infinitely fast reaction, becomes a boundary surface between the A-rich and

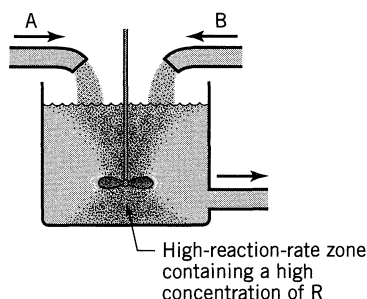
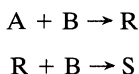


Figure 16.6 When reaction rate is very high, zones of nonhomogeneity exist in a reactor. This condition is detrimental to obtaining high yields of intermediate R from the reactions



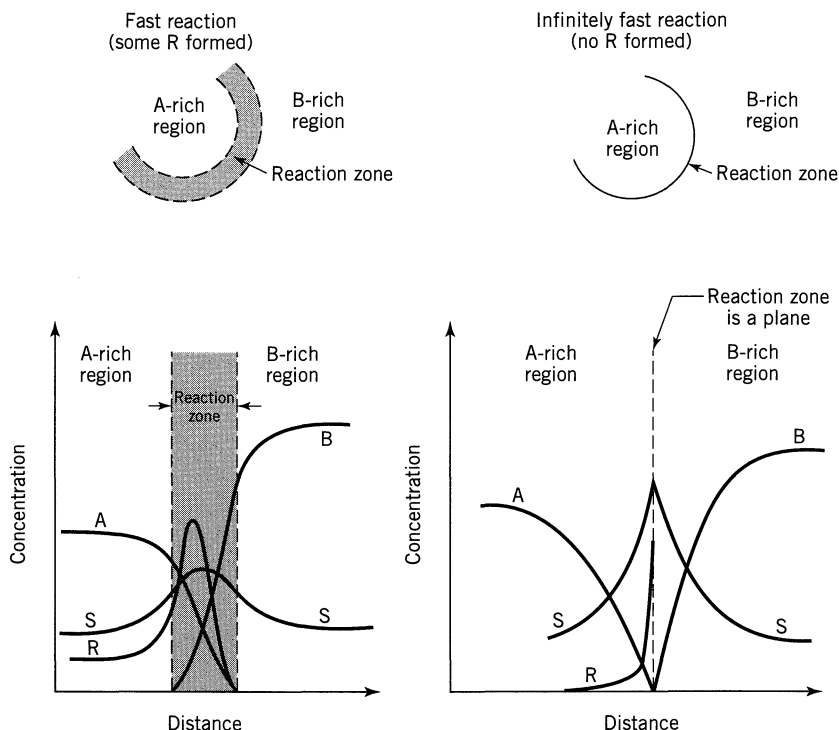


Figure 16.7 Concentration profiles of the components of the reactions



at a representative spot in the reactor between A-rich and B-rich fluid for a very fast and for an infinitely fast reaction.

B-rich regions. Now R will only be formed at this plane. What will happen to it? Consider a single molecule of R formed at the reaction plane. If it starts its random wanderings (diffusion) into the A zone and never moves back into the B zone, it will not react further and will be saved. However, if it starts off into the B zone or if at any time during its wanderings it moves through the reaction plane into the B zone, it will be attacked by B to form S. Interestingly enough, from probabilities associated with a betting game treated by Feller (1957), we can show that the odds in favor of a molecule of R never entering the B zone become smaller and smaller as the number of diffusion steps taken by a molecule gets larger and larger. This finding holds, no matter what pattern of wanderings is chosen for the molecules of R. Thus we conclude that no R is formed. Looked at from the point of view of Chapter 8, an infinitely fast reaction gives a maximum nonhomogeneity of A and R in the mixture, resulting in no R being formed. Figure 16.7 shows the concentration of materials at a typical reaction interface and illustrates these points.

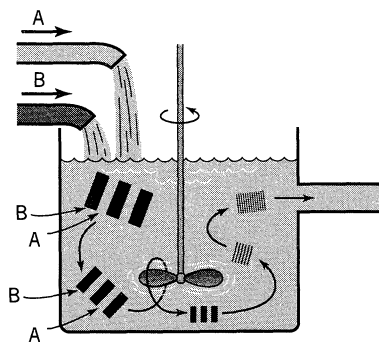


Figure 16.8 Stretching, folding, and thinning of sheets of very viscous A and B.

This behavior of multiple reaction could provide a powerful tool in the study of partial segregation in homogeneous systems. It has been used by Paul and Treybal (1971) who simply poured reactant B into a beaker of A and measured the amount of R formed for a very fast reaction of Eq. 14.

Ottino (1989, 1994) discuss the whole problem of intermixing of fluids A and B in terms of stretching, folding, thinning, and finally diffusional mixing of fluid elements. Figure 16.8 tries to illustrate this mechanism; however, we must now leave this fascinating subject.

These observations serve as a guide to the selection and design of equipment favoring the formation of intermediate when reaction is very fast. The important point is to achieve homogeneity in A and R throughout the reaction mixture before reaction has proceeded to any significant extent. This is done by:

- (a) making the reaction zone as large as possible by vigorous mixing.
- (b) dispersing B in A in as fine a form as possible, rather than A in B.
- (c) slowing the reaction.

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