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.

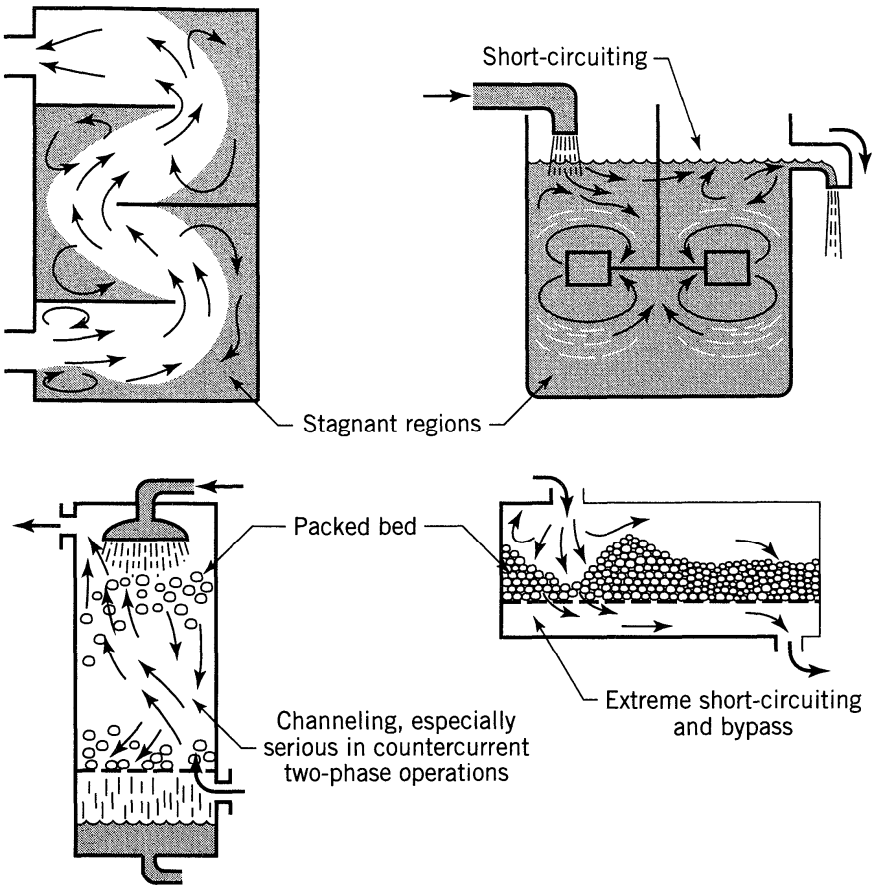


Figure 11.1 Nonideal flow patterns which may exist in process equipment.

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.

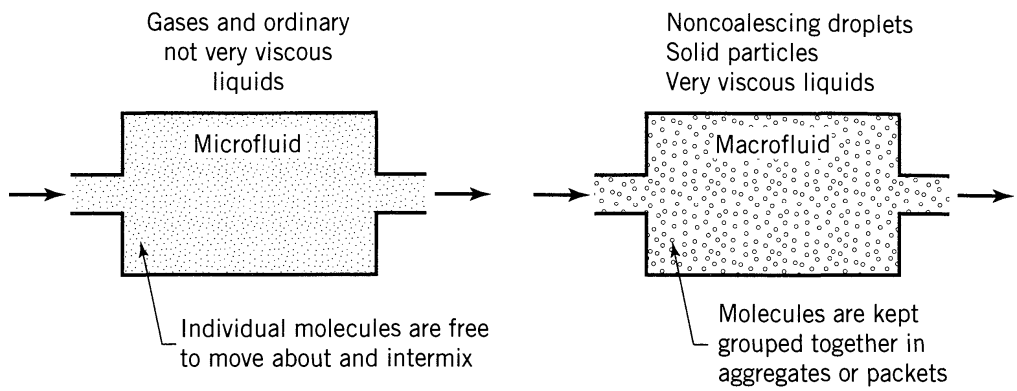


Figure 11.2 Two extremes of aggregation of fluid.

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

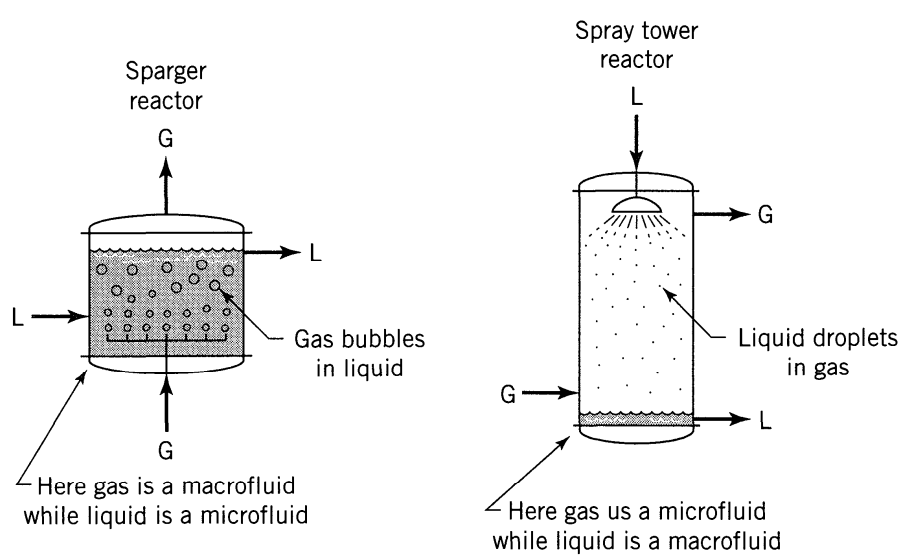


Figure 11.3 Examples of macro- and microfluid behavior.

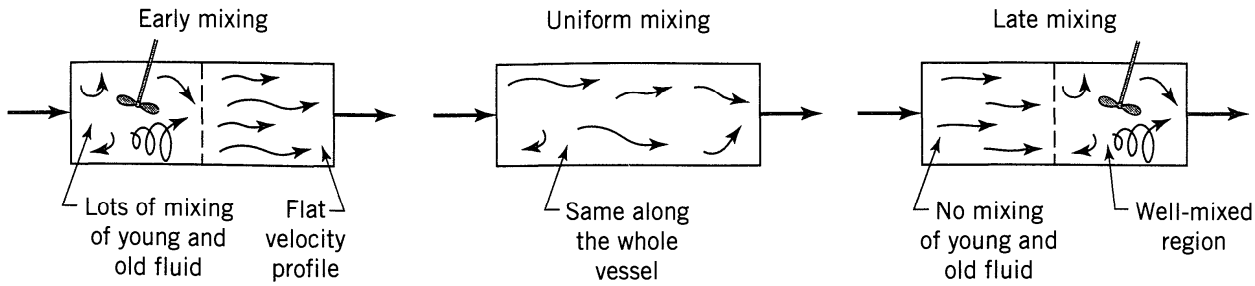


Figure 11.4 Examples of early and of late mixing of fluid.

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

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

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

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

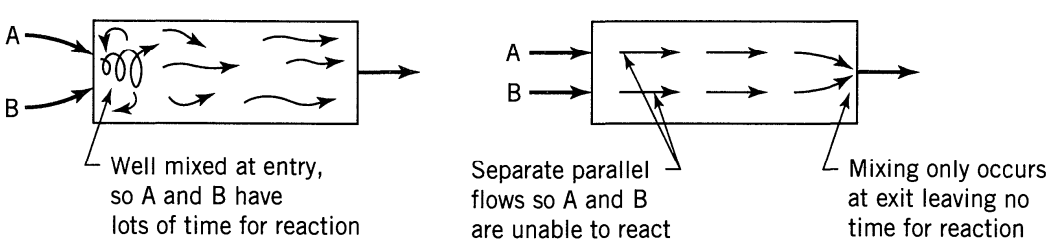


Figure 11.5 Early or late mixing affects reactor behavior.

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

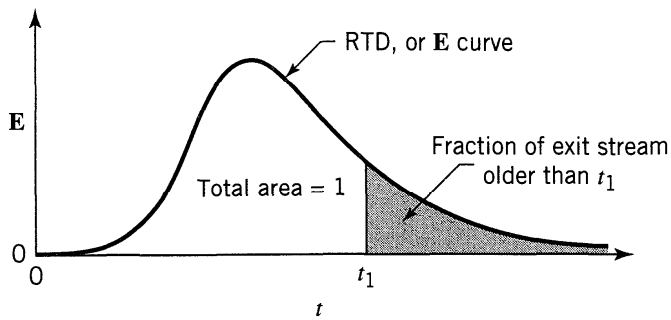


Figure 11.6 The exit age distribution curve **E** for fluid flowing through a vessel; also called the residence time distribution, or RTD.

the fraction younger than age t_1 is

$$\int_0^{t_1} \mathbf{E}\, dt \qquad [-] \tag{1}$$

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

$$\int_{t_1}^{\infty} \mathbf{E}\, dt = 1 - \int_0^{t_1} \mathbf{E}\, dt \qquad [-] \tag{2}$$

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.

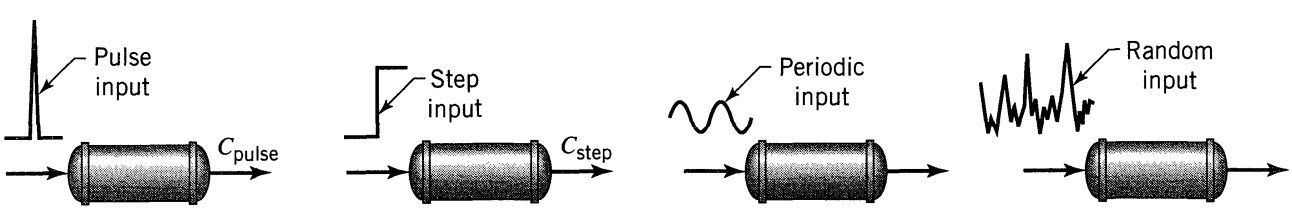


Figure 11.7 Various ways of studying the flow pattern in vessels.

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 m^3 through which flows v m^3/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

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

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

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.

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

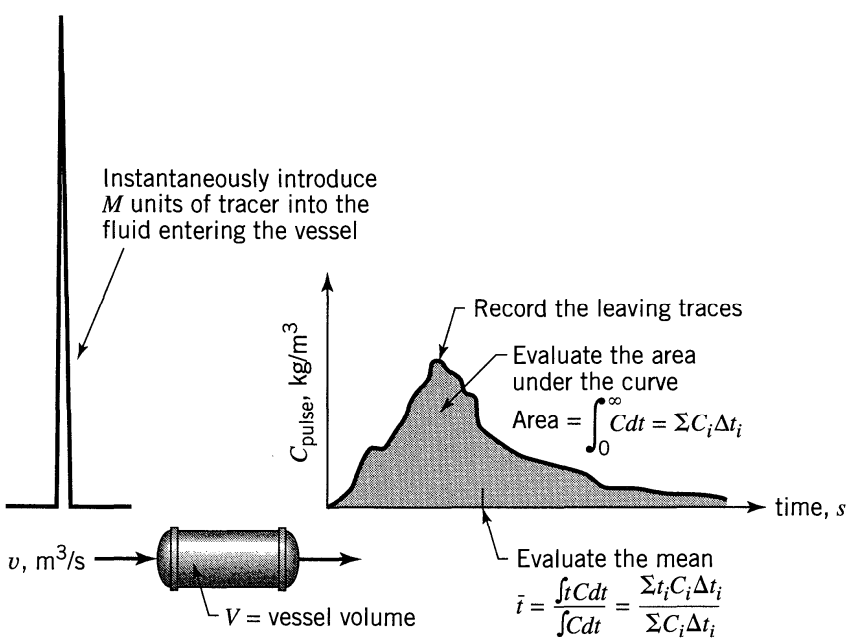


Figure 11.8 The useful information obtainable from the pulse trace experiment.

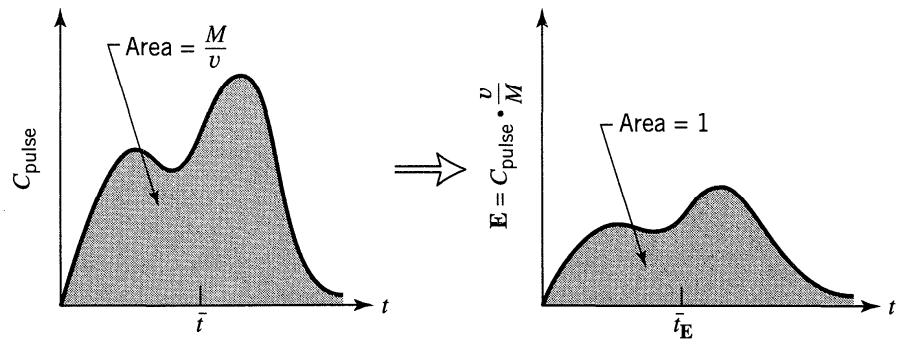


Figure 11.9 Transforming an experimental C_{pulse} curve into an **E** curve.

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

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

$\mathbf{E}_\theta$ 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 **E** into $\mathbf{E}_\theta$.

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

The Step Experiment

Consider v m^3/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 $C_{max} = \left[\frac{\text{kg or mol}}{\text{m}^3}\right]$, and measure the outlet tracer concentration C_{step} versus t, as shown in Fig. 11.11.

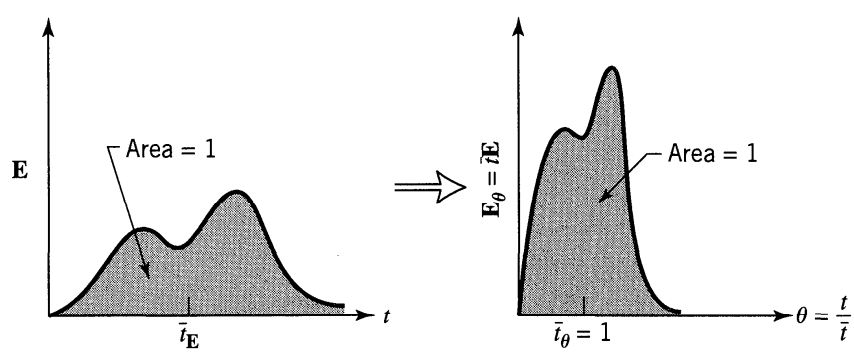


Figure 11.10 Transforming an **E** curve into an $\mathbf{E}_\theta$ curve.

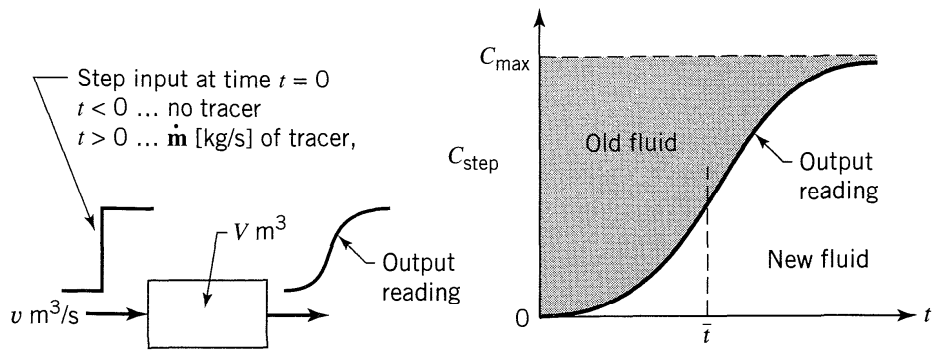


Figure 11.11 Information obtainable from a step tracer experiment.

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

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

and

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

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

where $\dot{\mathbf{m}}$ [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**

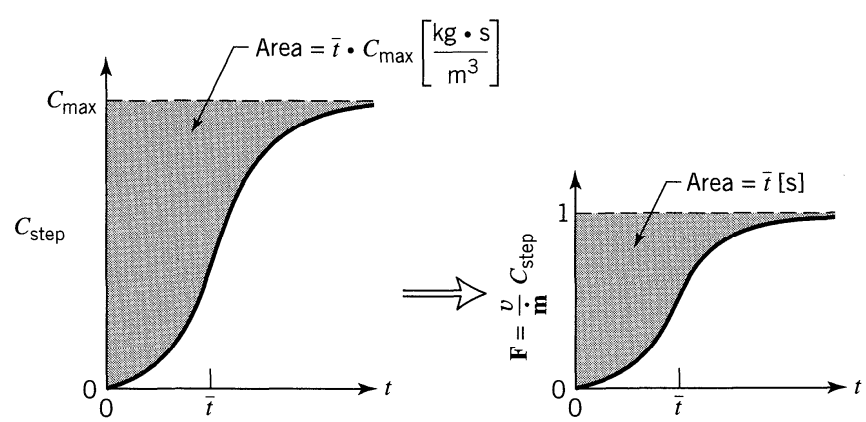


Figure 11.12 Transforming an experimental C_{step} curve to an **F** curve.

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

$$\begin{pmatrix}\text{fraction of red fluid}\\ \text{in the exit stream}\end{pmatrix} = \begin{pmatrix}\text{fraction of exit stream}\\ \text{younger than age } t\end{pmatrix}$$

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

$$\mathbf{F} = \int_0^t \mathbf{E}\, dt \tag{7}$$

and on differentiating

$$\frac{d\mathbf{F}}{dt} = \mathbf{E} \tag{8}$$

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 **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.

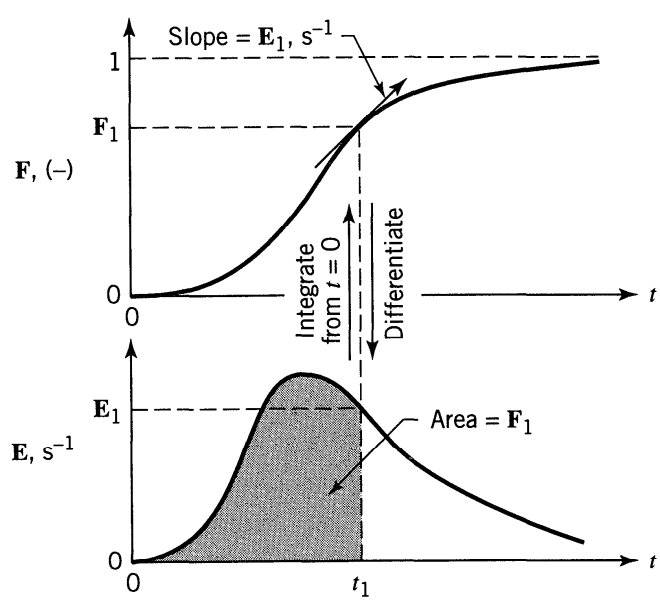


Figure 11.13 Relationship between the **E** and **F** curves.

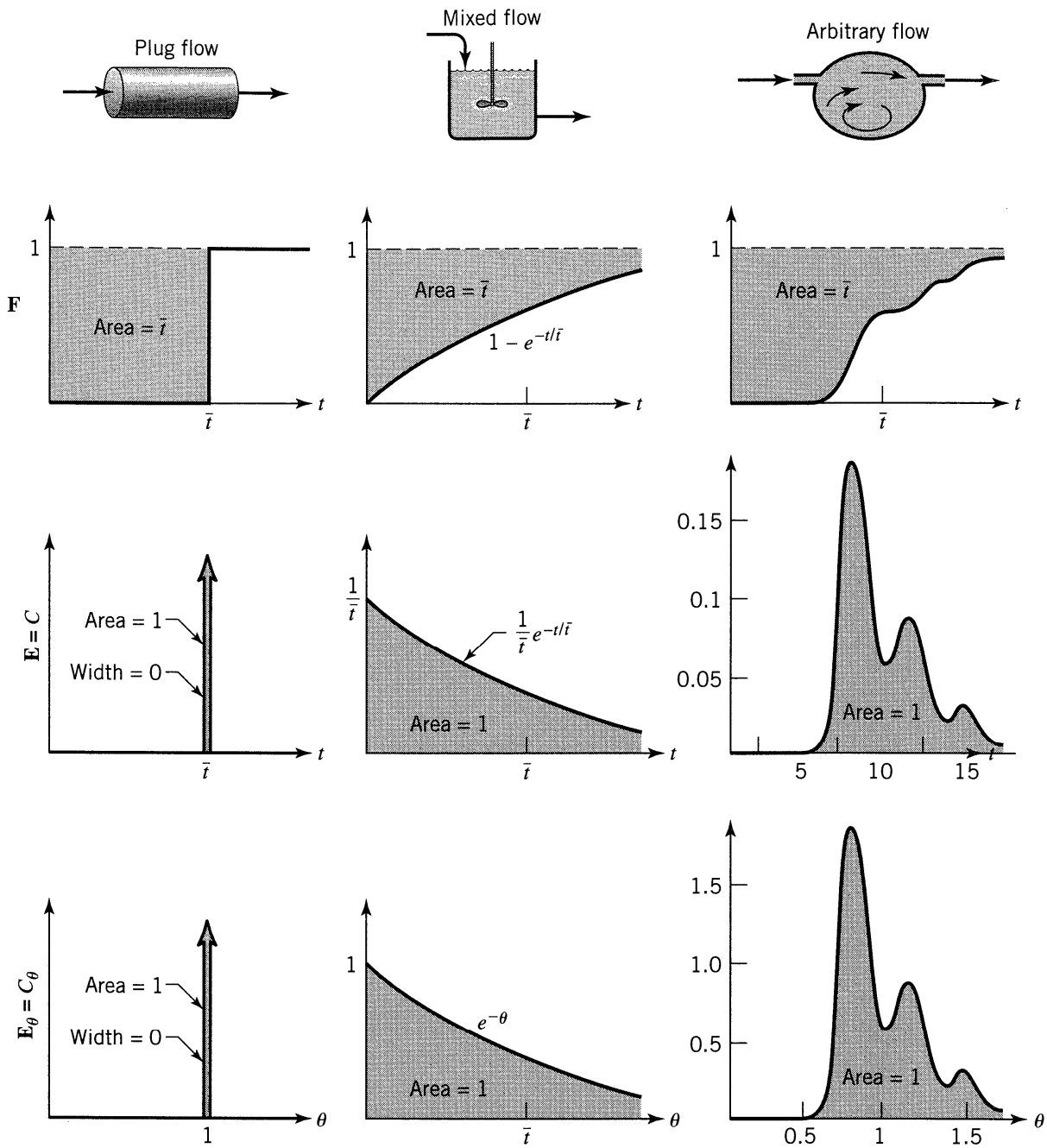


Figure 11.14 Properties of the **E** and **F** curves for various flows. Curves are drawn in terms of ordinary and dimensionless time units. Relationship between curves is given by Eqs. 7 and 8.

At any time these curves are related as follows:

$$\boxed{\begin{gathered} \mathbf{E} = \frac{v}{\dot{\mathbf{m}}} \cdot C_{\text{pulse}}, \quad \mathbf{F} = \frac{v}{\dot{\mathbf{m}}} \cdot C_{\text{step}}, \quad \mathbf{E} = \frac{d\mathbf{F}}{dt}, \\ \bar{t} = \frac{V}{v}, \quad \theta = \frac{t}{\bar{t}}, \quad \bar{\theta}_{\mathbf{E}} = 1, \quad \mathbf{E}_\theta = \bar{t}\mathbf{E} \\ \theta, \quad \mathbf{E}_\theta, \quad \mathbf{F} \ldots \text{ all dimensionless}, \quad \mathbf{E} = [\text{time}^{-1}] \end{gathered}} \tag{9}$$

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

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

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

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

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

Thus we have

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

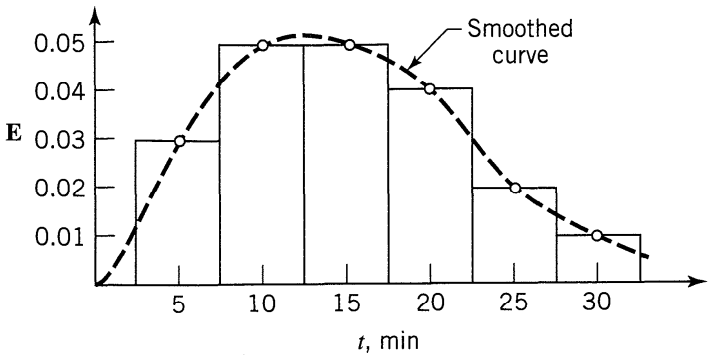


Figure E11.1

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. E11.2*a*.

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

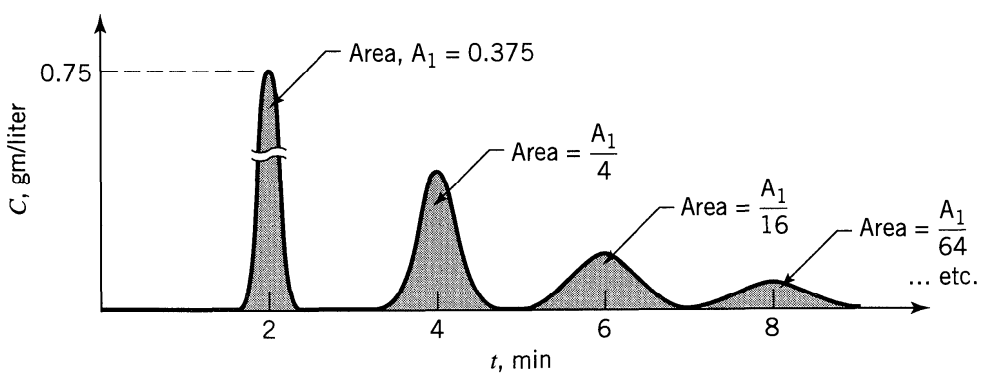


Figure E11.2*a*

SOLUTION

(a) 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

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

These values agree. The results are consistent. **(a)**

(b) For the liquid, Eq. 4 gives

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

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

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

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

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

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

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

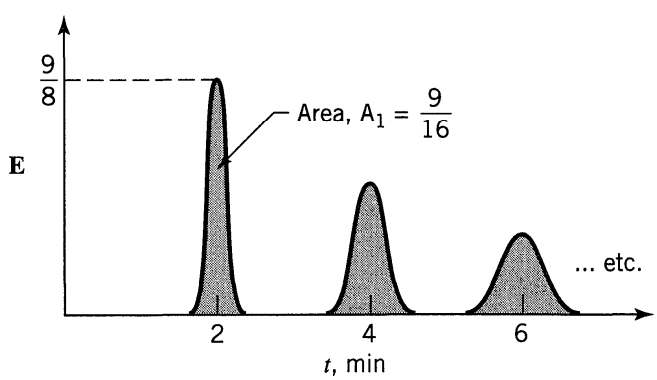


Figure E11.2*b*

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

$$\begin{pmatrix}\text{tracer leaving}\\ \text{in rectangle } B\end{pmatrix} = \begin{pmatrix}\text{all the tracer entering } t' \text{ seconds earlier than } t,\\ \text{and staying for time } t' \text{ in the vessel}\end{pmatrix}$$

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

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

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

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

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

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

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

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

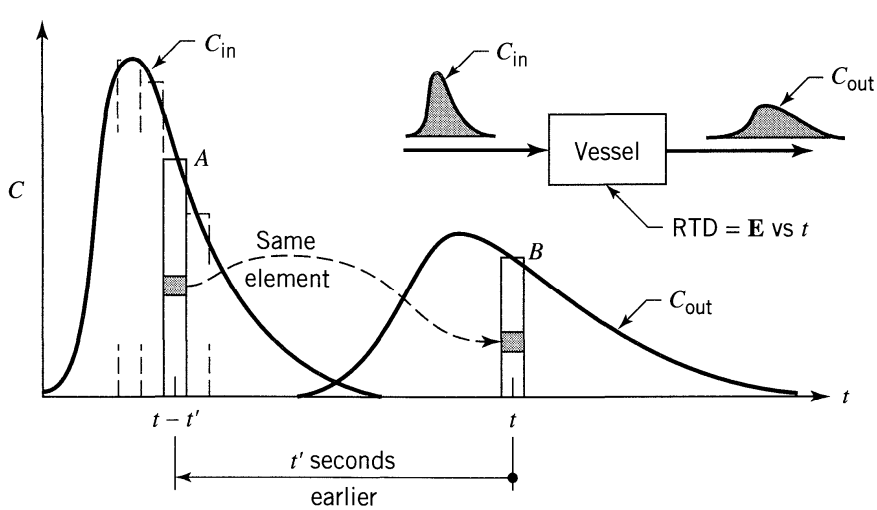


Figure 11.15 Sketch showing derivation of the convolution integral.

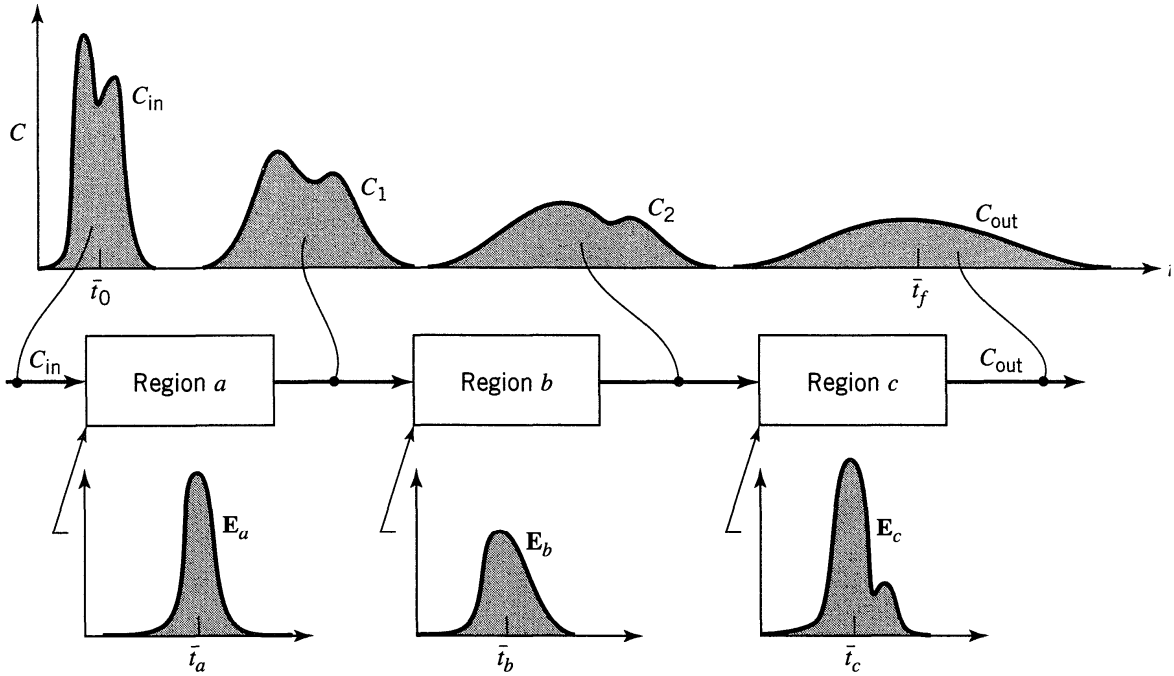


Figure 11.16 Modification of an input tracer signal C_{in} on passing through three successive regions.

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 $\mathbf{E}_a$, $\mathbf{E}_b$, and $\mathbf{E}_c$ are known, then C_1 is the convolution of $\mathbf{E}_a$ with C_{in} and so on, thus

$$C_1 = C_{in} * \mathbf{E}_a, \qquad C_2 = C_1 * \mathbf{E}_b, \qquad C_{out} = C_2 * \mathbf{E}_c$$

and on combining

$$C_{out} = C_{in} * \mathbf{E}_a * \mathbf{E}_b * \mathbf{E}_c \tag{11}$$

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

Problem 2. If we measure C_{in} and C_{out} and know $\mathbf{E}_a$ and $\mathbf{E}_c$ we can then extract the unknown $\mathbf{E}_b$. 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. E11.3*a*.

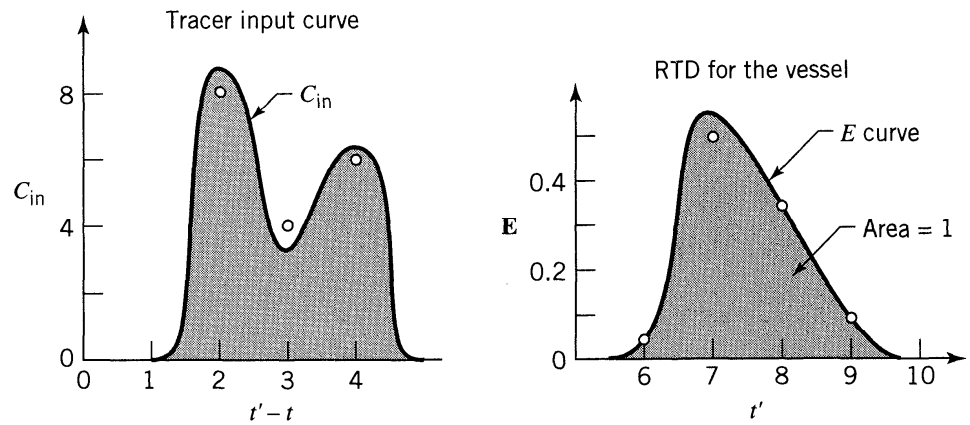


Figure E11.3*a*

SOLUTION

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

$t' - t$	C_{in}
0	0
1	0
2	8
3	4
4	6
5	0

t'	**E**
5	0
6	0.05
7	0.50
8	0.35
9	0.10
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. E11.3*b*. Note that the area under the C_{out} curve equals the area under the C_{in} curve.

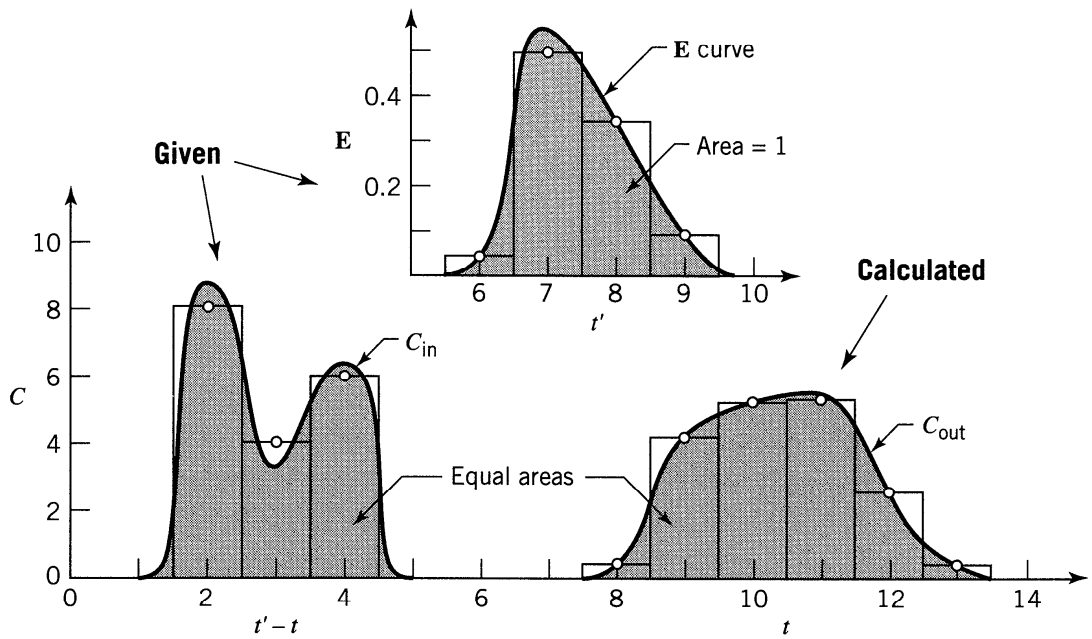


Figure E11.3*b*

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

$$\boxed{\begin{array}{c}\text{Late mixing favors reactions where } n > 1\\ \text{Early mixing favors reactions where } n < 1\end{array}} \qquad \textbf{(12)}$$

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

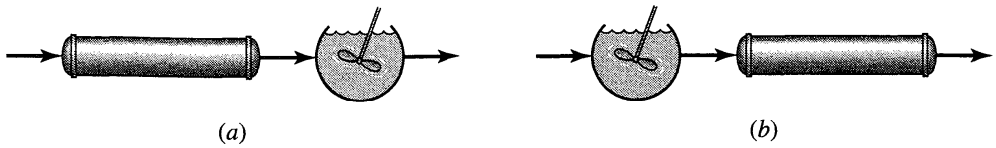


Figure 11.17 This shows the latest and the earliest mixing we can have for a given RTD.

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

$$\begin{pmatrix}\text{mean concentration}\\ \text{of reactant}\\ \text{in exit stream}\end{pmatrix} = \sum_{\substack{\text{all elements}\\ \text{of exit stream}}} \begin{pmatrix}\text{concentration of}\\ \text{reactant remaining}\\ \text{in an element of}\\ \text{age between } t\\ \text{and } t+dt\end{pmatrix}\begin{pmatrix}\text{fraction of exit}\\ \text{stream which is}\\ \text{of age between } t\\ \text{and } t+dt\end{pmatrix}$$

In symbols this becomes

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

or in terms of conversions

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

or in a form suitable for numerical integration

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

From Chapter 3 on batch reactors we have

- for first-order reactions $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = e^{-kt}$ **(14)**
- for second-order reactions $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = \frac{1}{1 + kC_{A0}t}$ **(15)**
- for an nth-order reaction $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = [1 + (n-1)C_{A0}^{n-1}kt]^{1/1-n}$ **(16)**

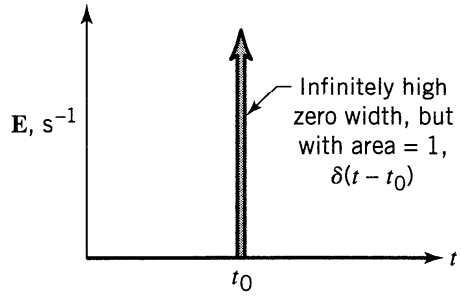


Figure 11.18 The **E** function for plug flow.

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

$$\delta(t - t_0) \tag{17}$$

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

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

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

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,

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

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

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

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

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}	$e^{-kt}\mathbf{E}\,\Delta t$
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	0.005	0.0001
30	0.01	9.21	0.0001	0
given				$\frac{C_A}{C_{A0}} = \sum e^{-kt}\mathbf{E}\,\Delta t = \underline{\underline{0.0469}}$

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·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.

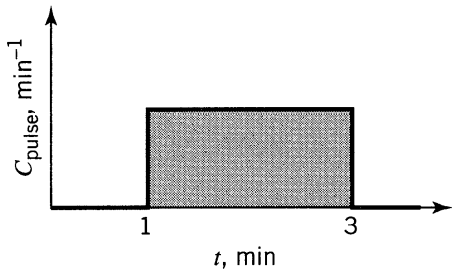


Figure E11.5

SOLUTION

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

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

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 $\mathbf{E}$ = 0.5 for $1 < t < 3$, Eq. 13 becomes

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

So

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

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.

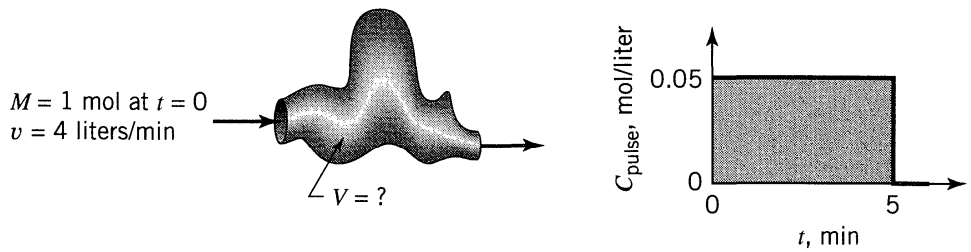


Figure P11.1

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

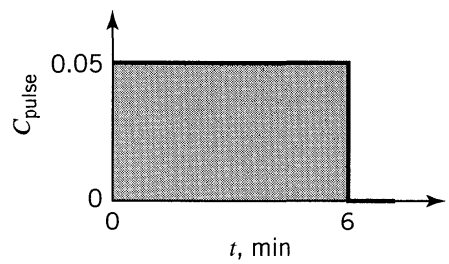


Figure P11.2

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.

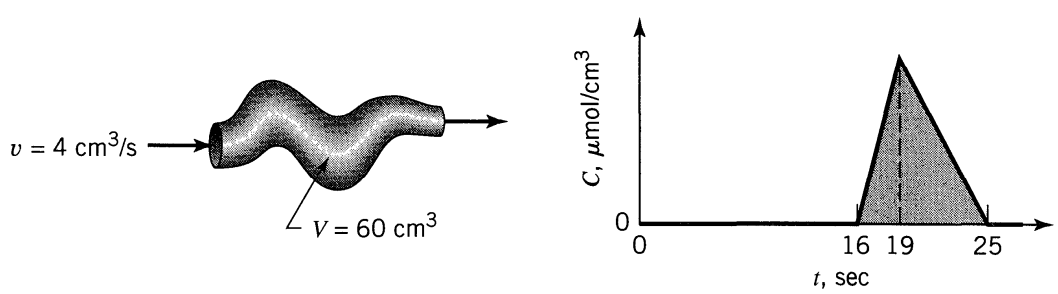


Figure P11.3

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.

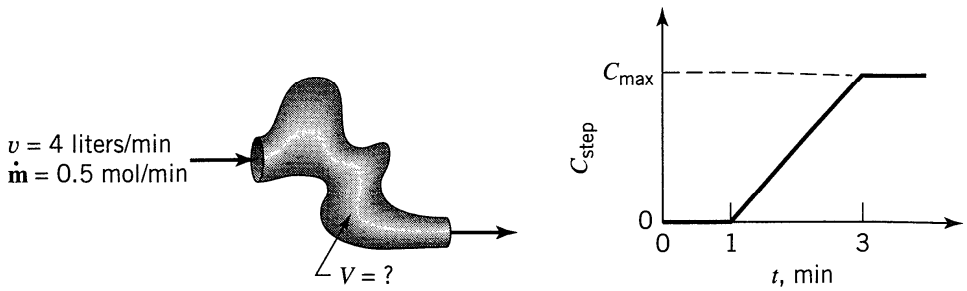


Figure P11.4

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 m^3/s) are monitored for a particular radioisotope ($t_{1/2} > 10$ 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?

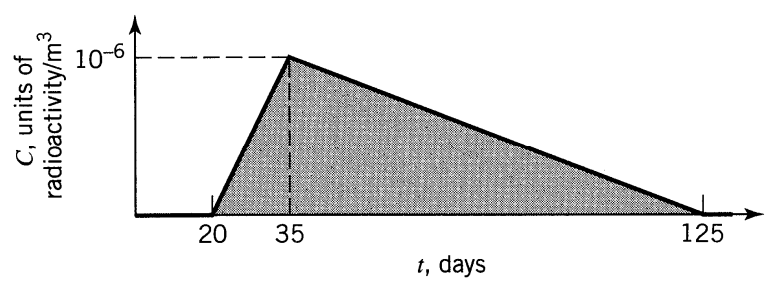


Figure P11.5

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 cm^3/s and 300 cm^3/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?

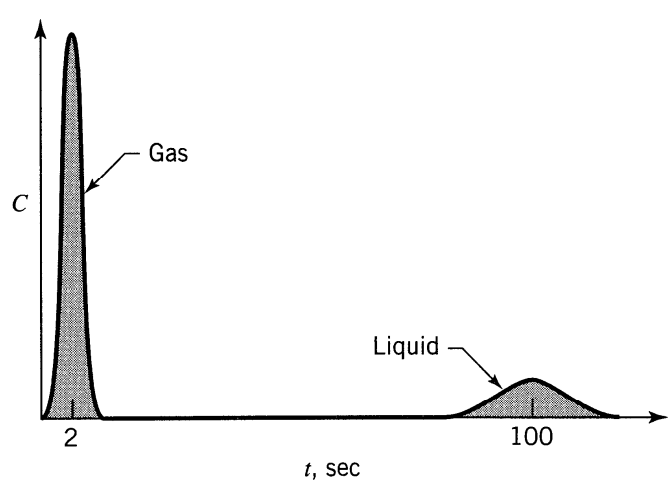
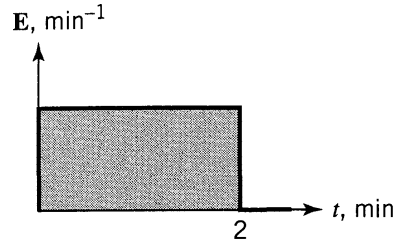


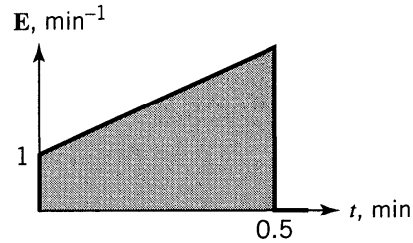
Figure P11.6

A liquid macrofluid reacts according to A → 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.

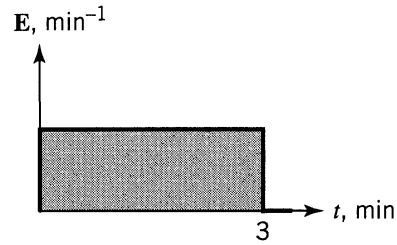
11.7. $C_{A0} = 1$ mol/liter
$-r_A = kC_A^{0.5}$
$k = 2$ mol$^{0.5}$/liter$^{0.5}$ · min



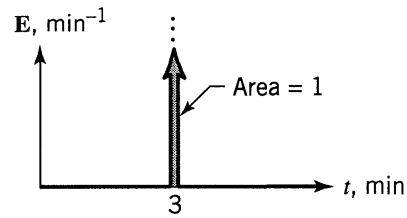
11.8. $C_{A0} = 2$ mol/liter
$-r_A = kC_A^2$
$k = 2$ liter/mol · min



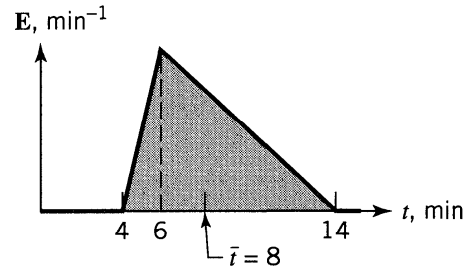
11.9. $C_{A0} = 6$ mol/liter
$-r_A = k$
$k = 3$ mol/liter · min



11.10. $C_{A0} = 4$ mol/liter
$-r_A = k$
$k = 1$ mol/liter · min



11.11. $C_{A0} = 0.1$ mol/liter
$-r_A = k$
$k = 0.03$ mol/liter · min



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

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

$$Fe_2O_3 \rightarrow FeS$$

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

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

and

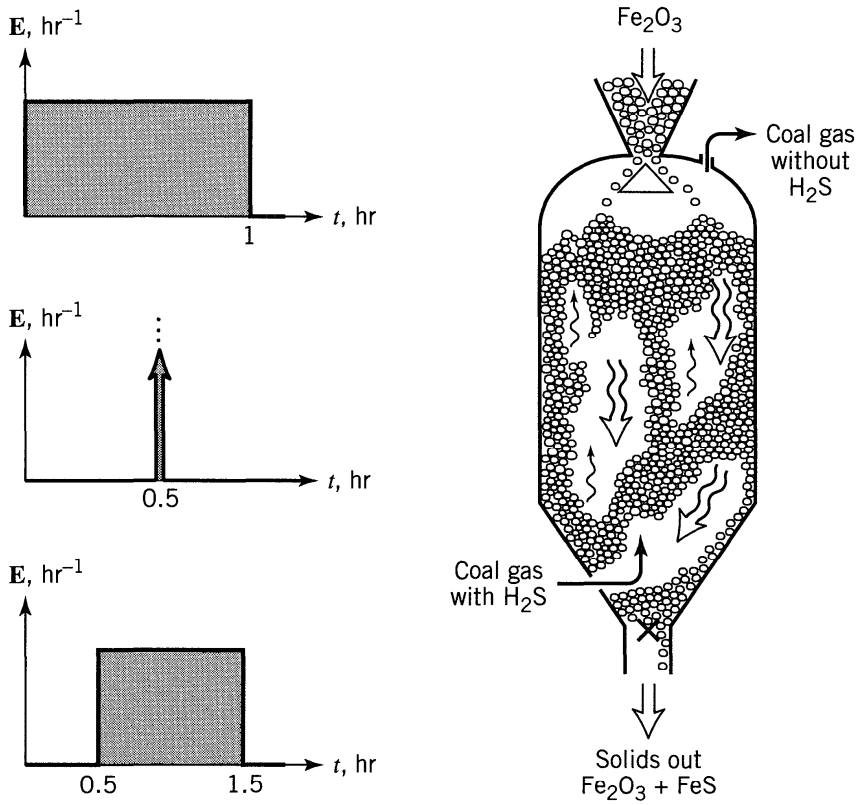
$$X = 1 \qquad \text{when } t \geq 1 \text{ hr}$$

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:
$\bar{t}_s = 15$ min, $\bar{t}_g = 2$ s for carrier gas
For the reaction: A $\rightarrow$ products, $-r_A = kC_A$, $k = 1\ \text{s}^{-1}$

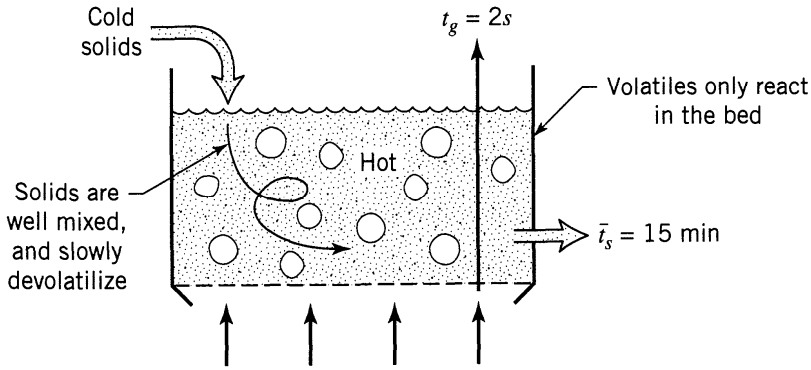


Figure P11.15

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

$$A \rightarrow R, \qquad -r_A = 0.005\, C_A^{1.5}, \text{ mol/m}^3 \cdot \text{s}$$

Determine the conversion of A if the stream is:
(a) a microfluid,
(b) a macrofluid.