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Chapter 2

CONTINUOUS FLOW REACTORS: HYDRAULIC CHARACTERISTICS

2.1 INTRODUCTION

Most natural and engineered systems in which reactions occur have a continuous flow of water through them. The mixing patterns in a reactor can make an important difference in the amount of reaction that occurs and in the composition of the effluent from the system. In this chapter, we focus strictly on the hydraulic and mixing characteristics of continuous flow reactors, i.e., no reactions are considered. With respect to the mass balances considered in Chapter 1, the concern is only with the terms for the mass crossing the boundary of the control volume and the consequent rate of change of mass within that control volume. In subsequent chapters, reaction kinetics are considered, first alone and then in combination with the concepts developed in this chapter, to analyze systems in which both flow and reaction occur.

A useful way of considering the hydraulic characteristics (or flow regime) of a continuous flow reactor is to imagine that we could keep track of all the water that came into the reactor over an infinitesimally brief period and determine the time periods for which parts of that aliquot of influent stayed in the reactor. We might find, for example, that 5% of the molecules stay in the reactor for less than one minute, 15% stay for between one and two minutes, 35% stay for between two and three minutes, and so forth until the full 100% was accounted for. The same information can be expressed in a cumulative fashion, i.e., 5% of the molecules that enter at some instant stay in the reactor for less than one minute, 20% stay for less than two minutes, 55% stay less than three minutes, etc. Such descriptions are called residence time distributions (RTDs). Much of this chapter is devoted to the subject of residence time distributions and what they tell us about the hydraulic or mixing characteristics of a reactor.

In reality, once an aliquot of influent enters the reactor, it is not possible to distinguish the water molecules in that aliquot from water molecules that enter earlier or later, i.e., it is not possible to label and keep track of water molecules to carry out the conceptual experiment described above. However, the same type of information about the residence time distribution of water can be obtained by adding tracers into the influent.

Tracer studies are used in water and wastewater treatment systems primarily to elucidate a reactor’s hydraulic behavior. Understanding this behavior is important because, as shown in Chapter 4, the hydraulic characteristics of a reactor can dramatically influence the treatment efficiency that the reactor achieves. Thus, for instance, a tracer study might be carried out to evaluate alternative models for the mixing that occurs in a reactor. The RTD derived from that study might then be used to predict the conversion (removal) efficiency that would be achieved for a particular contaminant in the reactor. Such an exercise might be carried out, for example, to predict the maximum contaminant concentration in an industrial wastewater treatment plant after an upset that results in a sudden dump of that material into the plant influent.
Tracer studies can also be used as diagnostic tools, e.g., to explore whether the reason that a reactor is not operating as efficiently as expected might be that the reactor has an undesirable mixing pattern. Finally, while most reactors used in water and wastewater treatment are constructed with the intention of facilitating a chemical reaction, some reactors (equalization reactors) are used not to carry out a chemical reaction, but only to mitigate fluctuations in the influent flow rate or solution composition. Achieving the desired hydraulic mixing pattern is usually the primary design objective in such cases. Again, tracer tests can be used to assess how well that design goal has been met.

The first part of the chapter introduces concepts about residence time distributions and mathematical representations of those distributions, followed by a section describing common ways of introducing tracers and of handling the resulting data to infer the residence time distributions of the reactor.

The extent of mixing in continuous flow reactors spans a spectrum. Reactors with absolutely zero mixing lie at one extreme, and reactors with complete and instantaneous mixing between the influent and all of the water already in the reactor lie at the other. In this chapter, the residence time distributions for the extreme conditions are described first, and intermediate degrees of mixing are investigated subsequently. The extremes are commonly called ideal cases, and the range between the two ideal cases defines non-ideal flow. The response to tracer studies in non-ideal reactors is investigated, and techniques for converting tracer responses to residence time distributions are presented. Mathematical models that characterize the non-ideal flow reactors with a few parameters are then described. The design and evaluation of equalization reactors are discussed in the final section of the chapter.

2.2 RESIDENCE TIME DISTRIBUTIONS

Cumulative and differential residence time distributions can be given in discrete terms, as described above. However, it is usually preferable to define continuous functions that accomplish the same task, i.e., that describe the fraction of the fluid in the effluent that has been in the reactor less than a certain time (the cumulative distribution) or the fraction of the fluid that has stayed in the reactor between any two times, $t_1$ and $t_2$. To see how such functions can be developed, imagine a system (a lake, an engineered reactor, or a segment of a river) with water flowing in and out at the same rate (so that the volume of water in the system is constant). Assume that the flow is steady, i.e., that it has been flowing in the same way for a long period and continues flowing in that way for at least the duration of the test. Imagine further that somehow we could label all the molecules that enter the system in an infinitesimal time period ending at the time defined as time zero; call the number of such labeled molecules $N_{\infty}$. Finally, imagine that we could easily measure (count) the labeled molecules as they left the reactor.

One possible result of such an experiment is shown in Figure 1A, in which the cumulative number of labeled molecules that have been counted in the effluent [$N(t)$] is shown as a function of time. The results shown in the figure suggest that, for this hypothetical system, not many
labeled molecules come out in the early time period, then they come out more rapidly for a while, and then their appearance at the detection point slows down once again; eventually, all of them come out, so that $N(t)$ reaches $N_\infty$.

Figure 1. Various presentations for results of a hypothetical experiment to evaluate the passage of labeled water molecules through a reactor.

The rate at which the labeled molecules come out can be found as the derivative of the curve shown in Figure 1A, i.e., as the limit of $\frac{\Delta N(t)}{\Delta t}$ as $\Delta t$ approaches zero. This derivative, evaluated at each time, is shown in Figure 1B and indicates directly that, in the example system, the rate at which the labeled molecules leave the system is small at the earliest times, higher for
intermediate times, and approaches zero at later times. Since the function described in part B of the figure is the derivative of the function in part A, the integral of the function in part B from time zero to any time $t$ yields $N(t)$. Taken over all time (from time zero to time infinity), that integral yields $N_\infty$.

Normalizing the derivative function shown in part B by dividing by $N_\infty$ makes the result independent of the absolute number of influent molecules that were labeled. The normalized result is called the *exit age distribution* of the system and is given the symbol $E(t)$; i.e.,

$$E(t) = \frac{dN / dt}{N_\infty} \quad (1)$$

$$E(t) \, dt = \frac{dN}{N_\infty} \quad (2)$$

This exit age distribution is shown in Part C of Figure 1. $E(t)$ has dimensions of inverse time. Since $dN$ is the number of labeled molecules that exit the reactor in the period $dt$, i.e., between $t$ and $t + dt$, $dN / N_\infty$ is the fraction of all labeled molecules that exit the reactor during this period. Therefore, since all the labeled molecules entered the reactor at $t = 0$, $E(t) \, dt$ can be identified as the fraction of the fluid that has residence time between $t$ and $t + dt$. Correspondingly, the fraction of the fluid with residence times between two discrete times is the time integral of $E(t) \, dt$ over that time period:

$$\text{Fraction of fluid in the system with residence time greater than } t_1 \text{ and less than } t_2 = \int_{t_1}^{t_2} E(\theta) \, d\theta \quad (3)$$

Note that, since 100% of the fluid must have a residence time less than infinity, the integral of $E(t)$ from $t = 0$ to $t = \infty$ must be 1; i.e.,

$$\int_{0}^{\infty} E(t) \, dt = 1 \quad (4)$$

Finally, it is useful to describe the cumulative age distribution, i.e., the fraction of the fluid with residence time less than or equal to a given value. This function can be derived by normalizing the data in part A of the figure by dividing by $N_\infty$. The result (shown in part D) has the same shape as that in part A but now has a range from 0 to 1; this cumulative age distribution is normally given the symbol $F(t)$ and is dimensionless. From the integral/derivative relationship described above between the functions shown in parts A and B of the figure, it should be clear that $F(t)$ is the integral of $E(t)$ from zero to time $t$; i.e.,

$$F(t) = \int_{0}^{t} E(t) \, dt \quad (5)$$
The differential and cumulative age distributions, i.e., $E(t)$ and $F(t)$, are useful descriptors of the flow characteristics (under steady flow conditions) of any system, as shown subsequently. Although we have not used statistical terminology in developing these functions, those familiar with statistical analysis will recognize $E(t)$ as a standard probability density function, and $F(t)$ as a cumulative probability function. These properties enable one to describe the flow characteristics in probabilistic terms. For example, we can say that the probability that a molecule will stay in a reactor less than time $t$ is $F(t)$, and the probability that a molecule will stay in the reactor between $t_1$ and $t_2$ is the integral expressed in Equation 3 above.

**Tracers**

The labeling of the influent water molecules at some instant and the subsequent measurement over time of those molecules in the effluent are, of course, not possible by any reasonable means. However, the same type of information about the residence time distribution can be obtained by introducing a tracer into the influent water and measuring its concentration in the effluent over time. Ideally, tracers used to analyze the RTD of a reactor meet four criteria: their hydraulic behavior is identical to that of water (e.g., they are neutrally buoyant); their addition does not change the properties of the solution (e.g., the viscosity) appreciably; they are non-reactive; and their concentration in water can be measured well, preferably at low concentrations. In essence, these characteristics assure that molecules of tracer behave identically to molecules of water in the reactor. However, because the tracer molecules can be differentiated easily from the water molecules, they serve the same function as the labeled molecules in the conceptual experiment. They therefore enable us to determine the differential and cumulative residence time distributions, $E(t)$ and $F(t)$, respectively.

Tracer studies are usually done by putting the tracer into the reactor influent either as a pulse or as a step input. In an ideal pulse input, a known amount of tracer is put in instantaneously, i.e., within an infinitesimally short time. The time at which the tracer is injected is usually defined as time zero. This input is similar to the labeling of all the molecules that come into the reactor in an infinitesimally short time as described above. In a step input, the tracer is put into the reactor at a constant concentration beginning at a defined instant (usually designated time zero) and continuing (ideally) forever; in reality, “forever” means for a sufficiently long time that the reactor response is essentially the same as it would be if the test were continued indefinitely.

For quantitative analysis of tracer experiments, it is necessary to describe these two different types of inputs mathematically. A step input function, starting at time zero and continuing forever, is shown in Figure 2a. Time zero is shown away from the vertical axis to emphasize that the tracer input is zero for all times prior to that time and equals a finite concentration $c_{\text{in}}$ for all times thereafter.

A step function whose value jumps from 0 to 1 when the value of an independent parameter $z$ is $z^*$ is called the Heaviside function of $z$, applied at $z^*$.  

---

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This function is shown in Figure 2b. With this terminology, the step input tracer test can be described as the product of \( c_{in} \) and the Heaviside function applied at time zero, i.e., 
\[
c_{in}(t) = c_{in} H_0(t).
\]

Figure 2. (a) The input tracer concentration for a step input test. (b) The Heaviside function of a variable \( z \), applied at \( z^* \). The function in part (a) can be described as \( c_{in} H_0(t) \).

The mathematical definition of the pulse input is a bit more obscure, as it includes the use of the Dirac delta function, \( \delta_{z^*}(z) \), where \( z \) is some variable of interest. This function, shown graphically in Figure 3a, is the derivative of the Heaviside function, so its value can be equated with the slope of Figure 2b, i.e., its value is infinite when \( z = z^* \) and zero at all other values of \( z \). The dimensions of \( \delta_{z^*} \) are the inverse dimensions of \( z \); e.g., if \( z \) is time, \( \delta_{z^*}(z) \) has dimensions of 1/time. The integral of the Dirac function over any interval \( z_1 \) to \( z_2 \) is \( H_{z^*}(z_2) - H_{z^*}(z_1) \). This difference is 1.0 over any interval that includes \( z^* \) and is zero over any interval that does not include it. In symbols, the Dirac delta function can be described as follows:

\[
\delta_{z^*}(z) = \frac{dH_{z^*}(z)}{dz} = \begin{cases} \infty & \text{at } z = z^* \\ 0 & \text{at all other } z \end{cases}
\]

\[
\int_{z_1}^{z_2} \delta_{z^*}(z) \, dz = H_{z^*}(z_2) - H_{z^*}(z_1) = \begin{cases} 1.0 & \text{if } z_1 < z^* < z_2 \\ 0 & \text{over any other interval} \end{cases}
\]
The Dirac function can also be defined as a limiting condition: if we imagine a continuous distribution \( f(z) \) defined from \( z = -\infty \) to \( z = +\infty \) with an integral over that range of one, and then imagine gradually shrinking the range of \( z \) values over which \( f(z) \) is non-zero, the limit as that range goes to zero is the delta function, and the value of \( z \) where \( f(z) \neq 0 \) is \( z^* \).

As noted above, the purpose of tracer tests is to gain information about the residence time distributions \( E(t) \) and \( F(t) \). We next consider how the concentration profile of tracer in the effluent of a reactor during a tracer test, whether that input is a pulse or a step, can be used to determine these residence time distributions.

**Pulse Input Response**

Consider the concentration of tracer in the effluent of some arbitrary reactor that has received a pulse input of mass \( M_{p,in} \), so that the profile of the input concentration is as shown in Figure 3b. Assume that the reactor contains a volume \( V \) of water and has been receiving a constant flow \( Q \) for sufficient time that steady flow conditions exist in the reactor. If we imagine, for example, that this arbitrary reactor is a large open tank in which the water comes in at one end and flows out the other, it is reasonable to think that the influent over some small time period will mix somewhat with the water that is in the vicinity of the influent port at that time, but that no tracer will be transported immediately to the other end of the reactor. A person taking samples at the effluent will detect no tracer immediately after the pulse injection; as time proceeds, the concentration of tracer will rise and subsequently fall. Eventually all of the tracer injected at time zero will have exited the reactor and the concentration of tracer will again be

![Figure 3. (a) The Dirac delta function of a variable \( z \); (b) The Dirac function characterizing the influent in a pulse input tracer study](image-url)
zero. This response of the reactor \( c_p(t) \), the effluent concentration as a function of time\(^1 \) is depicted in Figure 4A; the exact shape of the curve depends on the amount of mixing in the reactor, but that is not our concern now. It is sufficient to understand that a reactor could reasonably give the response shown.

\[^1\]The expression \( c(t) \) is used in this text to denote the concentration of a substance as a function of time. In the current context, \( c(t) \) is used for the time-varying concentration of tracer in the effluent from any reactor, \( c_p(t) \) is used to indicate the effluent tracer profile for a pulse input tracer test, and \( c_s(t) \) is used to indicate the corresponding profile for a step input tracer test.
We noted previously that $E(t)$ equals the rate at which labeled molecules of water exit the reactor, normalized to the total number of labeled molecules injected. The analog of the number of labeled molecules in the conceptual experiment is the mass of tracer in the real experiment. The exit age distribution, $E(t)$, can thus be evaluated as the rate at which tracer mass exits the reactor.

Figure 4. Experimental results for the tracer effluent concentration and the corresponding residence time distributions for a pulse input test in a hypothetical reactor.
reactor (the product of the flow and effluent concentration) divided by the total mass of tracer
put into the reactor, \( M_{p,\text{in}} \), i.e., in symbols\(^2\):

\[
E(t) = \frac{Q}{M_{p,\text{in}}} c_p(t)
\]  

(8)

The exit age distribution, \( E(t) \), is shown for the reactor under consideration in Figure 4B; the
shape is identical to that of \( c_p(t) \), but the units and values are different.

Equation 8 makes clear that \( E(t) \) can be thought of as a normalized response to a pulse
input tracer test; the normalization is accomplished by multiplying the direct response, \( c_p(t) \), by
the factor \( \frac{Q}{M_{p,\text{in}}} \). When the data are normalized in this way, if two different pulse input tracer
tests with different amounts of tracer are performed on the same reactor with the same flow
rate, \( c_p(t) \) would be different in the two tests but \( E(t) \) would be the same. Such a result is
essential, since \( E(t) \) is a function describing how water flows through the reactor (at a particular
flowrate \( Q \)) and is not intrinsically related to the tracer; tracers are simply a useful way of
determining the flow characteristics of the reactor.

Based on the various descriptions of \( E(t) \) to this point, we can think of the \( E(t) \) function in
three equivalent ways. First, for a sample of the influent, \( E(t) \) expresses the differing amounts of
time that the molecules of water will stay in the reactor. If, for example, \[
\int_{6 \text{ min}}^{10 \text{ min}} E(t) \, dt = 0.15,
\]
then 15% of the molecules will stay in the reactor between 6 and 10 minutes. Second, for an
aliquot of the effluent, \( E(t) \) characterizes the differing amounts of time that molecules were in the
reactor. So, using the same example, 15% of the molecules in any sample of effluent were in the
reactor between 6 and 10 minutes. Finally, \( E(t) \) is a probability density function so, for the same
example, any molecule that enters (or is in, or leaves) the reactor has a 15% probability that it
will (or did) stay in the reactor between 6 and 10 minutes.

The cumulative age distribution, \( F(t) \), can also be developed from a pulse input tracer test.
The cumulative mass of tracer that has come out of the reactor up to any time \( t \) can be
determined by integrating, from time zero to time \( t \), the rate at which the mass is leaving. As
noted just above, the rate at which tracer leaves the reactor is the product of flow and
concentration. Assigning the symbol \( M_p(t) \) to the mass that has come out in the effluent up until
time \( t \), this quantity is described as:

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\(^2\)The normalization can also be based on the total mass of tracer that is detected over all time in the
effluent from the reactor, \( M_{p,\text{out}} \). The following derivations are carried out using \( M_{p,\text{in}} \) as the normalizing
factor. A discussion about potential differences between \( M_{p,\text{in}} \) and \( M_{p,\text{out}} \) is provided subsequently.
\[ M_p(t) = Q \int_0^t c_p(t) \, dt \quad (9) \]

Equation 9 is a general expression for any reactor receiving a pulse input of tracer; for the arbitrary reactor under consideration, \( M_p(t) \) is shown graphically in Figure 4C. Again exploiting the analogy between hypothetical, labeled water molecules and the pulse input of tracer, we can equate \( F(t) \) with the fraction of the pulse input mass \( (M_{p, in}) \) that has exited the reactor up until time \( t \). Thus, \( F(t) \) can be computed as the ratio of \( M_p(t) \) to \( M_{p, in} \), i.e.,

\[ F(t) = \frac{M_p(t)}{M_{p, in}} = \frac{Q}{M_{p, in}} \int_0^t c_p(t) \, dt = \int_0^t E(t) \, dt \quad (10) \]

where the first two equalities are specific for the pulse input case, and the last equality is always true. For the case under consideration, \( F(t) \) is shown in Figure 4D; \( F(t) \) has the same shape as \( M_p(t) \) but is dimensionless and has a maximum value (asymptote) of one.

For a discrete data set, Equation 10 can be approximated using the trapezoidal rule as follows:

\[ F(t_i) = \sum_{all \ j \leq i} \left( \frac{E(t_j) + E(t_{j-1})}{2} \right) (t_j - t_{j-1}) = \sum_{all \ j \leq i} E_{ave}(t_j) \Delta t_j \quad (11) \]

where \( E_{ave}(t_j) \) is the average value of \( E(t) \) over the time interval \( \Delta t_j \).

**Step Input Response**

The exit age distribution, \( E(t) \), and cumulative age distribution, \( F(t) \), can also be developed using a step input tracer test. Recall that, in such a test, the non-reactive tracer is added at a concentration \( c_{in} \) beginning at time zero and continuing for all time thereafter. (Although the tracer is added at time zero, the water flow is assumed to have been established previously and to be steady throughout the test period.) Again, our question is: what is the response of the reactor to this test, i.e., how does the effluent concentration vary with time after the initiation of the tracer injection into the influent? Our intuition leads us to think that, for the reactor described above, no tracer will be found in the effluent immediately, but the effluent concentration will gradually rise from zero to the constant influent concentration. Such a result is shown graphically in Figure 5A.
Figure 5. Experimental results for the tracer effluent concentration and the corresponding residence time distributions for a step input test in a hypothetical reactor.

Any sample of effluent taken after the initiation of the tracer test can be thought of as a mixture of two parts: one fraction is water that came in before time zero and contains no tracer, and the other is water that came in after time zero and contains tracer at concentration $c_{\text{in}}$.

Consider an effluent sample collected at some time $t^*$. The fraction of the sample that entered the reactor less than time $t^*$ ago (between $t = 0$ and $t = t^*$) is, by definition, the value of the cumulative age distribution for $t^*$, i.e., it is $F(t^*)$. This fraction of the sample contained tracer molecules at concentration $c_{\text{in}}$ when it entered the reactor. The fraction that came in longer than $t^*$ ago (i.e., before $t = 0$, when water that contained no tracer was entering the reactor) is $1 - F(t^*)$. The tracer concentration in the sample is thus:

$$c(t^*) = F(t^*)c_{\text{in}} + (1 - F(t^*))c_{\text{in}}$$
so: \[ F(t^*) = \frac{c(t^*)}{c_n} \] (12a)

The above analysis can, of course, be applied at any time \( t \), so the relationship between the time record of the effluent concentration in a step-input tracer test, \( c_s(t) \), and the cumulative age distribution, \( F(t) \), can be generalized as:

\[ F(t) = \frac{c_s(t)}{c_n} \] (12b)

Hence, the \( F(t) \) curve can be obtained by normalizing the effluent concentration curve from a step input tracer, where the normalization involves simply dividing by the influent concentration. For the reactor under consideration, \( F(t) \) is shown in Figure 5B. Further, from the earlier discussion, it is clear that \( E(t) \) can be obtained as the derivative of \( F(t) \), and that function is shown in Figure 5C.

The cumulative age distribution, \( F(t) \), has three equivalent interpretations, analogous to those described above for the exit age distribution, \( E(t) \). First, \( F(t) \) expresses the anticipated cumulative residence time distribution of the influent water molecules that enter the reactor. If \( F(t_1) = 0.6 \), for example, 60% of the water molecules in any sample of influent will stay in the reactor for a period less than \( t_1 \). Second, \( F(t) \) expresses the cumulative residence time distribution of the molecules in the effluent. That is, if \( F(t_1) = 0.6 \), 60% of the water molecules in any sample of effluent spent a time less than \( t_1 \) in the reactor, while the rest (\( 1 - F(t_1) \)), or 40%, stayed in the reactor longer than \( t_1 \). Finally, \( F(t) \) expresses the probability that a single water (or tracer) molecule stays in the reactor less than a certain time; e.g., if \( F(t_1) = 0.6 \), the probability that a water molecule stays in the reactor less than \( t_1 \) is 60%.

We have now seen that both the exit age distribution, \( E(t) \), and the cumulative age distribution, \( F(t) \), can be determined from either pulse or step tracer tests. The \( E(t) \) and \( F(t) \) functions describe how water flows through a reactor, and that result is independent of the way in which the tracer test is conducted. Every sample of water, over all time in a reactor with steady flow, behaves identically to samples collected during the tracer test; the tracer test simply allows us to see and quantify that behavior.

**Example 1: Characterizing flow through a reactor from the results of a pulse tracer test.** A pulse input tracer test is conducted on a reactor with a water volume of 240 m³ and a flow rate of 4 m³/min. A mass of 10 kg of tracer is added to the reactor at time zero (pulse input), and the effluent concentration is recorded every 10 minutes as shown below. Determine and plot the differential and cumulative age distributions, \( E(t) \) and \( F(t) \).

<table>
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<th>Time, min</th>
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<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
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<td>34</td>
<td>40</td>
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<td>26</td>
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<td>6</td>
<td>3</td>
<td>1</td>
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Solution. The raw data are plotted in Figure Ex1-1, and the calculations needed to compute $E(t)$ and $F(t)$ are summarized in the subsequent Table. $E(t)$ is computed by substitution of the appropriate values into Equation 8. For example, the value in row 3 associated with $t = 20$ min is:

$$E(20 \text{ min}) = \left(\frac{4 \text{ m}^3/\text{min}}{10 \text{ kg}}\right) \left(\frac{34 \text{ mg}}{\text{L}}\right) \left(\frac{1 \text{ kg}}{10^6 \text{ mg}}\right) \left(\frac{10^3 \text{ L}}{\text{m}^3}\right)$$

$$= 0.0136 \text{ min}^{-1}$$

Figure Ex1-1. Tracer output curve ($c_p(t)$ vs. $t$) for Example 1.
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<thead>
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<th>B</th>
<th>C</th>
<th>D</th>
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<td>Time (min)</td>
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<td>(F(t)) (-)</td>
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<td>0</td>
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Column D has no entry in Row 1 because the values in this column are associated with intervals of time and are shown in the table at the end of the interval. For example, the entry of 0.100 shown for \(E(t)\Delta t\) at 20 minutes (in cell D3) is the product of the average value of \(E(t)\) during the preceding interval (\(\frac{0.0064 + 0.0136}{2}\) min⁻¹) and the duration of the time interval (20 − 10 minutes). This value can be equated with the approximate area under the \(E(t)\) versus \(t\) curve for the interval 10 to 20 minutes. \(E(t)\) and \(F(t)\) are plotted against \(t\) in Figure Ex1-2.

\(F(t)\) is computed as the integral of \(E(t)\) from time 0 to \(t\), which is approximated numerically as shown in Equation 11. Numerically, \(F(t)\) values in column E are the running sum of the values in column D. The value of \(F(t)\) in row 3, for example, is the value of \(F(t)\) in row 2 plus the value of \(E_{ave}(t)\Delta t\) in cell D3. Note that these data do not yield a final value of \(F(t) = 1.0\), although the final value is close to 1.0. We consider the implications of this outcome subsequently.
Figure Ex1-2. Differential and cumulative residence time distribution functions for the example data set.
Statistics of Probability Distributions and the Mean Hydraulic Detention Time

One important characteristic of the residence time distribution is the mean hydraulic detention time, i.e., the average amount of time that influent molecules spend in the reactor. We next consider how to determine the mean hydraulic residence time from residence time distributions or from tracer tests.

In any system with steady flow, each substance within the system is being replaced at an average rate given by the amount of the substance in the system divided by the rate at which it is entering or leaving the system. This is equally true if the substance of interest is a water molecule, another chemical species, or even people. For instance, if 120 people are in a department store, and 10 people leave while 10 others enter every minute, then the number in the store stays steady at 120, and the average length of time that a person stays in the store is 120 people/(10 people/min) = 12 minutes. Some may stay longer and some shorter, but 12 minutes is the average. Similarly, for a fluid moving through a control volume, the mass of fluid in the system is the product of the density and the volume ($\rho V$), and the rate at which fluid enters or leaves the system is $\rho Q$, so the average hydraulic residence time is $\frac{\rho V}{\rho Q} = \frac{V}{Q}$. As in the above example, some of the fluid may spend more time than $V/Q$ in the reactor, and some less, but the average is given by this value.

While the computation of the hydraulic residence time for a given reactor might appear to be a trivial matter, since $V$ and $Q$ are usually easy to measure, the evaluation is not as simple as it might seem. If, for instance, there is dead space in the corners of the reactor, the effective volume through which water flows might be less than the full, geometric volume of the reactor. In such a case, the actual mean hydraulic residence time is less than the value computed as $V/Q$. In this text, we use $\theta$ to represent the theoretical residence time of a reactor ($V/Q$) and $\bar{t}$ to represent the experimentally measured mean residence time. If water passes through the entire volume of the reactor, if the tracer has been well chosen (i.e., if it really does have the same mixing characteristics in the reactor as the water does), and if the experimental data are complete and accurate, then $\bar{t} = \theta$; if all the above constraints apply, except the reactor has some dead space, then $\bar{t} = V_{\text{eff}} / Q$, where $V_{\text{eff}}$ is the effective volume of the reactor, i.e., the total volume minus the volume of the dead space. Therefore, for a reactor with steady flow, it is possible for $\bar{t}$ to be less than $\theta$, but not to be greater than $\theta$. We next consider how tracer output can be used to compute $\bar{t}$ in a reactor receiving steady flow.

The average value of a variable is of interest in statistical analysis of many types of data, and some of the terms that appear in the analysis have been given special names. In particular, if events with various values of $x$ can occur, and if $G(x)$ is the differential probability density function describing the likelihood that a single event will occur with value between $x$ and $x + dx$, the mean value of $x$ is given by:
The term \( \int_0^\infty x^n G(x) \, dx \) is called the \( n^{th} \) moment of \( G \), so, according to Equation 13, the mean value of \( x \) can be defined as the first moment of \( G \) divided by the zeroth moment.

The probability density function of residence times in a reactor is identified above as the \( E(t) \) function, and the product \( E(t) \, dt \) is \( dF(t) \). Thus, taking into account the fact that \( F(t) = 1 \) when \( t = \infty \), the mean hydraulic detention time in a reactor can be computed from \( E(t) \) or \( F(t) \) as follows:

\[
\overline{t} = \frac{\int_0^\infty t E(t) \, dt}{\int_0^\infty E(t) \, dt} \quad \text{or} \quad \overline{t} = \frac{\int_0^1 t \, dF(t)}{\int_0^1 dF(t)} \quad (14a, b)
\]

As shown in Equation 8, \( E(t) \) can be equated with the normalized tracer effluent concentration from a pulse input test. Substituting from Equation 8 into Equation 14a, we find:

\[
\overline{t} = \frac{\int_0^\infty t \frac{Q}{M_{p, in}} c_p(t) \, dt}{\int_0^\infty \frac{Q}{M_{p, in}} c_p(t) \, dt} = \frac{\int_0^\infty t c_p(t) \, dt}{\int_0^\infty c_p(t) \, dt} \quad (15)
\]

For a discrete data set, Equation 15 can be approximated as follows:

\[
\overline{t} \approx \sum_{i} \frac{\left( t_i + t_{i-1} \right)}{2} \left( \frac{c_{p,i} + c_{p,i-1}}{2} \right) (t_i - t_{i-1}) = \frac{\sum c_{p,ave} \Delta t_i}{\sum c_{p,ave} \Delta t_i} \quad (16)
\]

An alternative way of manipulating Equation 14a is to recall that, since the probability of a water molecule having a residence time between zero and infinity is 100\%, \( \int_0^\infty E(t) \, dt = 1.0 \).

Therefore, Equation 14a can be simplified to:
\[ T = \int_0^\infty tE(t)\,dt = \frac{Q}{M_{p, in}} \int_0^\infty tc_p(t)\,dt = \frac{\int_0^\infty tc_p(t)\,dt}{M_{p, in}/Q} \quad (17) \]

or, for the analysis of a discrete data set:

\[ T \approx \sum_{i} \left( \frac{t_i + t_{i+1}}{2} \right) \frac{c_{p,i} + c_{p,i-1}}{2} \frac{(t_i - t_{i-1})}{M_{p, in}/Q} = \sum_{i} \frac{t_{ave,i}c_{p, iave} \Delta t_i}{M_{p, in}/Q} \quad (18) \]

By inspection, Equations 15 and 17 give the same result if and only if:

\[ \int_0^\infty c_p(t)\,dt = \frac{M_{p, in}}{Q} \quad (19) \]

\[ \int_0^\infty Qc_p(t)\,dt = M_{p, in} \quad (20) \]

The left-hand side of Equation 20 is the total mass of tracer exiting the reactor over all time, which we will designate \(M_{p, out}\), and the right-hand side is the total mass of tracer input, so it is clear that this equality should hold. However, as a practical matter, the mass of tracer detected in the effluent is often different from the amount injected. The discrepancy might arise because sampling was terminated while some tracer remained in the reactor, because flow and tracer data were inaccurate or incomplete, or a combination of those and other reasons. Regardless of the source of the discrepancy, the point is that the computed value of \(T\) can depend on the choice of which equation (Equation 15 or 17) is used to determine it.

The computed values of \(E(t)\) and \(F(t)\) according to Equations 8 and 10 also depend on whether the calculation is carried out treating \(M_{p, in}\) or \(M_{p, out}\) as the total mass of tracer used in the test. For example, if a tracer test was cut off too early, the correct value of \(F(t)\) for the last sample would be less than 1.0. Normalizing \(M_p(t)\) by \(M_{p, in}\) would cause the final, computed value of \(F(t)\) to be less than 1.0, and so would be the logical choice in this case. On the other hand, if a calibration error caused the measured values of \(c_p(t)\) to be in error by a consistent percentage, the evaluation of \(E(t)\) or \(F(t)\) using \(M_{p, out}(t)\) for the normalization would correct for the error and hence would be the best choice. Of course, we normally do not know whether these types of errors have occurred or their magnitude. Therefore, in general, it is probably a good idea to carry out the computation both ways and, if the results differ by a significant amount, to attempt to determine and correct for the cause of the discrepancy.
All of the equations for $\bar{t}$ shown above (Equations 15 to 18) can also be obtained from Equation 14b using $F(t)$ instead of $E(t)$. Alternatively, $\bar{t}$ can be computed directly from the $F(t)$ function by making the following substitution in Equation 14:

$$
\bar{t} = \frac{\int_0^\infty tE(t)dt}{\int_0^\infty E(t)dt} = \frac{\int_0^\infty t \frac{dF(t)}{dt} dt}{\int_0^\infty \frac{dF(t)}{dt} dt} = \frac{\int_0^\infty t dF(t)}{\int_0^\infty dF(t)} = \frac{\int_0^\infty t dF(t)}{F(\infty) - F(0)}
$$

(21)

Since $F(\infty) = 1$ and $F(0) = 0$, Equation 21 can be simplified for a continuous or a discrete data set, respectively, as follows:

$$
\bar{t} = \int_{F(0)}^{F(1)} t dF(t) = \int_0^1 t dF(t)
$$

(22)

$$
\bar{t} \approx \sum_{i} \left( \frac{t_i + t_{i-1}}{2} \right) \left( F_i(t) - F_{i-1}(t) \right) = \sum_{i} t_{i-1} \Delta F_i(t)
$$

(23)

In addition to the mean value of a distribution, it is useful to have a measure of the spread of data around the mean. In statistics, the parameter that describes this spread is the variance, $\sigma^2$, which is defined mathematically as the second moment around the mean divided by the zeroth moment, as follows:

$$
\sigma^2 = \frac{\int_{\infty}^{\infty} (x - \bar{x})^2 G(x) \, dx}{\int_{\infty}^{\infty} G(x) \, dx}
$$

(24a)

The variance can also be calculated as the difference between the second moment around the axis divided by the zeroth moment and the square of the mean:

$$
\sigma^2 = \frac{\int_{\infty}^{\infty} x^2 G(x) \, dx}{\int_{\infty}^{\infty} G(x) \, dx} - \bar{x}^2
$$

(24b)

As noted above, the value of $F(t)$ depends on whether $M_{p,in}$ or $M_{p,out}$ is used in the calculation. If $M_{p,in}$ is used, the computed value of $F(\infty)$ might not be 1.0.
Variance has the dimensions of $x^2$. The variance can be normalized and made dimensionless by dividing it by $\bar{x}^2$. In this text, we represent the normalized variance by the symbol $\bar{\sigma}^2$; thus, $\bar{\sigma}^2 = \frac{\sigma^2}{\bar{x}^2}$.

Two other functions related to the variance are often reported as indicators of the spread of a data set. These functions are the standard deviation ($\sigma$) of the data, which is simply the square root of the variance, and the coefficient of variation (CV), which is the standard deviation divided by the mean:

For $c_p(t)$ and $E(t)$ distributions, the variances for continuous and discrete data can be obtained by substituting directly into Equation 24. Thus, the variance of $c_p(t)$ is computed as follows:

$$\sigma_c^2 = \frac{\int (t - \bar{t})^2 c_p(t) \, dt}{\int c_p(t) \, dt} = \frac{\int \bar{t}^2 c_p(t) \, dt}{\int c_p(t) \, dt} - \bar{t}^2$$ (25)

$$\sigma_c^2 \approx \sum_{all \, i} \left( t_i + t_{i-1} \right) \frac{c_i + c_{i-1}}{2} \left( t_i - t_{i-1} \right) - \bar{t}^2$$ (26a)

$$\approx \frac{\sum_{all \, i} t_{i,ave}^2 c_{i,ave} \Delta t}{\sum_{all \, i} c_{i,ave} \Delta t} - \bar{t}^2$$ (26b)

The expression for the variance of $E(t)$, i.e., Equation 24 with $E(t)$ substituted for $G(x)$, can be simplified by noting that the denominator in the fraction on the right-hand side of the equation equals 1.0.\footnote{The denominator equals $F(\infty)$. As noted above, this value might not equal 1.0 if $M_{p,in}$ is used in the calculation of $E(t)$ and $F(t)$ values.} The variance of $E(t)$ can therefore be written as:

$$\sigma_E^2 = \frac{\int (t - \bar{t})^2 E(t) \, dt}{\int E(t) \, dt} = \int (t - \bar{t})^2 E(t) \, dt = \int t^2 E(t) \, dt - \bar{t}^2$$ (27)
Both $\sigma_c^2$ and $\sigma_E^2$ have dimensions of time squared. Note that, since $E(t)$ is the product of a constant and $c_p(t)$, this constant appears in both the numerator and denominator when one converts the variance of the $c_p(t)$ curve into the variance of the $E(t)$ curve. As a result, the variances of these two curves are identical. Also note that the dimensionless forms of the variance of the $c_p(t)$ and $E(t)$ functions can be obtained by dividing those functions by $\bar{T}^2$.

Example 2: Computing the mean hydraulic residence time and characterizing mixing in a reactor based on the $E(t)$ and $F(t)$ functions.

For the reactor characterized by the tracer output in Example 1:

(a) Determine the fraction of the tracer that is recovered during the course of the experiment.

(b) Determine the mean detention time in the reactor and the variance of the $c_p(t)$ and $E(t)$ functions.

(c) Compare the computed mean residence time to the theoretical mean detention time.

Solution. Information from Example 1 is repeated in Columns A through D in the following table, and Columns E through J show the calculations needed to determine the requested parameters. Once again, values that are associated with intervals of time are shown at the end of the interval, so they have no entry in Row 1.

(a) The mass of tracer exiting the reactor in any time period $\Delta t$ is $Q_c \Delta t$, and the total mass of tracer recovered during the test is the summation of the $Q_c \Delta t$ values over all $\Delta t$ (see Equation 20). Thus, the fraction of the tracer that was recovered can be computed as:

$$
\frac{M_{p,\text{out}}}{M_{p,\text{in}}} = \sum_{i} Q_{c,\text{ave}} \Delta t_i = \frac{Q \sum_{i} c_{p,\text{ave}} \Delta t_i}{M_{p,\text{in}}} = \left( \frac{4 \text{ m}^3}{\text{min}} \right) \left( 2490 \frac{\text{mg-min}}{L} \right) \left( 10^8 \frac{\text{mg}}{\text{kg}} \right) \left( \frac{10 \text{ kg}}{\text{L}} \right) = 0.996
$$
This value is necessarily the same as the final value of $F(t)$, because $E(t)$ and $F(t)$ were calculated based on $M_{p,in}$, i.e., $E(t_i)$ was calculated as $\frac{Q}{M_{p,in}} c_p(t_i)$, and $F(t)$ was computed from those calculated $E(t)$ values. The fact that the fraction of mass recovered is close to 1 suggests (but does not prove) that the tracer study was well done.
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(b) The mean hydraulic residence time can be computed from either Equation 16 or Equation 23. Column $E$ provides incremental terms for the denominator of Equation 16, and column $F$ provides the corresponding terms for the numerator. The sum of the terms in column $E$ (cell $E17$) is the zeroth moment of $c_p(t)$, and the sum of the terms in column $F$ (cell $F17$) is the first moment. According to Equation 16, the ratio of these two terms equals the mean hydraulic residence time:

$$\bar{t} = \frac{\sum_{all\ t} t_{ave} c_{ave} \Delta t}{\sum_{all\ t} c_{ave} \Delta t} \approx \frac{123300}{2490} \frac{\text{mg-min}}{\text{L}} = 49.5 \text{ min}$$

According to Equation 23, the mean hydraulic residence time can also be computed as the summation, over all time intervals, of the product of the average value of $t$ during an interval and the increment in $F(t)$ during that interval. Values of $t_{ave} \Delta F$ are shown in column $G$ of the table; the summation, shown in cell $G17$, is 49.3 minutes, which is close to the value of $\bar{t}$ computed by the first method. The slight discrepancy occurs because Equation 23 is based on the assumption that $F(t)$ reaches 1.0, but the maximum value of $F(t)$ in this data set is 0.996. If this fact is accounted for by using Equation 21) to calculate $\bar{t}$, and a value of 0.996 is inserted for $F(\infty)$, the calculated value of $\bar{t}$ becomes 49.3 min/0.996 = 49.5 min and the two values agree. If the tracer analysis were perfect and all of the input tracer were detected in the effluent, the original two estimates of $\bar{t}$ would be identical.

The variances of $c_p(t)$ and $E(t)$ can be calculated as the second moment around the mean divided by the zeroth moment (Equations 26 and 28). The data needed to evaluate these terms include $\bar{t}$, which is calculated above, and the summations shown in Row 17 of the columns $H$ and $I$. The calculations for $\sigma_c^2$ and for $\sigma_E^2$ are as follows:

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<td>26</td>
<td>$3211.7 \text{ min}^2 - (49.5 \text{ min})^2 = 760 \text{ min}^2$</td>
</tr>
<tr>
<td>$\sigma_E^2$</td>
<td>28a</td>
<td>$3211.7 \text{ min}^2 - (49.5 \text{ min})^2 = 760 \text{ min}^2$</td>
</tr>
</tbody>
</table>

(c) The theoretical mean detention time is $V/Q$, so:

$$\theta = \frac{240 \text{m}^3}{4 \text{m}^3/\text{min}} = 60 \text{min}$$

Thus, in this (made-up) example, the mean detention time calculated from the tracer results is only approximately 83% of the theoretical detention time $\theta$, suggesting that the effective volume of the tank is less than its geometrical volume. Since essentially all of the injected tracer was recovered, the discrepancy between $\theta$ and $\bar{t}$ is due to non-
ideality in the flow pattern and not to a failure to carry out the test over a long enough period to allow all the tracer to exit.

Having established the conceptual basis for residence time distributions and explored some experimental approaches for determining residence time distributions and representing them mathematically, we next consider what those residence time distributions can tell us about the mixing patterns in reactors.

2.3 IDEAL REACTORS

The flow regime of a reactor refers to the amount and characteristics of internal mixing in the reactor. The two extremes of mixing intensity are no mixing whatsoever and complete mixing; continuous flow reactors with these characteristics are known as plug flow reactors (PFRs) and continuous flow stirred tank reactors (CFSTRs), respectively. CFSTRs are also referred to as completely mixed reactors (CMRs) or continuous stirred tank reactors (CSTRs).

In a PFR, fluid moves steadily through the reactor along a defined path, without mixing at all with parcels of fluid ahead of or behind it in the axial direction. Mixing in the transverse direction is often considered complete, in which case there is no concentration gradient in that direction; however, that is not a core feature of the model. Axial diffusion and dispersion are both negligible in a PFR. Although ideal plug flow might never be achieved, some reactors and natural systems approach this behavior. Because no mixing occurs in the direction of flow, it is reasonable to imagine that each parcel of fluid in the reactor is physically isolated and behaves as if it were in a container moving through space without interaction with parcels upstream or downstream of it (as on a conveyor belt). Furthermore, any small parcel of fluid in the reactor contains molecules that all entered the reactor together at a specific earlier time. Thus, for instance, pesticides spilled into a river that behaves as an ideal plug flow system would move through the river system without spreading out into or being diluted by water that passed the point of the spill before or after the spill occurred.

At the other extreme of the mixing spectrum are CFSTRs, in which fluid mixing is so intense that, as soon as a parcel of water enters the system, it mixes with and dilutes into the water in the entire reactor volume. In such a reactor, any aliquot of fluid in the reactor contains molecules that entered the reactor at all prior times.

In water and wastewater treatment systems, some reactors behave closely enough to one of these limiting cases that they can be modeled as ideal reactors. For instance, some reactors, such as rapid mix tanks in a water treatment plants, are designed to have intense mixing so that the concentrated chemicals that are added to the water (e.g., coagulants, acids, bases, or disinfectant chemicals) are rapidly and uniformly distributed throughout the tank. Also, the contents of aeration tanks in activated sludge systems are often thoroughly mixed by bubbles.
that are injected through diffusers along the bottom of the tank and/or by mechanical mixers. These types of reactors can often be reasonably modeled as CFSTRs. At the other extreme, packed bed reactors (e.g., activated carbon adsorption columns, ion exchange columns, gas transfer towers for stripping or absorption) can often be treated as PFRs.

In the following subsections, we determine the residence time distribution for the two ideal reactors by determining the expected result of tracer studies and converting that information into the RTDs.

**Plug Flow Reactors**

Consider a plug flow reactor of volume $V$ that has operated with a steady flow $Q$ for a substantial period. What would be the response of the reactor to a pulse input tracer test in which a mass $M_{in}$ of tracer is put into the influent all at once at time 0?

From the conveyor belt description of a PFR given above, it should be obvious that all of the tracer would come out together after a time equal to the hydraulic residence time, $\theta$. While, as noted above, the average hydraulic residence time $\theta$ is $V/Q$ for any reactor, $\theta$ is the exact residence time of any parcel of fluid (including the parcel that contains the tracer) for a PFR. For the described conditions, the output of the reactor contains the entire mass $M_{in}$ at $t = \theta$ and contains no tracer at all other times. Thus, in mathematical terms, the mass of tracer in the output is $M_{in} \delta_\theta(t)$.

The $E(t)$ and $F(t)$ curves can also be determined easily based on this discussion. Because no tracer comes out prior to $\theta$ and all of it is out of the reactor after $t = \theta$, the cumulative age distribution $F(t)$ is the Heaviside function applied at $t = \theta$. Since $E(t)$ is the derivative of $F(t)$, $E(t)$ must be the Dirac delta applied at $t = \theta$. Thus,

$$F(t)_{\text{PFR}} = H_\theta(t) \quad \text{and} \quad E(t)_{\text{PFR}} = \delta_\theta(t)$$

These $E(t)$ and $F(t)$ functions are shown in Figure 6.
Although the $E(t)$ and $F(t)$ functions are presented above for the plug flow reactor based on conceptual arguments alone, it is useful to consider their derivation mathematically. The derivation is based on analysis of a differential control volume whose area is the cross-sectional area of the reactor, and whose length in the direction of flow is $dx$. Two choices for the boundaries of the control volume are reasonable, differing based on the frame of reference of the observer. In one choice, the control volume is a region of space that is fixed relative to an observer standing outside the reactor. This frame of reference is referred to as an Eulerian view. The other choice, called the Lagrangian view, is a region of space that is at the entrance of the reactor initially and that moves through the reactor at the average velocity of the fluid. The control volume in a Lagrangian view can be thought of as a region of space that is fixed relative to an observer who is traveling with the fluid. The PFR system is analyzed below using both approaches.

**Pulse Input to a PFR: Fixed Frame of Reference (Eulerian View)**

For a control volume fixed in space, as shown in Figure 7, the general mass balance for a tracer passing through a PFR can be written in words as follows:

$$\text{Rate of change of mass in differential volume} = \text{Rate of input of mass into control volume by advection} - \text{Rate of output of mass from control volume by advection}$$

**Figure 6. Age Distributions of a Plug Flow Reactor**
Figure 7. Definition Diagram for Mass Balance on PFR: Eulerian View

The mass balance contains no terms for input and output by dispersion/diffusion because, by the definition of a PFR, these terms are zero. The mass balance also lacks a reaction term, because the substance of interest is a non-reactive tracer. The volume of the small element of the reactor shown in Figure 7 is \( A \Delta x \), where \( A \) is the cross-sectional area. Translating this general mass balance into symbols yields:

\[
\begin{align*}
\frac{\Delta(cA\Delta x)}{\Delta t} &= Qc - Q(c + \Delta c) \quad (30a) \\
\frac{\Delta(cA\Delta x)}{\Delta t} &= -Q \Delta c \quad (30b)
\end{align*}
\]

If we divide through by \( A \Delta x \) and replace \( Q/A \) by the fluid velocity \( v_x \), we can then take the limit as \( \Delta x \) and \( \Delta t \) approach zero to obtain the following partial differential equation:

\[
\frac{\partial c}{\partial t} = -v_x \frac{\partial c}{\partial x} \quad (31)
\]

This differential equation is first order in both time and space and therefore requires one initial and one boundary condition. Both of these are contained in the description of the pulse input as a Dirac delta function at time zero: the tracer is injected all at once at \((x, t) = (0, 0)\) so the concentration at that instant at the influent end is infinite, and zero at all other locations in the reactor (initial condition); and, the tracer concentration at the influent end is zero at all other times (boundary condition).

To use the initial condition, we must define a concentration associated with the tracer input. In a real test, the tracer concentration in the input during a small interval around time zero would be large but finite, since all the tracer would be injected in a small volume of influent liquid. In the limit, this concentration is infinite, because the volume of solution containing the tracer is assumed to be infinitesimally small. In that case, the corresponding concentration can be defined as the mass \( M \) of the pulse input of tracer divided by the volume of an arbitrarily small aliquot of water. We identify this concentration as \( c'' \). The unusual characteristics of the Dirac delta function make the calculus unusual, but the solution is that the tracer (described by a Dirac delta
function) travels down the length of the reactor at the velocity \( v_x \), and therefore reaches the end of the reactor \((x = L)\) at \( t = \frac{L}{v_x} = \frac{V}{Q} = \theta \), i.e., the tracer output can be described by the following equation:

\[
c_{p}^{\text{PFR}}(x, t) = c^p \delta\left(\frac{x}{v_x}, t\right) \tag{32}
\]

The magnitude of the arbitrarily small aliquot of water turns out to be irrelevant to the result, because the Dirac function causes \( c_{p}^{\text{PFR}}(x, t) \) to be infinitely large if \( t = x / v_x \) and zero if \( t \) is any other value.

No molecule of water (or tracer) spends either more or less time in a plug flow reactor than \( \theta \). In probabilistic terms, we can say that the likelihood is 100% that a molecule will spend an amount of time equal to \( V/Q \) in the reactor, and the likelihood of it spending an amount of time other than \( \theta \) is nil. That statement completely defines the residence time distribution of a PFR.

The response of a PFR to a step input tracer test is a straightforward application of the same approach described above for a pulse input, and is left as an exercise (see Problem 1 at the end of the chapter).

**Pulse Input to a PFR: Moving Frame of Reference (Lagrangian View)**

In the Lagrangian view, the frame of reference is not a fixed point in space but a certain parcel of the fluid. As noted above, we can think of a plug flow reactor something like a conveyor belt; i.e., every parcel of fluid travels through the reactor as if it were a package on a conveyor belt with no interaction (dispersion/diffusion) with parcels upstream or downstream. The Lagrangian view of the system is based on a mass balance in which the control volume is a differential slice of space that travels from one end of the reactor to the other at the average fluid velocity. Stated another way, in the Lagrangian view, one imagines that the observer is in a packet of the fluid and travels with it; the mass balance then describes what such an observer sees.

Mathematically, the Lagrangian viewpoint can be represented by defining a coordinate system that moves with the water at velocity \( v_x \). Define axial distance on this coordinate system as \( x^* \). If the origin of the coordinate system \( (x^* = 0) \) is defined to coincide with the point \( x = 0 \) at time 0, the translation from values of \( x \) (on the fixed axis) to those of \( x^* \) at any future time can be made using the equation: \( x^* = x - v_x t \) (Figure 8). The coordinates of the two ends of the control volume are therefore always \( x^* = 0 \) and \( x^* = dx^* \), no matter how far the control volume has traveled through the reactor.
Figure 8. Definition diagram for a mass balance on a PFR: Lagrangian view. The coordinate system moves at the average velocity of the fluid, so $x^* = 0$ is at the upstream end of the control volume at all times.

The general word mass balance for the moving control volume, again recognizing the lack of dispersion in a PFR and the lack of reactivity of a tracer, would be the same as above, i.e.,

$$\text{Rate of change of mass in differential volume} = \text{Rate of input of mass into control volume by advection} - \text{Rate of output of mass from control volume by advection}$$

The Lagrangian view involves converting the word equation into a mathematical expression using $x^*$, rather than $x$, as the distance variable. Such a conversion turns out to be trivial: since the control volume is traveling with the fluid, no mass enters or leaves the control volume by advection, so the entire right-hand side of mass balance is zero. The mass balance can therefore be written as follows:

$$\frac{dV}{dt} \frac{\partial c(x^*, t)}{\partial t} = 0 \quad (33)$$

Because the control volume is always finite, $dV$ is non-zero, so this equation can be further simplified as follows:

$$\frac{\partial c(x^*, t)}{\partial t} = 0 \quad (34)$$

The solution to Equation 34 is that $c$ is a function of $x^*$ only, independent of time. The profile at time zero is given by $c(x^*, 0) = c^\ast \delta_0(x^*)$, i.e., it is a Dirac delta function applied at $x^* = 0$. Based on Equation 34, though, $c(x^*, t)$ does not change over time, so the concentration profile is given by $c^\ast \delta_0(x^*)$ at all times, i.e.:

$$c_p^{PFR}(x^*, t) = c^\ast \delta_0(x^*) \quad (35)$$

The result is that $c_p^{PFR}(x^*, t)$ equals $c^\ast$ times the Dirac spike whenever $x^* = 0$, and zero when $x^*$ has any non-zero value. Converting this result back to a function of $x$ (rather than $x^*$)
also converts it to a function of time. Since \( x^* = x - v_f t \), \( c_p^{PFR}(x, t) \) equals \( c^* \) times the Dirac spike whenever \( x - v_f t = 0 \), (i.e., whenever \( t = \frac{x}{v_f} \)), and zero at all other times and locations, i.e., \( c_p^{PFR}(x, t) = c^* \delta_{\frac{x}{v_f}}(t) \). As expected and necessary, the result with the Lagrangian view (moving reference) is the same as that obtained above (Equation 32) with the Eulerian view (fixed reference).

As noted above, the response of a PFR to a tracer input can be deduced easily from a qualitative understanding of the flow pattern in such reactors; the derivations provided above are useful as formal proofs of the validity of the qualitative analysis. More importantly, they serve as a simple introduction to the Eulerian and Lagrangian viewpoints and to the methodology used later in this chapter and in Chapter 4 to analyze more complex systems, including reactors with non-negligible diffusion/dispersion and in which chemical reactions are taking place.

**Continuous Flow Stirred Tank Reactors**

**Pulse Input to a CFSTR**

Consider next the response of a CFSTR, with steady flow \( Q \) in and out, to a pulse input. The situation is described pictorially in Figure 9. We focus first on what happens at time zero. By definition, the concentration in a CFSTR is the same at all locations, and the influent is mixed instantaneously with all the fluid in the reactor. Thus, at time zero, the mass \( M \) of tracer is mixed instantly into the entire volume \( V \), so that the concentration at any point in the reactor is \( \frac{M}{V} \); we designate this concentration \( c_o \). Because the effluent is taken from some point in the reactor, the concentration of the effluent at that instant (time 0) is also \( c_o \), i.e., \( c_p(0) = c_o \).

![Figure 9. Continuous Flow Stirred Tank Reactor: Pulse Input Tracer Study](image)

**Figure 9. Continuous Flow Stirred Tank Reactor: Pulse Input Tracer Study**
To determine what happens at all later times, we write a mass balance on the tracer in the system, defining the system boundaries to include all the fluid in the tank. The input and output are the influent and effluent, respectively, and, because the tracer is non-reactive, the mass balance contains no reaction term. In any mass balance, diffusion and dispersion are relevant only at the boundaries of the control volume. We assume that tracer cannot cross the boundaries of a CFSTR by these mechanisms, so these terms are omitted in the mass balance.\(^5\)

In summary, the mass balance can be described in words as follows:

\[
\text{Rate of change of mass of tracer in reactor = Rate of input of mass of tracer into reactor by advection} \quad \text{– Rate of output of mass of tracer from reactor by advection} \quad (36)
\]

As noted previously, the concentration is the same everywhere in the system, including in the effluent, so we can equate the concentration in the reactor at time \(t\) with \(c_p(t)\), the effluent concentration at that time. Also, after the initial dumping of tracer into the reactor at time zero, no further additions of tracer are made into the tank, so the input term (the first term on the right) is zero. Therefore, in symbols:

\[
\frac{dVc_p(t)}{dt} = 0 - Qc_p(t) \quad (37)
\]

The solution of this mass balance equation is straightforward. \(V\) is a constant and can be taken outside the derivative. Separating the variables, dividing by \(V\), and recognizing that \(\theta = \frac{V}{Q}\) leads to the following:

\[
\frac{dc_p(t)}{c_p(t)} = -\frac{1}{\theta} \, dt \quad (38)
\]

Integration of this equation from zero to an indefinite time \(t\) yields:

\[
\int_{c_{p0}}^{c_p(t)} \frac{dc_p(t)}{c_p(t)} = -\frac{1}{\theta} \int_{0}^{t} dt \quad (39)
\]

With the application of the initial condition that, at time zero, the (effluent) concentration is \(c_0\), the solution is as follows:

\[\]

\(^5\)The assumption that diffusion and dispersion are negligible across the inlet can be assured by a discontinuity in flow, e.g., by having the inlet pipe discharge freely from above the surface of the reactor. Negligible diffusion and dispersion across the outlet are assumed because the intense mixing in the reactor means that the effluent will have the same composition as the water inside the reactor, so no concentration gradient exists at that location.
\[
\ln \left( \frac{c_p^{\text{CFSTR}}(t)}{c_o} \right) = -\frac{1}{\theta} t
\]

(40a)

or:

\[
\begin{align*}
    c_p^{\text{CFSTR}}(t) &= c_o e^{-t/\theta} \\
\end{align*}
\]

(40b)

where the superscript has been added to emphasize that the result applies only for an ideal CFSTR. The results are shown graphically according to both the arithmetic (Equation 40b) and logarithmic (Equation 40a) forms of the equation in Figure 10.
Figure 10. Response of a CFSTR to a pulse input tracer test.

Immediately after the tracer is introduced and mixed throughout the reactor, the concentration is the highest it will ever be, because no more tracer is added after that time. The concentration is continually diluted by the (clean) influent, leading to a continual decline in the concentration in the reactor (and in its effluent). After one detention time \( t = \theta \), the concentration is still approximately 37\% \( (e^{-1} = 0.368) \) of what it was immediately after the input of tracer. Even after three detention times \( t = 3\theta \), the concentration is approximately 5\% \( (e^{-3} = 0.050) \) of the concentration at time zero. In fact, theoretically, an infinite time is required to get the last molecules of tracer out of the reactor. This result contrasts with that for a PFR, for which none of the tracer exits prior to time \( \theta \), and none remains in the reactor after time \( \theta \).

According to Equation 8, we can use the results from a pulse input tracer test to compute \( E(t) \) as the product \( c_p(t) \frac{Q}{M_{p,\text{in}}} \). For the particular case of a CFSTR, inserting Equation 40b into Equation 8 yields:

\[
E(t)_{\text{CFSTR}} = \frac{Q}{M_{p,\text{in}}} c_o e^{-t/\theta}
\]  

(41a)
Recognizing that \( c_0 = \frac{M_{p,\text{in}}}{V} \) and that \( \frac{Q}{V} = \frac{1}{\theta} \), leads to the following expression for the exit age distribution of a CFSTR:

\[
E(t)_{\text{CFSTR}} = \frac{1}{\theta} e^{-t/\theta}
\]  

(41b)

The mass of tracer that has come out of any reactor from time zero to any time \( t \) (i.e., \( M_p(t) \)) is given by Equation 9. For a CFSTR, inserting Equation 40b into Equation 9 and integrating the resulting expression yields the following relationship for \( M_p(t) \):

\[
M_p(t)_{\text{CFSTR}} = M_{\text{in}}(1 - e^{-t/\theta})
\]  

(42)

Finally, we can find the cumulative age distribution, \( F(t) \), as the integral to time \( t \) of \( E(t) \); for a CFSTR, the result is as follows:

\[
F(t)_{\text{CFSTR}} = 1 - e^{-t/\theta}
\]  

(43)

The four functions described above for the CFSTR are collected in Figure 11. Two of the functions, \( c_p(t) \) and \( M_p(t) \), have values that depend on the mass of tracer input, the volume of the reactor, and the mean hydraulic residence time \( (\theta) \), while the other two, \( E(t) \) and \( F(t) \), depend only on \( \theta \).

Based on the three ways of interpreting the \( E(t) \) and \( F(t) \) functions (influent view, effluent view, and probabilistic view), we can make the following statements about the residence time distribution in a CFSTR. The molecules of water (or any nonreactive substance in the water) that enter a CFSTR are dispersed immediately throughout the reactor. All of those molecules are in the reactor in the instant following their entry, so they are present at their highest concentration at that instant. Molecules that enter at any one time stay in the reactor for varying amounts of time. Many of the molecules that enter in one instant stay in the reactor for only a short time, and steadily smaller numbers of molecules stay for progressively longer times, with a very small number staying for extremely long periods. Correspondingly, the probability of the molecules leaving is highest immediately after their introduction. And, in any sample of the effluent, a large fraction of the molecules in an effluent aliquot came in a short period ago, while a much smaller fraction spent a much longer time in the reactor before making it into the effluent.
Figure 11. CFSTR Response to Pulse Input Tracer and Exit Age Distributions
**Step input to a CFSTR**

We now consider the response of a CFSTR to a step input of tracer. As always, we can carry out the analysis by writing a mass balance to describe the situation for any time after time zero. The system is again all of the fluid in the reactor, and the constituent of interest is again the tracer. Recognizing that the tracer is nonreactive so that no reaction term is necessary, the mass balance can be expressed in words identically as in Equation 36:

\[
\text{Rate of change of mass of tracer in reactor with time} = \text{Rate of input of tracer mass into reactor by advection} - \text{Rate of output of tracer mass from reactor by advection}
\]  

(36)

To convert this word equation into symbols, we note again that the mass of tracer in the CFSTR at any time is the product of the volume \(V\) and the concentration \(c\), and the rate of change of that mass with time is the time derivative of \(Vc\). The mass input and output are the products of the constant flow rate \(Q\) and the influent and effluent concentrations \(c_{in}\) and \(c_s(t)\), respectively. The concentration in the effluent is the same as the concentration in the reactor, so we can use \(c_s(t)\) for both; this situation is a consequence of the thorough mixing and is unique to a CFSTR. In symbols:

\[
\frac{dVc_s(t)}{dt} = Qc_{in} - Qc_s(t) 
\]  

(44)

Separating the variables, dividing through by \(V\), and recognizing that \(\frac{Q}{V} = \frac{1}{\theta}\), we obtain:

\[
\frac{dc_s(t)}{(c_{in} - c_s(t))} = \frac{1}{\theta} \, dt
\]  

(45)

To solve Equation 45, we need to know the initial condition. This condition can be slightly confusing, since the input concentration undergoes a step change at that time. The task is to find the concentration in the reactor (or in the effluent) at that time. As in the case of a pulse input, the approach is to consider the mass of tracer that enters the reactor between \(t = 0\) and an infinitesimal time later, which we designate \(t = \delta t\). In the step input case, this mass of tracer equals \(c_{in}Q\,\delta t\), so the concentration of tracer in the reactor at that time (ignoring mass released in the effluent) is \(c_{in}Q\,\delta t/V\). In the limit of \(\delta t\) approaching 0, the concentration of \(c(\delta t)\) goes to zero. Hence, the initial condition is \(c_s(0) = 0\). The integration of each side of Equation 45 from \(t = 0\) to the indefinite time \(t\) is then straightforward. The result, after algebraic manipulation, is as follows:

\[
c_s^{\text{CFSTR}}(t) = c_{in} \left(1 - e^{-t/\theta}\right)
\]  

(46)

The concentration profile indicated by the equation is as one might anticipate. At time zero, the concentration is zero. After very long periods (high values of \(t/\theta\)), the concentration
approaches the concentration of the influent. In the meanwhile, the concentration rises at an ever decreasing rate toward the asymptote, \( c_{\text{in}} \).

The cumulative age distribution follows easily from this equation describing the effluent concentration. According to Equation 12, the cumulative age distribution, \( F(t) \), is obtained by dividing \( c_s(t) \) by \( c_{\text{in}} \). Carrying out this normalization yields the same result as for the pulse input test (Equation 43):

\[
F(t)_{\text{CFSTR}} = 1 - e^{-t/\theta}
\]

Finally, the exit age distribution, \( E(t) \), can be obtained as the derivative of \( F(t) \), as follows:

\[
E(t)_{\text{CFSTR}} = \frac{1}{\theta} e^{-t/\theta}
\]

where, again, the result is the same as that obtained from the pulse input, as it must be. \( E(t) \) and \( F(t) \) reflect the mixing pattern of the water, so we must obtain the same result for these functions regardless of what type of tracer test (pulse or step) is performed.

2.4 NON-IDEAL REACTORS

Tracer Output from Non-Ideal Reactors

The two types of ideal reactors described above represent the two ends of the spectrum of mixing/no mixing. While these ideals are often approached in practice, most real reactors behave in a way that falls between the extreme cases. In this section, we consider such reactors, which are commonly referred to as being non-ideal.

As is the case for ideal reactors, the hydraulic behavior of non-ideal reactors is described most completely by their \( E(t) \) or \( F(t) \) functions. The determination of these functions as well as other parameters of interest (e.g., the mean and variance of the residence time distribution) from tracer test data was demonstrated in Examples 1 and 2. In the preceding section, we determined the expected response of ideal reactors to specific patterns of tracer input. We next address the more general question: what output profile can be expected for any arbitrary input of a non-reactive substance into a reactor?

Relating Tracer Input and Output Curves Via the Convolution Integral

In almost all cases, flow through a reactor causes the concentration profile of a conservative tracer to spread out and flatten, as shown in the upper part of Figure 12. Only a PFR does not change the shape of the profile, and even a PFR shifts the curve to later times. In this section, we develop an approach for predicting the output concentration profile from knowledge of the input profile, \( c_{\text{in}}(t) \), for a reactor with any given residence time distribution, \( E(t) \). The analysis presented here is adapted from Levenspiel (1972).
To accomplish this task, it is useful to plot both the input and output concentration profiles on the same axes, as shown in the lower part of Figure 12. Consider the effluent during a small $\Delta t$ around time $t$, as shown. Each molecule of tracer that is in the output came into the reactor at some time earlier, but later than time zero. For instance, some part of the tracer that comes out in the time interval labeled $\Delta t$ came into the reactor within a small interval of time $t'$ earlier, i.e., around time $t - t'$ in the interval labeled $\Delta t'$. Stated another way, the small cross-hatched section of the output in the time interval $\Delta t$ represents the same molecules of tracer that are indicated by the small cross-hatched section of the input in the time interval $\Delta t'$. Extending the analysis, we see that the entire output in the small increment of time $\Delta t$ is composed of parts of the input that came in at various times between 0 and $t$. Therefore, the total tracer output during time $\Delta t$ can be obtained by considering each prior period $\Delta t'$, multiplying the concentration of tracer in the input at time $t$ by the fraction of that input that stays in the reactor for time $t'$, and then summing up the contributions for all possible $\Delta t'$ periods. Translating that sentence to a word equation yields the following:

$$\text{Mass of tracer that comes out in interval } \Delta t = \sum_{\text{all intervals } \Delta t'} \left( \text{Mass of tracer that enters during interval } \Delta t' \right) \left( \frac{\text{Fraction of input that stays in the reactor for a time between } t' \text{ and } t' + \Delta t'}{\Delta t'} \right)$$

(47)
Figure 12. Transformation of input of conservative substance as it travels through a reactor system.

The term on the left hand side of Equation 47 is simply the product of the flow rate, $Q$, the (average) effluent concentration in the time interval $\Delta t$, and the time increment $\Delta t$, i.e., $Qc_{\text{out}}(t)\Delta t$. Similarly, the first term within the summation on the right side is $Qc_{\text{in}}(t-t')\Delta t'$. The second term within the summation is $E(t')\Delta t'$. Thus, the equation can be written in symbols as follows:

$$Qc_{\text{out}}(t)\Delta t = \sum_{\text{all intervals } \Delta t' \text{ for } t' \lt t} \left\{ Qc_{\text{in}}(t-t')\Delta t' E(t')\Delta t' \right\}$$

(48)

Assuming that the entire distribution is broken into equivalent increments, $\Delta t'$ is constant and can be taken out of the summation on the right. The flow rate is also constant and so can come out of the summation. The equation can therefore be simplified as follows:

$$Qc(t)\Delta t = Q\Delta t' \sum_{\text{all intervals } \Delta t' \text{ for } t' \lt t} \left\{ c_{\text{in}}(t-t') E(t')\Delta t' \right\}$$

(49)

Although the actual times $t$ and $t'$ are offset from one another, the durations $\Delta t$ and $\Delta t'$ can be chosen to be identical, in which case we can write:
\[ c(t) = \sum_{\text{all intervals}} \left\{ c_{\text{in}}(t - t') E(t') \Delta t' \right\} \] (50)

When the increment is allowed to shrink to infinitesimal size, the summation can be replaced by an integral, with the following result:

\[ c(t) = \int_{t'=0}^{t'=\infty} c_{\text{in}}(t - t') E(t') dt' \] (51)

This integration is a special mathematical operation known as convolution; in words, we say that \( c(t) \) is the convolution of \( c_{\text{in}}(t) \) and \( E(t) \). The symbol * is used to represent the convolution process, so, equivalently to Equation 51, we can write:

\[ c(t) = c_{\text{in}}(t) * E(t) \] (52)

If \( E(t) \) is described only at discrete points, as it often is from the results of a tracer test, a numerical convolution can be performed as described by Equation 49 or 50. When the input and residence time distributions can be described by mathematical functions, Equation 52 is often simple to solve using Laplace Transforms because of the following property of the convolution integral\(^6\):

\[ \mathcal{L}\{F(t) * G(t)\} = \mathcal{L}\{F(t)\} \cdot \mathcal{L}\{G(t)\} \] (53)

where \( \mathcal{L}\{F(t)\} \) is the Laplace transform of the function \( F(t) \).\(^7\) According to Equation 53, the Laplace transform of the convolution integral is the product of the Laplace transforms of the two functions being convolved. This property means that the integration can be avoided; to find \( c(t) \), one simply looks up the Laplace transforms of \( c_{\text{in}}(t) \) and of \( E(t) \), multiplies them, and uses Laplace transform tables to find the inverse transform of that product. An example of the utility of this property of the convolution process is given below.

\(^6\)A brief explanation of LaPlace transforms and some examples of their use are given in the Appendix at the end of the chapter.

\(^7\)By convention, Laplace transform functions are almost always represented by the symbol \( f(s) \), and inverse transforms are written as \( F(t) \). Do not confuse the generic \( F(t) \) inverse Laplace function with the cumulative distribution function, which is also given the symbol \( F(t) \).
Example 3: Determining the Response of a CFSTR to a Step Input of Tracer, Using the Convolution Integral.

The response of a CFSTR to a step tracer input was determined earlier in the chapter by using the appropriate mass balance and initial condition. Derive the same result using a convolution integral.

Solution. According to Equation 51b, the effluent concentration as a function of time can be found as the convolution of the input \( c_{\text{in}} \) and the \( E(t) \) function for a CFSTR,

\[
E(t)_{\text{CFSTR}} = \frac{1}{\theta} \exp \left( -\frac{t}{\theta} \right), \quad \text{i.e.,}
\]

\[
c_{\text{s, out}}^{\text{CFSTR}}(t) = c_{\text{in}} * \frac{1}{\theta} \exp \left( -\frac{t}{\theta} \right) \quad (54)
\]

Taking the Laplace transform of both sides of this equation, we obtain:

\[
\mathcal{L}\{c_{\text{out}}(t)\} = \mathcal{L}\{c_{\text{in}}\} \left( \mathcal{L}\left\{ \frac{1}{\theta} \exp \left( -\frac{t}{\theta} \right) \right\} \right) \quad (55)
\]

From Laplace transform tables, we find the three properties or formulas needed here:
(1) that the Laplace transform of a constant is that constant divided by \( s \), (2) that the Laplace transform of a constant times a function is that constant times the Laplace transform of the function, and (3) that the Laplace transform of \( e^{at} \) is \( \frac{1}{s-a} \). Using these properties yields:

\[
\mathcal{L}\{c_{\text{out}}(t)\} = \left( \frac{c_{\text{in}}}{s} \right) \left( \frac{1}{s} \right) \left( \frac{1}{s-a} \right) = \frac{c_{\text{in}}}{\theta} \left( \frac{1}{s} \right) \left( \frac{1}{s+\frac{1}{\theta}} \right) \quad (56)
\]

The inverse transformation requires the use of the second property noted above and the following inverse transform:

\[
\mathcal{L}\{F(t)\} = \frac{1}{(s-a)(s-b)} \quad \text{Inverse transform} \quad F(t) = \frac{1}{a-b} \left( e^{at} - e^{bt} \right)
\]

With \( a = 0 \) and \( b = -\frac{1}{\theta} \), the inverse transformation yields:
\[
\begin{align*}
\frac{c_{in}(t)}{c_{in}} &= \frac{1}{\theta} \left( \frac{1}{\theta} \right) (e^0 - e^{-t/\theta}) \\
&= c_{in} (1 - e^{-t/\theta})
\end{align*}
\]  

(57a)

(57b)

This result, of course, agrees with that found earlier by using the mass balance approach.

**Modeling Residence Time Distributions of Non-Ideal Reactors**

Establishing the residence time distributions \(E(t)\) and \(F(t)\) is the most complete way to characterize the net hydraulic behavior of a reactor between the influent and the effluent. (One could go into greater detail to describe the hydraulic behavior in a smaller section inside a reactor, but the concern here is only for the overall hydraulic behavior.) Although the numerical results from a tracer test capture all of the available information about these functions, using the results as a collection of individual data points is often inconvenient and, more importantly, can obscure important trends and similarities among different reactors. To overcome those drawbacks, it is often useful to fit the data to a mathematical model that allows the description of the functions to be compressed into a few parameters. Because such models rarely fit the data exactly, modeling usually includes some loss of information (or loss of precision), but the added convenience is often deemed to be worth the sacrifice. Recognizing the loss of information (i.e., comparing the model to the data) is an important part of the modeling process.

In this section, reactor models are presented in three categories, although the distinction between categories is somewhat arbitrary. In the first category, models that consider reactors to have hydraulic characteristics that are closely related to the ideal reactors (PFRs and CFSTRs) are presented; these models include one parameter in addition to the average hydraulic residence time to fit the data. In these models, the idea is to describe the mixing in the reactor relative to the complete mixing of a CFSTR or the complete absence of mixing of a PFR as a base case, with the added fitting parameter describing the extent of deviation from the idealized conditions. In the second category, models that include the possibility of dead space in the reactor (i.e., space in which the water is stagnant so that the reactor behaves as if that space were not in the reactor) are presented. These models are combined with those in the first category and require two parameters beyond the hydraulic residence time: one characterizing the amount of dead space in the reactor and one characterizing the non-ideal mixing. In the third category, more complex models with several parameters are presented; these models can be used to model almost any residence time distribution with some stated accuracy. The greatest attention is on the first category, not only because these are the most commonly used models but also because they satisfy the goal of simplifying the use of \(E(t)\) or \(F(t)\) most completely. As the models become more complex, using all of the data for \(E(t)\) or \(F(t)\) might become simpler than finding the parameter values and using the model.
Models for Systems With Mixing Patterns Intermediate Between PFRs and CFSTRs

PFR with Dispersion

The first model we will consider assumes that the non-ideal behavior of a reactor is caused by (or at least can be described by) some dispersion in a flow pattern that is nearly that of an ideal PFR. In this model, the constraint of zero mixing in the axial direction within a plug flow reactor is relaxed by considering dispersion (or, more properly, the sum of diffusion and dispersion) to be non-zero. To determine the residence time distribution of such a reactor, one could perform a tracer study and analyze the results in terms of the Eulerian (fixed frame of reference) mass balance for the system, as developed in Chapter 1:

\[
\frac{\partial C(x,t)}{\partial t} = -v_x \frac{\partial C(x,t)}{\partial x} + D \frac{\partial^2 C(x,t)}{\partial x^2} \tag{58}
\]

where \(v_x\) is the (average) velocity in the axial \((x)\) direction, and \(D\) is the sum of the dispersion and diffusion coefficients (recall that in the vast majority of engineered systems, the dispersivity is much larger than the diffusivity).

Equation 58 applies to any profile for a tracer input into a PFR with dispersion; the details of the input function for a given situation are included in the boundary and initial conditions. Although we could write those boundary and initial conditions to solve Equation 58 for a particular situation, the mass balance turns out to be simpler to analyze if written from a Lagrangian point of view, i.e., if written for a control volume that is moving with the fluid at velocity \(v_x\). Recall that, on the Lagrangian axis, distance is defined by a variable \(x^*\), which is related to \(x\) by the equation: \(x^* = x - v_x t\). Recall also that, from the Lagrangian viewpoint, fluid is not entering or leaving the control volume by advection, so the advective term can be set to zero. As a result, the mass balance can be written in terms of \(x^*\) as follows:

\[
\frac{\partial c(x^*,t)}{\partial t} = D \frac{\partial^2 c(x^*,t)}{\partial (x^*)^2} \tag{59}
\]

which is the equation describing simple one-dimensional diffusion/ dispersion from a planar source.

It is convenient to transform Equations 58 and 59 into dimensionless forms; in that way, the results can be understood most generally and be broadly applicable. To do so, we can define dimensionless distance, time, and concentration as follows:
Dimensionless distance $\tilde{x}$:

$$\tilde{x} \equiv \frac{x}{L} \quad (60a)$$

Dimensionless time $\tilde{t}$:

$$\tilde{t} = \frac{t}{\theta} = \frac{t}{V/Q} = \frac{t}{L/v_x} \quad (60b)$$

Dimensionless concentration $\tilde{c}$:

$$\tilde{c} = \frac{c}{M/V} = \frac{c}{c_o} \quad (60c)$$

After these substitutions, Equation 58 is transformed into the following:

$$\frac{\partial \tilde{c}(\tilde{x},\tilde{t})}{\partial \tilde{t}} = -\frac{\partial \tilde{c}(\tilde{x},\tilde{t})}{\partial \tilde{x}} + \frac{D}{v_x L} \frac{\partial^2 \tilde{c}(\tilde{x},\tilde{t})}{\partial \tilde{x}^2} \quad (61)$$

and Equation 59 becomes:

$$\frac{\partial \tilde{c}(\tilde{x}^*,\tilde{t})}{\partial \tilde{t}} = \frac{D}{v_x L} \frac{\partial^2 \tilde{c}(\tilde{x}^*,\tilde{t})}{(\partial \tilde{x}^*)^2} \quad (62)$$

where $\tilde{x}^* \equiv \tilde{x} - \tilde{t}$. The dimensionless term $\frac{D}{v_x L}$ appears in both Equations 61 and 62 and represents the single parameter of the model. $\frac{D}{v_x L}$ is often referred to as the dispersion number, and its inverse is called the Peclet number, Pe. The dispersion number gives a relative measure of the importance of dispersion and advection in the mass balance equation: the larger the dispersion number, the more significant dispersion is relative to advection. Note that $\frac{D}{v_x L}$ is a single number; for the purposes of the model, there is no significance to (nor, in many situations, any way to identify) the values of the individual components ($D$, $v_x$, or $L$) that affect the composite parameter.

Whether written in dimensional or dimensionless form, the defining equation is first order in time and second order in space. Therefore, to solve for the concentration profile, one initial and two boundary conditions are required. For a pulse input tracer test, the initial condition is described by the pulse input at time zero at the influent boundary and the absence of tracer elsewhere in the reactor. The boundary conditions are more difficult to specify; approaches that have been considered include statements of the flux at the boundaries or statements of the concentrations either at the physical boundaries (the inlet and outlet of the reactor) or the mathematical boundaries ($x^* = \pm \infty$). For engineered reactors, it is often not possible for dispersion to occur across the boundary in the reverse direction of the flow, i.e., it is not possible for a molecule to re-enter the reactor through the effluent end once it has exited, nor for a molecule that has entered the reactor to exit by crossing the boundary where the influent flow
enters. This condition is known as a *closed boundary*. For natural systems such as the reaches of a river or different fields of a groundwater system, dispersion might be possible across the boundaries, so that situation is different. This condition is known as an *open boundary*.

The boundary condition problem has been discussed by Wehner and Wilhelm (1956) and Levenspiel (1972). The problem can be solved analytically only if one considers open boundaries at the physical limits and boundary conditions of zero concentration at \( x^* = \pm \infty \). For a pulse input into a system with open boundaries, the solution can be expressed for the dimensionless and dimensional formulations as follows (after Bear, 1972):

\[
\tilde{c}(\tilde{x},\tilde{t}) = \frac{1}{2\sqrt{\pi \left( \frac{D}{v_L} \right) \tilde{t}}} \exp \left\{ -\frac{\left( \tilde{x} - \tilde{t} \right)^2}{4 \left( \frac{D}{v_L} \right) \tilde{t}} \right\}
\]

(63)

\[
c(x,t) = \frac{c_o}{2\sqrt{\pi \left( \frac{D}{v_L} \right) \frac{t}{\theta}}} \exp \left\{ -\frac{(x - v_L t)^2}{4 \left( \frac{D}{v_L} \right) \frac{t}{\theta}} \right\}
\]

(64)

These equations give the concentration distribution over time and space for a pulse input at time zero. They define a profile that spreads out with a diminishing peak as the tracer moves through the reactor. For any fixed value of \( t \) or \( \tilde{t} \), the profile is a gaussian distribution along the distance axis. A family of curves from this equation, depicting the spread of tracer as it travels through the reactor, is shown in Figure 13a. The curves represent the tracer concentration throughout the reactor at different times, so the set of curves can be thought of as a time series of snapshots of the tracer profile.
Figure 13. Snapshots of the tracer profile in a pulse input test, according to the dispersion model for $D / (v_x L) = 0.002$. (a) Concentration as a function of distance using an Eulerian distance axis. (b) Concentration as a function of distance using a Lagrangian distance axis.

Figure 13a describes the tracer concentration as a function of distance at various times, i.e., each curve is for a fixed value of time and various values of distance. Note that, when plotted in this way, the profile is always symmetric around its peak value. This property is emphasized by plotting the profile using a Lagrangian distance scale (Figure 13b). However, in an actual tracer study, the variable that is almost always measured is the tracer concentration as a function of time at a fixed location (i.e., in the reactor effluent, at $x = L$). An observer standing at this point first sees tracer that has been in the system for a short time and has dispersed downstream to reach the reactor effluent. Later, the observer sees a higher concentration of tracer, but this tracer has been in the system longer and has therefore been subject to more dispersion than the tracer seen earlier. Still later, after the peak has passed the observer, he or she sees tracer that has been in the reactor and has been affected by dispersion quite a long time. The fact that the parcels of fluid being observed at different times have been affected by dispersion to differing extents leads to a tracer profile that is skewed, with the tracer concentration increasing more rapidly at early times than it decreases at later times. A family of curves showing this trend for
different values of $\frac{D}{v_xL}$ is presented in Figure 14. At low values of $\frac{D}{v_xL}$, the curves are approximately symmetric and gaussian, but as $\frac{D}{v_xL}$ increases, they become more skewed.
Figure 14. Tracer profile in the effluent of a plug flow reactor with open boundaries and in which dispersion is occurring, for a pulse input of tracer at $t = 0$. (a) Normalized tracer concentration as a function of time at various locations in the reactor, for $\frac{D}{v_x L} = 0.2$; (b) Normalized tracer concentration at $x/L = 1.0$ for various values of the dispersion number, $\frac{D}{v_x L}$. 
As is clear from the preceding discussion, the dispersion model uses the dispersion number (or, equivalently, the Peclet number) as the single parameter that specifies where a system lies on the spectrum between plug flow and complete mixing. The larger the dispersion number, the sooner a tracer can be detected downstream of its injection point, and the longer it takes for the total mass of tracer injected to be completely flushed out of the system. In the limit of extremely large dispersion, the system behaves very much like a CFSTR. Thus, a true PFR has zero dispersion, a CFSTR has infinite dispersion, and in the PFR-with-dispersion model, non-ideal reactors can be characterized by various, intermediate amounts of dispersion.

The $E(t)$ function according to the dispersion model for a reactor with open boundaries is easily determined by specifying that $x = L$ in Equation 64 and applying Equation 8 to Equation 64 to obtain the following:

$$E(t) = \frac{1}{2\theta^2 \sqrt{\pi}} \exp \left\{ \frac{1}{\theta^2} \left( \frac{1-t}{\theta} \right)^2 \right\}$$  \hspace{1cm} (65)

Using Equation 65, we can predict the $E(t)$ curve for a reactor that behaves like a PFR that has open boundaries and in which there is some dispersion. Of course, that conceptual image of a reactor is still highly idealized, albeit not as idealized as a PFR with no dispersion. In reality, even reactors in which the flow pattern seems to approximate plug flow with dispersion might have peculiarities that cause localized mixing beyond that induced by dispersion, or regions where the dispersion coefficient differs from elsewhere in the reactor. Therefore, having established the expected $E(t)$ function for a reactor that follows the PFR-with-dispersion model exactly, we need to choose the value of the dispersion number that provides the best fit to the residence time distribution of the real reactor, and to assess how close that best-fit modeling scenario comes to reproducing the observed behavior in the system.

Traditionally, the approach used to estimate the dispersion number that best describes a reactor relies on matching the normalized variance of the experimental $E(t)$ curve with that of the $E(t)$ curve predicted by the model. The former value can be calculated as described earlier, using Equation 26 or 28, and the latter can be calculated using either Equation 66 or 67, depending on whether the system is to be modeled as having open or closed boundary, respectively.

$$\sigma^2_e \left|_{\text{model, open boundaries}} \right. = \frac{2}{v_x L} + 8 \left( \frac{D}{v_x L} \right)^2$$  \hspace{1cm} (66)

$$\sigma^2_e \left|_{\text{model, closed boundaries}} \right. = \frac{2}{v_x L} - 2 \left( \frac{D}{v_x L} \right)^2 \left( 1 - \exp \left( -\frac{v_x L}{D} \right) \right)$$  \hspace{1cm} (67)
To find the dispersion number that best fits the experimental data, one inserts the experimental value of the normalized variance on the left hand side of Equation 66 or 67 and solves by trial and error for the value of $\frac{D}{v_s L}$ that satisfies the equation. An example of this process is provided below.

Alternatively, non-linear regression techniques (available in many spreadsheet and graphics programs) can be used to identify the values of parameters in the dispersion model that minimize the errors between the experimental and model $c_p(t)$ or $E(t)$ curves. When this approach is used, the model curves can be generated using Equation 63, 64, or 65, in which case the dispersion number and the hydraulic residence time can be adjusted to improve the fit. The latter parameter (the hydraulic residence time) is identified in the equations as $\theta$, but here we consider assigning values other than $V_{tot}/Q$ to that parameter, so we represent it more generically as $\bar{T}_D$.

Two reasonable choices are available for assigning a value to $\bar{T}_D$: we can either assign it the value of $\bar{T}$ calculated from tracer data, or we can leave it unconstrained and use whatever value causes the model $c_p(t)$ or $E(t)$ curve to best fit the experimental data. In the latter case, the match between the model and the data is always better, and sometimes dramatically better, than if $\bar{T}_D$ is forced to equal $\bar{T}$ and only $\frac{D}{v_s L}$ used to fit the data (this outcome is also demonstrated in the following example).

The choice of which parameter estimation approach to use depends on the intended use of the results. In general, if the data are to be used to predict the extent of reaction that can be expected in a reactor (as is described in Chapter 4), using both $\frac{D}{v_s L}$ and $\bar{T}_D$ as fitting parameters is preferable. On the other hand, if the data are to be used to test whether the model is a true representation of the mixing in a reactor (e.g., that the dispersion is one-dimensional) or to assess how the dispersion number varies as a function of other system parameters, setting $\bar{T}_D$ to the value of $\bar{T}$ (assuming that $\bar{T}$ has been carefully evaluated) and using only $\frac{D}{v_s L}$ to fit the data is probably more appropriate. In the end, such decisions must be made on a case-by-case basis.

**Example 4.** Estimate the best-fit value of the dispersion number for the data in Example 1, and compare the $E(t)$ curve of the experimental data with that of the predicted tracer output curve for a PFR with the estimated dispersion number. Assume the PFR has open boundaries.

**Solution.** The variance of $E(t)$ for the experimental data was estimated in Example 2 to be $760 \text{ min}^2$ or $747 \text{ min}^2$, depending on whether the estimate is made using Equation 28a or 28b. Using the value from Equation 28b and normalizing it by
dividing by $\overline{t}^2$ (i.e., $49.5^2 \text{ min}^2$) gives a value for the normalized variance of 0.305. Solving Equation 66 by trial and error, the dispersion number corresponding to this value of the normalized variance is 0.107.

The model $E(t)$ curve for a reactor with a dispersion number of 0.107 can be developed using Equation 65. This curve is compared with the experimental $E(t)$ curve in Figure Ex4-1a. The model does not fit the data very well at early times. Depending on how one intends to use the model, the lack of exact fit might or might not be of concern.

A better fit to the data can be obtained by allowing both the dispersion number and the mean hydraulic residence time to be adjusted as we seek to model the data. Using a non-linear regression analysis to minimize the errors between the experimental data and model predictions, the best-fit parameter values are determined to be $\frac{D}{v_r L} = 0.27$, $\overline{t}_D = 36.4 \text{ minutes}$. The predicted output curve using these parameters is also shown in the figure; except at long times, this curve provides a dramatically better fit to the data than does the model in which $\overline{t}_D$ is constrained to equal the experimental value of $\overline{t}$ ($= 49.5 \text{ minutes}$).

The model $F(t)$ curves are compared with the cumulative tracer output profile in Figure Ex4-1b.
Figure Ex4-1. Experimental values and model curves based on the PFR-with-dispersion model, using two sets of model parameters for (a) $E(t)$ and (b) $F(t)$.

Model 1: $\frac{D}{v_x L} = 0.107$, $\bar{t}_D = \bar{t} = 49.5$ minutes, Model 2: $\frac{D}{v_x L} = 0.27$, $\bar{t}_D = 36.4$ minutes.
**CFSTRs in Series**

A second model that is sometimes used to describe non-ideal flow in a reactor represents the reactor as a series of $N$ equi-sized smaller CFSTRs. To envision the model, one can imagine installing baffles in a reactor so that the water follows a path from one part of the reactor to the next with no possibility of returning to an earlier section. A schematic representation of the model is shown in Figure 15. With no baffles (Figure 15a), the reactor is simply a single CFSTR; as already discussed, some molecules of water appear in the effluent of such a reactor quite rapidly. With one baffle, the reactor has two sections. In such a case, even if each section is well mixed, there is less overall mixing than in the system without the baffle. With two or three baffles, the reactor has three or four sections (as in Figure 15b), respectively, and still less mixing. In such a case, molecules that enter the first section at some instant are unlikely to mix with those that have been in the system for a long time, as the latter molecules are predominantly in downstream sections.

As the number of sections (equal to the number of baffles plus one) increases, the mixing that takes place in each CFSTR affects smaller and smaller volumes of water. At very large $N$, a parcel of liquid moves through the series of reactors, mixing minimally with liquid ahead of or behind it. That is, as $N$ increases, the reactor behaves increasingly like a PFR. This model is, logically enough, excellent at fitting tracer data for reactors that have real baffles (as, for example, disinfection reactors frequently do), but it is also useful for fitting tracer data for reactors with no physical baffles. In the latter case, the hydraulic equivalent of physical baffles might be provided by the combined effects of the arrangement of entry ports, the momentum of fluid entering the reactor, and the style of the effluent collection system.
Figure 15. (a) A single CFSTR with volume $V$, and (b) the same tank divided by baffles into four, equi-sized ($V/4$) CFSTRs in series.

The derivation of the expressions for $E(t)$ and $F(t)$ for this model is straightforward; a guide to the process is provided in Problem 2 at the end of the chapter. The result for any integer value of $N$ is as follows:

$$E(t) = \frac{1}{\theta} \frac{N^N}{(N-1)!} \left( \frac{t}{\theta} \right)^{N-1} \exp \left( -\frac{Nt}{\theta} \right)$$  \hspace{1cm} (68)$$

$$F(t) = 1 - e^{-N\theta} \sum_{i=1}^{N} \frac{1}{(i-1)!} \left( \frac{Nt}{\theta} \right)^{i-1}$$  \hspace{1cm} (69a)$$
or

\[
F(t) = 1 - e^{-\frac{N t}{\theta}} - \frac{N t}{\theta} e^{-\frac{N t}{\theta}} - \frac{1}{2!} \left( \frac{N t}{\theta} \right)^2 e^{-\frac{N t}{\theta}} - \cdots - \frac{1}{(N-1)!} \left( \frac{N t}{\theta} \right)^{N-1} e^{-\frac{N t}{\theta}}
\]  

(69b)

where \( \theta \) is the hydraulic detention time of the complete tank and \( N \) is the (conceptual) number of tanks into which the complete tank is divided. A family of curves showing the effluent concentration profile for different values of \( N \) is shown in Figure 16. The ordinate is the dimensionless product of \( E(t) \) and \( \theta \). This ordinate is chosen to make the figure independent of \( \theta \); note that, for a pulse input tracer study, the ordinate is also equivalent to \( \frac{c_p(t)}{c_o} \), where \( c_o \) is calculated based on the volume of water in the entire reactor. As \( N \) increases, the behavior of the reactor goes from that of a CFSTR (\( N = 1 \)) to that of a PFR (\( N = \infty \)).

Figure 16. Residence time distribution for the CFSTRs-in-series model, for various values of \( N \).

To use the CFSTRs-in-series model, the parameter \( N \) must be determined. As we sometimes do when determining the best-fit value of the dispersion number in the dispersion model, we can use the variance of the data from a tracer test to find the best value of \( N \). The variance of the predicted \( E(t) \) curve for \( N \) CFSTRs in series can be computed by substituting
Equation 68 into Equation 27. Integration of the resulting equation yields the following simple relationship between the number of ideal CFSTRs in series and the variance of $E(t)$:

$$N = \frac{T^2}{\sigma_E^2}$$  \hspace{1cm} (70)$$

The use of this approach for estimating $N$ is demonstrated in the following example.

**Example 5.** Estimate the best-fit number of equi-sized CFSTRs in series to model the data in Example 1, and compare the model-predicted $E(t)$ curve with the experimental $E(t)$ curve, as was done in Example 4 for the PFR-with-dispersion model.

*Solution.* The normalized variance of the experimental $E(t)$ curve was determined in Example 4 to be 0.305. The best-fit number of equi-sized CFSTRs in series is the inverse of this number, or 3.28. While the number of CFSTRs in a real system would obviously have to be an integer, this is not necessarily a restriction for a hypothetical system. That is, if our goal is simply to use the CFSTRs-in-series model to describe the tracer pattern from the real reactor as best we can in a compact form, treating $N$ as a continuous variable might be acceptable.

Equation 68 gives the value of $E(t)$ for $N$ ideal CFSTRs in series; for comparison with experimental data, however, $\bar{T}$ should be substituted for $\theta$. Thus, the $E(t)$ curve for 3.28 CFSTRs can be estimated by the following modification of Equation 68, with $N = 3.28$:

$$E(t) = \frac{1}{\bar{T}} \frac{N^N}{(N-1)!} \left( \frac{t}{\bar{T}} \right)^{N-1} e^{-Nt/\bar{T}}$$  \hspace{1cm} (71)$$

The value of $(N-1)!$ is defined only for integral values of $N$. However, a continuous function that is closely related to $(N-1)!$ has been identified that allows one, in essence, to estimate values of $(N-1)!$ when $N$ is not an integer. This function, commonly represented as $\Gamma(x)$, has the property that, if $x$ is an integer $\Gamma(x) = (N-1)!$. Thus, for instance, $\Gamma(5) = 4!$. The value of $\Gamma(3.28)$, therefore, is a good approximation of 2.28!. This value is 2.63. By inserting this value into Equation 71 for $(N-1)!$, along with the value of $\bar{T}$ computed in Example 1, we can calculate the expected $E(t)$ curve for $N = 3.28$. The $E(t)$ curves for $N$ values of 3.00 and 3.28 are compared with the experimentally determined $E(t)$ values below. The curves for $N = 3$ and $N = 3.28$ are not substantially different from one another, and both match the experimental data quite well. Thus, for this particular (hypothetical) data set, the CFSTRs-in-series model appears to match the experimental data significantly better than the PFR-with-dispersion model, when both models are constrained to match the experimental mean hydraulic detention time.
Models for Systems in Which the Non-Ideality Applies to Only a Portion of the Reactor: Short-Circuiting and Dead Space

The above discussion describes how various degrees of mixing in a system might be represented, based on the implicit assumptions that all the fluid participates in the same flow pattern and that the entire volume of the reactor is involved in that flow pattern. However, either of these assumptions might not be valid in a given reactor. Two specific cases can be identified in which these assumptions are violated, and the terms *dead space* and *short-circuiting* are used to describe these cases.

Dead space is the simpler of the two cases to describe. As the name implies, this condition means that some part of the available space in the reactor is not used. The water in that portion of the reactor is essentially stagnant, and that portion of the reactor might as well be filled with concrete as with water (or packing in packed bed reactors). The effective volume of a reactor with dead space is less than the actual volume, and the entire flow passes through the effective volume. When this problem occurs, it usually is associated with corners or other specific regions of tanks where mixing is very poor. It can also occur because of differences in the density between the influent and water already in the tank, a situation that is most likely to occur in tanks with no mechanical mixing, such as tanks designed for sedimentation. If the influent water is at a different temperature and therefore has a different density than the water in the reactor, it can
sink to the bottom or float across the top of the water in the tank, reducing the effective volume of the reactor.

Dead space is directly quantifiable from tracer studies. In any reactor in which all of the volume is used in the flow pattern (regardless of that flow pattern), the mean detention time of the tracer, $\bar{t}$, should equal the theoretical detention time, $\theta \left( = \frac{V_{\text{tot}}}{Q} \right)$. In a reactor with dead space, the entire flow $Q$ passes through the effective reactor volume, $V_{\text{eff}}$, where $V_{\text{eff}} < V_{\text{tot}}$. The dead space, $V_{\text{dead}}$, is the difference between the total and effective volumes, i.e.,

$$V_{\text{dead}} = V_{\text{total}} - V_{\text{eff}}$$

(72)

The fractional dead space, $m$, is defined as

$$m = 1 - \frac{V_{\text{eff}}}{V_{\text{tot}}} = 1 - \frac{\bar{t}}{\theta}$$

(73)

Example 6: Testing CFSTR Behavior Based on Response to a Tracer Test

The results of a spike-input tracer test on a reactor, using a dye as the tracer, are provided below. The volume of the reactor, based on its geometry, is 50 m$^3$, and the influent and effluent flow rates during the test were both 0.1 m$^3$/min.

<table>
<thead>
<tr>
<th>Time, h</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye Conc., mg/L</td>
<td>35</td>
<td>31.6</td>
<td>24.1</td>
<td>21.6</td>
<td>17.9</td>
<td>17.2</td>
<td>13.8</td>
<td>11.9</td>
<td>11.1</td>
<td>9.1</td>
<td>7.6</td>
</tr>
</tbody>
</table>

(a) Determine whether the reactor behaves as a CFSTR.

(b) Estimate the mean hydraulic residence time in the reactor based on its geometry, based on Equation 40b, and based on Equation 16. Discuss the different estimates and indicate which one you find most trustworthy.

Solution. (a) Whether a reactor behaves as a CFSTR can be determined by comparing the outcome of a tracer test with the expected outcome for an ideal CFSTR. According to Equation 40b, a plot of $\ln c(t)$ vs. $t$ for an ideal CFSTR should be linear with a slope of $-1/\bar{t}$ and an intercept of $\ln c_o$. The data are plotted using semi-logarithmic coordinates below, and are seen to fit the straight line expectation quite well. The best-fit slope is $-0.149$/h, corresponding to a hydraulic residence time of 6.7 hours.
(b) The theoretical hydraulic residence time of a reactor is \( V/Q \), which for this reactor is 500 min, or 8.33 hours. The residence time computed according to Equation 40b is the result obtained in part (a), i.e., 6.7 hours. A numerical estimate of the residence time, based on Equation 16, suggests that the residence time is smaller still: only 3.8 hours. These values are vastly different; which one, if any, is right?

A reasonable hypothesis for the difference between the first estimate (based on geometry) and the other two is that the effective volume of the reactor is significantly less than the total volume, i.e., that some portion of the reactor is not participating in the mixing regime. As a result, the total flow is passing through only a portion of the geometric volume, causing the actual residence time to be less than that calculated based on the system geometry.

The explanation for the difference between the estimates of \( \bar{t} \) using Equations 40b and 16 is a bit more subtle, and is based on the fact that the graphical approach is based on the change in tracer concentration during the period of analysis, whereas the numerical method represents an attempt to integrate the tracer data over all time. That is, the numerical approach involves approximating the values of \( \int_0^\infty cdt \) and \( \int_0^\infty cdt \) as \( \sum_{t=0}^{\text{max}} cdt \) and \( \sum_{c=0}^{\text{max}} cdt \), respectively. The approximation of the integrals as summations turns out to be acceptable; the problem arises not from that approximation but from the fact that the summation must extend to \( t = \infty \), or at least to the time at which all the tracer has exited the reactor. From the fact that the tracer concentration in the final sample is > 20% of \( c_o \), it is clear that this requirement is not met. The data at long residence times has a disproportionate effect on the estimation of \( \bar{t} \), so that computing \( \bar{t} \)
without sufficient data at long times can lead to a severe underestimate. By contrast, the
graphical approach to estimating $\bar{T}$ (or a corresponding numerical approach) relies on the
existing data rather than a simulated integration to long times, and therefore is not subject to the
same bias. The result highlights the greater reliability of this latter approach. It also suggests that,
if one has to use a numerical integration to estimate $\bar{T}$, it is probably worthwhile to extrapolate
the data as best one can to the time when all the tracer has exited the reactor; such an
extrapolation certainly involves some risk, but it is still likely to improve the estimate of $\bar{T}$.

Short circuiting is a term that has been used with less precision than dead space. Generally,
it means that at least some of the fluid follows a different path through the reactor than the
intended one and exits after a shorter-than-desired residence time. Here, we use the term to
describe a situation in which the system behaves as though the effective volume of the reactor is
divided into two or more sections in parallel. If part of the fluid passes through each section, the
fluid with an average residence time less than the mean hydraulic residence time of the whole
reactor is said to be short circuiting. Short circuiting is then characterized by an $E(t)$ function
that is a linear addition of the $E(t)$ functions for the reactor sections, with one or more of the
individual $E(t)$ curves having a mean value less than $\theta$.

Short circuiting can occur, for instance, in packed bed reactors when some portion of the
flow travels along the walls of the reactor while the rest travels through the packed bed. In open
reactors, the influent distribution system might direct a substantial portion of the flow through a
small segment of the reactor, and a smaller portion through a larger segment; the former portion
would be the short circuiting portion of the flow. Similarly, the weir system that controls the
effluent might draw a substantial portion of the flow into a small portion of the reactor, creating
an imbalance in the spread of the flow throughout the reactor volume. In a CFSTR, of course, a
portion of the influent exits after a very short time due to random mixing processes. In short-
circuiting, the process is different because it is not random, i.e., a portion of the influent is
envisioned to follow a defined, non-random path through the reactor to the effluent port.

Models that account for short-circuiting and dead space are intrinsically more complex than
those that assume that all of the flow utilizes all of the volume of the reactor. Some models that
allow for these effects are described next.

Models for Complex Mixing Behavior

PFRs in Parallel

Often, mixing patterns are more complex than those represented by any of the models
described above. In such cases, a more complex network of ideal reactors must be used to
model mixing in the real reactor. One conceptual approach for modeling complex mixing is to
restrict the model network to several PFRs in parallel. Theoretically, one could define a different
PFR for each parcel of water entering, and thereby accurately model the exit age distribution of
virtually any real system. A schematic showing a reactor that is represented by five PFRs in
parallel, with various amounts of flow entering the various reactors (and, therefore, each reactor having a different detention time), is shown in Figure 17.

The $E(t)$ curve for the model system represented in Figure 17 is a linear summation of the $E(t)$ curves for the individual reactors, weighted according to the flows through those reactors. That is, if 30% of the flow into the overall reactor could be modeled as though it passed through a PFR with a residence time of 10 minutes, then in a spike input tracer test, 30% of the tracer input would enter that portion of the reactor and exit as a spike 10 minutes later. Others of the hypothetical reactors would contribute to the $E(t)$ curve at times corresponding to their respective residence times, yielding an $E(t)$ function for the model system consisting of five spikes, as shown in Figure 18a.

Figure 17. Schematic of PFRs-in-parallel model. The meaning of the dashed lines is discussed in the text.
Figure 18. Residence Time Distributions Modeled As Five PFRs in Parallel. (a) $E(t)$ Curves; (b) $F(t)$ Curves. The values of $\theta_i$ correspond to the residence times in the various model reactors. The spikes in part (a) are infinitely thin and high, and each encloses an area equal to the product of the overall average residence time and the fraction of the total flow that passes through the corresponding reactor. The height of each step in part (b) corresponds to the fraction of the of the total flow that passes through the corresponding reactor.
It is not possible to identify a set of $Q_i$ and $\theta_i$ values for the hypothetical reactors that would cause the $E(t)$ function for the model system to match that of the experimental system, because the model $E(t)$ curve comprises a series of infinitely high and thin spikes. However, an appropriate set of $Q_i$ and $\theta_i$ values can be chosen so that the model $F(t)$ curve is well matched to the experimental $F(t)$ curve. As can be seen in Figure 18b, the $F(t)$ curve for the model system consists of a stair-step plot; the height of each step corresponds to $Q_i/Q_{tot}$ and the location of the step on the abscissa corresponds to $\theta_i$. It should be apparent that we could model any empirical $F(t)$ curve to any chosen degree of accuracy by using enough model PFRs in parallel. Thus, the PFRs-in-parallel model can represent either of the ideal extremes of mixing: a true PFR is represented as a single PFR which has residence time $\theta$ and receives all the flow, and an ideal CFSTR is represented as an infinite number of PFRs, each with a different value of $\theta$, and each receiving a small fraction of the flow. The model can also represent degrees of mixing intermediate between these two extremes or much more complex mixing patterns.

While the PFRs-in-parallel model is more flexible than the models discussed previously in terms of its ability to model a wide range of tracer output curves, it also has significant drawbacks. The two models of ideal reactors (ideal PFRs or CFSTRs) are each characterized by a single parameter: $\theta$. The PFR-with-dispersion and CFSTRs-in-series models each add an adjustable parameter (dispersion number or number of equal-sized CFSTRs in series) to incorporate and characterize the degree of non-ideality. By contrast, the PFRs-in-parallel model contains an arbitrarily large number of fitting parameters: the volume and flow rate through each of the hypothetical reactors. Because of this, the PFRs-in-parallel model has the advantage that it is capable of modeling virtually any arbitrary flow pattern in any reactor and the disadvantage that it is more complex and has more parameters to be evaluated than the other models presented here.

**PFRs in Series**

It is instructive to re-draw Figure 17 so that the various sections of reactors that operate in parallel are merged, i.e., so that each group of reactor sections enclosed in dotted lines in Figure 17 is treated as a single PFR. In such a case, the conceptual picture of the system is converted to a group of PFRs in series (Figure 19a). However, only a portion of the flow exiting each reactor enters the subsequent reactor; the remainder of the flow is shunted directly to the effluent of the entire reactor network, where it combines and mixes with the flow that has passed through the other reactors. It should be obvious that the mixing patterns in Figures 17 and 19a are identical, so the tracer outputs would be identical also. In each case, the influent water enters the entire reactor system, portions of the water exit the system at various times thereafter, and all the portions are mixed at the most downstream point in the system. The resulting $E(t)$ curves can be obtained by inspection, or more formally using the convolution integral (see Problem 9).
Plug flow reactors can be combined in yet another way to yield the same tracer response as the systems characterized in Figures 17 and 19a. Specifically, Figure 19b describes a reactor system that is very similar to that of Figure 19a, but differs in a subtle way. In Figure 19a, all of the flow enters the system together, and portions of the flow are then steadily withdrawn and shunted past the downstream part of the system to the outlet. By contrast, in Figure 19b, portions of the influent are shunted past the upstream part of the system, and all the flow exits the system together. In fact, a little thought shows that the system described by Figure 19b is simply the system described by Figure 19a run in reverse. If we eliminate the space between the
various reactors, we see that Figure 19a can be described as a single PFR with multiple outlets placed along the length of the reactor, and Figure 19b can be described as a single PFR with multiple inlets (Figure 20). Once again, either purely conceptual arguments or a mathematical analysis can be applied to predict the tracer response of these systems; the conclusion is that the $E(t)$ functions for all the systems in Figures 17, 19, and 20 are identical.

![Diagram](image-url)

**Figure 20.** Representations of Figures 19a and b, respectively, as single reactors with multiple outlets or inlets. Figures a and b represent complete segregation and maximum mixedness, respectively.

In the system with multiple outlets along the reactor length (which is equivalent to a system with completely independent PFRs in parallel), the separate flow streams are mixed at the latest possible point (the final effluent point). This model is sometimes referred to as the *complete segregation* model. By contrast, in the system with multiple inlets (Figure 19b or 20b), the streams are mixed at the earliest possible point that is consistent with the tracer data; this system is sometimes referred to as the *maximum mixedness* model. As shown in Chapter 4, despite responding identically in tracer tests, these systems sometimes behave quite differently if the input is a reactive substance.

**Example 7.** Describe the parameters of a model reactor system containing five PFRs in parallel that might be a reasonable representation of the reactor described in
Example 1. Compare the model-predicted $E(t)$ and $F(t)$ curves with the corresponding experimental curves, as was done above for the PFR-with-dispersion and CFSTRs-in-series models.

Solution. As in the previous approaches for modeling the experimental data, the goal is to define a model system that has residence time distribution functions that are similar to the experimental ones. However, unlike those approaches, the use of the PFRs in parallel model does not involve use of the variance of $E(t)$ curve. The expected tracer output from a group of five PFRs in parallel is simply five spikes, each infinitely high and infinitely thin. Clearly, no matter how we configure the model system, an $E(t)$ curve that consists of five such spikes and values of zero at all other times will not match the experimental $E(t)$ curve. This result is an outcome of the assumption that the tracer was injected over an infinitesimally small period; an assumption that the tracer entered the system over a short, but finite period would lead to a predicted tracer output profile that had several short periods of high concentration separated by periods with no tracer, and an assumption that some dispersion occurred in each PFR would lead to finite tracer concentrations appearing in the effluent between the periods of high concentration.

In any case, as noted above, the best approach for carrying out the modeling exercise is to try to match the predicted and experimental $F(t)$ curves, rather than the $E(t)$ curves. The $F(t)$ curve for the model system will be a stair-step function, because each model PFR contributes zero tracer to the effluent at times less than its hydraulic residence time and then will contribute all the tracer that entered it exactly at its residence time. The fraction of the total tracer that enters a given reactor $i$ in the model system is $Q_i/Q_{tot}$. Therefore, $F(t)$ of the model system will be zero at all times less than $\theta_1$, where $\theta_1$ is the shortest hydraulic residence time of any reactor in the system. At $t = \theta_1$, $F(t)$ will jump to a value equal to $Q_1/Q_{tot}$, where it will remain until $t = \theta_2$, the second shortest residence time of the five reactors. At that time, $F(t)$ will instantly increase to $(Q_1 + Q_2)/Q_{tot}$. This pattern will continue until $t$ equals the longest residence time of the five PFRs, at which point $F(t)$ becomes 1.0.

The modeling approach is therefore to draw the experimental $F(t)$ curve and to overlay a second curve that consists of five steps. The time and height of these steps can be chosen to provide the best match to the experimental data; often an eyeball fit is satisfactory. Such a plot is shown in Figure Ex7-1.
Figure Ex7-1. Experimental and model $F(t)$ curves. The model curve is for a system of five PFRs in parallel.

The times of the five vertical increases in $F(t)$ correspond to the residence times of the five model reactors, and the increase in $F(t)$ at each step indicates the fraction of the total flow that passes through that reactor. The model parameters can therefore be summarized as follows:

<table>
<thead>
<tr>
<th>Reactor #</th>
<th>$\theta$, min</th>
<th>$Q/Q_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>0.21</td>
</tr>
<tr>
<td>3</td>
<td>48</td>
<td>0.17</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>96</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The model $E(t)$ curve is shown in Figure Ex7-2. Although the $E(t)$ curve does not match the experimental curve well, the $F(t)$ curves are reasonably well matched. It should be apparent that by increasing the number of hypothetical reactors being considered, we could improve the fit of the model $F(t)$ curve to the point where it provided an extremely good fit to the data, but the $E(t)$ curves could never be made to match.
Non-Equivalent CFSTRs in Series

Complex mixing can be modeled in numerous other ways. For instance, one might add flexibility to the CFSTR-in-series model by allowing the individual reactors to have different volumes. In such a model, the volume of each reactor would have to be specified, rather than just the total number of hypothetical reactors. Ultimately, no matter how complex the hydraulic flow pattern in a reactor, it can always be represented by some combination of CFSTRs and PFRs, in some combination of parallel and series connections. However, identifying a network of such reactors that is both physically reasonable and leads to a mathematically tractable mass balance can be difficult. Furthermore, with each additional component in the model system, additional fitting parameters need to be used to describe it, and the use of more than three or four fitting parameters is rarely justified by available data, unless the physical structure of the reactor provides support for the proposed model.

2.5 EQUALIZATION

The principles described in this chapter are applied directly in equalization, a pretreatment process sometimes used in wastewater treatment plants. Equalization is the process of reducing or eliminating temporal fluctuations in the water flow rate and/or the concentration of some constituent. For flow equalization, a tank in which the fluid volume can vary with time is used to

Figure Ex7-2. Experimental and model $E(t)$ curves. The five spikes are for a system of five PFRs in parallel.
dampen the flow fluctuations; ideally, the effluent flow from this tank is the average flow. When
the influent flow is greater than the average flow, the amount of water stored in the tank
increases and, when the influent flow is less than average, the water level decreases. Similarly,
for concentration equalization of a conservative chemical, a CFSTR with constant volume can
dampen the concentration variations. When the influent concentration is greater than the
concentration in the tank, the concentration in the tank (and its effluent) increases, but it remains
less than that of the influent; when the influent concentration is less than that in the tank, the
concentration in the tank decreases, while remaining greater than that of the influent.

Equalization is a pretreatment process, i.e., it accomplishes no treatment (removal of
pollutants) itself. As a result, its use can only be justified based on the effect of variation of flow
or influent concentration on downstream treatment processes. Equalization can make operation
of treatment processes simpler, particularly when a chemical must be fed to a process in
stoichiometric proportion to the mass flux of a pollutant in the influent. The design issue is how
large the equalization volume must be to reduce the fluctuations in the flow or concentration to
acceptable levels. To address that issue, the effect of time-variant influent conditions on
subsequent treatment processes must be assessed.

**Flow Equalization**

When considering flow equalization, the composition of the influent is irrelevant; the mass
balance of interest is for water alone. The mass balance is written using the entire reactor as the
control volume. In words, the mass balance is as follows:

Rate of change of mass of water in the reactor = Mass rate at which water enters the reactor − Mass rate at which water exits the reactor

Translating into symbols:

\[
\frac{d}{dt} \rho V(t) = \rho Q_{in}(t) - \rho Q_{out}(t) \tag{74}
\]

Recognizing that the density of water, \( \rho \), is a constant converts Equation 74 into a simple
volume balance for water in the tank:

\[
\frac{dV(t)}{dt} = Q_{in}(t) - Q_{out}(t) \tag{75}
\]

As written, \( V, Q_{in}, \) and \( Q_{out} \) are all functions of time. The goal of flow equalization is to fix
\( Q_{out} \) at a constant value, namely its average value over some time period, \( \tau \). The choice of that
time period depends on the situation. For an industry with large flow variations over short
cycles, a several hour period might be a satisfactory choice for \( \tau \). For plants with a diurnal
cycle, a 24-hour period is likely the proper choice. For industries with negligible flow on
weekends, storing water for the weekend (especially, for example, to keep a microorganism population alive in a biological treatment facility) might necessitate a choice of several days or a week as the averaging period. Once that choice is made (and assuming data are available), the determination of the average flow is straightforward.

Assuming that equalization works perfectly, \( Q_{\text{out}} \) can be set at the (constant) average flow \( (Q_{\text{ave}}) \) over the selected period. With that substitution, a separation of variables in Equation 75 leads to the following:

\[
\int_{V(0)}^{V(t)} dV = \int_{0}^{t} Q_{\text{in}}(t) \, dt - Q_{\text{ave}} \int_{0}^{t} dt 
\]

(76)

Upon integration, the result is:

\[
V(t) - V(0) = \int_{0}^{t} Q_{\text{in}}(t) \, dt - Q_{\text{ave}} t 
\]

(77a)

\[
V(t) = V(0) + \int_{0}^{t} Q_{\text{in}}(t) \, dt - Q_{\text{ave}} t 
\]

(77b)

In words, Equation 77b states that the volume of water in the reactor at time \( t \) is the volume present at time zero plus the cumulative volume of water input to the reactor since time zero minus the cumulative volume of water taken out of the reactor since time zero. The design problem is to find the maximum value of \( V(t) \) and provide that much storage capacity. Because the choice of time zero is arbitrary in a continuous flow reactor, \( V(0) \) is also unknown and reflects the history prior to that time.

The analysis is carried out using Equation 78**a. Both sides of this equation represent the cumulative difference between the input and output from (the arbitrary) time zero to time \( t \). If a set of flow values at various intervals is available, the cumulative difference can be calculated using the right hand side of the equation. At times for which the cumulative difference is positive, the basin contains more water than at time zero, and at times for which the cumulative difference is negative, the basin has less water than at time zero. Equalization can only be accomplished if the basin had enough water at time zero to offset the largest cumulative negative difference during the time period under consideration; otherwise the basin would be dry at some time, and the outflow could only equal the inflow. Hence, the minimum value of \( V(0) \) is chosen as the absolute value of the maximum negative cumulative difference in the set of data. With that choice, \( V(t) \) can be calculated from Equation 78b. The volume of the basin, then, has to be at least the maximum value of \( V(t) \), or else the basin would overflow (or the effluent flow would have to be increased). That design value for the basin volume \( (V(t)_{\text{max}}) \) can be found without ever finding all of the values of \( V(t) \) as the sum of the maximum positive cumulative difference and the absolute value of the maximum negative cumulative difference of the input and output. In
Example 8. Consider a small industry with a varying production of wastewater. To discharge to the local Publicly Owned Treatment Works (POTW), the flow must be equalized before entrance to the sewer. A typical set of hourly flow rates for one day (midnight to midnight) is shown in columns A and B of the spreadsheet below. What is the minimum volume of the equalization tank needed to allow the industry to discharge its waste at a steady rate on a day with typical flows?
### Table

<table>
<thead>
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<th>A</th>
<th>B</th>
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<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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<td><strong>Avg. Flow During Previous Hour (m³/h)</strong></td>
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<td><strong>Cum. Volume Output Since t = 0 (m³)</strong></td>
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<td>42.5</td>
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</table>

**Solution.** The cumulative input \( \sum_{i=1}^{j} Q_{in,i} \Delta t_i \) of the flows is shown in column D of the preceding table. The \( \Delta t_i \) values are all one hour, so the volume input in any hour (m³) is numerically equal to the flow rate (m³/h). Thus, column D shows the running sum of the input volume. The final value, 336 m³, can be used to calculate the average flow, which is 14.0 m³/h.
Since the goal is to maintain a steady output rate, the effluent flow is fixed at $Q_{ave}$. The cumulative output volume ($Q_{ave}t$) is shown in column E. Obviously, at the end, the cumulative output must equal the cumulative input. The differences between the cumulative input and output volumes, i.e., the values associated with the right hand side of Equation 77a, are shown in column F. These values are negative for the first several hours because the influent flow is less than the average (i.e., effluent) flow during those times. The maximum negative and maximum positive values in column F are $-42.5$ m$^3$ at $t = 8$ h and $13.5$ m$^3$ at $t = 20$ h, respectively. Thus, at least $42.5$ m$^3$ of water had to be present at time zero to allow the desired flow rate to be maintained through the whole period, and after $t = 20$ h, there will be $13.5$ m$^3$ more water in the tank than at time zero. The sum of these volumes is the required design volume ($56.0$ m$^3$). A tank with this volume would be able to maintain a constant flow rate of $14.0$ m$^3$/h despite the fluctuating influent flows, if this pattern of the flow variation was repeated daily. The data from column F are plotted in Figure Ex8-1, from which the same result is easily seen.

![Figure Ex8-1. Variation in inflow for example system.](image)

Assume that, at time zero, the tank contained the minimum acceptable value of $42.5$ m$^3$ of water. With this information, another column (column G) can be added to the spreadsheet to show the volume of water in the tank at various times, computed according to Equation 77b.
As noted above, in most situations, flow patterns are somewhat cyclical, although the period of the cycle might be anywhere from hours to many days. The flow patterns will not be the same every cycle, and therefore the required volume to equalize the flows will also vary. In such a case (again assuming data are available), one can carry out the analysis shown above for a large number \((N)\) of time periods. For each time period, a different value for the required volume is obtained. These values of required volumes can be rank-ordered from lowest to highest. Thus, if 25 cases have been analyzed, 25 values of the required volume \((V)\) would have been computed, associated with \(k\) values of 1 to 25; the smallest value of \(V\) is assigned a \(k\) value of 1, the next smallest value of \(V\) is assigned a \(k\) value of 2, etc.

The rank number \((k)\) is then converted to a fraction \(f\) by dividing it by \(N+1\) (26 in the example system), and that fraction is interpreted as the probability that a given volume will be required. For example, the third lowest value of \(V\) has a \(k\) of 3, so the corresponding \(f\) value \((= k/(N + 1))\) is 0.115. The interpretation is that this volume will provide the desired amount of equalization 11.5% of the time. (The addition of one to \(N\) in the denominator is a common technique used in statistics to account for the fact that the available data might not include the most extreme condition that will ever occur. That is, using a value of \(N + 1\) in the denominator assures that \(f\) never reaches 100%, thereby allowing for the possibility that the required volume might exceed the largest value required in the past.)

A graph is then made of \(f\) versus the required volume, \(V\). Using such a graph, the design can be statistically based. For example, if the objective is to be able to equalize the flow 90% of the time, the required volume is the value of \(V\) corresponding to \(f = 0.9\). One might also use statistical techniques to attempt to predict the likelihood of extreme flows that are even larger or smaller than those during the period for which data are available.

**Example 9.** The wastewater flows entering a municipal treatment plant were recorded at 15-minute intervals. Twenty-eight days of data were analyzed to find the required volume necessary to completely equalize the flow for each day, using the methodology shown in the previous example. The resulting 28 values of volumes required are shown in the table below; in this table, the values have already been rank ordered from lowest to highest although they did not happen in this sequence. Find the required volumes that would be required to equalize the flow for 80, 85, 90, and 95% of the cases.

---

\(^8\)In preparing such graphs, a probability axis is sometimes used for the ordinate. Such a scale can linearize the data, if the data can be described by a standard probability function.
Solution. The rank number for each case needs to be converted into a fraction (or percent) of cases with required volume less than the value for that case. So, for example, the value of 878 m$^3$ is ranked seventh of the 28 cases; the associated fraction is 7/29, or 0.241. This means that 24.1\% of the cases have a required volume less than or equal to 878 m$^3$. The data analyzed this way can then be plotted as shown in Figure Ex.9.1; because the data of interest are those associated with the upper portion of the data, those data are re-plotted in Part B of the figure.
To find the volumes required for each specified fraction (or percent), horizontal lines are drawn from given fractions on the ordinate to the graphed data, and then vertical lines are drawn from that point to the abscissa to find the associated volumes. The four required values are shown on the figure. Note that, in these real data from a wastewater plant in Texas, the highest value for required volume in this 28-day period (3292 m$^3$, the last value in the table) is more than twice as high as the second highest value. In the analysis, the effect is a dramatic difference between the volume required to be able to equalize for 90% of the cases and that required for the 95% case. The example points up the problem of using a small data set; data for several months rather than four weeks should be used.

### Concentration Equalization

Many wastewater treatment plants experience broad variations in the influent concentration. Because any CFSTR contains a mixture of the water and contaminants that came into the tank at all previous times (in proportions described by the exponentially decaying $E(t)$ distribution), CFSTRs tend to equalize the concentration, i.e., the variation in concentration is less in the effluent than in the influent. This fact, intrinsically true for any CFSTR, has led to the use of CFSTRs as designed concentration equalization facilities. In the analysis that follows, the constituent of interest is considered non-reactive in the equalization facility. That same
constituent is, generally, reactive in some subsequent treatment process, in which the chemical, physical, or biological conditions might be different from those in the equalization tank. If the species is in fact slightly reactive in the equalization facility, ignoring the reactivity should lead to a somewhat conservative design, which is usually an acceptable result.

The extent of concentration equalization that is accomplished in a CFSTR can be determined using the approach described above for the response of CFSTRs to tracer inputs. For instance, consider a situation in which the flow is reasonably constant and the influent concentration to a CFSTR suddenly jumps to a new value. Imagine, for now, that the new influent concentration \( c_2 \) remains constant for some time period. If the instant of the change is defined as time zero, the concentration in the tank at the instant the influent changes is \( c(0) \), and it reflects the previous history of the influent to the tank. The mass balance on the CFSTR for any time after time zero is:

\[
\frac{dVc_{\text{out}}}{dt} = Qc_2 - Qc_{\text{out}}
\]  

(78)

Dividing through by \( V \) and noting that \( Q/V = 1/\theta \), this equation yields:

\[
\frac{dc_{\text{out}}}{dt} = -\frac{1}{\theta}c_2 - \frac{1}{\theta}c_{\text{out}}
\]  

(79a)

\[
\frac{dc_{\text{out}}}{dt} + \frac{1}{\theta}c_{\text{out}} = \frac{1}{\theta}c_2
\]  

(79b)

Rearranging and taking the Laplace transform of both sides, we obtain:

\[
s f(s) - \left[ c_{\text{out}}(0) \right] + \frac{1}{\theta} f(s) = \frac{1}{\theta}c_2 \frac{1}{s}
\]  

(80)

where \( f(s) \) is the Laplace transform of \( c_{\text{out}}(t) \). Rearranging again, \( f(s) \) is found to be:

\[
f(s) = \frac{1}{s + \frac{1}{\theta}} + c_2 \frac{1}{s \left( s + \frac{1}{\theta} \right)}
\]  

(81)

Taking the inverse Laplace transform yields:

\[
c(t) = c(0) \exp\left(-\frac{t}{\theta}\right) + c_2 \left( 1 - \exp\left(-\frac{t}{\theta}\right) \right)
\]  

(82)

Equation 82 describes the change in the concentration over time of the effluent concentration from the reactor. Examining the two terms on the right hand side is instructive. The first term is identical to the response of a CFSTR to a pulse input of a tracer.
(Equation 40b) with the mass of tracer sufficient to yield the concentration \( c(0) \) throughout the reactor at time zero. That term alone would characterize a CFSTR that contained tracer at a concentration \( c(0) \) at time zero, and that received tracer-free influent from that time forward. The second term on the right hand side is identical to the response of a CFSTR that contained no tracer at time zero and that is then subjected to a step input of tracer (Equation 46) at concentration \( c_2 \). Overall, the response of the CFSTR shown in Equation 82 is the superposition of these two responses – the exponential die-off of the existing concentration and the rise toward the asymptote defined by the new influent concentration.

Equation 82 can be used, with minor alteration, to predict the changes in concentration in the effluent of a CFSTR that is receiving a time-varying input of a conservative substance. If input data are available at discrete times, the average input concentration for an interval \( \Delta t \) can be calculated and represented as \( c_{in,\Delta t} \). The response of the CFSTR (i.e., its concentration) at the end of that interval (time \( t + \Delta t \)) will reflect the exponential decay of the concentration at the start of the interval (time \( t \)) plus the exponential rise associated with the influent during the interval, i.e.,

\[
c(t + \Delta t) = c(t) \exp\left(-\frac{\Delta t}{\theta}\right) + c_{in,\Delta t} \left(1 - \exp\left(-\frac{\Delta t}{\theta}\right)\right)
\]

(Equation 83)

Equation 83 is a recursive equation, i.e., the concentration at one time is calculated based on the conditions in the tank at the previous discrete time and the influent during the interval. The equation is used successively to step through time.

To begin the analysis of concentration equalization in a CFSTR receiving a time-varying influent, one chooses an arbitrary concentration that is assumed to exist in the tank at time zero \( (c(0)) \); a long-term average might be a reasonable choice, but any value that is in the range of possible influent concentrations is acceptable. Since this value is an arbitrary guess, though, one would want to discard the concentrations computed for the first few detention times when making a design decision, in order to avoid any significant influence of that choice.

For a given situation, the key design decision (the choice of \( \theta \)) involves straightforward spreadsheet work. First, the influent concentrations and associated times are entered, and the time intervals of interest (\( \Delta t \) values) are selected. The average influent concentration during each interval is then calculated. Finally, an initial concentration is guessed, a trial hydraulic detention time (\( \theta \)) is chosen, and Equation 83 is used successively to calculate the expected effluent concentrations over time. Different values of \( \theta \) are used until a predetermined criterion for the variation of the effluent concentration is attained. Possible criteria include not exceeding a maximum difference between the high and low values in the entire data set or in any chosen time period, a maximum standard deviation, or a maximum coefficient of variation (standard deviation divided by the mean).

The approach to concentration equalization given above is completely general and therefore can be applied in any situation. A more restrictive situation, but one that is often reasonably
approximated in wastewater flows, is also instructive to investigate. Consider a situation where 
the flow is reasonably constant and the variation in concentration over time can be adequately 
described as a sine function. The concentration in such an influent is expressed mathematically 
as follows:

\[
c_{\text{in}}(t) = c_{\text{ave}} + c_{\text{amp}} \sin(\omega t)
\]  

where \(c_{\text{ave}}\) is the average concentration in the influent, \(c_{\text{amp}}\) is the amplitude of the variation, and 
\(\omega\) is the frequency of the sine function. The frequency, \(\omega\), is defined as \(\frac{2\pi}{T}\), where \(T\) is the 
period. If such an influent enters a CFSTR, it can be shown\(^9\) that the effluent concentration 
varies as follows:

\[
c_{\text{out}}(t) = c_{\text{ave}} + \frac{c_{\text{amp}}}{\sqrt{1 + \omega^2 \theta^2}} \sin(\omega t - \arctan(\omega \theta))
\]  

Equation 85 indicates that the effluent concentration has the same long term average 
concentration as the influent (because no reactions are considered to occur) and that it also has 
a sine variation like the influent. However, the amplitude of the sine curve is mitigated (divided) 
by the term \(\sqrt{1 + \omega^2 \theta^2}\), and the entire sine function is offset in time from the influent’s sine 
function by the arc tangent term. An example of these effects is shown in Figure 21. Results for 
two choices of the design detention time, \(\theta\), are shown. Generally, the offset of the effluent sine 
curve is unimportant; what is valuable is the reduction of the amplitude. For the examples shown 
in the figure, the amplitudes after equalization are 69% and 54% of the original amplitude with 
the 4- and 6-hour detention times, respectively.

---

\(^9\)The solution is reasonably straightforward using LaPlace transforms. The mass balance, as before, 
yields: 
\[
\frac{dc_{\text{out}}}{dt} = \frac{1}{\theta} c_{\text{in}} - \frac{1}{\theta} c_{\text{in}}.
\]  
To solve the equation, one needs to choose an initial condition. With the 
choice that \(c(0) = c_{\text{ave}}\), the solution contains a third term not shown in Equation 64. That extra term is 
\[
c(0) \frac{\omega t}{\theta} \exp\left(-\frac{t}{\theta}\right) \frac{1}{1 + \omega^2 \theta^2}.
\]  
The exponential decay with time makes this term infinitesimally small after a few 
periods and therefore irrelevant from the point of view of design, which is concerned with what happens 
over the long term.
Figure 21. Concentration Equalization of a Sinusoidal Influent.

If the desired reduction in the amplitude is known, the required detention time can be calculated directly from:

\[
\frac{c_{\text{amp,new}}}{c_{\text{amp,orig}}} = \frac{1}{\sqrt{1 + \omega^2 \theta^2}}
\]

If almost complete equalization is necessary, the time lag between the sine functions for the influent and effluent can be made to be half the period, so that blending a fraction of the unequalized influent with the equalization tank effluent results in a further reduction of the variation. This option, however, requires a large equalization volume. In a more general sense, the results in the figure demonstrate that the concentration in the effluent increases when the concentration of the influent is greater than that in the tank, and vice versa, i.e., the maxima and minima of the effluent curves occur at the intersections with the influent curve.

**Concurrent Flow and Concentration Equalization**

Some situations, especially those encountered in industrial wastewater treatment, require that both flow and concentration be equalized, i.e., the variation in each is unacceptably high. The approach to equalization analysis and design in such situations is a combination of the methods described for each separately. Concentration equalization occurs naturally in any CFSTR. Therefore, if a tank designed for flow equalization is provided with mixing,
concentration equalization will occur to some degree at all times except when the tank is (nearly) empty. How much equalization occurs can be predicted by Equation 83, except in this case, the detention time is no longer a constant, i.e. \( \theta = \theta(t) \). At any instant (or small interval), the mean hydraulic detention time is the ratio of the volume of water in the tank \( V(t) \) (from Equation 77b) and the effluent flow rate \( Q_{ave} \).

If a preliminary design volume is determined based on flow equalization alone, \( V(t) \) can be calculated as shown in Example 8 above (column F in the spreadsheet). The time-varying value of the hydraulic residence time, \( \theta(t) \), can then be computed as \( V(t)/Q_{ave} \), and Equation 87 (which is just Equation 83 modified to include the possibility that \( \theta(t) \) values depend on \( t \)) can be used recursively to compute \( c(t) \) throughout the period of flow and concentration variation:

\[
c(t + \Delta t) = c(t) \exp\left(-\frac{\Delta t}{\theta(t)}\right) + c_{in,\Delta t} \left(1 - \exp\left(-\frac{\Delta t}{\theta(t)}\right)\right)
\]

(87)

If the concentration equalization that results naturally from flow equalization is insufficient, then a greater equalization volume must be allowed for in design, causing some water to remain in the tank at all times. The value of \( V(t) \) for such a tank equals the value for the minimum size flow equalization tank (i.e., a tank that is designed for flow equalization alone) plus the incremental volume to improve concentration equalization. That is, \( V(t) \) in the larger tank equals \( V(t) \) as computed in column F of the spreadsheet in Example 8, plus a constant value \( V_{xc} \), the extra volume added for concentration equalization. Various values of \( V_{xc} \) can be considered, and the concentration versus time profile for each can be computed according to Equation 87 until an acceptable degree of concentration equalization is achieved.

**Example 10.** (a) The concentration of a contaminant during the period described in Example 8 varies as shown below. Compute the concentration equalization that results from flow equalization alone, for initial concentrations in the system of 100 and 200 mg/L.
(b) Assuming an initial concentration in the system of 100 mg/L, compare the fluctuations in the influent concentration with those in the effluent for basin volumes of 56.0 m³ (the minimum for flow equalization), 75 m³, and 150 m³.

Solution. (a) The concentration equalization for the two values of \( c_0 \), calculated according to Equation 87 is shown in Figure Ex10-1. Despite the relatively large difference in the initial values, the curves virtually coincide after just a few hours.

![Figure Ex10-1. Concentration equalization for two assumptions about the initial condition.](image-url)
(b) The three scenarios are characterized in Figure Ex 10-2, again based on application of Equation 87 to the given data. The results shown are for the expected concentrations during day 2, for an assumed concentration of 155 mg/L at the beginning of day 1. By focusing on the second day of operation, the effect of the arbitrary assumption regarding the concentration at the beginning of day 1 is effectively eliminated. Larger equalization volume clearly leads to more damping of the concentration. In the scenarios shown, the ratios of the maximum to the minimum concentration are 3.4, 2.2, 1.6, and 1.1 for equalization volumes 0, 56.5, 75, and 150 m³, respectively.

![Figure Ex10-2. Concentration equalization in the system described in Examples 8 and 9.](image)

When designing for either flow or concentration equalization, it is unwise to assume that a short period of observation will include the most extreme conditions ever experienced, so the preliminary data collection should be conducted over a large enough time span that these extremes are likely to be approached. If the flow and concentration vary in a somewhat regular pattern, the analysis can be conducted for each cycle to yield a value of the corresponding required volume for that cycle. These values can then be rank-ordered and converted to a cumulative probability distribution, as described above for flow equalization alone, and the design value can be chosen on the basis of a predetermined objective stated in statistical terms.
When designing for simultaneous flow and concentration equalization, the required volume depends on variations in both flow and concentration, and the risk that use of a small amount of data in the analysis will lead to an underestimate of the required equalization volume might be even higher than when designing for only one of these objectives. If the data for flow and concentration are negatively correlated (one increases when the other decreases), the design for flow equalization is likely to be sufficient for concentration equalization. If the data for these two variables are positively correlated, additional volume for concentration equalization is likely to be necessary, but the risk in the analysis is not much higher than in the flow equalization case; i.e., the range of required volumes will be equally well characterized with the same number of data points. However, if the variations in flow and concentration are not correlated, the risk that a small number of data points will not characterize the variation in required volume rises --- the data are less likely to include the extreme cases in which concentration is high when the flow is high and/or the volume in the tank is low. In this case, the designer needs to use a much greater number of data points in the analysis (if available), include a larger safety factor, design for a stricter objective, or use some combination of these approaches to ensure that the design meets the objectives.

2.6 SUMMARY

Various ways to evaluate and model the hydraulic characteristics (or mixing intensity) of reactors with continuous, steady flow have been presented in this chapter. The extremes of mixing intensity are represented as ideal reactor types: in an ideal plug-flow reactor (PFR), there is zero mixing in the axial direction, and in an ideal continuous flow stirred tank reactor (CFSTR), the mixing is infinitely intense. Both ideal and non-ideal reactors can be characterized most completely by their residence time distributions (the exit age distribution, \(E(t)\), and/or the cumulative age distribution, \(F(t)\)). Alternatively, non-ideal reactors can sometimes be modeled quite well either by modifying the assumptions applicable to the ideal reactors or by representing the non-ideal reactor as a linked network of ideal reactors. The models used most often to represent non-ideal reactors include:

1) a PFR with dispersion;

2) a number of equal-sized CFSTRs in series;

3) a combination of a few ideal CFSTRs and PFRs connected in series and/or parallel, perhaps with dead space included; or

4) a network of a large number of PFRs in parallel or in series with multiple inlets and outlets.

For ideal reactors (CFSTRs and PFRs), a single parameter (\(\theta\)) is sufficient to describe the reactor hydraulics completely. For the first two models for non-ideality listed above, one additional parameter is needed. In the latter two models, the number of parameters needed
depends on the number of model reactors used to represent the real system. At some point of complexity, one might decide that the advantage of modeling is small in comparison to using the empirical $E(t)$ or $F(t)$ data (obtained from tracer tests).

The predicted tracer output curve using the best-fit values of the defining parameters for each model can be compared with the actual output curve. If a model gives a good fit, then one might infer that the hydraulics of the reactor have been characterized reasonably well. If chosen models do not give a good match to the experimental output, the conclusion is that the actual flow pattern in the reactor is not like the model flow patterns investigated, and others may have to be postulated.

The decision of how many fitting parameters to use is a judgment which must be made based on the reliability of the residence time distribution data, the need for an accurate representation, and the cost of improving the fit. However, in carrying out the analysis and interpreting the result, one must keep in mind that each of the mathematical models is based on a physical model of the flow pattern. If the physical model is correct, the results predicted by the mathematical model will fit the experimental ones. There may also be incorrect models of the physical process which nevertheless fit the tracer data quite well. No one model is universally better than the others; the best model is the one that give a sufficiently accurate representation of the reactor behavior for the intended use.

Some real reactors often closely approximate one or another of the ideal cases. Rapid mix basins and flocculators are usually small open reactors with sufficient mixing to approximate a CFSTR. Packed beds (adsorption or ion exchange columns, deep bed filters, and perhaps even stripping towers) are close to being PFRs, although they are likely to have a small amount of dispersion. On the other hand, many reactors are non-ideal. Aeration basins have intense mixing induced by the air movement itself or by mechanical aerators, but this mixing is usually relatively local, and such basins might be modeled as a small number of CFSTRs in series. Baffled reactors, such as disinfection chambers, might also act as a number of CFSTRs in series. Reactors (or pipes or channels) with a high ratio of length to width (or depth) will approximate plug flow, although some dispersion is likely. For accurate description, tracer studies and the types of analyses presented in this chapter are necessary.

Analysis of reactor hydraulics is directly applicable to the design of reactors for flow and/or concentration equalization. In such situations, the varying water volume stored in the equalization basin can allow a steady flow of water to downstream processes, even if the influent flow rate varies significantly. Similarly, the dilution of influent into a substantial volume of water collected during earlier times dampens the fluctuations in the composition of the feed to downstream processes. Although equalization accomplishes no pollutant removal itself, it can greatly facilitate smooth operation of the pollutant removal steps that follow it.
APPENDIX

Introduction to Laplace Transforms as a Method of Solving (Certain) Differential Equations

The process of using Laplace transforms for solving differential equations is similar to the well-known process of using logarithms to solve exponential problems. (Unfortunately, in this age of calculators, some readers might be a bit rusty on the logarithm transform process, but the analogy is still useful.) Consider the following exponential equation:

\[ x^a = b \]

where \( a \) and \( b \) are known and \( x \) is the unknown. To solve, we take the logarithmic transform of both sides of the equation to obtain:

\[ \log x^a = \log b. \]

With this equation, we can say that we have transformed the problem onto the logarithmic plane. We then use the properties of logarithms to find:

\[ a \log x = \log b \]

and do algebra to find the solution on this logarithmic plane:

\[ \log x = \frac{\log b}{a} \]

Finally, we do the inverse transformation (i.e., take the antilog) to find the solution on the normal plane:

\[ x = \text{antilog} \left( \frac{\log b}{a} \right) \]

For example, following each of these steps to find the value of \( x \) in the equation:

\[ x^{3.7} = 196.4 \]

leads to the result \( x = 4.17 \).

The Laplace process for solving differential equations is similar to this logarithm process. We start with a differential equation in \( F(t) \); \( F(t) \) here is any (qualifying) function of time and not specifically the cumulative age distribution. The choice of this symbol for the function is perhaps unfortunate in this chapter, but its use by mathematicians is almost universal, and so it is used here for consistency with published mathematical tables. After taking the Laplace transform of both sides of the equation, we have an algebraic equation in the Laplace transform of \( F(t) \),
usually written alternately as either $\mathbf{L}\{F(t)\}$ or $f(s)$; the meaning of $s$ is explained below. We then do algebra on the Laplace plane to solve for $f(s)$, and finally perform the inverse Laplace transformation, often written as $\mathbf{L}^{-1}$, to find $F(t)$.

The Laplace transform is defined as follows:

$$\mathbf{L}\{F(t)\} \equiv f(s) \equiv \int_{t=0}^{\infty} e^{-st} F(t) \, dt$$

where $s$ is a number sufficiently large to make the integral converge (i.e., $s$ is not a variable), $F(t)$ must be continuous (or piecewise continuous) for all $t > 0$, and $F(t)$ must be bounded near $t = 0$. This transformation lends itself to situations in which $F(t)$ is defined for $t \geq 0$ (but not for $t < 0$).

Fortunately, one is not often required to use the definition and perform the integration to apply Laplace transforms. Operations with Laplace transforms and transforms of many common functions have been tabulated; a convenient (although small) listing is given in the CRC Standard Mathematical Tables, and several other listings are available in mathematical reference books.

The three most common operations (at least for use associated with tracers in environmental systems) are easily derived from the definition. They are as follows.

1. \(\mathbf{L}\{A F(t)\} = A f(s)\)

i.e., the Laplace transform of the product of a constant ($A$) and a function ($F(t)$) is the product of that constant and the Laplace transform of the function.

2. \(\mathbf{L}\{F_1(t) + F_2(t)\} = f_1(s) + f_2(s)\)

i.e., the Laplace transform of a sum is the sum of the associated Laplace transforms.

3. \(\mathbf{L}\{F'(t)\} = \mathbf{L}\left\{\frac{dF(t)}{dt}\right\} = s f(s) - F(0)\)

i.e., the Laplace transform of the derivative of a function is the product of $s$ and the Laplace transform of the function, minus the value of the function at time zero. (The $+0$ means that, if there is a discontinuity at zero, the limit as $t$ approaches zero from positive $t$ is used.) It is this operation that allows one to solve differential equations, because the transform of the time derivative of $F(t)$ is a function of $F(t)$ and not of the differential of $F(t)$.

A fourth operation is also often useful and was noted in the text, namely:
i.e., the Laplace transform of the convolution of two functions is the product of the Laplace transforms of the two functions.

A short listing of Laplace transforms of common functions is given in Table A1; again, the reader is referred to the CRC Standard Mathematical Tables or other reference books for additional listings.

**Table A1. Laplace Transform of Common Functions**

<table>
<thead>
<tr>
<th>Number</th>
<th>Function ((F(t)))</th>
<th>Laplace Transform of Function ((f(s)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>(\frac{1}{s})</td>
</tr>
<tr>
<td>2</td>
<td>(t)</td>
<td>(\frac{1}{s^2})</td>
</tr>
<tr>
<td>3</td>
<td>(\frac{t^{n-1}}{(n-1)!}) ((n = 1, 2, \ldots))</td>
<td>(\frac{1}{s^n})</td>
</tr>
<tr>
<td>4</td>
<td>(\frac{1}{\sqrt{\pi t}})</td>
<td>(\frac{1}{\sqrt{s}})</td>
</tr>
<tr>
<td>5</td>
<td>(t^{k-1}) ((k&gt;0))</td>
<td>(\frac{\Gamma(k)}{s^k})</td>
</tr>
<tr>
<td>6</td>
<td>(e^{at})</td>
<td>(\frac{1}{s-a})</td>
</tr>
<tr>
<td>7</td>
<td>(te^{at})</td>
<td>(\frac{1}{(s-a)^2})</td>
</tr>
<tr>
<td>8</td>
<td>(\frac{1}{(n-1)!} e^{at}) ((n = 1, 2, \ldots))</td>
<td>(\frac{1}{(s-a)^n})</td>
</tr>
<tr>
<td>9</td>
<td>(t^{k-1} e^{at}) ((k &gt; 0))</td>
<td>(\frac{\Gamma(k)}{(s-a)^k})</td>
</tr>
<tr>
<td>10</td>
<td>(\frac{1}{a-b} \left(e^{at} - e^{bt}\right))</td>
<td>(\frac{1}{(s-a)(s-b)})</td>
</tr>
</tbody>
</table>
Note: $\Gamma(k)$, which appears in transforms 5 and 9, is an integral function that, for positive values of $k$, is closely related to the factorial function. The formal definition and values of this function can be found in mathematical handbooks.

**Examples of the Use of Laplace Transforms**

**Example A-1. CFSTR with Pulse Input of Conservative Tracer at $t = 0$.**

The mass balance for this situation has been described in the chapter as follows:

$$V \frac{dc}{dt} = Q(0) - Qc$$

The reaction term is zero (the tracer is chosen to be non-reactive) and $c$ is a function of time. As indicated, the input concentration is zero after time zero. Dividing by the volume of the reactor, $V$, yields:

$$\frac{dc}{dt} = -\frac{1}{\theta} c$$

Taking the Laplace transform of each side gives:

$$s f(s) - c(0) = -\frac{1}{\theta} f(s)$$

where the concentration in the reactor at time zero, $(c(0))$, is $\frac{M}{V}$. Rearranging and factoring yields:

$$f(s) \left( s + \frac{1}{\theta} \right) = c(0)$$

Solving for $f(s)$, the solution on the Laplace plane, gives:
\[ f(s) = c(0) \frac{1}{s + \frac{1}{\theta}} \]

Using transform number (6) from the table of transforms given above with the value of \( a = -\frac{1}{\theta} \), and recognizing that the constant \( c(0) \) will carry through into the equation during the inverse transformation (operation 1 shown above) yields the following:

\[ c(t) = c(0) e^{-\theta t} \]

This result is, of course, the same as that found by straightforward integration and shown in the chapter. The value here is in recognizing the utility and simplicity of the Laplace transform method.

**Example A-2. CFSTR with Step Input of Conservative Tracer at Time Zero**

The mass balance for this situation (also given in the chapter) is:

\[ V \frac{dc}{dt} = Qc_{in} - Qc \]

where again \( c \) is a function of time, defined for all positive values of \( t \), so the Laplace transform method is useful. After dividing by \( V \), recognizing that \( \frac{Q}{V} = \frac{1}{\theta} \), and rearranging, this equation becomes:

\[ \frac{dc}{dt} + \frac{1}{\theta} c = \frac{c_{in}}{\theta} \]

Taking the Laplace transform of both sides of this equation yields:

\[ s f(s) - c(0) + \frac{1}{\theta} f(s) = \frac{c_{in}}{\theta} \frac{1}{s} \]

Recognizing that the concentration of tracer in the reactor at time 0 is zero (i.e., \( c(0) = 0 \)) and rearranging yields the solution on the Laplace plane:

\[ f(s) = \frac{c_{in}}{\theta} \frac{1}{s \left( s + \frac{1}{\theta} \right)} \]

Finally, applying transform #10 with \( a = 0 \) and \( b = -\frac{1}{\theta} \) gives the solution as:
\[ c(t) = \frac{c_{in}}{\theta} \frac{1}{0 + \frac{1}{\theta}} \left( e^{0t} - e^{-\theta t} \right) = c_{in} \left( 1 - e^{-\theta t} \right) \]

Of course, the solution is the same as derived earlier in two different ways (direct integration of the differential equation for the mass balance and by convolution of the \( E(t) \) function for the CFSTR and the input function). In comparison to the integration method, the Laplace transform method is easier primarily because, after the transformation, the solution is found via algebra rather than calculus. For more complex problems, this benefit is even more apparent than in the two examples given here. The CFSTRs-in-series problem (Problem 2) or the sinusoidal concentration equalization problem are examples where the solution methodology using Laplace transforms is considerably easier than other methods (e.g., the integrating factor method).
**Problems**

1. a) For a single CFSTR, at what value of \( t/\theta \) is the concentration of the effluent 85% of the initial concentration in a pulse input tracer test?

   (b) For the same system as in part (a), at what value of \( t/\theta \) is the total mass of tracer that has left the reactor 85% of the mass initially injected?

   (c) For a single CFSTR, at what value of \( t/\theta \) is the concentration of the effluent 85% of the influent concentration in a step input tracer test?

2. You are the owner of a company that makes a chemical product in a large, continuous flow stirred tank reactor (CFSTR) with a theoretical detention time \( \theta \). Production has not been as good as you had hoped and you have just hired a smart young engineer to help solve problems in the plant. She suggests putting baffles in the reactor, effectively dividing it into a series of CFSTRs.

   (a) Write out the mass balance and the resulting equation describing the effluent concentration as a function of time for a pulse input tracer test before any baffles are installed.

   (b) Repeat part (a) for the concentration of the effluent from the tank once one baffle has been installed, dividing the tank into two identical CFSTRs. Solve the problem using the convolution process described in the chapter.

   (c) Repeat part (a) for the concentration of the effluent from the tank once two baffles have been installed, dividing the tank into three identical CFSTRs.

   (d) Generalize your answers from parts (b) and (c) to develop the equation for a case where the tank is divided into \( n \) tanks.

   (e) Assume that the detention time in the tank is 60 minutes, and that the amount of tracer injected is enough to cause the initial concentration in the unbaffled tank to be 100 mg/L. Plot, on a single graph, the effluent tracer concentration as a function of time for the cases of zero, one, and four baffles installed, for \( t = 0 \) to 200 min.

3. The data shown below are from a tracer study of an aerobic sludge digester for which the design mean hydraulic residence time is several weeks. The work was conducted by Monteith and Stephens and was reported in J. Water Pollution Control Federation (v.53, p.78, 1981). A schematic showing the conceptual model they used to represent the digester is provided below. The total reactor volume (\( V_{\text{tot}} \)) is assumed to be distributed between an active fraction, \( f_a \) (\( V_a = f_a V_{\text{tot}} \)), and an inactive fraction (dead space). Also, a fraction \( f_{sc} \) of the total flow (\( f_{sc} Q_{\text{tot}} \)) is short-circuiting fluid that is assumed to pass through the reactor without mixing with the other fluid (as a plug); the flow entering the mixed portion of the reactor is designated \( f_m Q_{\text{tot}} \). The volume \( V_a \) (the active volume) is assumed to be well-mixed, and \( V_d \) is dead space; \( f_a \) is the
fraction of the total reactor volume that is well-mixed. \( c_o \) is defined as the mass of tracer injected divided by the total reactor volume.

\[
\frac{t}{\theta} \quad \frac{c}{c_o} \quad \frac{t}{\theta} \quad \frac{c}{c_o}
\]

<table>
<thead>
<tr>
<th>( t/\theta )</th>
<th>( c/c_o )</th>
<th>( t/\theta )</th>
<th>( c/c_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05( ^a )</td>
<td>1.78</td>
<td>0.38</td>
<td>0.33</td>
</tr>
<tr>
<td>0.05( ^a )</td>
<td>1.02</td>
<td>0.44</td>
<td>0.32</td>
</tr>
<tr>
<td>0.05( ^a )</td>
<td>0.79</td>
<td>0.47</td>
<td>0.29</td>
</tr>
<tr>
<td>0.05( ^a )</td>
<td>0.53</td>
<td>0.63</td>
<td>0.26</td>
</tr>
<tr>
<td>0.05( ^a )</td>
<td>0.53</td>
<td>0.78</td>
<td>0.15</td>
</tr>
<tr>
<td>0.05( ^a )</td>
<td>0.53</td>
<td>0.84</td>
<td>0.14</td>
</tr>
<tr>
<td>0.17</td>
<td>0.47</td>
<td>1.00</td>
<td>0.12</td>
</tr>
<tr>
<td>0.26</td>
<td>0.40</td>
<td>1.05</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\( ^a \) These samples were the first ones collected. They were collected in the order shown (top to bottom) at various times during the first sampling date, at \( t/\theta \) near 0.05.

\[
V_{sc} = f_{sc} Q_{tot} \\
Q_m = f_m Q_{tot} \\
V_a = f_a V \\
V_d = f_d V
\]

(a) Why were such vastly different tracer output concentrations obtained over a relatively short sampling period after the tracer was injected (the first six data points)?

(b) Recall that, for any tracer output curve, \( \int_{t_1}^{t_2} Q c dt \) is the total mass of tracer exiting the reactor from time \( t_1 \) to time \( t_2 \). By manipulating that integral, determine the significance of the area under a tracer output curve that is normalized in the way that the authors of this study normalized their data, i.e., explain in words the significance of the integral \( \int_{t}^{\infty} \frac{c}{c_o} \frac{dt}{\theta} \). What value would you expect to obtain for \( \int_{t}^{\infty} \frac{c}{c_o} \frac{dt}{\theta} \) for any reactor?

(c) Write a mass balance around the active portion of the reactor, and develop an expression for the tracer concentration exiting that portion of the reactor (i.e., \( c_a(t) \)) in terms of \( Q, V, f_m, \) and \( f_a \).
(d) Write another mass balance, this time around the point where the short-circuiting fluid joins the fluid that has passed through the active part of the reactor, and develop an expression for the concentration of tracer exiting the entire reactor as a function of time \(c(t)\), in terms of the parameters shown in the system definition diagram. Note that this is the concentration that would be detected by the investigators, who sampled a mixture of whatever water exited the reactor.

(e) Estimate the value of the integral \(\int_0^\infty \frac{c}{c_0} \frac{dt}{\theta}\) for the experimental data. To do this, you will need to extrapolate the given data back to time zero and forward to times well beyond when the investigators stopped collecting data. Try to carry out this extrapolation using the equation you developed in part (d). Why is the experimental value of \(\int_0^\infty \frac{c}{c_0} \frac{dt}{\theta}\) different from the expected value determined in part b?

(f) Use the experimental data in conjunction with the equation you developed in part (d) to estimate the values of \(f_{sc}\), and \(f_a\) in the digester.

(g) It is not clear whether the investigators captured the peak of the tracer output as the short-circuiting fluid exited the system. Use your results to evaluate whether they did.

4. Draw a flowsheet to model a reactor with 10 percent of the tank volume being “nearly-dead” space with a residence time of 20 \(\theta\) and 30 percent of the influent flow short-circuiting through the reactor with a residence time of 0.1 \(\theta\), where \(\theta\) is the hydraulic residence time based on the total volume of water in the reactor and the total flow through the reactor. Assume that the overall reactor can be modeled as three ideal reactors in parallel-- CFSTRs representing the main part of the reactor and the dead space, and a PFR representing the short-circuiting fluid. Write the equation and draw a curve showing the product \(E(t) \theta\) as a function of \(t/\theta\) for the reactor.

5. Determine and plot the \(E(t)\) curve for a reactor system consisting of two CFSTRs in series, with hydraulic detention times of one hour and two hours, respectively. Compare the result with that for the same reactors in the reverse order (or, equivalently, for the same reactors with the direction of flow reversed). You may wish to use the approach of Problem 2 as a guide.

6. There are a number of situations in which two reactors may operate semi-independently. For instance, in a stratified lake, the epilimnion and hypolimnion may have quite different compositions and reaction characteristics, yet have some continuous, relatively low level of water exchange between them across the thermocline. Similarly, engineered reactors often have zones in corners or along edges that are largely, but not completely, isolated from the “core.” Consider such a reactor whose total volume is 100 m\(^3\). Of this volume, 80 m\(^3\) is a well-mixed core zone, and 20 m\(^3\) is distributed in various zones that are well-mixed themselves and may all
be considered equivalent to one another but are not thoroughly mixed with the core. The flow pattern is such that the flow of 5 m$^3$/min into and out of the reactor enters and leaves through pipes that are in the core zone. The exchange of fluid between the core and secondary zones is at a steady rate of about 0.1 m$^3$/min. (Note: the performance of this system is investigated further in the problems at the end of Chapter 4.)

(a) Ten grams of a tracer is injected as a spike into the inlet pipe at $t = 0$. Write the mass balance equations describing the concentration of tracer in each part of the reactor as a function of time, and calculate and plot those concentrations from $t = 0$ until the time when 9.9 g of tracer has exited the overall reactor. Show the results for both reactors on the same graph. Discuss briefly the significance of the point of intersection of the two lines. (Hint: the mass balances yield two simultaneous differential equations that can be solved simultaneously, once initial conditions are established. Once the equations are identified, they can be solved any of several ways, including numerically, by direct integration, or by integration in Laplace space (which might be the easiest approach)).

(b) If you were to model the reactor as a group of equal-volume CFSTRs in series, how many CFSTRs would you use in the model?

7. A hydraulic study of the flow-through characteristics of a sedimentation basin was made using NaCl as a tracer by injecting a slug of salt at the inlet and measuring the salt concentration at the outlet. The tank was designed to operate as a PFR. The results of the study are shown below:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentration of NaCl (mg/L at outlet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>trace</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>30</td>
<td>130</td>
</tr>
<tr>
<td>40</td>
<td>110</td>
</tr>
<tr>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>120</td>
<td>30</td>
</tr>
<tr>
<td>140</td>
<td>20</td>
</tr>
<tr>
<td>160</td>
<td>10</td>
</tr>
<tr>
<td>180</td>
<td>5</td>
</tr>
</tbody>
</table>

(Note: the performance of this system is investigated further in the problems at the end of Chapter 4.)
(a) What is the mean fluid residence time in the tank? Can you draw any conclusion about short-circuiting or dead space in the tank?

(b) Determine the appropriate parameter values to model the tracer output as best you can for the following four physical models of the system:

i) a PFR with dispersion, for open boundaries.

ii) a PFR with dispersion, for closed boundaries.

iii) seven ideal PFRs in parallel.

iv) n equal sized CFSTRs in series.

(c) Draw $E(t)$ and $F(t)$ vs. $t/\theta$ curves for the model systems characterized in parts i, iii, and iv in part (b), i.e., the expected $E(t)$ and $F(t)$ curve for each model, if that model represented the system exactly. Compare these curves with the experimental $E(t)$ and $F(t)$ data. Would you choose of these models to represent the data? If so, which one? If not, what other model might you test?

Hint: $c_o$ can be found by writing an expression for $M_{in}$ as a function of $c_o$, writing another expression for $M_{out}$ in terms of the (known) effluent tracer concentrations, and assuming that $M_{in} = M_{out}$.

8. The average hydraulic residence time in a system can be computed by injecting a tracer and analyzing its concentration in the output stream. During such tests, if the reactor is not an ideal PFR, some of the tracer will remain in the reactor indefinitely, at least in theory. In such cases, it is often unclear exactly how long one should collect and analyze the data in order to get a good estimate of the true residence time.

Consider a tracer test on an ideal CFSTR with an average hydraulic residence time of 60 minutes.

(a) Determine the average hydraulic residence time that you would compute based on the tracer output, if you collected perfect data starting at $t = 0$, but stopped collecting data at various times up to $10 \theta$. Recalling that $\tilde{t}$ can be computed from the tracer data based on either $M_{in}$ or $M_{out}$ as the measure of total tracer used in the test, carry out the calculations twice, once using $M_{in}$ and once using $M_{out}$.

(b) Repeat the calculations in part (a), but assume that a systematic error occurred in the analysis of tracer, so that all the measured values were 5% lower that the actual values.

(c) How long would you have to collect data in order to compute a value of $\tilde{T}$ that is within 10% of $\theta$?
9. Prove using the convolution integral that the responses of the reactor systems shown in Figures 17a, b, and c to a pulse input of tracer are identical.

10. During an 8-hour testing period, an industrial plant produced wastewater at a rate and with a contaminant concentration that varied as shown in the following table.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Avg. Flow (m³/h)</th>
<th>Avg. Conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1</td>
<td>11</td>
<td>109</td>
</tr>
<tr>
<td>1-2</td>
<td>12</td>
<td>121</td>
</tr>
<tr>
<td>2-3</td>
<td>14</td>
<td>140</td>
</tr>
<tr>
<td>3-4</td>
<td>18</td>
<td>164</td>
</tr>
<tr>
<td>4-5</td>
<td>20</td>
<td>202</td>
</tr>
<tr>
<td>5-6</td>
<td>25</td>
<td>201</td>
</tr>
<tr>
<td>6-7</td>
<td>50</td>
<td>124</td>
</tr>
<tr>
<td>7-8</td>
<td>10</td>
<td>112</td>
</tr>
</tbody>
</table>

(a) How large a tank is required to achieve complete flow equalization? Plot the volume of water in such tank as a function of time, using 5-minute intervals.

(b) What is the long-term average contaminant concentration in the wastewater?

(c) The treatment process works best if the maximum concentration entering the process is no greater than 1.5 times the minimum concentration (i.e., \( c_{\text{max}}/c_{\text{min}} < 1.5 \)). If the flow equalization tank is a CFSTR, will it achieve this degree of concentration equalization? If not, approximately how large must the tank be to do so?

(c) What is the key assumption that was implicit in the analysis performed to answer parts (a) and (c)?

REFERENCES


Wehner and Wilhelm (1956)

Levenspiel (1972).