Distributions of Residence Times for Chemical Reactors

DVD 13

> Nothing in life is to be feared. It is only to be understood.
> Marie Curie

Overview In this chapter we learn about nonideal reactors, that is, reactors that do not follow the models we have developed for ideal CSTRs, PFRs, and PBRs. In Part 1 we describe how to characterize these nonideal reactors using the residence time distribution function $E(t)$, the mean residence time t_m, the cumulative distribution function $F(t)$, and the variance σ^2. Next we evaluate $E(t)$, $F(t)$, t_m, and σ^2 for ideal reactors, so that we have a reference point as to how far our real (i.e., nonideal) reactor is off the norm from an ideal reactor. The functions $E(t)$ and $F(t)$ will be developed for ideal PPRs, CSTRs and laminar flow reactors. Examples are given for diagnosing problems with real reactors by comparing t_m and $E(t)$ with ideal reactors. We will then use these ideal curves to help diagnose and troubleshoot bypassing and dead volume in real reactors.

In Part 2 we will learn how to use the residence time data and functions to make predictions of conversion and exit concentrations. Because the residence time distribution is not unique for a given reaction system, we must use new models if we want to predict the conversion in our nonideal reactor. We present the five most common models to predict conversion and then close the chapter by applying two of these models, the segregation model and the maximum mixedness model, to single and to multiple reactions.

After studying this chapter the reader will be able to describe the cumulative $F(t)$ and external age $E(t)$ and residence-time distribution functions, and to recognize these functions for PFR, CSTR, and laminar flow reactors. The reader will also be able to apply these functions to calculate the conversion and concentrations exiting a reactor using the segregation model and the maximum mixedness model for both single and multiple reactions.

From *Elements of Chemical Reaction Engineering, Fourth Edition,* by H. Scott Fogler.

13.1 General Characteristics

The reactors treated in the book thus far—the perfectly mixed batch, the plug-flow tubular, the packed bed, and the perfectly mixed continuous tank reactors—have been modeled as ideal reactors. Unfortunately, in the real world we often observe behavior very different from that expected from the exemplar; this behavior is true of students, engineers, college professors, and chemical reactors. Just as we must learn to work with people who are not perfect, so the reactor analyst must learn to diagnose and handle chemical reactors whose performance deviates from the ideal. Nonideal reactors and the principles behind their analysis form the subject of this chapter and the next.

We want to analyze and characterize nonideal reactor behavior.

Part 1 Characterization and Diagnostics

The basic ideas that are used in the distribution of residence times to characterize and model nonideal reactions are really few in number. The two major uses of the residence time distribution to characterize nonideal reactors are

1. To diagnose problems of reactors in operation
2. To predict conversion or effluent concentrations in existing/available reactors when a new reaction is used in the reactor

System 1 In a gas–liquid continuous-stirred tank reactor (Figure 13-1), the gaseous reactant was bubbled into the reactor while the liquid reactant was fed through an inlet tube in the reactor's side. The reaction took place at the gas–liquid interface of the bubbles, and the product was a liquid. The continuous liquid phase could be regarded as perfectly mixed, and the reaction rate was proportional to the total bubble surface area. The surface area of a particular bubble depended on the time it had spent in the reactor. Because of their different sizes, some gas bubbles escaped from the reactor almost immediately, while others spent so much time in the reactor that they were almost com-

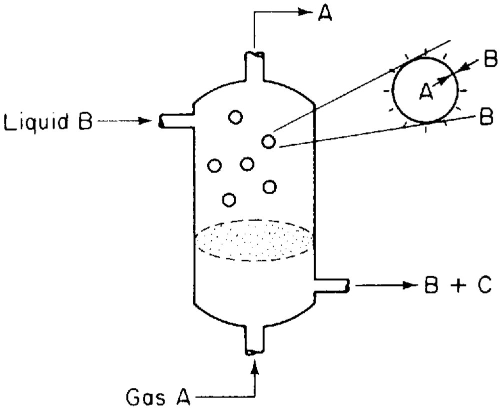

Figure 13-1 Gas–liquid reactor.

pletely consumed. The time the bubble spends in the reactor is termed the *bubble residence time*. What was important in the analysis of this reactor was not the average residence time of the bubbles but rather the residence time of each bubble (i.e., the residence time distribution). The total reaction rate was found by summing over all the bubbles in the reactor. For this sum, the distribution of residence times of the bubbles leaving the reactor was required. An understanding of residence-time distributions (RTDs) and their effects on chemical reactor performance is thus one of the necessities of the technically competent reactor analyst.

Not all molecules are spending the same time in the reactor.

System 2 A packed-bed reactor is shown in Figure 13-2. When a reactor is packed with catalyst, the reacting fluid usually does not flow through the reactor uniformly. Rather, there may be sections in the packed bed that offer little resistance to flow, and as a result a major portion of the fluid may channel through this pathway. Consequently, the molecules following this pathway do not spend as much time in the reactor as those flowing through the regions of high resistance to flow. We see that there is a distribution of times that molecules spend in the reactor in contact with the catalyst.

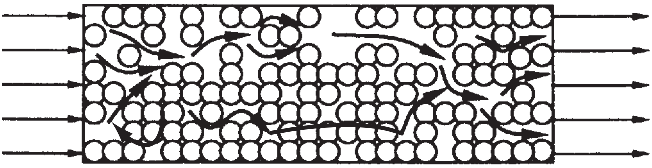

Figure 13-2 Packed-bed reactor.

System 3 In many continuous-stirred tank reactors, the inlet and outlet pipes are close together (Figure 13-3). In one operation it was desired to scale up pilot plant results to a much larger system. It was realized that some short circuiting occurred, so the tanks were modeled as perfectly mixed CSTRs with a bypass stream. In addition to short circuiting, stagnant regions (dead zones) are often encountered. In these regions there is little or no exchange of material with the well-mixed regions, and, consequently, virtually no reaction occurs

We want to find ways of determining the dead volume and amount of bypassing.

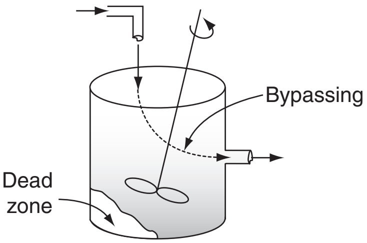

Figure 13-3 CSTR.

there. Experiments were carried out to determine the amount of the material effectively bypassed and the volume of the dead zone. A simple modification of an ideal reactor successfully modeled the essential physical characteristics of the system and the equations were readily solvable.

The three concepts
- RTD
- Mixing
- Model

Three concepts were used to describe nonideal reactors in these examples: *the distribution of residence times in the system, the quality of mixing*, and *the model used to describe the system*. All three of these concepts are considered when describing deviations from the mixing patterns assumed in ideal reactors. The three concepts can be regarded as characteristics of the mixing in nonideal reactors.

One way to order our thinking on nonideal reactors is to consider modeling the flow patterns in our reactors as either CSTRs or PFRs as a *first* approximation. In real reactors, however, nonideal flow patterns exist, resulting in ineffective contacting and lower conversions than in the case of ideal reactors. We must have a method of accounting for this nonideality, and to achieve this goal we use the next-higher level of approximation, which involves the use of *macromixing* information (RTD) (Sections 13.1 to 13.4). The next level uses microscale (*micromixing*) information to make predictions about the conversion in nonideal reactors. We address this third level of approximation in Sections 13.6 to 13.9 and in Chapter 14.

13.1.1 Residence-Time Distribution (RTD) Function

The idea of using the distribution of residence times in the analysis of chemical reactor performance was apparently first proposed in a pioneering paper by MacMullin and Weber.[1] However, the concept did not appear to be used extensively until the early 1950s, when Prof. P. V. Danckwerts[2] gave organizational structure to the subject of RTD by defining most of the distributions of interest. The ever-increasing amount of literature on this topic since then has generally followed the nomenclature of Danckwerts, and this will be done here as well.

In an ideal plug-flow reactor, all the atoms of material leaving the reactor have been inside it for exactly the same amount of time. Similarly, in an ideal batch reactor, all the atoms of materials within the reactor have been inside it for an identical length of time. The time the atoms have spent in the reactor is called the *residence time* of the atoms in the reactor.

The idealized plug-flow and batch reactors are the only two classes of reactors in which all the atoms in the reactors have the same residence time. In all other reactor types, the various atoms in the feed spend different times inside the reactor; that is, there is a distribution of residence times of the material within the reactor. For example, consider the CSTR; the feed introduced into a CSTR at any given time becomes completely mixed with the material already in the reactor. In other words, some of the atoms entering the CSTR

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[1] R. B. MacMullin and M. Weber, Jr., *Trans. Am. Inst. Chem. Eng.*, *31*, 409 (1935).

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

The "RTD": Some molecules leave quickly, others overstay their welcome.

leave it almost immediately because material is being continuously withdrawn from the reactor; other atoms remain in the reactor almost forever because all the material is never removed from the reactor at one time. Many of the atoms, of course, leave the reactor after spending a period of time somewhere in the vicinity of the mean residence time. In any reactor, the distribution of residence times can significantly affect its performance.

We will use the RTD to characterize nonideal reactors.

The *residence-time distribution* (RTD) of a reactor is a characteristic of the mixing that occurs in the chemical reactor. There is no axial mixing in a plug-flow reactor, and this omission is reflected in the RTD. The CSTR is thoroughly mixed and possesses a far different kind of RTD than the plug-flow reactor. As will be illustrated later, not all RTDs are unique to a particular reactor type; markedly different reactors can display identical RTDs. Nevertheless, the RTD exhibited by a given reactor yields distinctive clues to the type of mixing occurring within it and is one of the most informative characterizations of the reactor.

13.2 Measurement of the RTD

The RTD is determined experimentally by injecting an inert chemical, molecule, or atom, called a *tracer*, into the reactor at some time $t = 0$ and then measuring the tracer concentration, C, in the effluent stream as a function of time. In addition to being a nonreactive species that is easily detectable, the tracer should have physical properties similar to those of the reacting mixture and be completely soluble in the mixture. It also should not adsorb on the walls or other surfaces in the reactor. The latter requirements are needed so that the tracer's behavior will honestly reflect that of the material flowing through the reactor. Colored and radioactive materials along with inert gases are the most common types of tracers. The two most used methods of injection are *pulse input* and *step input*.

Use of tracers to determine the RTD

13.2.1 Pulse Input Experiment

In a pulse input, an amount of tracer N_0 is suddenly injected in one shot into the feedstream entering the reactor in as short a time as possible. The outlet concentration is then measured as a function of time. Typical concentration–time curves at the inlet and outlet of an arbitrary reactor are shown in Figure 13-4. The effluent concentration–time curve is referred to as the C curve in RTD analysis. We shall analyze the injection of a tracer pulse for a single-input and single-output system in which *only flow* (i.e., no dispersion) carries the tracer material across system boundaries. First, we choose an increment of time Δt sufficiently small that the concentration of tracer, $C(t)$, exiting between time t and $t + \Delta t$ is essentially the same. The amount of tracer material, ΔN, leaving the reactor between time t and $t + \Delta t$ is then

The ***C*** curve

$$\Delta N = C(t)v\,\Delta t \tag{13-1}$$

where v is the effluent volumetric flow rate. In other words, ΔN is the amount of material exiting the reactor that has spent an amount of time between t and $t + \Delta t$ in the reactor. If we now divide by the total amount of material that was injected into the reactor, N_0, we obtain

$$\frac{\Delta N}{N_0} = \frac{vC(t)}{N_0}\,\Delta t \tag{13-2}$$

which represents the fraction of material that has a residence time in the reactor between time t and $t + \Delta t$.

For pulse injection we define

$$E(t) = \frac{vC(t)}{N_0} \tag{13-3}$$

so that

$$\frac{\Delta N}{N_0} = E(t)\,\Delta t \tag{13-4}$$

Interpretation of $E(t)\,dt$

The quantity ***E(t)*** is called the ***residence-time distribution function***. It is the function that describes in a quantitative manner how much time different fluid elements have spent in the reactor. The quantity $E(t)dt$ is the fraction of fluid exiting the reactor that has spent between time t and $t + dt$ inside the reactor.

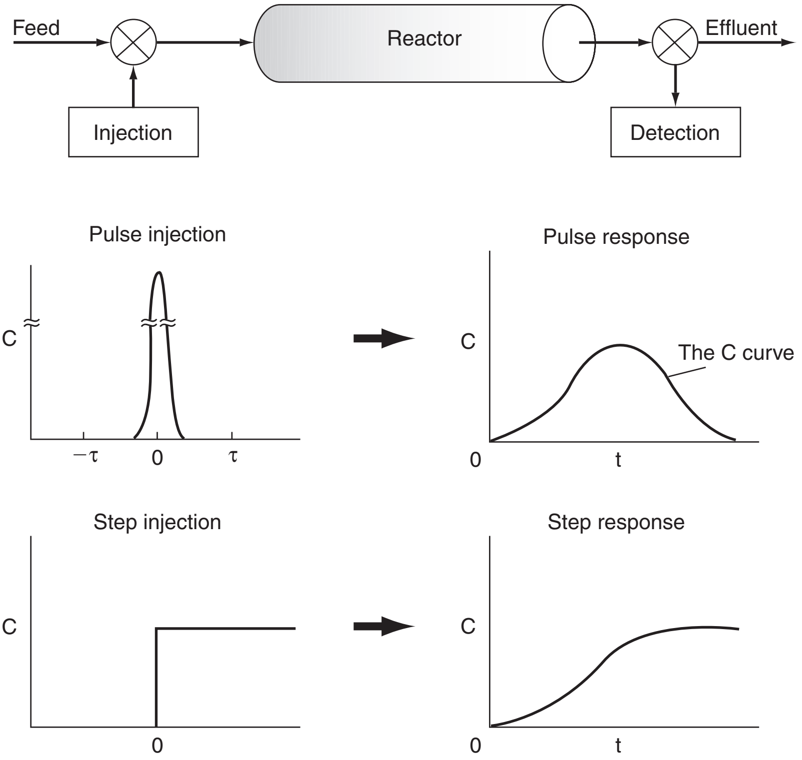
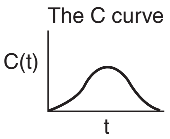


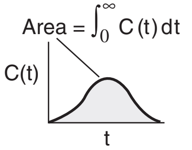
Figure 13-4 RTD measurements.



If N_0 is not known directly, it can be obtained from the outlet concentration measurements by summing up all the amounts of materials, ΔN, between time equal to zero and infinity. Writing Equation (13-1) in differential form yields

$$dN = vC(t)\,dt \tag{13-5}$$

and then integrating, we obtain

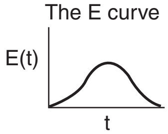


$$N_0 = \int_0^\infty vC(t)\,dt \tag{13-6}$$

We find the RTD function, ***E(t)***, from the tracer concentration ***C(t)***

The volumetric flow rate v is usually constant, so we can define $E(t)$ as

$$\boxed{E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}} \tag{13-7}$$



The integral in the denominator is the area under the C curve.

An alternative way of interpreting the residence-time function is in its integral form:

$$\left[\begin{array}{c}\text{Fraction of material leaving the reactor}\\ \text{that has resided in the reactor}\\ \text{for times between } t_1 \text{ and } t_2\end{array}\right] = \int_{t_1}^{t_2} E(t)\,dt$$

We know that the fraction of all the material that has resided for a time t in the reactor between $t = 0$ and $t = \infty$ is 1; therefore,

Eventually all must leave

$$\int_0^\infty E(t)\,dt = 1 \tag{13-8}$$

The following example will show how we can calculate and interpret $E(t)$ from the effluent concentrations from the response to a pulse tracer input to a real (i.e., nonideal) reactor.

Example 13–1 Constructing the C(t) and E(t) Curves

A sample of the tracer hytane at 320 K was injected as a pulse to a reactor, and the effluent concentration was measured as a function of time, resulting in the data shown in Table E13–1.1.

Pulse Input

TABLE E13–1.1 TRACER DATA

t (min)	0	1	2	3	4	5	6	7	8	9	10	12	14
C (g/m^3)	0	1	5	8	10	8	6	4	3.0	2.2	1.5	0.6	0

The measurements represent the exact concentrations at the times listed and not average values between the various sampling tests. **(a)** Construct figures showing $C(t)$ and $E(t)$ as functions of time. **(b)** Determine both the fraction of material leaving the reactor that has spent between 3 and 6 min in the reactor and the fraction of material leaving that has spent between 7.75 and 8.25 min in the reactor, and **(c)** determine the fraction of material leaving the reactor that has spent 3 min or less in the reactor.

Solution

(a) By plotting C as a function of time, using the data in Table E13-1.1, the curve shown in Figure E13-1.1 is obtained.

The ***C*** curve

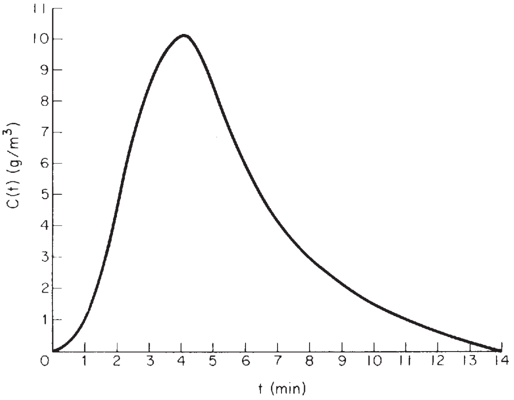


Figure E13-1.1 The C curve.

To obtain the $E(t)$ curve from the $C(t)$ curve, we just divide $C(t)$ by the integral $\int_0^\infty C(t)\,dt$, which is just the area under the C curve. Because one quadrature (integration) formula will not suffice over the entire range of data in Table E13-1.1, we break the data into two regions, 0-10 minutes and 10 to 14 minutes. The area under the C curve can now be found using the numerical integration formulas (A-21) and (A-25) in Appendix A.4:

$$\int_0^\infty C(t)\,dt = \int_0^{10} C(t)\,dt + \int_{10}^{14} C(t)\,dt \tag{E13-1.1}$$

$$\begin{aligned}\int_0^{10} C(t)\,dt &= \tfrac{1}{3}[1(0)+4(1)+2(5)+4(8)\\ &\quad +2(10)+4(8)+2(6)\\ &\quad +4(4)+2(3.0)+4(2.2)+1(1.5)]\\ &= 47.4\ \text{g}\cdot\text{min/m}^3\end{aligned} \tag{A-25}$$

$$\int_{10}^{14} C(t)\,dt = \tfrac{2}{3}[1.5+4(0.6)+0] = 2.6\ \text{g}\cdot\text{min/m}^3 \tag{A-21}$$

$$\int_0^\infty C(t)\,dt = 50.0\ \text{g}\cdot\text{min/m}^3 \tag{E13-1.2}$$

We now calculate

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C(t)}{50\ \text{g}\cdot\text{min/m}^3} \tag{E13-1.3}$$

with the following results:

Table E13–1.2 $C(t)$ and $E(t)$

t (min)	1	2	3	4	5	6	7	8	9	10	12	14
$C(t)$ (g/m^3)	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
$E(t)$ (min^{-1})	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

(b) These data are plotted in Figure E13-1.2. The shaded area represents the fraction of material leaving the reactor that has resided in the reactor between 3 and 6 min.

The ***E*** curve

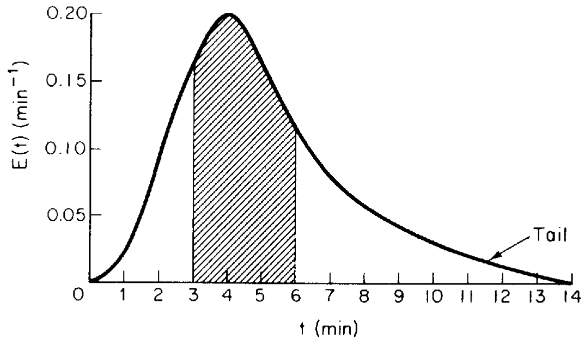


Figure E13-1.2 Analyzing the E curve.

Using Equation (A-22) in Appendix A.4:

$$\int_3^6 E(t)\,dt = \text{shaded area} \tag{A-22}$$

$$= \tfrac{3}{8}\Delta t(f_1 + 3f_2 + 3f_3 + f_4)$$

$$= \tfrac{3}{8}(1)[0.16 + 3(0.2) + 3(0.16) + 0.12] = 0.51$$

Evaluating this area, we find that 51% of the material leaving the reactor spends between 3 and 6 min in the reactor.

Because the time between 7.75 and 8.25 min is very small relative to a time scale of 14 min, we shall use an alternative technique to determine this fraction to reinforce the interpretation of the quantity $E(t)\,dt$. The average value of $E(t)$ between these times is 0.06 min^{-1}:

$$E(t)\,dt = (0.06\ \text{min}^{-1})(0.5\ \text{min}) = 0.03$$

The tail

Consequently, 3.0% of the fluid leaving the reactor has been in the reactor between 7.75 and 8.25 min. The long-time portion of the $E(t)$ curve is called the *tail*. In this example the tail is that portion of the curve between *say* 10 and 14 min.

(c) Finally, we shall consider the fraction of material that has been in the reactor for a time t or less, that is, the fraction that has spent between 0 and t minutes in the reactor. This fraction is just the shaded area under the curve up to $t = t$ minutes. This area is shown in Figure E13-1.3 for $t = 3$ min. Calculating the area under the curve, we see that 20% of the material has spent 3 min *or less* in the reactor.

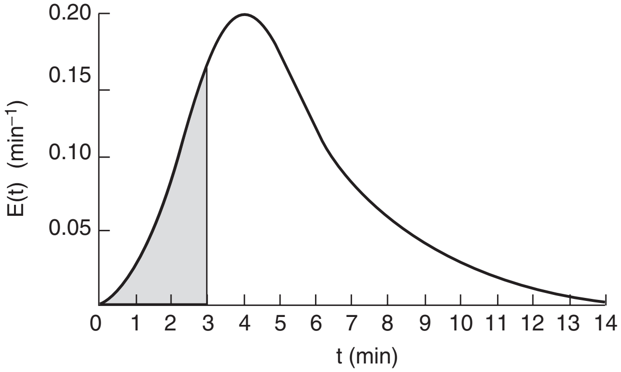


Figure E13-1.3 Analyzing the E curve.

Drawbacks to the pulse injection to obtain the RTD

The principal difficulties with the pulse technique lie in the problems connected with obtaining a reasonable pulse at a reactor's entrance. The injection must take place over a period which is very short compared with residence times in various segments of the reactor or reactor system, and there must be a negligible amount of dispersion between the point of injection and the entrance to the reactor system. If these conditions can be fulfilled, this technique represents a simple and direct way of obtaining the RTD.

There are problems when the concentration–time curve has a long tail because the analysis can be subject to large inaccuracies. This problem principally affects the denominator of the right-hand side of Equation (13-7) [i.e., the integration of the $C(t)$ curve]. It is desirable to extrapolate the tail and analytically continue the calculation. The tail of the curve may sometimes be approximated as an exponential decay. The inaccuracies introduced by this assumption are very likely to be much less than those resulting from either truncation or numerical imprecision in this region. Methods of fitting the tail are described in the *Professional Reference Shelf* 13 R.1.

Reference Shelf

13.2.2 Step Tracer Experiment

Now that we have an understanding of the meaning of the RTD curve from a pulse input, we will formulate a more general relationship between a time-varying tracer injection and the corresponding concentration in the effluent. We shall state without development that the output concentration from a vessel is related to the input concentration by the convolution integral:[3]

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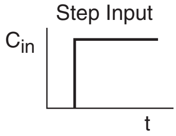
[3] A development can be found in O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. (New York: Wiley, 1972), p. 263.

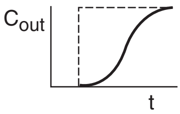
$$C_{\text{out}}(t) = \int_0^t C_{\text{in}}(t - t')E(t')\,dt \tag{13-9}$$

The inlet concentration most often takes the form of either a perfect *pulse input* (Dirac delta function), *imperfect pulse injection* (see Figure 13-4), or a *step input*.

Just as the RTD function $E(t)$ can be determined directly from a pulse input, the cumulative distribution $F(t)$ can be determined directly from a step input. We will now analyze a *step input* in the tracer concentration for a system with a constant volumetric flow rate. Consider a constant rate of tracer addition to a feed that is initiated at time $t = 0$. Before this time no tracer was added to the feed. Stated symbolically, we have



$$C_0(t) = \begin{cases} 0 & t < 0 \\ (C_0)\text{ constant} & t \geq 0 \end{cases}$$



The concentration of tracer in the feed to the reactor is kept at this level until the concentration in the effluent is indistinguishable from that in the feed; the test may then be discontinued. A typical outlet concentration curve for this type of input is shown in Figure 13-4.

Because the inlet concentration is a constant with time, C_0, we can take it outside the integral sign, that is,

$$C_{\text{out}} = C_0 \int_0^t E(t')\,dt'$$

Dividing by C_0 yields

$$\left[\frac{C_{\text{out}}}{C_0}\right]_{\text{step}} = \int_0^t E(t')\,dt' = F(t)$$

$$F(t) = \left[\frac{C_{\text{out}}}{C_0}\right]_{\text{step}} \tag{13-10}$$

We differentiate this expression to obtain the RTD function $E(t)$:

$$E(t) = \frac{d}{dt}\left[\frac{C(t)}{C_0}\right]_{\text{step}} \tag{13-11}$$

Advantages and drawbacks to the step injection

The positive step is usually easier to carry out experimentally than the pulse test, and it has the additional advantage that the total amount of tracer in the feed over the period of the test does not have to be known as it does in the pulse test. One possible drawback in this technique is that it is sometimes difficult to maintain a constant tracer concentration in the feed. Obtaining the RTD from this test also involves differentiation of the data and presents an additional and probably more serious drawback to the technique, because differentiation of data can, on occasion, lead to large errors. A third problem lies with the large amount of tracer required for this test. If the tracer is very expensive, a pulse test is almost always used to minimize the cost.

Other tracer techniques exist, such as negative step (i.e., elution), frequency-response methods, and methods that use inputs other than steps or pulses. These methods are usually much more difficult to carry out than the ones presented and are not encountered as often. For this reason they will not be treated here, and the literature should be consulted for their virtues, defects, and the details of implementing them and analyzing the results. A good source for this information is Wen and Fan.[4]

13.3 Characteristics of the RTD

From $E(t)$ we can learn how long different molecules have been in the reactor.

Sometimes $E(t)$ is called the *exit-age distribution function*. If we regard the "age" of an atom as the time it has resided in the reaction environment, then $E(t)$ concerns the age distribution of the effluent stream. It is the most used of the distribution functions connected with reactor analysis because it characterizes the lengths of time various atoms spend at reaction conditions.

13.3.1 Integral Relationships

The fraction of the exit stream that has resided in the reactor for a period of time shorter than a given value t is equal to the sum over all times less than t of $E(t)\,\Delta t$, or expressed continuously,

The cumulative RTD function $F(t)$

$$\int_0^t E(t)\,dt = \begin{bmatrix} \text{Fraction of effluent} \\ \text{that has been in reactor} \\ \text{for less than time } t \end{bmatrix} = F(t) \qquad (13\text{-}12)$$

Analogously, we have

$$\int_t^\infty E(t)\,dt = \begin{bmatrix} \text{Fraction of effluent} \\ \text{that has been in reactor} \\ \text{for longer than time } t \end{bmatrix} = 1 - F(t) \qquad (13\text{-}13)$$

Because t appears in the integration limits of these two expressions, Equations (13-12) and (13-13) are both functions of time. Danckwerts[5] defined Equation (13-12) as a *cumulative distribution function and called it* $F(t)$. We can calculate $F(t)$ at various times t from the area under the curve of an $E(t)$ versus t plot. For example, in Figure E13-1.3 we saw that $F(t)$ at 3 min was 0.20, meaning that 20% of the molecules spent 3 min or less in the reactor. Similarly, using Figure E13-1.3 we calculate $F(t) = 0.4$ at 4 minutes. We can continue in this manner to construct $F(t)$. The shape of the $F(t)$ curve is shown in Figure 13-5. One notes from this curve that 80% $[F(t)]$ of the molecules spend 8 min or less in the reactor, and 20% of the molecules $[1 - F(t)]$ spend longer than 8 min in the reactor.

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[4] C. Y. Wen and L. T. Fan, *Models for Flow Systems and Chemical Reactors* (New York: Marcel Dekker, 1975).

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

The *F* curve

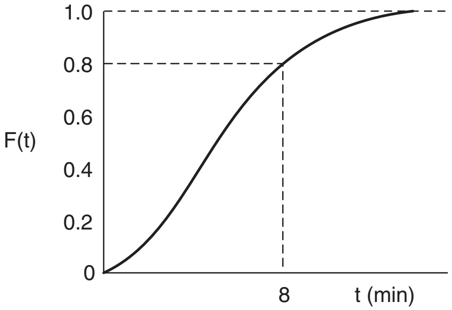


Figure 13-5 Cumulative distribution curve, $F(t)$.

The *F* curve is another function that has been defined as the normalized response to a particular input. Alternatively, Equation (13-12) has been used as a definition of $F(t)$, and it has been stated that as a result it can be obtained as the response to a positive-step tracer test. Sometimes the *F* curve is used in the same manner as the RTD in the modeling of chemical reactors. An excellent example is the study of Wolf and White,[6] who investigated the behavior of screw extruders in polymerization processes.

13.3.2 Mean Residence Time

In previous chapters treating ideal reactors, a parameter frequently used was the space time or average residence time τ, which was defined as being equal to V/v. It will be shown that, in the absence of dispersion, and for constant volumetric flow ($v = v_0$) no matter what RTD exists for a particular reactor, ideal or nonideal, this nominal space time, τ, is equal to the mean residence time, t_m.

As is the case with other variables described by distribution functions, the mean value of the variable is equal to the first moment of the RTD function, $E(t)$. Thus the mean residence time is

The first moment gives the average time the effluent molecules spent in the reactor.

$$\boxed{t_m = \frac{\int_0^\infty tE(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty tE(t)\,dt} \tag{13-14}$$

We now wish to show how we can determine the total reactor volume using the cumulative distribution function.

---

[6] D. Wolf and D. H. White, *AIChE J.*, *22*, 122 (1976).

What we are going to do now is prove $t_m = \tau$ for constant volumetric flow, $v = v_0$. You can skip what follows and go directly to Equation (13–21) if you can accept this result.

Consider the following situation: We have a reactor completely filled with maize molecules. At time $t = 0$ we start to inject blue molecules to replace the maize molecules that currently fill the reactor. Initially, the reactor volume V is equal to the volume occupied by the maize molecules. Now, in a time dt, the volume of molecules that will leave the reactor is $(v\,dt)$. The fraction of these molecules that have been in the reactor a time t or greater is $[1 - F(t)]$. Because only the maize molecules have been in the reactor a time t or greater, the volume of maize molecules, dV, leaving the reactor in a time dt is

$$dV = (v\,dt)[1 - F(t)] \tag{13-15}$$

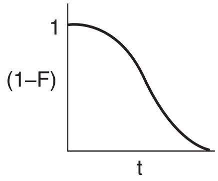
If we now sum up all of the maize molecules that have left the reactor in time $0 < t < \infty$, we have

All we are doing here is proving that the space time and mean residence time are equal.

$$V = \int_0^\infty v\,[1 - F(t)]\,dt \tag{13-16}$$

Because the volumetric flow rate is constant,[†]

$$V = v \int_0^\infty [1 - F(t)]\,dt \tag{13-17}$$



Using the integration-by-parts relationship gives

$$\int x\,dy = xy - \int y\,dx$$

and dividing by the volumetric flow rate gives

$$\frac{V}{v} = t[1 - F(t)]\Big|_0^\infty + \int_0^1 t\,dF \tag{13-18}$$

At $t = 0$, $F(t) = 0$; and as $t \to \infty$, then $[1 - F(t)] = 0$. The first term on the right-hand side is zero, and the second term becomes

$$\frac{V}{v} = \tau = \int_0^1 t\,dF \tag{13-19}$$

However, $dF = E(t)\,dt$; therefore,

$$\boxed{\tau = \int_0^\infty tE(t)\,dt} \tag{13-20}$$

The right-hand side is just the mean residence time, and we see that the mean residence time is just the space time τ:

[†] *Note:* For gas-phase reactions at constant temperature and no pressure drop $t_m = \tau/(1 + \varepsilon X)$.

$\tau = t_m$, Q.E.D.

$$\boxed{\tau = t_m} \tag{13-21}$$

and no change in volumetric flow rate. For gas-phase reactions, this means no pressure drop, isothermal operation, and no change in the total number of moles (i.e., $\varepsilon \equiv 0$, as a result of reaction).

End of proof!

This result is true *only* for a *closed system* (i.e., no dispersion across boundaries; see Chapter 14). The exact reactor volume is determined from the equation

$$\boxed{V = v t_m} \tag{13-22}$$

13.3.3 Other Moments of the RTD

It is very common to compare RTDs by using their moments instead of trying to compare their entire distributions (e.g., Wen and Fan[7]). For this purpose, three moments are normally used. The first is the mean residence time. The second moment commonly used is taken about the mean and is called the variance, or square of the standard deviation. It is defined by

The second moment about the mean is the variance.

$$\boxed{\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)\, dt} \tag{13-23}$$

The magnitude of this moment is an indication of the "spread" of the distribution; the greater the value of this moment is, the greater a distribution's spread will be.

The third moment is also taken about the mean and is related to the *skewness*. The skewness is defined by

The two parameters most commonly used to characterize the RTD are τ and σ^2

$$s^3 = \frac{1}{\sigma^{3/2}} \int_0^\infty (t - t_m)^3 E(t)\, dt \tag{13-24}$$

The magnitude of this moment measures the extent that a distribution is skewed in one direction or another in reference to the mean.

Rigorously, for complete description of a distribution, all moments must be determined. Practically, these three are usually sufficient for a reasonable characterization of an RTD.

Example 13–2 Mean Residence Time and Variance Calculations

Calculate the mean residence time and the variance for the reactor characterized in Example 13-1 by the RTD obtained from a pulse input at 320 K.

Solution

First, the mean residence time will be calculated from Equation (13-14):

---

[7] C. Y. Wen and L. T. Fan, *Models for Flow Systems and Chemical Reactors* (New York: Decker, 1975), Chap. 11.

$$t_m = \int_0^\infty tE(t)\,dt \tag{E13-2.1}$$

The area under the curve of a plot of $tE(t)$ as a function of t will yield t_m. Once the mean residence time is determined, the variance can be calculated from Equation (13-23):

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)\,dt \tag{E13-2.2}$$

To calculate t_m and σ^2, Table E13-2.1 was constructed from the data given and interpreted in Example 13-1. One quadrature formula will not suffice over the entire range. Therefore, we break the integral up into two regions, 0 to 10 min and 10 to 14 (minutes), i.e., infinity (∞).

$$t_m = \int_0^\infty tE(t)\,dt = \int_0^{10} tE(t)\,dt + \int_{10}^\infty tE(t)\,dt$$

Starting with Table E13-1.2 in Example 13-1, we can proceed to calculate $tE(t)$, $(t - t_m)$ and $(t - t_m)^2\,E(t)$ and $t^2E(t)$ shown in Table E13-2.1.

TABLE E13-2.1. CALCULATING $E(t)$, t_m, AND σ^2

t	$C(t)$	$E(t)$	$tE(t)$	$(t - t_m)^a$	$(t - t_m)^2E(t)^a$	$t^2E(t)^a$
0	0	0	0	−5.15	0	0
1	1	0.02	0.02	−4.15	0.34	0.02
2	5	0.10	0.20	−3.15	0.992	0.4
3	8	0.16	0.48	−2.15	0.74	1.44
4	10	0.20	0.80	−1.15	0.265	3.2
5	8	0.16	0.80	−0.15	0.004	4.0
6	6	0.12	0.72	0.85	0.087	4.32
7	4	0.08	0.56	1.85	0.274	3.92
8	3	0.06	0.48	2.85	0.487	3.84
9	2.2	0.044	0.40	3.85	0.652	3.56
10	1.5	0.03	0.30	4.85	0.706	3.0
12	0.6	0.012	0.14	6.85	0.563	1.73
14	0	0	0	8.85	0	0

[a] The last two columns are completed after the mean residence time (t_m) is found.

Again, using the numerical integration formulas (A-25) and (A-21) in Appendix A.4, we have

$$t_m = \int_0^h f(x)dx = \frac{h_1}{3}\,(f_1 + 4f_2 + 2f_3 + 4f_4 + \cdots + 4f_{n-1} + f_n) \tag{A-25}$$

$$+\frac{h_2}{3}\,(f_{n+1} + 4f_{n+2} + f_{n+3}) \tag{A-21}$$

Numerical integration to find the mean residence time, t_m

$$\begin{aligned} t_m &= \tfrac{1}{3}[1(0) + 4(0.02) + 2(0.2) + 4(0.48) + 2(0.8) + 4(0.8) \\ &\quad + 2(0.72) + 4(0.56) + 2(0.48) + 4(0.40) + 1(0.3)] \\ &\quad + \tfrac{2}{3}[0.3 + 4(0.14) + 0] \\ &= 4.58 + 0.573 = 5.15 \text{ min} \end{aligned}$$

Calculating the mean residence time,

$$\tau = t_m = \int_0^\infty tE(t)\,dt$$

Note: One could also use the spreadsheets in Polymath or Excel to formulate Table E13-2.1 and to calculate the mean residence time t_m and variance σ.

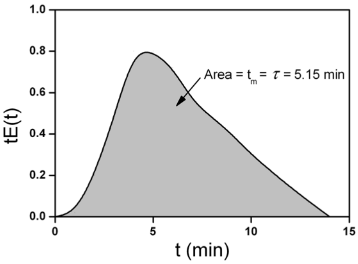


Figure E13-2.1 Calculating the mean residence time.

Plotting $tE(t)$ versus t we obtain Figure E13-2.1. The area under the curve is 5.15 min.

$$\boxed{t_m = 5.15 \text{ min}}$$

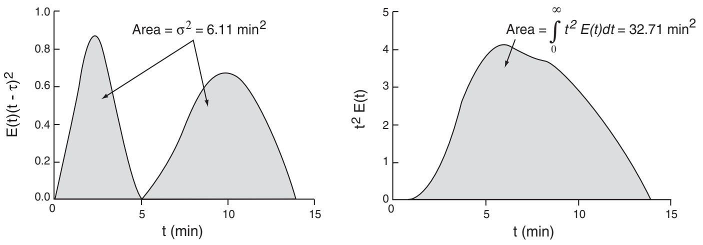
Calculating the variance,

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)\,dt$$

$$\sigma^2 = \int_0^\infty t^2 E(t)dt - t_m^2$$

Now that the mean residence time has been determined, we can calculate the variance by calculating the area under the curve of a plot of $(t - t_m)^2 E(t)$ as a function of t (Figure E13-2.2[a]). The area under the curve(s) is 6.11 min^2.

One could also use Polymath or Excel to make these calculations.



(a) (b)

Figure E13-2.2 Calculating the variance.

Expanding the square term in Equation (13-23)

$$\sigma^2 = \int_0^\infty t^2 E(t)dt - 2t_m \int_0^\infty tE(t)dt + t_m^2 \int_0^\infty E(t)dt \qquad \text{(E13-2.2)}$$

$$= \int_0^\infty t^2 E(t)dt - 2t_m^2 + t_m^2$$

$$\boxed{\sigma^2 = \int_0^\infty t^2 E(t)dt - t_m^2} \qquad \text{(E13-2.3)}$$

We will use quadrature formulas to evaluate the integral using the data (columns 1 and 7) in Table E13-2.1. Integrating between 1 and 10 minutes and 10 and 14 minutes using the same form as Equation (E13-2.3)

$$\int_0^\infty t^2E(t)dt = \int_0^{10} t^2E(t)dt + \int_0^{14} t^2E(t)dt$$

$$= \frac{1}{3}[0 + 4(0.02) + 2(0.4) + 4(1.44) + 2(3.2)$$

$$+4(4.0) + 2(4.32) + 4(3.92) + 2(3.84)$$

$$+4(3.56) + 3.0] + \frac{2}{3}[3.0 + 4(1.73) + 0]\ \text{min}^2$$

$$= 32.71\ \text{min}^2$$

This value is also the shaded area under the curve in Figure E13-2.2(b).

$$\boxed{\sigma^2 = \int_0^\infty t^2E(t)dt - t_m^2 = 32.71\ \text{min}^2 - (5.15\ \text{min})^2 = 6.19\ \text{min}^2}$$

The square of the standard deviation is $\sigma^2 = 6.19\ \text{min}^2$, so $\sigma = 2.49$ min.

13.3.4 Normalized RTD Function, $E(\Theta)$

Frequently, a normalized RTD is used instead of the function $E(t)$. If the parameter Θ is defined as

$$\Theta \equiv \frac{t}{\tau} \tag{13-25}$$

a dimensionless function $E(\Theta)$ can be defined as

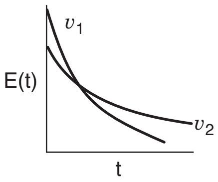
$$E(\Theta) \equiv \tau E(t) \tag{13-26}$$

and plotted as a function of Θ. The quantity Θ represents the number of reactor volumes of fluid based on entrance conditions that have flowed through the reactor in time t.

Why we use a normalized RTD

The purpose of creating this normalized distribution function is that the flow performance inside reactors of different sizes can be compared directly. For example, if the normalized function $E(\Theta)$ is used, *all* perfectly mixed CSTRs have numerically the same RTD. If the simple function $E(t)$ is used, numerical values of $E(t)$ can differ substantially for different CSTRs. As will be shown later, for a perfectly mixed CSTR,

$E(t)$ for a CSTR



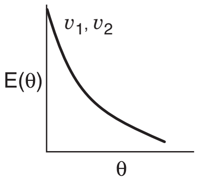
$v_1 > v_2$

$$\boxed{E(t) = \frac{1}{\tau}e^{-t/\tau}} \tag{13-27}$$

and therefore

$$\boxed{E(\Theta) = \tau E(t) = e^{-\Theta}} \tag{13-28}$$

From these equations it can be seen that the value of $E(t)$ at identical times can be quite different for two different volumetric flow rates, say v_1 and v_2. But for



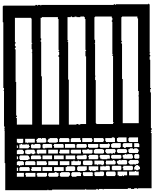
the same value of Θ, the value of $E(\Theta)$ is the same irrespective of the size of a perfectly mixed CSTR.

It is a relatively easy exercise to show that

$$\int_0^\infty E(\Theta)\, d\Theta = 1 \tag{13-29}$$

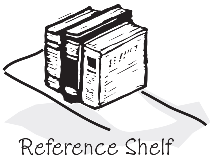
and is recommended as a 93-s divertissement.

13.3.5 Internal-Age Distribution, $I(\alpha)$



Tombstone jail
How long have you
been here? $I(\alpha)$
When do you
expect to get out?

Although this section is not a prerequisite to the remaining sections, the internal-age distribution is introduced here because of its close analogy to the external-age distribution. We shall let α represent the age of a molecule inside the reactor. The internal-age distribution function $I(\alpha)$ is a function such that $I(\alpha)\Delta\alpha$ is the fraction of material *inside the reactor* that has been inside the reactor for a period of time between α and $\alpha + \Delta\alpha$. It may be contrasted with $E(\alpha)\Delta\alpha$, which is used to represent the material *leaving the reactor* that has spent a time between α and $\alpha + \Delta\alpha$ in the reaction zone; $I(\alpha)$ characterizes the time the material has been (and still is) in the reactor at a particular time. The function $E(\alpha)$ is viewed outside the reactor and $I(\alpha)$ is viewed inside the reactor. In unsteady-state problems it can be important to know what the particular state of a reaction mixture is, and $I(\alpha)$ supplies this information. For example, in a catalytic reaction using a catalyst whose activity decays with time, the internal age distribution of the catalyst in the reactor $I(\alpha)$ is of importance and can be of use in modeling the reactor.



The internal-age distribution is discussed further on the Professional Reference Shelf where the following relationships between the cumulative internal age distribution $I(\alpha)$ and the cumulative external age distribution F(α)

$$I(\alpha) = (1 - F(\alpha))/\tau \tag{13-30}$$

and between E(t) and I(t)

$$E(\alpha) = -\frac{d}{d\alpha}[\tau I(\alpha)] \tag{13-31}$$

are derived. For a CSTR it is shown that the internal age distribution function is

$$I(\alpha) = -\frac{1}{\tau} e^{-\alpha/\tau}$$

13.4 RTD in Ideal Reactors

13.4.1 RTDs in Batch and Plug-Flow Reactors

The RTDs in plug-flow reactors and ideal batch reactors are the simplest to consider. All the atoms leaving such reactors have spent precisely the same amount of time within the reactors. The distribution function in such a case is a spike of infinite height and zero width, whose area is equal to 1; the spike occurs at $t = V/v = \tau$, or $\Theta = 1$. Mathematically, this spike is represented by the Dirac delta function:

$E(t)$ for a plug-flow reactor

$$\boxed{E(t) = \delta(t-\tau)} \tag{13-32}$$

The Dirac delta function has the following properties:

Properties of the Dirac delta function

$$\delta(x) = \begin{cases} 0 & \text{when } x \neq 0 \\ \infty & \text{when } x = 0 \end{cases} \tag{13-33}$$

$$\int_{-\infty}^{\infty} \delta(x)\,dx = 1 \tag{13-34}$$

$$\int_{-\infty}^{\infty} g(x)\,\delta(x-\tau)\,dx = g(\tau) \tag{13-35}$$

To calculate τ the mean residence time, we set g(x) = t

$$t_m = \int_0^{\infty} tE(t)\,dt = \int_0^{\infty} t\,\delta(t-\tau)\,dt = \tau \tag{13-36}$$

But we already knew this result. To calculate the variance we set, $g(t) = (t-\tau)^2$, and the variance, σ^2, is

$$\sigma^2 = \int_0^{\infty} (t-\tau)^2\,\delta(t-\tau)\,dt = 0 \tag{13-37}$$

All material spends exactly a time τ in the reactor, there is no variance! The cumulative distribution function $F(t)$ is

$$F(t) = \int_0^t E(t)dt = \int_0^t \delta(t-\tau)dt$$

The $E(t)$ function is shown in Figure 13-6(a), and $F(t)$ is shown in Figure 13-6(b).

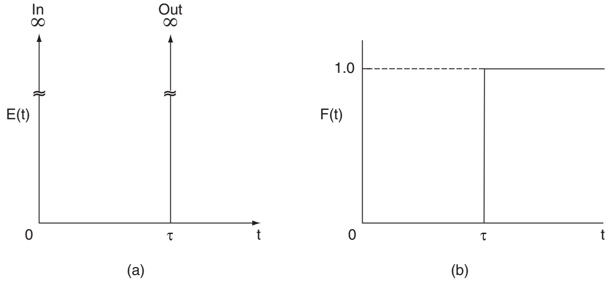


Figure 13-6 Ideal plug-flow response to a pulse tracer input.

13.4.2 Single-CSTR RTD

From a tracer balance we can determine $E(t)$.

In an ideal CSTR the concentration of any substance in the effluent stream is identical to the concentration throughout the reactor. Consequently, it is possible to obtain the RTD from conceptual considerations in a fairly straightforward manner. A material balance on an inert tracer that has been injected as a pulse at time $t = 0$ into a CSTR yields for $t > 0$

$$\overbrace{0}^{\text{In}} - \overbrace{vC}^{\text{Out}} = \overbrace{V\frac{dC}{dt}}^{\text{Accumulation}} \tag{13-38}$$

Because the reactor is perfectly mixed, C in this equation is the concentration of the tracer either in the effluent or within the reactor. Separating the variables and integrating with $C = C_0$ at $t = 0$ yields

$$C(t) = C_0 e^{-t/\tau} \tag{13-39}$$

This relationship gives the concentration of tracer in the effluent at any time t.

To find $E(t)$ for an ideal CSTR, we first recall Equation (13-7) and then substitute for $C(t)$ using Equation (13-39). That is,

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C_0 e^{-t/\tau}}{\int_0^\infty C_0 e^{-t/\tau}\,dt} = \frac{e^{-t/\tau}}{\tau} \tag{13-40}$$

Evaluating the integral in the denominator completes the derivation of the RTD for an ideal CSTR given by Equations (13-27) and (13-28):

$E(t)$ and $E(\Theta)$ for a CSTR

$$\boxed{E(t) = \frac{e^{-t/\tau}}{\tau}} \tag{13-27}$$

$$\boxed{E(\Theta) = e^{-\Theta}} \tag{13-28}$$

Recall $\Theta = t/\tau$ and $E(\Theta) = \tau E(t)$.

Response of an ideal CSTR

$$\boxed{\begin{aligned} E(\Theta) &= e^{-\Theta} \\ F(\Theta) &= 1 - e^{-\Theta} \end{aligned}}$$

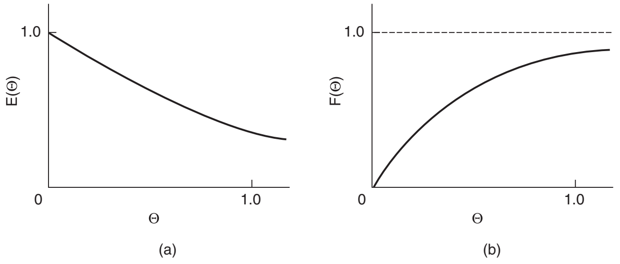


Figure 13-7 $E(\Theta)$ and $F(\Theta)$ for an Ideal CSTR.

The cumulative distribution $F(\Theta)$ is

$$F(\Theta) = \int_0^{\theta} E(\Theta)d\Theta = 1 - e^{-\Theta}$$

The $E(\Theta)$ and $F(\Theta)$ functions for an Ideal CSTR are shown in Figure 13-7 (a) and (b), respectively.

Earlier it was shown that for a constant volumetric flow rate, the mean residence time in a reactor is equal to V/v, or τ. This relationship can be shown in a simpler fashion for the CSTR. Applying the definition of the mean residence time to the RTD for a CSTR, we obtain

$$t_m = \int_0^{\infty} tE(t)\,dt = \int_0^{\infty} \frac{t}{\tau}\, e^{-t/\tau}\,dt = \tau \tag{13-20}$$

Thus the nominal holding time (space time) $\tau = V/v$ is also the mean residence time that the material spends in the reactor.

The second moment about the mean is a measure of the spread of the distribution about the mean. The variance of residence times in a perfectly mixed tank reactor is (let $x = t/\tau$)

For a perfectly mixed CSTR: $t_m = \tau$ and $\sigma = \tau$.

$$\sigma^2 = \int_0^{\infty} \frac{(t-\tau)^2}{\tau}\, e^{-t/\tau}\,dt = \tau^2 \int_0^{\infty} (x-1)^2 e^{-x}\,dx = \tau^2 \tag{13-41}$$

Then $\sigma = \tau$. The standard deviation is the square root of the variance. For a CSTR, the standard deviation of the residence-time distribution is as large as the mean itself!!

13.4.3 Laminar Flow Reactor (LFR)

Before proceeding to show how the RTD can be used to estimate conversion in a reactor, we shall derive $E(t)$ for a laminar flow reactor. For laminar flow in a tubular reactor, the velocity profile is parabolic, with the fluid in the center of the tube spending the shortest time in the reactor. A schematic diagram of the fluid movement after a time t is shown in Figure 13-8. The figure at the left shows how far down the reactor each concentric fluid element has traveled after a time t.

Molecules near the center spend a shorter time in the reactor than those close to the wall.

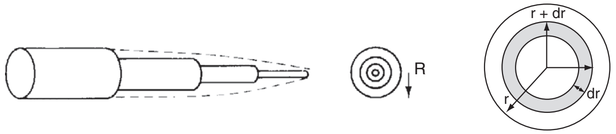
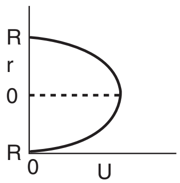


Figure 13-8 Schematic diagram of fluid elements in a laminar flow reactor.



Parabolic Velocity Profile

The velocity profile in a pipe of outer radius R is

$$U = U_{\max}\left[1-\left(\frac{r}{R}\right)^2\right] = 2U_{\text{avg}}\left[1-\left(\frac{r}{R}\right)^2\right] = \frac{2v_0}{\pi R^2}\left[1-\left(\frac{r}{R}\right)^2\right] \tag{13-42}$$

where $U_{\max}$ is the centerline velocity and U_{avg} is the average velocity through the tube. U_{avg} is just the volumetric flow rate divided by the cross-sectional area.

The time of passage of an element of fluid at a radius r is

$$\begin{aligned} t(r) &= \frac{L}{U(r)} = \frac{\pi R^2 L}{v_0} \frac{1}{2[1-(r/R)^2]} \\ &= \frac{\tau}{2[1-(r/R)^2]} \end{aligned} \tag{13-43}$$

The volumetric flow rate of fluid out between r and $(r + dr)$, dv, is

$$dv = U(r)\, 2\pi r dr$$

The fraction of total fluid passing between r and $(r + dr)$ is dv/v_0, i.e.

$$\frac{dv}{v_0} = \frac{U(r)2(\pi r dr)}{v_0} \tag{13-44}$$

The fraction of fluid between r and $(r + dr)$ that has a flow rate between v and $(v + dv)$ spends a time between t and $(t + dt)$ in the reactor is

$$E(t)dt = \frac{dv}{v_0} \tag{13-45}$$

We now need to relate the fluid fraction [Equation (13-45)] to the fraction of fluid spending between time t and $t + dt$ in the reactor. First we differentiate Equation (13-43):

$$dt = \frac{\tau}{2R^2} \frac{2r\,dr}{[1-(r/R)^2]^2} = \frac{4}{\tau R^2} \left\{ \frac{\tau/2}{[1-(r/R)^2]} \right\}^2 r\,dr$$

and then substitute for t using Equation (13-43) to yield

$$dt = \frac{4t^2}{\tau R^2}\, r\,dr \tag{13-46}$$

Combining Equations (13-44) and (13-46), and then using Equation (13-43) for $U(r)$, we now have the fraction of fluid spending between time t and $t + dt$ in the reactor:

$$E(t)dt = \frac{dv}{v_0} = \frac{L}{t}\left(\frac{2\pi r\,dr}{v_0}\right) = \frac{L}{t}\left(\frac{2\pi}{v_0}\right)\frac{\tau R^2}{4t^2}\,dt = \frac{\tau^2}{2t^3}\,dt$$

$$E(t) = \frac{\tau^2}{2t^3}$$

The minimum time the fluid may spend in the reactor is

$$t = \frac{L}{U_{\text{max}}} = \frac{L}{2U_{\text{avg}}}\left(\frac{\pi R^2}{\pi R^2}\right) = \frac{V}{2v_0} = \frac{\tau}{2}$$

Consequently, the complete RTD function for a laminar flow reactor is

$E(t)$ for a laminar flow reactor

$$\boxed{E(t) = \begin{cases} 0 & t < \dfrac{\tau}{2} \\ \dfrac{\tau^2}{2t^3} & t \geq \dfrac{\tau}{2} \end{cases}} \tag{13-47}$$

The cumulative distribution function for $t \geq \tau/2$ is

$$F(t) = \int_0^t E(t)dt = 0 + \int_{\tau/2}^t E(t)dt = \int_{\tau/2}^t \frac{\tau^2}{2t^3}\,dt = \frac{\tau^2}{2}\int_{\tau/2}^t \frac{dt}{t^3} = 1 - \frac{\tau^2}{4t^2} \tag{13-48}$$

The mean residence time t_m is

For LFR $t_m = \tau$

$$t_m = \int_{\tau/2}^{\infty} tE(t)\,dt = \frac{\tau^2}{2}\int_{\tau/2}^{\infty}\frac{dt}{t^2}$$

$$= \frac{\tau^2}{2}\left[-\frac{1}{t}\right]_{\tau/2}^{\infty} = \tau$$

This result was shown previously to be true for any reactor. The mean residence time is just the space time τ.

The dimensionless form of the RTD function is

Normalized RTD function for a laminar flow reactor

$$\boxed{E(\Theta) = \begin{cases} 0 & \Theta < 0.5 \\ \dfrac{1}{2\Theta^3} & \Theta \geq 0.5 \end{cases}} \tag{13-49}$$

and is plotted in Figure 13-9.

The dimensionless cumulative distribution, F(Θ) for $\Theta \geq 1/2$, is

$$F(\Theta) = 0 + \int_{\frac{1}{2}}^{\Theta} E(\Theta)d\Theta = \int_{\frac{1}{2}}^{\Theta}\frac{d\Theta}{2\Theta^3} = \left(1 - \frac{1}{4\Theta^2}\right)$$

$$\boxed{F(\Theta) = \left\{\begin{matrix} 0 & \Theta < \dfrac{1}{2} \\ \left(1 - \dfrac{1}{4\Theta^2}\right) & \Theta \geq \dfrac{1}{2} \end{matrix}\right\}}$$

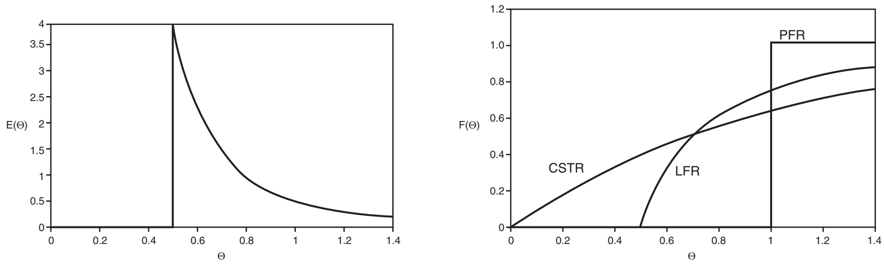


Figure 13-9 (a) $E(\Theta)$ for an LFR; (b) $F(\Theta)$ for a PFR, CSTR, and LFR.

Figure 13-9(a) shows $E(\Theta)$ for a laminar flow reactor (LFR), while Figure 9-13(b) compares $F(\Theta)$ for a PFR, CSTR, and LFR.

Experimentally injecting and measuring the tracer in a laminar flow reactor can be a difficult task if not a nightmare. For example, if one uses as a tracer chemicals that are photo-activated as they enter the reactor, the analysis and interpretation of $E(t)$ from the data become much more involved.[8]

13.5 Diagnostics and Troubleshooting

13.5.1 General Comments

As discussed in Section 13.1, the RTD can be used to diagnose problems in existing reactors. As we will see in further detail in Chapter 14, the RTD functions $E(t)$ and $F(t)$ can be used to model the real reactor as combinations of ideal reactors.

Figure 13-10 illustrates typical RTDs resulting from different nonideal reactor situations. Figures 13-10(a) and (b) correspond to nearly ideal PFRs and CSTRs, respectively. In Figure 13-10(d) one observes that a principal peak occurs at a time smaller than the space time ($\tau = V/v_0$) (i.e., early exit of fluid) and also that some fluid exits at a time greater than space-time τ. This curve could be representative of the RTD for a packed-bed reactor with channeling and dead zones. A schematic of this situation is shown in Figure 13-10(c). Figure 13-10(f) shows the RTD for the nonideal CSTR in Figure 13-10(e), which has dead zones and bypassing. The dead zone serves to reduce the effective reactor volume, so the active reactor volume is smaller than expected.

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[8] D. Levenspiel, *Chemical Reaction Engineering,* 3rd ed. (New York: Wiley, 1999), p. 342.

RTDs that are commonly observed

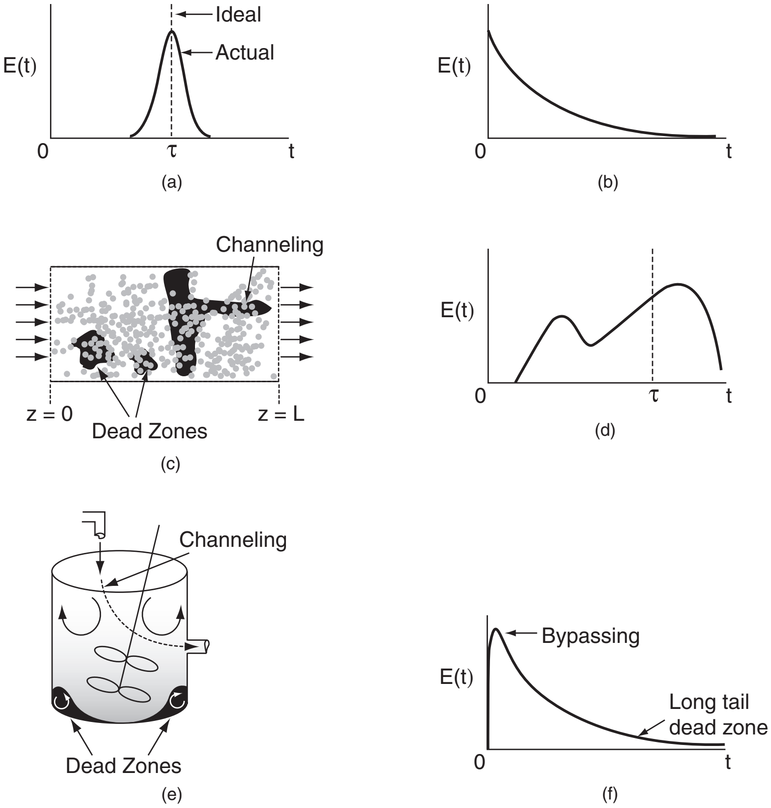

Figure 13-10 (a) RTD for near plug-flow reactor; (b) RTD for near perfectly mixed CSTR; (c) Packed-bed reactor with dead zones and channeling; (d) RTD for packed-bed reactor in (c); (e) tank reactor with short-circuiting flow (bypass); (f) RTD for tank reactor with channeling (bypassing or short circuiting) and a dead zone in which the tracer slowly diffuses

13.5.2 Simple Diagnostics and Troubleshooting Using the RTD for Ideal Reactors

13.5.2A The CSTR

We will first consider a CSTR that operates (a) normally, (b) with bypassing, and (c) with a dead volume. For a well-mixed CSTR, the mole (mass) balance on the tracer is

$$\frac{VdC}{dt} = -v_0 C$$

Rearranging, we have

$$\frac{dC}{dt} = -\frac{1}{\tau}C$$

We saw the response to a pulse tracer is

Concentration: $C(t) = C_{T0}e^{-t/\tau}$

RTD Function: $E(t) = \frac{1}{\tau}e^{-t/\tau}$

Cumulative Function: $F(t) = 1 - e^{-t/\tau}$

$$\tau = \frac{V}{v_0}$$

where τ is the space time—the case of perfect operation.

a. Perfect Operation (P)

Here we will measure our reactor with a yardstick to find V and our flow rate with a flow meter to find v_0 in order to calculate $\tau = V/v_0$. We can then compare the curves shown below for the perfect operation in Figure 13-11 with the subsequent cases, which are for imperfect operation.

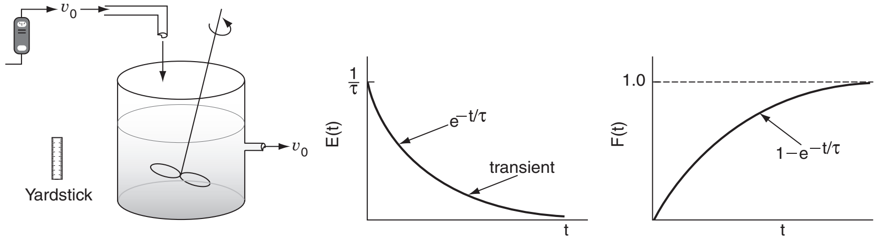

Figure 13-11 Perfect operation of a CSTR.

$$\tau = \frac{V}{v_0}$$

If τ is large, there will be a slow decay of the output transient, $C(t)$, and $E(t)$ for a pulse input. If τ is small, there will be rapid decay of the transient, $C(t)$, and $E(t)$ for a pulse input.

b. Bypassing (BP)

A volumetric flow rate v_b bypasses the reactor while a volumetric flow rate v_{SB} enters the system volume and $v_0 = v_{SB} + v_b$. The reactor system volume V_S is the well-mixed portion of the reactor, and the volumetric flow rate entering the system volume is v_{SB}. The subscript SB denotes that part of the flow has bypassed and only v_{SB} enters the system. Because some of the fluid bypasses, the flow passing through the system will be less than the total volumetric rate, $v_{SB} < v_0$, consequently $\tau_{SB} > \tau$. Let's say the volumetric flow rate that bypasses the reactor, v_b, is 25% of the total (e.g., $v_b = 0.25\ v_0$). The volumetric flow rate entering the reactor system, v_{SB} is 75% of the total ($v_{SB} = 0.75\ v_0$) and the corresponding true space time (τ_{SB}) for the system volume with bypassing is

$$\tau_{SB} = \frac{V}{v_{SB}} = \frac{V}{0.75 v_0} = 1.33\tau$$

The space time, τ_{SB}, will be greater than that if there were no bypassing. Because τ_{SB} is greater than τ there will be a slower decay of the transients $C(t)$ and $E(t)$ than that of perfect operation.

An example of a corresponding $E(t)$ curve for the case of bypassing is

$$E(t) = \frac{v_b}{v_0}\delta(t-0) + \frac{v_{SB}^2}{V v_0} e^{-t/\tau_{SB}}$$

The CSTR with bypassing will have RTD curves similar to those in Figure 13-12.

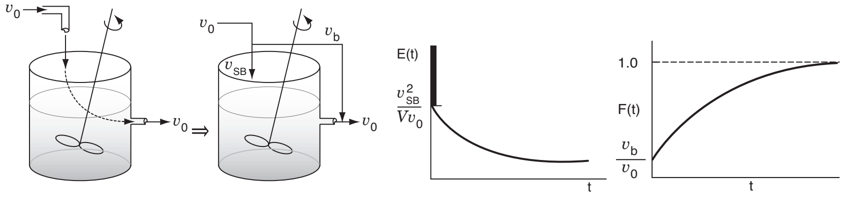

Figure 13-12 Ideal CSTR with bypass.

We see from the $F(t)$ curve that we have an initial jump equal to the fraction by-passed.

c. Dead Volume (DV)

Consider the CSTR in Figure 13-13 without bypassing but instead with a stagnant or dead volume.

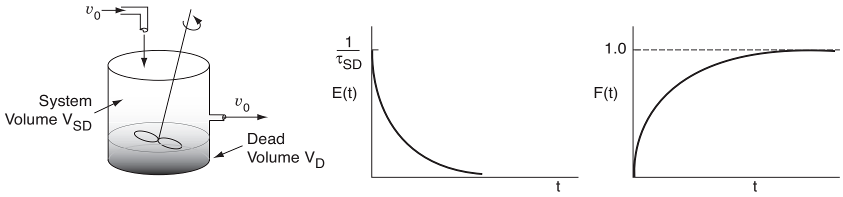

Figure 13-13 Ideal CSTR with dead volume.

The total volume, V, is the same as that for perfect operation, $V = V_D + V_{SD}$.

We see that because there is a dead volume which the fluid does not enter, there is less system volume, V_{SD}, than in the case of perfect operation, $V_{SD} < V$. Consequently, the fluid will pass through the reactor with the dead volume more quickly than that of perfect operation, i.e., $\tau_{SD} < \tau$.

$$\text{If} \qquad V_D = 0.2V,\ V_{SD} = 0.8V, \text{ then } \tau_{SD} = \frac{0.8V}{v_0} = 0.8\tau$$

Also as a result, the transients $C(t)$ and $E(t)$ will decay more rapidly than that for perfect operation because there is a smaller system volume.

Summary

A summary for ideal CSTR mixing volume is shown in Figure 13-14.

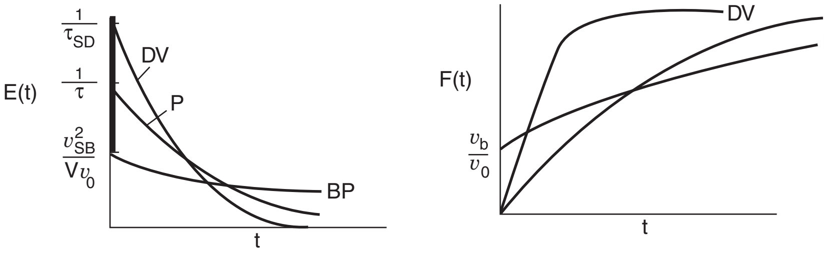

Figure 13-14 Comparison of $E(t)$ and $F(t)$ for CSTR under perfect operation, bypassing, and dead volume. (BP = bypassing, P = perfect, and DV = dead volume).

Knowing the volume V measured with a yardstick and the flow rate v_0 entering the reactor measured with a flow meter, one can calculate and plot $E(t)$ and $F(t)$ for the ideal case (P) and then compare with the measured RTD $E(t)$ to see if the RTD suggests either bypassing (BP) or dead zones (DV).

13.5.2B Tubular Reactor

A similar analysis to that for a CSTR can be carried out on a tubular reactor.

a. Perfect Operation of PFR (P)

We again measure the volume V with a yardstick and v_0 with a flow meter. The $E(t)$ and $F(t)$ curves are shown in Figure 13-15. The space time for a perfect PFR is

$$\tau = V/v_0$$

b. PFR with Channeling (Bypassing, BP)

Let's consider channeling (bypassing), as shown in Figure 13-16, similar to that shown in Figures 13-2 and 13-10(d). The space time for the reactor system with bypassing (channeling) τ_{SB} is

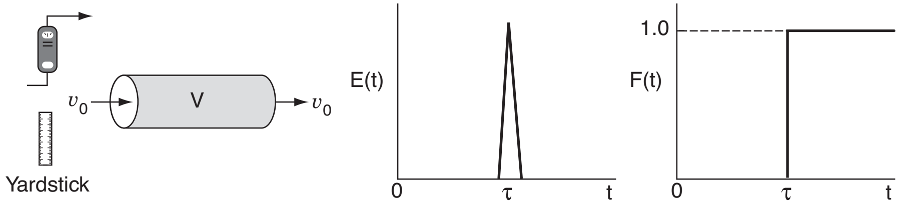

Figure 13-15 Perfect operation of a PFR.

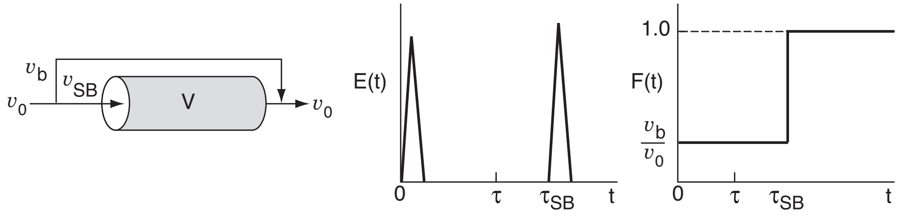

Figure 13-16 PFR with bypassing similar to the CSTR.

$$\tau_{SB} = \frac{V}{v_{SB}}$$

Because $v_{SB} < v_0$, the space time for the case of bypassing is greater when compared to perfect operation, i.e.,

$$\tau_{SB} > \tau$$

If 25% is bypassing (i.e., $v_b = 0.25\ v_0$) and 75% is entering the reactor system (i.e., $v_{SB} = 0.75\ v_0$), then $\tau_{SB} = V/(0.75v_0) = 1.33\tau$. The fluid that does enter the reactor system flows in plug flow. Here we have two spikes in the $E(t)$ curve. One spike at the origin and one spike at τ_{SB} that comes after τ for perfect operation. Because the volumetric flow rate is reduced, the time of the second spike will be greater than τ for perfect operation.

c. **PFR with Dead Volume (DV)**
The dead volume, V_D, could be manifested by internal circulation at the entrance to the reactor as shown in Figure 13-17.

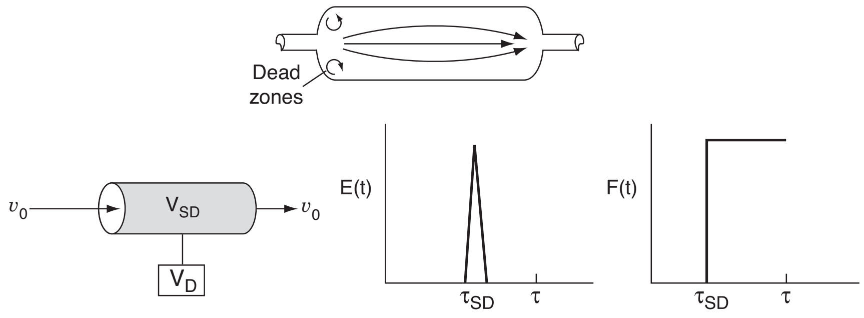

Figure 13-17 PFR with dead volume.

The system V_{SD} is where the reaction takes place and the total reactor volume is ($V = V_{SD} + V_D$). The space time, τ_{SD}, for the reactor system with only dead volume is

$$\tau_{SD} = \frac{V_{SD}}{v_0}$$

Compared to perfect operation, the space time τ_{SD} is smaller and the tracer spike will occur before τ for perfect operation.

$$\tau_{SD} < \tau$$

Here again, the dead volume takes up space that is not accessible. As a result, the tracer will exit early because the system volume, V_{SD}, through which it must pass is smaller than the perfect operation case.

Summary

Figure 13-18 is a summary of these three cases.

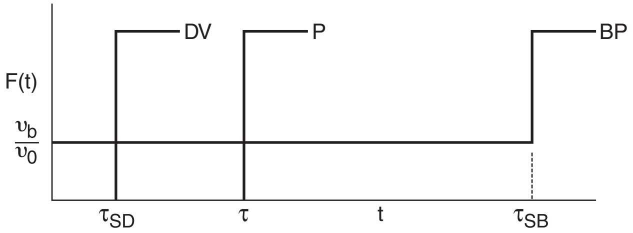

Figure 13-18 Comparison of PFR under perfect operation, bypassing, and dead volume (DV = dead volume, P = perfect PFR, BP = bypassing).

In addition to its use in diagnosis, the RTD can be used to predict conversion in existing reactors when a new reaction is tried in an old reactor. However, as we will see in Section 13.5.3, the RTD is not unique for a given system, and we need to develop models for the RTD to predict conversion.

13.5.3 PFR/CSTR Series RTD

Modeling the real reactor as a CSTR and a PFR in series

In some stirred tank reactors, there is a highly agitated zone in the vicinity of the impeller that can be modeled as a perfectly mixed CSTR. Depending on the location of the inlet and outlet pipes, the reacting mixture may follow a somewhat tortuous path either before entering or after leaving the perfectly mixed zone—or even both. This tortuous path may be modeled as a plug-flow reactor. Thus this type of tank reactor may be modeled as a CSTR in series with a plug-flow reactor, and the PFR may either precede or follow the CSTR. In this section we develop the RTD for this type of reactor arrangement.

First consider the CSTR followed by the PFR (Figure 13-19). The residence time in the CSTR will be denoted by τ_s and the residence time in the PFR by τ_p. If a pulse of tracer is injected into the entrance of the CSTR, the

Side Note: Medical Uses of RTD The application of RTD analysis in biomedical engineering is being used at an increasing rate. For example, Professor Bob Langer's* group at MIT used RTD analysis for a novel Taylor-Couette flow device for blood detoxification while Lee et al.† used an RTD analysis to study arterial blood flow in the eye. In this later study, sodium fluorescein was injected into the anticubical vein. The cumulative distribution function $F(t)$ is shown schematically in Figure 13.5.N-1. Figure 13.5N-2 shows a laser ophthalmoscope image after injection of the sodium fluorescein. The mean residence time can be calculated for each artery to estimate the mean circulation time (ca. 2.85 s). Changes in the retinal blood flow may provide important decision-making information for sickle-cell disease and retinitis pigmentosa.

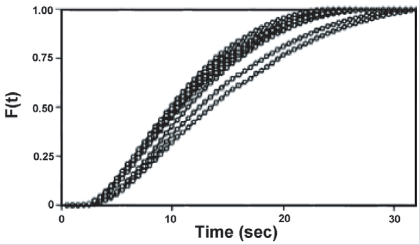

Figure 13.5.N-1 Cumulative RTD function for arterial blood flow in the eye. Courtesy of *Med. Eng. Phys.*†

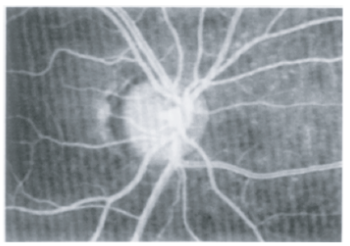

Figure 13.5.N-2 Image of eye after tracer injection. Courtesy of *Med. Eng. Phys.*†

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* G. A. Ameer, E. A. Grovender, B. Olradovic, C. L. Clooney, and R. Langer, *AIChE J. 45*, 633 (1999).

† E. T. Lee, R. G. Rehkopf, J. W. Warnicki, T. Friberg, D. N. Finegold, and E. G. Cape, *Med. Eng. Phys. 19*, 125 (1997).

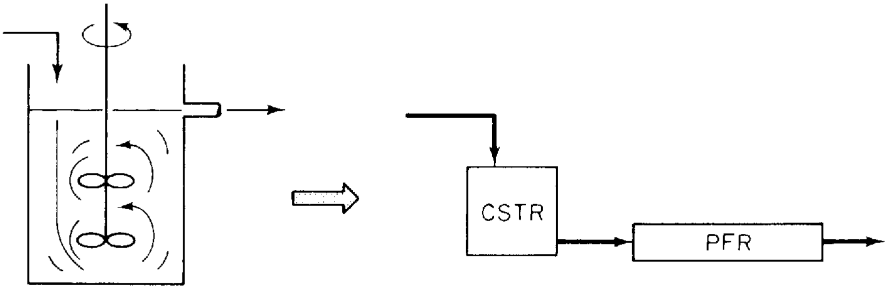

Figure 13-19 Real reactor modeled as a CSTR and PFR in series.

CSTR output concentration as a function of time will be

$$C = C_0 e^{-t/\tau_s}$$

This output will be delayed by a time τ_p at the outlet of the plug-flow section of the reactor system. Thus the RTD of the reactor system is

$$\boxed{E(t) = \begin{cases} 0 & t < \tau_p \\ \dfrac{e^{-(t-\tau_p)/\tau_s}}{\tau_s} & t \geq \tau_p \end{cases}} \tag{13-50}$$

See Figure 13-20.

The RTD is not unique to a particular reactor sequence.

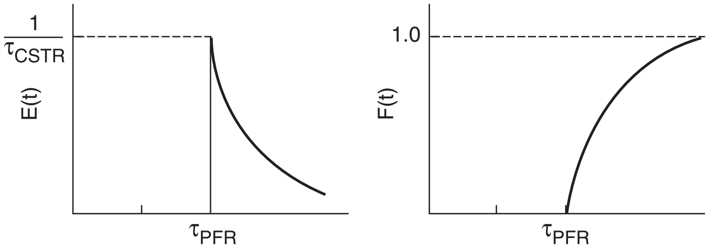

Figure 13-20 RTD curves $E(t)$ and $F(t)$ for a CSTR and a PFR in series.

Next the reactor system in which the CSTR is preceded by the PFR will be treated. If the pulse of tracer is introduced into the entrance of the plug-flow section, then the same pulse will appear at the entrance of the perfectly mixed section τ_p seconds later, meaning that the RTD of the reactor system will be

$E(t)$ is the same no matter which reactor comes first.

$$\boxed{E(t) = \begin{cases} 0 & t < \tau_p \\ \dfrac{e^{-(t-\tau_p)/\tau_s}}{\tau_s} & t \geq \tau_p \end{cases}} \tag{13-51}$$

which is *exactly* the same as when the CSTR was followed by the PFR.

It turns out that no matter where the CSTR occurs within the PFR/CSTR reactor sequence, the same RTD results. Nevertheless, this is not the entire story as we will see in Example 13-3.

Example 13–3 Comparing Second-Order Reaction Systems

Examples of *early* and late mixing for a given RTD

Consider a second-order reaction being carried out in a *real* CSTR that can be modeled as two different reactor systems: In the first system an ideal CSTR is followed by an ideal PFR; in the second system the PFR precedes the CSTR. Let τ_s and τ_p each equal 1 min, let the reaction rate constant equal 1.0 m^3/kmol·min, and let the initial concentration of liquid reactant, C_{A0}, equal 1 kmol/m^3. Find the conversion in each system.

Solution

Again, consider first the CSTR followed by the plug-flow section (Figure E13-3.1). A mole balance on the CSTR section gives

$$v_0(C_{A0} - C_{Ai}) = kC_{Ai}^2 V \tag{E13-3.1}$$

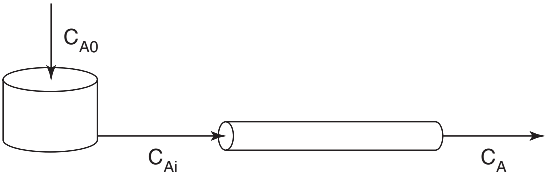

Figure E13-3.1 Early mixing scheme.

Rearranging, we have

$$\tau_s k C_{Ai}^2 + C_{Ai} - C_{A0} = 0$$

Solving for C_{Ai} gives

$$C_{Ai} = \frac{\sqrt{1 + 4\tau_s k C_{A0}} - 1}{2\tau_s k} \qquad \text{(E13-3.2)}$$

Then

$$C_{Ai} = \frac{-1 + \sqrt{1+4}}{2} = 0.618 \text{ kmol/m}^3 \qquad \text{(E13-3.3)}$$

This concentration will be fed into the PFR. The PFR mole balance

$$\frac{dF_A}{dV} = v_0 \frac{dC_A}{dV} = \frac{dC_A}{d\tau_p} = r_A = -kC_A^2 \qquad \text{(E13-3.4)}$$

$$\frac{1}{C_A} - \frac{1}{C_{Ai}} = \tau_p k \qquad \text{(E13-3.5)}$$

Substituting $C_{Ai} = 0.618$, $\tau_p = 1$, and $k = 1$ in Equation (E13-3.5) yields

$$\frac{1}{C_A} - \frac{1}{0.618} = (1)(1)$$

Solving for C_A gives

CSTR → PFR
$X = 0.618$

$$C_A = 0.382 \text{ kmol/m}^3$$

as the concentration of reactant in the effluent from the reaction system. Thus, the conversion is 61.8%—i.e., $X = ([1 - 0.382]/1) = 0.618$.

When the perfectly mixed section is preceded by the plug-flow section (Figure E13-3.2) the outlet of the PFR is the inlet to the CSTR, C_{Ai}:

$$\frac{1}{C_{Ai}} - \frac{1}{C_{A0}} = \tau_p k$$

$$\frac{1}{C_{Ai}} - \frac{1}{1} = (1)(1) \qquad \text{(E13-3.6)}$$

$$C_{Ai} = 0.5 \text{ kmol/m}^3$$

and a material balance on the perfectly mixed section (CSTR) gives

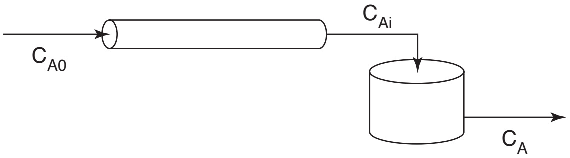

Figure E13-3.2 Late mixing scheme.

PFR → CSTR
$X = 0.634$

$$\tau_s k C_A^2 + C_A - C_{Ai} = 0 \tag{E13-3.7}$$

$$C_A = \frac{\sqrt{1+4\tau_s k C_{Ai}} - 1}{2\tau_s k} \tag{E13-3.8}$$

$$= \frac{-1+\sqrt{1+2}}{2} = 0.366 \text{ kmol/m}^3$$

Early Mixing
$X = 0.618$
Late Mixing
$X = 0.634$

as the concentration of reactant in the effluent from the reaction system. The corresponding conversion is 63.4%. That is $X = 1 - (C_A/C_{A0}) = 1 - \frac{0.366}{1.0} = 63.4\%$

In the first configuration, a conversion of 61.8% was obtained; in the second, 63.4%. While the difference in the conversions is small for the parameter values chosen, **the point is that there is a difference**.

While $E(t)$ was the same for both reaction systems, the conversion was not.

The conclusion from this example is of extreme importance in reactor analysis: **The RTD is not a complete description of structure for a particular reactor or system of reactors**. The RTD is unique for a particular reactor. However, the reactor or reaction system is not unique for a particular RTD. When analyzing nonideal reactors, the RTD alone is not sufficient to determine its performance, and more information is needed. It will be shown that in addition to the RTD, an adequate model of the nonideal reactor flow pattern and knowledge of the quality of mixing or "degree of segregation" are both required to characterize a reactor properly.

There are many situations where the fluid in a reactor neither is well mixed nor approximates plug flow. The idea is this: We have seen that the RTD can be used to diagnose or interpret the type of mixing, bypassing, etc., that occurs in an existing reactor that is currently on stream and is not yielding the conversion predicted by the ideal reactor models. Now let's envision another use of the RTD. Suppose we have a nonideal reactor either on line or sitting in storage. We have characterized this reactor and obtained the RTD function. What will be the conversion of a reaction with a known rate law that is carried out in a reactor with a known RTD?

The Question

How can we use the RTD to predict conversion in a real reactor?

In Part 2 we show how this question can be answered in a number of ways.

Part 2 Predicting Conversion and Exit Concentration

13.6 Reactor Modeling Using the RTD

Now that we have characterized our reactor and have gone to the lab to take data to determine the reaction kinetics, we need to choose a model to predict conversion in our real reactor.

The Answer

$$\boxed{\text{RTD + MODEL + KINETIC DATA} \quad \Rightarrow \left\{ \frac{\text{EXIT CONVERSION and}}{\text{EXIT CONCENTRATION}} \right.}$$

We now present the five models shown in Table 13-1. We shall classify each model according to the number of adjustable parameters. We will discuss the first two in this chapter and the other three in Chapter 14.

Ways we use the RTD data to predict conversion in nonideal reactors

TABLE 13-1. MODELS FOR PREDICTING CONVERSION FROM RTD DATA

1. **Zero adjustable parameters**
   - **a. Segregation model**
   - **b. Maximum mixedness model**
2. **One adjustable parameter**
   - **a. Tanks-in-series model**
   - **b. Dispersion model**
3. **Two adjustable parameters**

   Real reactors modeled as combinations of ideal reactors

The RTD tells us how long the various fluid elements have been in the reactor, but it does not tell us anything about the exchange of matter between the fluid elements (i.e., *the mixing*). The mixing of reacting species is one of the major factors controlling the behavior of chemical reactors. Fortunately for first-order reactions, knowledge of the length of time each molecule spends in the reactor is all that is needed to predict conversion. For first-order reactions the conversion is independent of concentration (recall Equation E9-1.3):

$$\frac{dX}{dt} = k(1 - X) \tag{E9-1.3}$$

Consequently, mixing with the surrounding molecules is not important. Therefore, once the RTD is determined, we can predict the conversion that will be achieved in the real reactor provided that the specific reaction rate for the first-order reaction is known. However, for reactions other than first order, knowledge of the RTD is not sufficient to predict conversion. In these cases the degree of mixing of molecules must be known in addition to how long each molecule spends in the reactor. Consequently, we must develop models that account for the mixing of molecules inside the reactor.

The more complex models of nonideal reactors necessary to describe reactions other than first order must contain information about *micromixing* in addition to that of *macromixing*. **Macromixing** produces a distribution of residence times *without*, however, specifying how molecules of different ages encounter one another in the reactor. **Micromixing**, on the other hand, describes how molecules of different ages encounter one another in the reactor. There are two extremes of *micromixing*: (1) all molecules of the same age group remain together as they travel through the reactor and are not mixed with any other age until they exit the reactor (i.e., complete segregation); (2) molecules of different age groups are completely mixed at the molecular level as soon as they enter the reactor (complete micromixing). For a given state of macromixing (i.e., a given RTD), these two extremes of micromixing will give the upper and lower limits on conversion in a nonideal reactor. For reaction orders greater than one or less than zero, the segregation model will predict the highest conversion. For reaction orders between zero and one, the maximum mixedness model will predict the highest conversion. This concept is discussed further in Section 13.7.3.

Reference Shelf

We shall define a globule as a fluid particle containing millions of molecules all of the same age. A fluid in which the globules of a given age do not mix with other globules is called a macrofluid. A *macrofluid* could be visualized as a noncoalescent globules where all the molecules in a given globule have the same age. A fluid in which molecules are not constrained to remain in the globule and are free to move everywhere is called a *microfluid*.[9] There are two extremes of mixing of the *macrofluid* globules to form a *microfluid* we shall study—early mixing and late mixing. These two extremes of late and early mixing are shown in Figure 13-21 (a) and (b), respectively. These extremes can also be seen by comparing Figures 13-23 (a) and 13-24 (a). The extremes of late and early mixing are referred to as *complete segregation* and *maximum mixedness*, respectively.

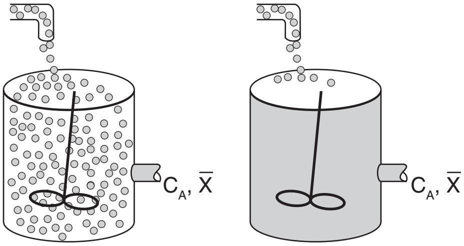

Figure 13-21 (a) Macrofluid; and (b) microfluid mixing on the molecular level.

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[9] J. Villermaux, *Chemical Reactor Design and Technology* (Boston: Martinus Nijhoff, 1986).

13.7 Zero-Parameter Models

13.7.1 Segregation Model

In a “perfectly mixed” CSTR, the entering fluid is assumed to be distributed immediately and evenly throughout the reacting mixture. This mixing is assumed to take place even on the microscale, and elements of different ages mix together thoroughly to form a completely micromixed fluid. If fluid elements of different ages do not mix together at all, the elements remain segregated from each other, and the fluid is termed *completely segregated*. The extremes of complete micromixing and complete segregation are the limits of the micromixing of a reacting mixture.

In developing the segregated mixing model, we first consider a CSTR because the application of the concepts of mixing quality are illustrated most easily using this reactor type. In the segregated flow model we visualize the flow through the reactor to consist of a continuous series of globules (Figure 13-22).

In the segregation model globules behave as batch reactors operated for different times

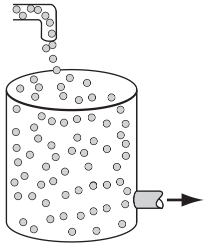

Figure 13-22 Little batch reactors (globules) inside a CSTR.

These globules retain their identity; that is, they do not interchange material with other globules in the fluid during their period of residence in the reaction environment, i.e., they remain segregated. In addition, each globule spends a different amount of time in the reactor. In essence, what we are doing is lumping all the molecules that have exactly the same residence time in the reactor into the same globule. The principles of reactor performance in the presence of completely segregated mixing were first described by Danckwerts[10] and Zwietering.[11]

The segregation model has mixing at the latest possible point.

Another way of looking at the segregation model for a continuous flow system is the PFR shown in Figures 13-23(a) and (b). Because the fluid flows down the reactor in plug flow, each exit stream corresponds to a specific residence time in the reactor. Batches of molecules are removed from the reactor at different locations along the reactor in such a manner as to duplicate the RTD function, $E(t)$. The molecules removed near the entrance to the reactor correspond to those molecules having short residence times in the reactor.

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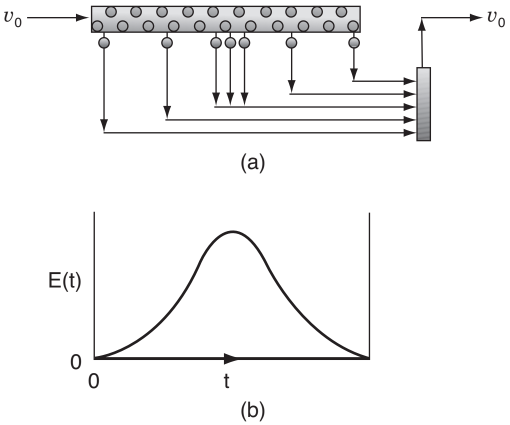
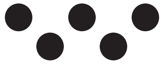
[10] P. V. Danckwerts, *Chem. Eng. Sci.*, *8*, 93 (1958).

[11] T. N. Zwietering, *Chem. Eng. Sci.*, *11*, 1 (1959).



E(t) matches the removal of the batch reactors

Figure 13-23 Mixing at the latest possible point.



Little batch reactors

Physically, this effluent would correspond to the molecules that channel rapidly through the reactor. The farther the molecules travel along the reactor before being removed, the longer their residence time. The points at which the various groups or batches of molecules are removed correspond to the RTD function for the reactor.

Because there is no molecular interchange between globules, each acts essentially as its own batch reactor. The reaction time in any one of these tiny batch reactors is equal to the time that the particular globule spends in the reaction environment. The distribution of residence times among the globules is given by the RTD of the particular reactor.

$$\boxed{\text{RTD + MODEL + KINETIC DATA} \quad \Rightarrow \left\{ \frac{\text{EXIT CONVERSION and}}{\text{EXIT CONCENTRATION}} \right.}$$

To determine the mean conversion in the effluent stream, we must average the conversions of all of the various globules in the exit stream:

$$\begin{bmatrix} \text{Mean} \\ \text{conversion} \\ \text{of those globules} \\ \text{spending between} \\ \text{time } t \text{ and } t+dt \\ \text{in the reactor} \end{bmatrix} = \begin{bmatrix} \text{Conversion} \\ \text{achieved in a globule} \\ \text{after spending a time } t \\ \text{in the reactor} \end{bmatrix} \times \begin{bmatrix} \text{Fraction} \\ \text{of globules that} \\ \text{spend between } t \\ \text{and } t+dt \text{ in the} \\ \text{reactor} \end{bmatrix}$$

then

$$d\overline{X} = X(t) \times E(t)\, dt$$

$$\boxed{\frac{d\bar{X}}{dt} = X(t)E(t)} \tag{13-52}$$

Summing over all globules, the mean conversion is

Mean conversion for the segregation model

$$\boxed{\bar{X} = \int_0^\infty X(t)E(t)\,dt} \tag{13-53}$$

Summary Notes

Consequently, if we have the batch reactor equation for $X(t)$ and measure the RTD experimentally, we can find the mean conversion in the exit stream. *Thus, if we have the RTD, the reaction rate expression, then for a segregated flow situation (i.e., model), we have sufficient information to calculate the conversion.* An example that may help give additional physical insight to the segregation model is given in the Summary Notes on the CD-ROM, click the More back button just before section 4A.2.

Consider the following first-order reaction:

$$\mathrm{A} \xrightarrow{k} \text{products}$$

For a batch reactor we have

$$-\frac{dN_A}{dt} = -r_A V$$

For constant volume and with $N_A = N_{A0}(1 - X)$,

$$N_{A0}\frac{dX}{dt} = -r_A V = kC_A V = kN_A = kN_{A0}(1 - X)$$

$$\boxed{\frac{dX}{dt} = k(1 - X)} \tag{13-54}$$

Solving for $X(t)$, we have

$$X(t) = 1 - e^{-kt}$$

Mean conversion for a first-order reaction

$$\bar{X} = \int_0^\infty X(t)E(t)dt = \int_0^\infty (1 - e^{-kt})E(t)\,dt = \int_0^\infty E(t)\,dt - \int_0^\infty e^{-kt}E(t)\,dt \tag{13-55}$$

$$\bar{X} = 1 - \int_0^\infty e^{-kt}E(t)\,dt \tag{13-56}$$

We will now determine the mean conversion predicted by the segregation model for an ideal PFR, a CSTR, and a laminar flow reactor.

Example 13–4 Mean Conversion in an Ideal PFR, an Ideal CSTR, and a Laminar Flow Reactor

Derive the equation of a first-order reaction using the segregation model when the RTD is equivalent to (a) an ideal PFR, (b) an ideal CSTR, and (c) a laminar flow reactor. Compare these conversions with those obtained from the design equation.

Solution

(a) For the **PFR**, the RTD function was given by Equation (13-32)

$$E(t) = \delta(t - \tau) \tag{13-32}$$

Recalling Equation (13-55)

$$\bar{X} = \int_0^\infty X(t)E(t)\,dt = 1 - \int_0^\infty e^{-kt}E(t)\,dt \tag{13-55}$$

Substituting for the RTD function for a PFR gives

$$\bar{X} = 1 - \int_0^\infty (e^{-kt})\delta(t - \tau)\,dt \tag{E13-4.1}$$

Using the integral properties of the Dirac delta function, Equation (13-35) we obtain

$$\bar{X} = 1 - e^{-k\tau} = 1 - e^{-Da} \tag{E13-4.2}$$

where for a first-order reaction the Damköhler number is $Da = \tau k$. Recall that for a PFR after combining the mole balance, rate law, and stoichiometric relationships (cf. Chapter 4), we had

$$\frac{dX}{d\tau} = k(1 - X) \tag{E13-4.3}$$

Integrating yields

$$X = 1 - e^{-k\tau} = 1 - e^{-Da} \tag{E13-4.4}$$

which is identical to the conversion predicted by the segregation model $\bar{X}$.

(b) For the **CSTR**, the RTD function is

$$E(t) = \frac{1}{\tau}e^{-t/\tau} \tag{13-27}$$

Recalling Equation (13-56), the mean conversion for a first-order reaction is

$$\bar{X} = 1 - \int_0^\infty e^{-kt}E(t)\,dt \tag{13-56}$$

$$\bar{X} = 1 - \int_0^\infty \frac{e^{-(1/\tau + k)t}}{\tau}\,dt$$

$$\bar{X} = 1 + \frac{1}{k + 1/\tau}\frac{1}{\tau}e^{-(k+1/\tau)t}\Big|_0^\infty$$

$$\bar{X} = \frac{\tau k}{1+\tau k} = \frac{Da}{1+Da} \tag{E13-4.5}$$

As expected, using the $E(t)$ for an ideal PFR and CSTR with the segregation model gives a mean conversion $\bar{X}$ identical to that obtained by using the algorithm in Ch. 4.

Combining the CSTR mole balance, the rate law, and stoichiometry, we have

$$F_{A0}X = -r_A V$$

$$v_0 C_{A0} X = kC_{A0}(1-X)V$$

$$X = \frac{\tau k}{1+\tau k} \tag{E13-4.6}$$

which is identical to the conversion predicted by the segregation model $\bar{X}$.

(c) For a **laminar flow reactor** the RTD function is

$$E(t) = \begin{Bmatrix} 0 & \text{for } (t < \tau/2) \\ \dfrac{\tau^2}{2t^3} & \text{for } (t \geq \tau/2) \end{Bmatrix} \tag{13-47}$$

The dimensionless form is

$$E(\Theta) = \begin{Bmatrix} 0 & \text{for } \Theta < 0.5 \\ \dfrac{1}{2\Theta^3} & \text{for } \Theta \geq 0.5 \end{Bmatrix} \tag{13-49}$$

From Equation (13-15), we have

$$\bar{X} = 1 - \int_0^\infty e^{-kt}E(t)dt = 1 - \int_0^\infty e^{-\tau k\Theta}E(\Theta)d\Theta \tag{E13-4.7}$$

$$\bar{X} = 1 - \int_{0.5}^\infty \frac{e^{-\tau k\Theta}}{2\Theta^3}d\Theta \tag{E13-4.8}$$

Integrating twice by parts

$$\boxed{\bar{X} = 1 - (1-0.5\tau k)e^{-0.5k\tau} - (0.5\tau k)^2\int_{0.5}^\infty \frac{e^{-\tau k\Theta}}{\Theta}d\Theta} \tag{E13-4.9}$$

The last integral is the *exponential integral* and can be evaluated from tabulated values. Fortunately, Hilder[12] developed an approximate formula ($\tau k = Da$).

---

[12] M. H. Hilder, *Trans. I. ChemE*, *59*, 143 (1979).

$$\boxed{\begin{gathered}\bar{X} = 1 - \frac{1}{(1+0.25\tau k)e^{0.5\tau k} + 0.25\tau k} \equiv 1 - \frac{1}{(1+0.25\,Da)\,e^{0.5Da} + 0.25\,Da} \\ \bar{X} = \frac{(4+Da)e^{0.5Da} + Da - 4}{(4+Da)e^{0.5Da} + Da} \qquad \text{(E13-4.10)}\end{gathered}}$$

A comparison of the exact value along with Hilder's approximation is shown in Table E13-4.1 for various values of the Damköhler number, τk, along with the conversion in an ideal PFR and an ideal CSTR.

TABLE E13-4.1. COMPARISON OF CONVERSION IN PFR, CSTR, AND LAMINAR FLOW REACTOR FOR DIFFERENT DAMKÖHLER NUMBERS FOR A FIRST-ORDER REACTION

$Da = \tau k$	$X_{\text{L.F. Exact}}$	$X_{\text{L.F. Approx.}}$	X_{PFR}	X_{CSTR}
0.1	0.0895	0.093	0.0952	0.091
1	0.557	0.56	0.632	0.501
2	0.781	0.782	0.865	0.667
4	0.940	0.937	0.982	0.80
10	0.9982	0.9981	0.9999	0.90

where $X_{\text{L.F. Exact}}$ = exact solution to Equation (E13-4.9) and $X_{\text{L.F. Approx.}}$ = Equation (E13-4.10).

For large values of the Damköhler number then, there is complete conversion along the streamlines off the center streamline so that the conversion is determined along the pipe axis such that

$$\bar{X} = 1 - \int_{0.5}^{\infty} 4e^{-\tau k\Theta}\,d\Theta = 1 - 4e^{-0.5\tau k}/\tau k \qquad \text{(E13-4.11)}$$

Figure E13-4.1 shows a comparison of the mean conversion in an LFR, PFR, and CSTR as a function of the Damköhler number for a first-order reaction.

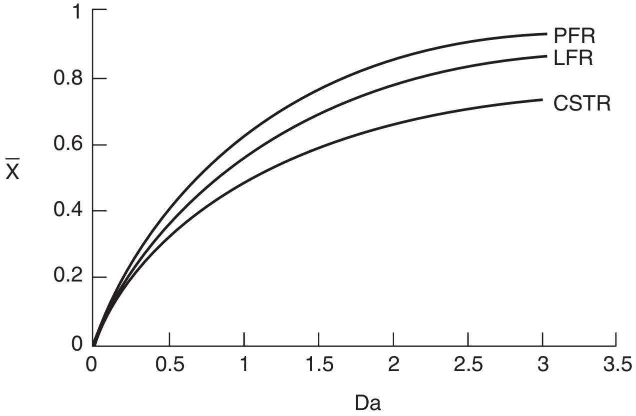


Figure E13-4.1 Conversion in a PFR, LFR, and CSTR as a function of the Damköhler number (Da) for a first-order reaction ($Da = \tau k$).

Important Point:

For a first-order reaction, knowledge of $E(t)$ is sufficient.

We have just shown for a first-order reaction that whether you assume complete micromixing [Equation (E13-4.6)] or complete segregation [Equation (E13-4.5)] in a CSTR, the same conversion results. This phenomenon occurs because the rate of change of conversion for a first-order reaction does *not* depend on the concentration of the reacting molecules [Equation (13-54)]; it does not matter what kind of molecule is next to it or colliding with it. Thus the extent of micromixing does not affect a first-order reaction, so the segregated flow model can be used to calculate the conversion. As a result, *only the RTD is necessary to calculate the conversion for a first-order reaction in any type of reactor* (see Problem P13-3_c). Knowledge of neither the degree of micromixing nor the reactor flow pattern is necessary. We now proceed to calculate conversion in a real reactor using RTD data.

Example 13–5 Mean Conversion Calculations in a Real Reactor

Calculate the mean conversion in the reactor we have characterized by RTD measurements in Examples 13-1 and 13-2 for a first-order, liquid-phase, irreversible reaction in a completely segregated fluid:

$$\text{A} \longrightarrow \text{products}$$

The specific reaction rate is 0.1 min^{-1} at 320 K.

Solution

Because each globule acts as a **batch reactor** of constant volume, we use the batch reactor design equation to arrive at the equation giving conversion as a function of time:

$$X = 1 - e^{-kt} = 1 - e^{-0.1t} \tag{E13-5.1}$$

These calculations are easily carried out with the aid of a spreadsheet such as Excel or Polymath.

To calculate the mean conversion we need to evaluate the integral:

$$\bar{X} = \int_0^\infty X(t)E(t)\,dt \tag{13-53}$$

The RTD function for this reactor was determined previously and given in Table E13-2.1 and is repeated in Table E13-5.1. To evaluate the integral we make a plot of $X(t)E(t)$ as a function of t as shown in Figure E13-5.1 and determine the area under the curve.

For a given RTD, the segregation model gives the upper bound on conversion for reaction orders less than zero or greater than 1.

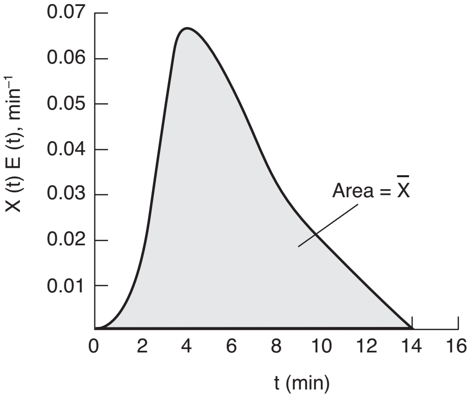


Figure E13-5.1 Plot of columns 1 and 4 from the data in Table E13-5.1.

TABLE E13-5.1 PROCESSED DATA TO FIND THE MEAN CONVERSION $\bar{X}$

t (min)	$E(t)$ (min^{-1})	$X(t)$	$X(t)E(t)$ (min^{-1})
0	0.000	0	0
1	0.020	0.095	0.0019
2	0.100	0.181	0.0180
3	0.160	0.259	0.0414
4	0.200	0.330	0.0660
5	0.160	0.393	0.0629
6	0.120	0.451	0.0541
7	0.080	0.503	0.0402
8	0.060	0.551	0.0331
9	0.044	0.593	0.0261
10	0.030	0.632	0.01896
12	0.012	0.699	0.0084
14	0.000	0.75	0

Using the quadature formulas in Appendix A.4

$$\int_0^\infty X(t)E(t)\,dt = \int_0^{10} X(t)E(t)\,dt + \int_{10}^{14} X(t)E(t)\,dt$$

$$= \tfrac{1}{3}[0 + 4(0.0019) + 2(0.018) + 4(0.0414) + 2(0.066)$$

$$+ 4(0.0629) + 2(0.0541) + 4(0.0402) + 2(0.0331)$$

$$+ 4(0.0261) + 0.01896] + \tfrac{2}{3}[0.01896 + 4(0.0084) + 0]$$

$$= (0.350) + (0.035) = 0.385$$

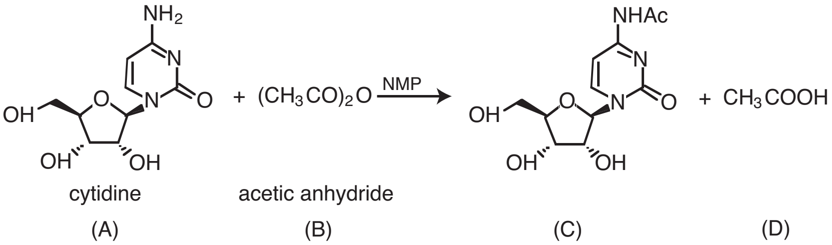
$$\bar{X} = \text{area} = 0.385$$

The mean conversion is 38.5%. Polymath or Excel will easily give $\bar{X}$ after setting up columns 1 and 4 in Table E13-5.1. The area under the curve in Figure E13-5.1 is the mean conversion $\bar{X}$.

As discussed previously, because the reaction is *first order*, the conversion calculated in Example 13-5 would be valid for a reactor with complete mixing, complete segregation, or any degree of mixing between the two. Although early or late mixing does not affect a first-order reaction, micromixing or complete segregation can modify the results of a second-order system significantly.

Example 13–6 Mean Conversion for a Second-Order Reaction in a Laminar Flow Reactor

The liquid-phase reaction between cytidine and acetic anhydride



$$A + B \rightarrow C + D$$

is carried out isothermally in an inert solution of *N*-methyl-2-pyrrolidone (NMP) with $\Theta_{NMP} = 28.9$. The reaction follows an elementary rate law. The feed is equal molar in A and B with $C_{A0} = 0.75$ mol/dm^3, a volumetric flow rate of 0.1 dm^3/s and a reactor volume of 100 dm^3. Calculate the conversion in (a) a PFR, (b) a batch reactor, and (c) a laminar flow reactor.

Additional information:[13]

$k = 4.93 \times 10^{-3}$ dm^3/mol · s at 50°C with $E = 13.3$ kcal/mol, $\Delta H_{RX} = -10.5$ kcal/mol

Heat of mixing for $\Theta_{NMP} = \dfrac{F_{NMP}}{F_{A0}} = 28.9$, $\Delta H_{mix} = -0.44$ kcal/mol

Solution

The reaction will be carried out isothermally at 50˚C. The space time is

$$\tau = \frac{V}{v_0} = \frac{100 \text{ dm}^3}{0.1 \text{ dm}^3/\text{s}} = 1000 \text{ s}$$

(a) **For a PFR**

Mole Balance

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} \tag{E13-6.1}$$

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[13] J. J. Shatynski and D. Hanesian, *Ind. Eng. Chem. Res., 32*, 594 (1993).

Rate Law

$$-r_A = kC_AC_B \tag{E13-6.2}$$

Stoichiometry, $\Theta_B = 1$

$$C_A = C_{A0}(1 - X) \tag{E13-6.3}$$

$$C_B = C_A \tag{E13-6.4}$$

Combining

$$\frac{dX}{dV} = \frac{kC_{A0}(1-X)^2}{v_0} \tag{E13-6.5}$$

PFR Calculation

Solving with $\tau = V/v_0$ and $X = 0$ for $V = 0$ gives

$$X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}} = \frac{Da_2}{1 + Da_2} \tag{E13-6.6}$$

where Da_2 is the Damköhler number for a second-order reaction.

$$Da_2 = \tau k C_{A0} = (1000\text{s})(4.9 \times 10^{-3}\ \text{dm}^3/\text{s} \cdot \text{mol})(0.75\ \text{mol/dm}^3)$$

$$= 3.7$$

$$X = \frac{3.7}{4.7}$$

$$\boxed{X = 0.787}$$

(b) **Batch Reactor**

$$\frac{dX}{dt} = \frac{-r_A}{C_{A0}} \tag{E13-6.7}$$

Batch Calculation

$$\frac{dX}{dt} = kC_{A0}(1-X)^2 \tag{E13-6.8}$$

$$X(t) = \frac{kC_{A0}t}{1 + kC_{A0}t} \tag{E13-6.9}$$

If the batch reaction time is the same time as the space time the batch conversion is the same as the PFR conversion $X = 0.787$.

(c) **Laminar Flow Reactor**

The differential form for the mean conversion is obtained from Equation (13-52)

$$\frac{d\bar{X}}{dt} = X(t)E(t) \tag{13-52}$$

We use Equation (E13-6.9) to substitute for $X(t)$ in Equation (13-52). Because E(t) for the LFR consists of two parts, we need to incorporate the IF statement in our ODE solver program. For the laminar flow reaction, we write

$$E_1 = 0 \text{ for } t < \tau/2 \tag{E13-6.10}$$

$$E_2 = \frac{\tau^2}{2t^3} \quad \text{for } t \geq \tau/2 \tag{E13-6.11}$$

Let $t_1 = \tau/2$ so that the IF statement now becomes

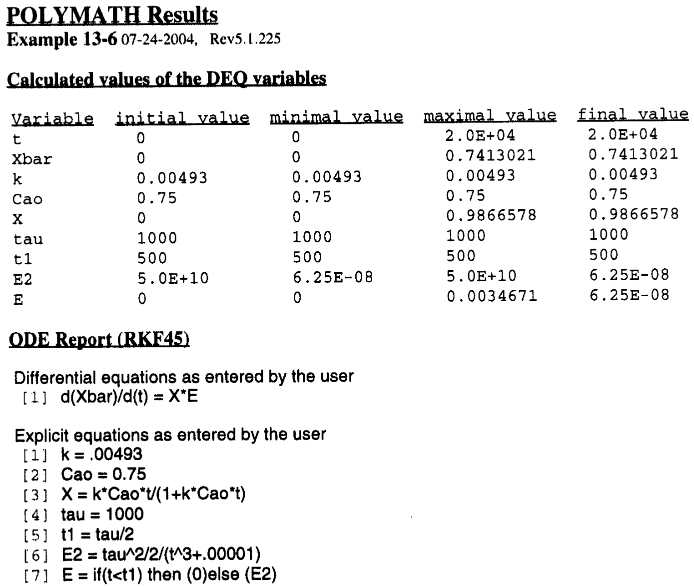
LFR Calculation

$$E = \text{If } (t < t_1) \text{ then } (E_1) \text{ else } (E_2) \tag{E13-6.12}$$

One other thing is that the ODE solver will recognize that $E_2 = \infty$ at $t = 0$ and refuse to run. So we must add a very small number to the denominator such as (0.001); for example,

$$E_2 = \frac{\tau^2}{(2t^3 + 0.001)} \tag{E13-6.13}$$

The integration time should be carried out to 10 or more times the reactor space time τ. The Polymath Program for this example is shown below.



```
POLYMATH Results
Example 13-6 07-24-2004, Rev5.1.225

Calculated values of the DEQ variables

Variable  initial value  minimal value  maximal value  final value
t         0              0              2.0E+04        2.0E+04
Xbar      0              0              0.7413021      0.7413021
k         0.00493        0.00493        0.00493        0.00493
Cao       0.75           0.75           0.75           0.75
X         0              0              0.9866578      0.9866578
tau       1000           1000           1000           1000
t1        500            500            500            500
E2        5.0E+10        6.25E-08       5.0E+10        6.25E-08
E         0              0              0.0034671      6.25E-08

ODE Report (RKF45)

Differential equations as entered by the user
 [1] d(Xbar)/d(t) = X*E

Explicit equations as entered by the user
 [1] k = .00493
 [2] Cao = 0.75
 [3] X = k*Cao*t/(1+k*Cao*t)
 [4] tau = 1000
 [5] t1 = tau/2
 [6] E2 = tau^2/2/(t^3+.00001)
 [7] E = if(t<t1) then (0)else (E2)
```

Living Example Problem

We see that the mean conversion Xbar ($\overline{X}$) for the LFR is 74.1%.
In summary,

$$\boxed{\begin{aligned} X_{\text{PFR}} &= 0.786 \\ X_{\text{LFR}} &= 0.741 \end{aligned}}$$

Compare this result with the exact analytical formula[14] for the laminar flow reactor with a second-order reaction

Analytical Solution

$$\boxed{\overline{X} = Da[1 - (Da/2)\ln(1+2/Da)]}$$

where $Da = kC_{A0}\tau$. For $Da = 3.70$ we get $\overline{X} = 0.742$.

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[14] K. G. Denbigh, *J. Appl. Chem., 1,* 227 (1951).

13.7.2 Maximum Mixedness Model

Segregation model mixing occurs at the latest possible point.

In a reactor with a segregated fluid, mixing between particles of fluid does not occur until the fluid leaves the reactor. The reactor exit is, of course, the *latest* possible point that mixing can occur, and any effect of mixing is postponed until after all reaction has taken place as shown in Figure 13-23. We can also think of completely segregated flow as being in a state of *minimum mixedness*. We now want to consider the other extreme, that of *maximum mixedness* consistent with a given residence-time distribution.

We return again to the plug-flow reactor with side entrances, only this time the fluid enters the reactor along its length (Figure 13-24). As soon as the fluid enters the reactor, it is completely mixed radially (but not longitudinally) with the other fluid already in the reactor. The entering fluid is fed into the reactor through the side entrances in such a manner that the RTD of the plug-flow reactor with side entrances is identical to the RTD of the real reactor.

Maximum mixedness: mixing occurs at the earliest possible point

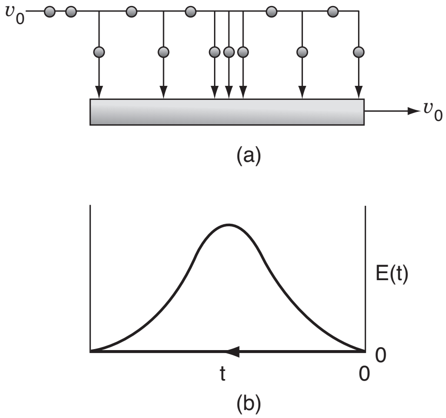

Figure 13-24 Mixing at the earliest possible point.

The globules at the far left of Figure 13-24 correspond to the molecules that spend a long time in the reactor while those at the far right correspond to the molecules that channel through the reactor. In the reactor with side entrances, mixing occurs at the *earliest* possible moment consistent with the RTD. Thus the effect of mixing occurs as early as possible throughout the reactor, and this situation is termed the condition of *maximum mixedness*.[15] The approach to calculating conversion for a reactor in a condition of maximum mixedness will now be developed. In a reactor with side entrances, let λ be the time it takes for the fluid to move from a particular point to the end of the reactor. In other words, λ is the life expectancy of the fluid in the reactor at that point (Figure 13-25).

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[15] T. N. Zwietering, *Chem. Eng. Sci.*, *11*, 1 (1959).

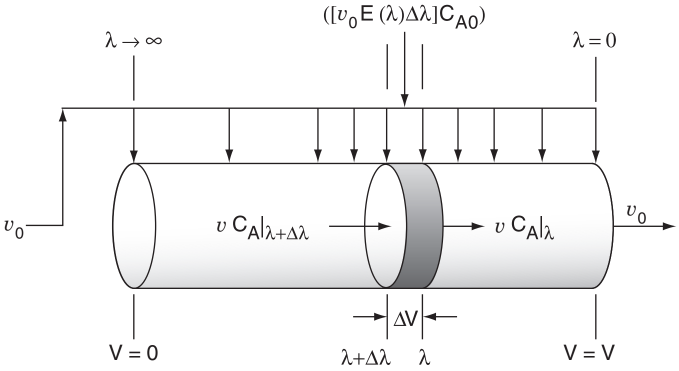
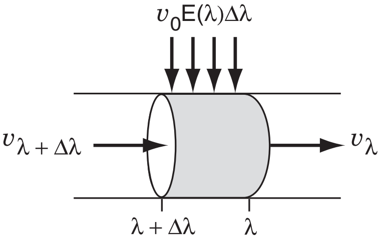


Figure 13-25 Modeling maximum mixedness by a plug-flow reactor with side entrances.

Moving down the reactor from left to right, λ decreases and becomes zero at the exit. At the left end of the reactor, λ approaches infinity or the maximum residence time if it is other than infinite.

Consider the fluid that enters the reactor through the sides of volume ΔV in Figure 13-25. The fluid that enters here will have a life expectancy between λ and λ+Δλ. The fraction of fluid that will have this life expectancy between λ and λ+Δλ is E(λ)Δλ. The corresponding volumetric flow rate IN through the sides is $[v_0 E(\lambda)\Delta\lambda]$.



The volumetric flow rate at λ, v_λ, is the flow rate that entered at λ+Δλ, $v_{\lambda+\Delta\lambda}$ plus what entered through the sides $v_0\,E(\lambda)\Delta\lambda$, i.e.,

$$v_\lambda = v_{\lambda+\Delta\lambda} + v_0 E(\lambda)\Delta\lambda$$

Rearranging and taking the limit as $\Delta\lambda \to 0$

$$\frac{dv_\lambda}{d\lambda} = -v_0 E(\lambda) \tag{13-57}$$

The volumetric flow rate v_0 at the entrance to the reactor ($X = 0$) is zero because the fluid only enters through the sides along the length.

Integrating equation (13-57) with limits $v_\lambda = 0$ at $\lambda = \infty$ and $v_\lambda = v_\lambda$ at $\lambda = \lambda$, we obtain

$$\boxed{v_\lambda = v_0 \int_\lambda^\infty E(\lambda)d\lambda = v_0[1 - F(\lambda)]} \tag{13-58}$$

The volume of fluid with a life expectancy between λ and λ + Δλ is

$$\Delta V = v_0[1 - F(\lambda)]\,\Delta\lambda \tag{13-59}$$

The rate of generation of the substance A in this volume is

$$r_A \Delta V = r_A v_0[1 - F(\lambda)]\,\Delta\lambda \tag{13-60}$$

We can now carry out a mole balance on substance A between λ and λ + Δλ:

Mole balance

$$\begin{bmatrix}\text{In}\\ \text{at } \lambda + \Delta\lambda\end{bmatrix} + \begin{bmatrix}\text{In}\\ \text{through side}\end{bmatrix} - \begin{bmatrix}\text{Out}\\ \text{at } \lambda\end{bmatrix} + \begin{bmatrix}\text{Generation}\\ \text{by reaction}\end{bmatrix} = 0$$

$$v_0[1 - F(\lambda)]C_A|_{\lambda+\Delta\lambda} + v_0 C_{A0}E(\lambda)\,\Delta\lambda$$
$$- v_0[1 - F(\lambda)]C_A|_\lambda + r_A v_0[1 - F(\lambda)]\,\Delta\lambda = 0 \tag{13-61}$$

Dividing Equation (13-61) by $v_0\,\Delta\lambda$ and taking the limit as $\Delta\lambda \to 0$ gives

$$E(\lambda)C_{A0} + \frac{d\{[1 - F(\lambda)]C_A(\lambda)\}}{d\lambda} + r_A[1 - F(\lambda)] = 0$$

Taking the derivative of the term in brackets

$$C_{A0}E(\lambda) + [1 - F(\lambda)]\frac{dC_A}{d\lambda} - C_A E(\lambda) + r_A[1 - F(\lambda)] = 0$$

or

$$\boxed{\frac{dC_A}{d\lambda} = -r_A + (C_A - C_{A0})\frac{E(\lambda)}{1 - F(\lambda)}} \tag{13-62}$$

We can rewrite Equation (13-62) in terms of conversion as

$$-C_{A0}\frac{dX}{d\lambda} = -r_A - C_{A0}X\frac{E(\lambda)}{1 - F(\lambda)} \tag{13-63}$$

or

$$\boxed{\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1 - F(\lambda)}(X)} \tag{13-64}$$

The boundary condition is as $\lambda \rightarrow \infty$, then $C_A = C_{A0}$ for Equation (13-62) [or $X = 0$ for Equation (13-64)]. To obtain a solution, the equation is integrated backwards numerically, starting at a very large value of λ and ending with the final conversion at $\lambda = 0$. For a given RTD and reaction orders greater than one, the maximum mixedness model gives the lower bound on conversion.

MM gives the lower bound on X.

Example 13–7 Conversion Bounds for a Nonideal Reactor

Living Example Problem

The liquid-phase, second-order dimerization

$$2A \longrightarrow B \qquad r_A = -kC_A^2$$

for which $k = 0.01\ \text{dm}^3/\text{mol}\cdot\text{min}$ is carried out at a reaction temperature of 320 K. The feed is pure A with $C_{A0} = 8\ \text{mol/dm}^3$. The reactor is nonideal and perhaps could be modeled as two CSTRs with interchange. The reactor volume is 1000 dm^3, and the feed rate for our dimerization is going to be 25 dm^3/min. We have run a tracer test on this reactor, and the results are given in columns 1 and 2 of Table E13-7.1. We wish to know the bounds on the conversion for different possible degrees of micromixing for the RTD of this reactor. What are these bounds?

Tracer test on tank reactor: $N_0 = 100$ g, $v = 25\ \text{dm}^3/\text{min}$.

Table E13-7.1 Raw and Processed Data

t (min)	C (mg/dm^3)	$E(t)$ (min^{-1})	$1 - F(t)$	$E(t)/[1 - F(t)]$ (min^{-1})	λ (min)
0	112	0.0280	1.000	0.0280	0
5	95.8	0.0240	0.871	0.0276	5
10	82.2	0.0206	0.760	0.0271	10
15	70.6	0.0177	0.663	0.0267	15
20	60.9	0.0152	0.584	0.0260	20
30	45.6	0.0114	0.472	0.0242	30
40	34.5	0.00863	0.353	0.0244	40
50	26.3	0.00658	0.278	0.0237	50
70	15.7	0.00393	0.174	0.0226	70
100	7.67	0.00192	0.087	0.0221	100
150	2.55	0.000638	0.024	0.0266	150
200	0.90	0.000225	0.003	0.075	200
1	2	3	4	5	6

Columns 3 through 5 are calculated from columns 1 and 2.

Solution

The bounds on the conversion are found by calculating conversions under conditions of complete segregation and maximum mixedness.

Conversion if fluid is completely segregated. The batch reactor equation for a second-order reaction of this type is

$$X = \frac{kC_{A0}t}{1 + kC_{A0}t}$$

Spreadsheets work quite well here.

The conversion for a completely segregated fluid in a reactor is

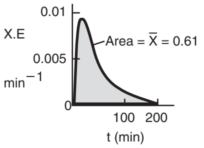
$$\overline{X} = \int_0^\infty X(t)E(t)\,dt$$

The calculations for this integration are carried out in Table E13-7.2. The numerical integration uses the simple trapezoid rule. The conversion for this system if the fluid were completely segregated is 0.61 or 61%.

Table E13-7.2. Segregation Model

t (min)	$X(t)$	$X(t)E(t)$ (min^{-1})	$X(t)E(t)\,\Delta t$
0	0	0	0
5	0.286	0.00686	0.0172†
10	0.444	0.00916	0.0400
15	0.545	0.00965	0.0470
20	0.615	0.00935	0.0475
30	0.706	0.00805	0.0870
40	0.762	0.00658	0.0732
50	0.800	0.00526	0.0592
70	0.848	0.00333	0.0859
100	0.889	0.00171	0.0756
150	0.923	0.000589	0.0575
200	0.941	0.000212	0.0200
			0.610

†For the first point we have X(t)E(t)Δt = (0 + 0.00686) (5/2) = 0.0172



Conversion for maximum mixedness. The Euler method will be used for numerical integration:

$$X_{i+1} = X_i + (\Delta\lambda)\left[\frac{E(\lambda_i)}{1-F(\lambda_i)}X_i - kC_{A0}(1-X_i)^2\right]$$

Integrating this equation presents some interesting results. If the equation is integrated from the exit side of the reactor, starting with λ = 0, the solution is unstable and soon approaches large negative or positive values, depending on what the starting value of X is. We want to find the conversion at the exit to the reactor λ = 0. Consequently, we need to integrate backwards.

$$X_{i-1} = X_i - \Delta\lambda\left[\frac{E(\lambda_i)X_i}{1-F(\lambda_i)} - kC_{A0}(1-X_i)^2\right]$$

If integrated from the point where $\lambda \longrightarrow \infty$, oscillations may occur but are damped out, and the equation approaches the same final value no matter what initial value of X between 0 and 1 is used. We shall start the integration at $\lambda = 200$ and let $X = 0$ at this point. If we set $\Delta\lambda$ too large, the solution will blow up, so we will start out with $\Delta\lambda = 25$ and use the average of the measured values of $E(t)/[(1 - F(t)]$ where necessary. We will now use the data in column 5 of Table E13-7.1 to carry out the integration.

At $\lambda = 200$, $X = 0$

$\lambda = 175$:

$$X(\lambda = 175) = X(\lambda = 200) - \Delta\lambda\left[\frac{E(200)X(200)}{1 - F(200)} - kC_{A0}(1 - X(200))^2\right]$$

$$X = 0 - (25)[(0.075)(0) - ((0.01)(8)(1))^2] = 2$$

$\lambda = 150$:

$$X(\lambda = 150) = X(\lambda = 175) - \Delta\lambda\left[\frac{E(175)X(175)}{1 - F(175)} - kC_{A0}(1 - X(175))^2\right]$$

We need to take an average of $E\,/\,(1 - F)$ between $\lambda = 200$ and $\lambda = 150$.

$$X\,(\lambda = 150) = 2 - (25)\left[\left(\frac{0.075 + 0.0266}{2}\right)(2) - (0.01)(8)(1 - 2)^2\right] = 1.46$$

$\lambda = 125$:

$$X\,(\lambda = 125) = 1.46 - (25)[(0.0266)(1.46) - (0.01)(8)(1 - 1.46)^2] = 0.912$$

$\lambda = 100$:

$$X\,(\lambda = 100) = 0.912 - (25)\left[\left(\frac{0.0266 + 0.0221}{2}\right)(0.912) - (0.01)(8)(1 - 0.912)^2\right]$$

$$= 0.372$$

$\lambda = 70$:

$$X = 0.372 - (30)[(0.0221)(0.372) - (0.01)(8)(1 - 0.372)^2] = 1.071$$

$\lambda = 50$:

$$X = 1.071 - (20)[(0.0226)(1.071) - (0.01)(8)(1 - 1.071)^2] = 0.595$$

$\lambda = 40$:

$$X = 0.595 - (10)[(0.0237)(0.595) - (0.01)(8)(1 - 0.595)^2] = 0.585$$

Summary	
PFR	76%
Segregation	61%
CSTR	58%
Max. mix	56%

Running down the values of X along the right-hand side of the preceding equation shows that the oscillations have now damped out. Carrying out the remaining calculations down to the end of the reactor completes Table E13-7.3. The conversion for a condition of maximum mixedness in this reactor is 0.56 or 56%. It is interesting to note that there is little difference in the conversions for the two conditions of complete segregation (61%) and maximum mixedness (56%). With bounds this narrow, there may not be much point in modeling the reactor to improve the predictability of conversion.

For comparison it is left for the reader to show that the conversion for a PFR of this size would be 0.76, and the conversion in a perfectly mixed CSTR with complete micromixing would be 0.58.

Solved Problems

TABLE E13-7.3. MAXIMUM MIXEDNESS MODEL

λ (min)	X
200	0.0
175	2.0
150	1.46
125	0.912
100	0.372
70	1.071
50	0.595
40	0.585
30	0.580
20	0.581
10	0.576
5	0.567
0	0.564

Calculate backwards to reactor exit.

The Intensity Function, $\Lambda(t)$ can be thought of as the probability of a particle escaping the system between a time t and $(t + dt)$ provided the particle is still in the system. Equations (13-62) and (13-64) can be written in a slightly more compact form by making use of the **intensity function**.[16] The intensity function $\Lambda(\lambda)$ is the fraction of fluid in the vessel with age λ that will leave between λ and $\lambda + d\lambda$. We can relate $\Lambda(\lambda)$ to $I(\lambda)$ and $E(\lambda)$ in the following manner:

$$\begin{bmatrix} \text{Volume of} \\ \text{fluid leaving} \\ \text{between times} \\ \lambda \text{ and } \lambda + d\lambda \end{bmatrix} = \begin{bmatrix} \text{Volume of fluid} \\ \text{remaining at} \\ \text{time } \lambda \end{bmatrix} \begin{bmatrix} \text{Fraction of} \\ \text{the fluid with} \\ \text{age } \lambda \text{ that} \\ \text{will leave between} \\ \text{time } \lambda \text{ and } \lambda + d\lambda \end{bmatrix}$$

$$[v_0 E(\lambda)\, d\lambda] = [V I(\lambda)][\Lambda(\lambda)\, d\lambda] \tag{13-65}$$

Then

$$\Lambda(\lambda) = \frac{E(\lambda)}{\tau I(\lambda)} = -\frac{d \ln[\tau I(\lambda)]}{d\lambda} = \frac{E(\lambda)}{1 - F(\lambda)} \tag{13-66}$$

Combining Equations (13-64) and (13-66) gives

$$\frac{dX}{d\lambda} = \frac{r_A(\lambda)}{C_{A0}} + \Lambda(\lambda) X(\lambda) \tag{13-67}$$

We also note that the exit age, t, is just the sum of the internal age, α, and the life expectancy, λ:

$$t = \alpha + \lambda \tag{13-68}$$

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[16] D. M. Himmelblau and K. B. Bischoff, *Process Analysis and Simulation* (New York: Wiley, 1968).

In addition to defining *maximum mixedness* discussed above, Zwietering[17] also generalized a measure of micromixing proposed by Danckwerts[18] and defined the **degree of segregation**, J, as

$$J = \frac{\text{variance of ages between fluid "points"}}{\text{variance of ages of all molecules in system}}$$

A fluid “point” contains many molecules but is small compared to the scale of mixing. The two extremes of the *degree of segregation* are

$J = 1$: complete segregation
$J = 0$: maximum mixedness

Equations for the variance and J for the intermediate cases can be found in Zwietering.[17]

13.7.3 Comparing Segregation and Maximum Mixedness Predictions

Reference Shelf

In the previous example we saw that the conversion predicted by the segregation model, X_{seg}, was greater than that by the maximum mixedness model $X_{\max}$. Will this always be the case? No. To learn the answer we take the second derivative of the rate law as shown in the Professional Reference Shelf R13.3 on the CD-ROM.

Comparing X_{seg} and X_{mm}

$$\boxed{\begin{array}{llll} \text{If} & \dfrac{\partial^2(-r_A)}{\partial C_A^2} > 0 & \text{then} & X_{\text{seg}} > X_{\text{mm}} \\[2ex] \text{If} & \dfrac{\partial^2(-r_A)}{\partial C_A^2} < 0 & \text{then} & X_{\text{mm}} > X_{\text{seg}} \\[2ex] \text{If} & \dfrac{\partial^2(-r_A)}{\partial C_A^2} = 0 & \text{then} & X_{\text{mm}} = X_{\text{seg}} \end{array}}$$

For example, if the rate law is a power law model

$$-r_A = kC_A^n$$

$$\frac{\partial(-r_A)}{\partial C_A} = nkC_A^{n-1}$$

$$\frac{\partial^2(-r_A)}{\partial C_A^2} = n(n-1)kC_A^{n-2}$$

From the product $[(n)(n-1)]$, we see

If $n > 1$, then $\dfrac{\partial^2(-r_A)}{\partial C_A^2} > 0$ and $X_{\text{seg}} > X_{\text{mm}}$

If $n < 0$, then $\dfrac{\partial^2(-r_A)}{\partial C_A^2} > 0$ and $X_{\text{seg}} > X_{\text{mm}}$

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[17] T. N. Zwietering, *Chem. Eng. Sci.*, *11*, 1 (1959).

[18] P. V. Danckwerts, *Chem. Eng. Sci.*, *8*, 93 (1958).

$$\text{If} \quad 0 < n < 1, \qquad \text{then} \quad \frac{\partial^2(-r_A)}{\partial C_A^2} < 0 \qquad \text{and} \qquad X_{mm} > X_{seg}$$

We note that in some cases X_{seg} is not too different from X_{mm}. However, when one is considering the destruction of toxic waste where $X > 0.99$ is desired, then even a small difference is significant!!

Important point

In this section we have addressed the case where all we have is the RTD and no other knowledge about the flow pattern exists. Perhaps the flow pattern cannot be assumed because of a lack of information or other possible causes. Perhaps we wish to know the extent of possible error from assuming an incorrect flow pattern. We have shown how to obtain the conversion, using only the RTD, for two limiting mixing situations: the earliest possible mixing consistent with the RTD, or maximum mixedness, and mixing only at the reactor exit, or complete segregation. Calculating conversions for these two cases gives bounds on the conversions that might be expected for different flow paths consistent with the observed RTD.

13.8 Using Software Packages

Example 13-7 could have been solved with an ODE solver after fitting $E(t)$ to a polynomial.

Fitting the E(t) Curve to a Polynomial

Some forms of the equation for the conversion as a function of time multiplied by $E(t)$ will not be easily integrated analytically. Consequently, it may be easiest to use ODE software packages. The procedure is straightforward. We recall Equation (13-52)

$$\frac{d\bar{X}}{dt} = X(t)E(t) \tag{13-52}$$

where $\bar{X}$ is the mean conversion and $X(t)$ is the batch reactor conversion at time t. The mean conversion $\bar{X}$ is found by integrating between $t = 0$ and $t = \infty$ or a very large time.

Next we obtain the mole balance on $X(t)$ from a batch reactor

$$\frac{dX}{dt} = -\frac{r_A}{C_{A0}}$$

and would write the rate law in terms of conversion, e.g.,

$$-r_A = kC_{A0}^2(1-X)^2$$

The ODE solver will combine these equations to obtain $X(t)$ which will be used in Equation (13-52). Finally we have to specify $E(t)$. This equation can be an analytical function such as those for an ideal CSTR,

$$E(t) = \frac{e^{-t/\tau}}{\tau}$$

or it can be polynomial or a combination of polynomials that have been used to fit the experimental RTD data

$$E(t) = a_0 + a_1 t + a_2 t^2 + \cdots \tag{13-69}$$

or

$$F(t) = b_0 + b_1 t + b_2 t^2 + \cdots \tag{13-70}$$

CAUTION

We now simply combine Equations (13-52), (13-69), and (13-70) and use an ODE solver. There are three cautions one must be aware of when fitting $E(t)$ to a polynomial. First, you use one polynomial $E_1(t)$ as $E(t)$ increases with time to the top of the curve shown in Figure 13-27. A second polynomial $E_2(t)$ is used from the top as $E(t)$ decreases with time. One needs to match the two curves at the top.

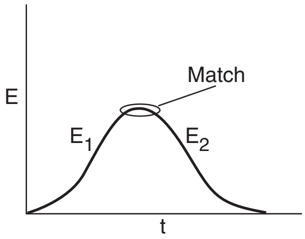


Figure 13-27 Matching $E_1(t)$ and $E_2(t)$.

Summary Notes

Polymath Tutorial

Second, one should be certain that the polynomial used for $E_2(t)$ does not become negative when extrapolated to long times. If it does, then constraints must be placed on the fit using **IF** statements in the fitting program. Finally, one should check that the area under the $E(t)$ curve is virtually one and that the cumulative distribution $F(t)$ at long times is never greater than 1. A tutorial on how to fit the $C(t)$ and $E(t)$ data to a polynomial is given in the *Summary Notes* for Chapter 5 on the CD-ROM and on the web.

Segregation Model

Here we simply use the coupled set of differential equations for the mean or exit conversion, $\bar{X}$, and the conversion $X(t)$ inside a globule at any time, t.

$$\frac{d\bar{X}}{dt} = X(t)E(t) \tag{13-52}$$

$$\frac{dX}{dt} = \frac{-r_A}{C_{A0}} \tag{13-71}$$

The rate of reaction is expressed as a function of conversion: for example,

$$-r_A = k_A C_{A0}^2 (1 - X)^2$$

and the equations are then solved numerically with an ODE solver.

Maximum Mixedness Model

Because most software packages won't integrate backwards, we need to change the variable such that the integration proceeds forward as λ decreases from some large value to zero. We do this by forming a new variable, z, which is the difference between the longest time measured in the $E(t)$ curve, $\bar{T}$, and λ. In the case of Example 13-7, the longest time at which the tracer concentration was measured was 200 minutes (Table E13-7.1). Therefore we will set $\bar{T} = 200$.

$$z = \bar{T} - \lambda = 200 - \lambda$$

$$\lambda = \bar{T} - z = 200 - z$$

Then,

$$\frac{dX}{dz} = -\frac{r_A}{C_{A0}} - \frac{E(\bar{T} - z)}{1 - F(\bar{T} - z)} X \tag{13-72}$$

One now integrates between the limit $z = 0$ and $z = 200$ to find the exit conversion at $z = 200$ which corresponds to $\lambda = 0$.

In fitting $E(t)$ to a polynomial, one has to make sure that the polynomial does not become negative at large times. Another concern in the maximum mixedness calculations is that the term $1 - F(\lambda)$ does not go to zero. Setting the maximum value of $F(t)$ at 0.999 rather than 1.0 will eliminate this problem. It can also be circumvented by integrating the polynomial for $E(t)$ to get $F(t)$ and then setting the maximum value of $F(t)$ at 0.999. If $F(t)$ is ever greater than one when fitting a polynomial, the solution will blow up when integrating Equation (13-72) numerically.

Example 13–8 Using Software to Make Maximum Mixedness Model Calculations

Use an ODE solver to determine the conversion predicted by the **maximum mixedness model** for the $E(t)$ curve given in Example E13-7.

Solution

Because of the nature of the $E(t)$ curve, it is necessary to use two polynomials, a third order and a fourth order, each for a different part of the curve to express the RTD, $E(t)$, as a function of time. The resulting $E(t)$ curve is shown in Figure E13-8.1.

To use Polymath to carry out the integration, we change our variable from λ to z using the largest time measurements that were taken from $E(t)$ in Table E13-7.1, which is 200 min:

First, we fit $E(t)$.

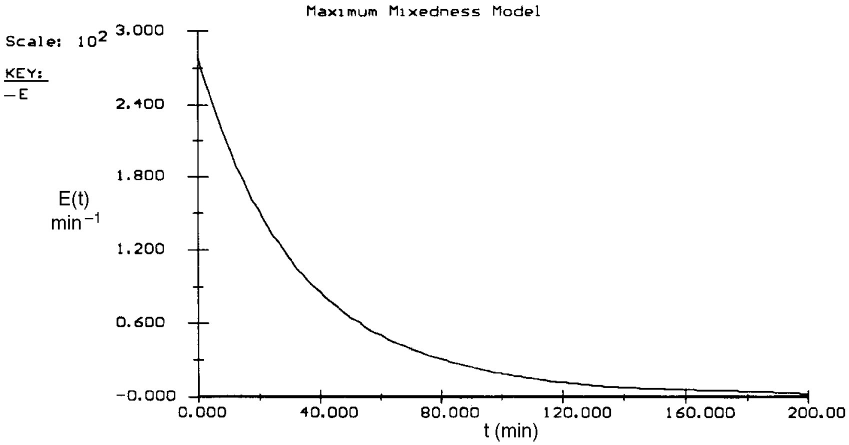


Figure E13-8.1 Polynomial fit of $E(t)$.

$$z = 200 - \lambda$$

The equations to be solved are

$$\lambda = 200 - z \tag{E13-8.1}$$

Maximum mixedness model

$$\frac{dX}{dz} = -\frac{r_A}{C_{A0}} - \frac{E(200-z)}{1-F(200-z)}X \tag{E13-8.2}$$

For values of λ less than 70, we use the polynomial

$$E_1(\lambda) = 4.447e^{-10}\lambda^4 - 1.180e^{-7}\lambda^3 + 1.353e^{-5}\lambda^2 - 8.657e^{-4}\lambda + 0.028 \tag{E13-8.3}$$

For values of λ greater than 70, we use the polynomial

$$E_2(\lambda) = -2.640e^{-9}\lambda^3 + 1.3618e^{-6}\lambda^2 - 2.407e^{-4}\lambda + 0.015 \tag{E13-8.4}$$

$$\frac{dF}{d\lambda} = E(\lambda) \tag{E13-8.5}$$

CAUTION

with $z = 0$ ($\lambda = 200$), $X = 0$, $F = 1$ [i.e., $F(\lambda) = 0.999$]. **Caution:** Because $[1 - F(\lambda)]^{-1}$ tends to infinity at $F = 1$, ($z = 0$), we set the maximum value of F at 0.999 at $z = 0$.

The Polymath equations are shown in Table E13-8.1. The solution is

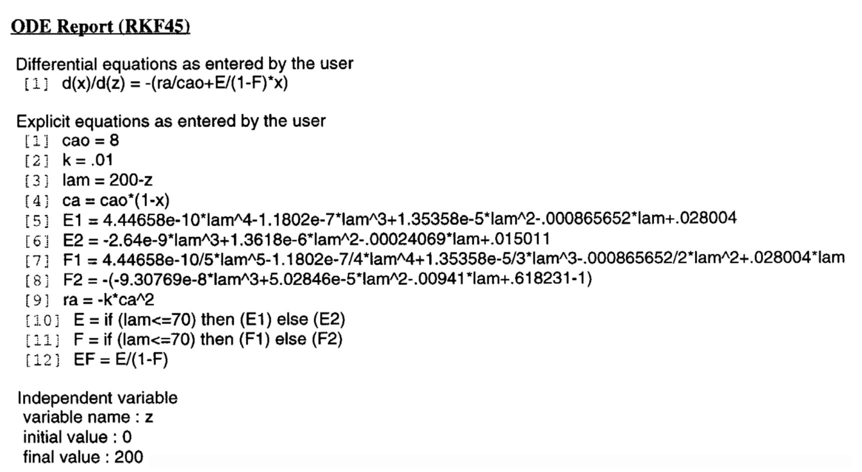
$$\text{at } z = 200 \qquad X = 0.563$$

The conversion predicted by the maximum mixedness model is 56.3%.

Living Example Problem

Polynomials used to fit $E(t)$ and $F(t)$

TABLE E13-8.1. POLYMATH PROGRAM FOR MAXIMUM MIXEDNESS MODEL



```
ODE Report (RKF45)

Differential equations as entered by the user
 [1]  d(x)/d(z) = -(ra/cao+E/(1-F)*x)

Explicit equations as entered by the user
 [1]  cao = 8
 [2]  k = .01
 [3]  lam = 200-z
 [4]  ca = cao*(1-x)
 [5]  E1 = 4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.000865652*lam+.028004
 [6]  E2 = -2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
 [7]  F1 = 4.44658e-10/5*lam^5-1.1802e-7/4*lam^4+1.35358e-5/3*lam^3-.000865652/2*lam^2+.028004*lam
 [8]  F2 = -(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.618231-1)
 [9]  ra = -k*ca^2
 [10]  E = if (lam<=70) then (E1) else (E2)
 [11]  F = if (lam<=70) then (F1) else (F2)
 [12]  EF = E/(1-F)

Independent variable
 variable name : z
 initial value : 0
 final value : 200
```

13.8.1 Heat Effects

If tracer tests are carried out isothermally and then used to predict nonisothermal conditions, one must couple the segregation and maximum mixedness models with the energy balance to account for variations in the specific reaction rate. This approach will only be valid for liquid phase reactions because the volumetric flow rate remains constant. For adiabatic operation and $\Delta C_P = 0$,

$$T = T_0 + \frac{(-\Delta H^\circ_{\mathrm{Rx}})}{\sum \Theta_i C_{P_i}} X \tag{T8-1.B}$$

As before, the specific reaction rate is

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \tag{T8-2.3}$$

Assuming that $E(t)$ is unaffected by temperature variations in the reactor, one simply solves the segregation and maximum mixedness models, accounting for the variation of k with temperature [i.e., conversion; see Problem P13-2$_{\mathrm{A}}$(i)].

13.9 RTD and Multiple Reactions

As discussed in Chapter 6, when multiple reactions occur in reacting systems, it is best to work in concentrations, moles, or molar flow rates rather than conversion.

13.9.1 Segregation Model

In the **segregation model** we consider each of the globules in the reactor to have different concentrations of reactants, C_{A}, and products, C_{P}. These globules are mixed together immediately upon exiting to yield the exit concentration of A, $\overline{C_A}$, which is the average of all the globules exiting:

$$\overline{C_A} = \int_0^{\infty} C_A(t)E(t)\,dt \tag{13-73}$$

$$\overline{C_B} = \int_0^{\infty} C_B(t)E(t)\,dt \tag{13-74}$$

The concentrations of the individual species, $C_A(t)$ and $C_B(t)$, in the different globules are determined from batch reactor calculations. For a constant-volume batch reactor, where q reactions are taking place, the coupled mole balance equations are

$$\frac{dC_A}{dt} = r_A = \sum_{i=1}^{i=q} r_{iA} \tag{13-75}$$

$$\frac{dC_B}{dt} = r_B = \sum_{i=1}^{i=q} r_{iB} \tag{13-76}$$

These equations are solved simultaneously with

$$\frac{d\overline{C_A}}{dt} = C_A(t)E(t) \tag{13-77}$$

$$\frac{d\overline{C_B}}{dt} = C_B(t)E(t) \tag{13-78}$$

to give the exit concentration. The RTDs, $E(t)$, in Equations (13-77) and (13-78) are determined from experimental measurements and then fit to a polynomial.

13.9.2 Maximum Mixedness

For the **maximum mixedness model,** we write Equation (13-62) for each species and replace r_A by the net rate of formation

$$\frac{dC_A}{d\lambda} = -\sum r_{iA} + (C_A - C_{A0})\frac{E(\lambda)}{1-F(\lambda)} \tag{13-79}$$

$$\frac{dC_B}{d\lambda} = -\sum r_{iB} + (C_B - C_{B0})\frac{E(\lambda)}{1-F(\lambda)} \tag{13-80}$$

After substitution for the rate laws for each reaction (e.g., $r_{1A} = k_1C_A$), these equations are solved numerically by starting at a very large value of λ, say $\overline{T} = 200$, and integrating backwards to $\lambda = 0$ to yield the exit concentrations C_A, C_B, ….

We will now show how different RTDs with the *same* mean residence time can produce different product distributions for multiple reactions.

Example 13–9 RTD and Complex Reactions

Living Example Problem

Consider the following set of liquid-phase reactions:

$$A + B \xrightarrow{k_1} C$$

$$A \xrightarrow{k_2} D$$

$$B + D \xrightarrow{k_3} E$$

which are occurring in two different reactors with the same mean residence time $t_m = 1.26$ min. However, the RTD is very different for each of the reactors, as can be seen in Figures E13-9.1 and E13-9.2.

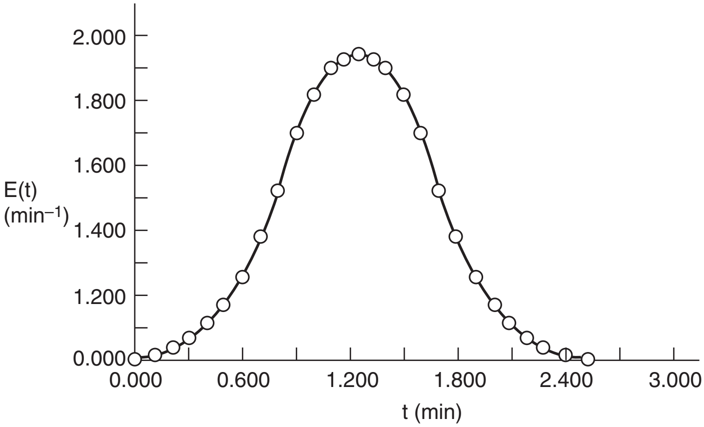


Figure E13-9.1 $E_1(t)$: asymmetric distribution.

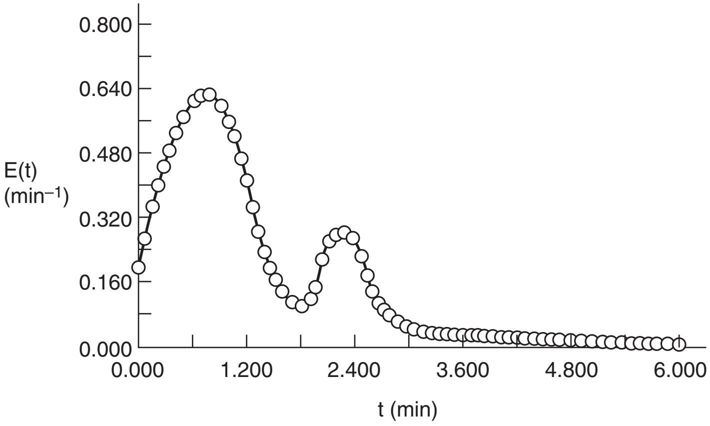


Figure E13-9.2 $E_2(t)$: bimodal distribution.

(a) Fit a polynomial to the RTDs.

(b) Determine the product distribution (e.g., $S_{C/D}$, $S_{D/E}$) for
   1. The segregation model
   2. The maximum mixedness model

Additional Information

$k_1 = k_2 = k_3 = 1$ in appropriate units at 350K.

Solution

Segregation Model

Combining the mole balance and rate laws for a constant-volume batch reactor (i.e., globules), we have

$$\frac{dC_A}{dt} = r_A = r_{1A} + r_{2A} = -k_1 C_A C_B - k_2 C_A \tag{E13-9.1}$$

$$\frac{dC_B}{dt} = r_B = r_{1B} + r_{3B} = -k_1 C_A C_B - k_3 C_B C_D \tag{E13-9.2}$$

$$\frac{dC_C}{dt} = r_C = r_{1C} = k_1 C_A C_B \tag{E13-9.3}$$

$$\frac{dC_D}{dt} = r_D = r_{2D} + r_{3D} = k_2 C_A - k_3 C_B C_D \tag{E13-9.4}$$

$$\frac{dC_E}{dt} = r_E = r_{3E} = k_3 C_B C_D \tag{E13-9.5}$$

and the concentration for each species exiting the reactor is found by integrating the equation

$$\frac{d\overline{C_i}}{dt} = C_i E(t) \tag{E13-9.6}$$

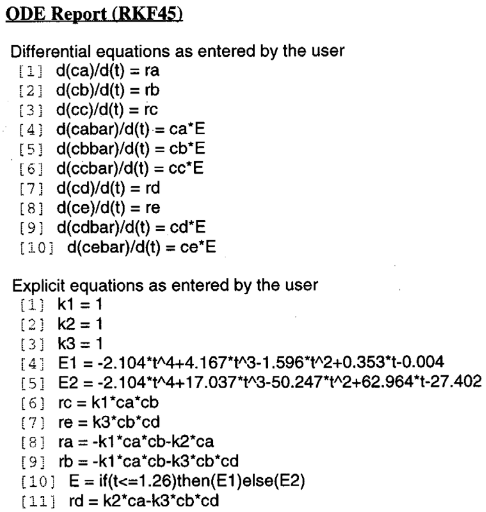
over the life of the $E(t)$ curve. For this example the life of the $E_1(t)$ is 2.42 minutes (Figure E13-9.1), and the life of $E_2(t)$ is 6 minutes (Figure E13-9.2).

The initial conditions are $t = 0$, $C_A = C_B = 1$, and $C_C = C_D = C_E = 0$.

The Polymath program used to solve these equations is shown in Table E13-9.1 for the asymmetric RTD, $E_1(t)$.

With the exception of the polynomial for $E_2(t)$, an identical program to that in Table E13-9.1 for the bimodal distribution is given on the CD-ROM. A comparison of the exit concentration and selectivities of the two RTD curves is shown in Table E13-9.2.

TABLE E13-9.1. POLYMATH PROGRAM FOR SEGREGATION MODEL WITH ASYMMETRIC RTD (MULTIPLE REACTIONS)



ODE Report (RKF45)

```
Differential equations as entered by the user
 [1]  d(ca)/d(t) = ra
 [2]  d(cb)/d(t) = rb
 [3]  d(cc)/d(t) = rc
 [4]  d(cabar)/d(t) = ca*E
 [5]  d(cbbar)/d(t) = cb*E
 [6]  d(ccbar)/d(t) = cc*E
 [7]  d(cd)/d(t) = rd
 [8]  d(ce)/d(t) = re
 [9]  d(cdbar)/d(t) = cd*E
 [10]  d(cebar)/d(t) = ce*E

Explicit equations as entered by the user
 [1]  k1 = 1
 [2]  k2 = 1
 [3]  k3 = 1
 [4]  E1 = -2.104*t^4+4.167*t^3-1.596*t^2+0.353*t-0.004
 [5]  E2 = -2.104*t^4+17.037*t^3-50.247*t^2+62.964*t-27.402
 [6]  rc = k1*ca*cb
 [7]  re = k3*cb*cd
 [8]  ra = -k1*ca*cb-k2*ca
 [9]  rb = -k1*ca*cb-k3*cb*cd
 [10]  E = if(t<=1.26)then(E1)else(E2)
 [11]  rd = k2*ca-k3*cb*cd
```

Living Example Problem

TABLE E13-9.2. SEGREGATION MODEL RESULTS

Asymmetric Distribution		*Bimodal Distribution*	
The solution for $E_1(t)$ is:		The solution for $E_2(t)$ is:	
$\overline{C_A} = 0.151$	$\overline{C_E} = 0.178$	$\overline{C_A} = 0.245$	$\overline{C_E} = 0.162$
$\overline{C_B} = 0.454$	$\overline{X} = 84.9\%$	$\overline{C_B} = 0.510$	$\overline{X} = 75.5\%$
$\overline{C_C} = 0.357$	$S_{C/D} = 1.18$	$\overline{C_C} = 0.321$	$S_{C/D} = 1.21$
$\overline{C_D} = 0.303$	$S_{D/E} = 1.70$	$\overline{C_D} = 0.265$	$S_{D/E} = 1.63$

Maximum Mixedness Model

The equations for each species are

$$\frac{dC_A}{d\lambda} = k_1 C_A C_B + k_2 C_A + (C_A - C_{A0}) \frac{E(\lambda)}{1 - F(\lambda)} \tag{E13-9.7}$$

$$\frac{dC_B}{d\lambda} = k_1 C_A C_B + k_3 C_B C_D + (C_B - C_{B0}) \frac{E(\lambda)}{1 - F(\lambda)} \tag{E13-9.8}$$

$$\frac{dC_C}{d\lambda} = -k_1 C_A C_B + (C_C - C_{C0}) \frac{E(\lambda)}{1 - F(\lambda)} \tag{E13-9.9}$$

$$\frac{dC_D}{d\lambda} = -k_2 C_A + k_3 C_B C_D + (C_D - C_{D0}) \frac{E(\lambda)}{1 - F(\lambda)} \tag{E13-9.10}$$

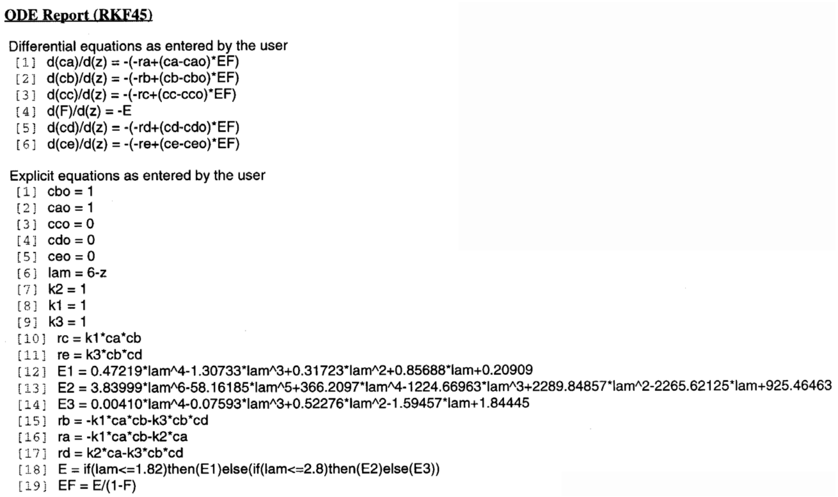
$$\frac{dC_E}{d\lambda} = -k_3 C_B C_D + (C_E - C_{E0}) \frac{E(\lambda)}{1 - F(\lambda)} \tag{E13-9.11}$$

Solved Problems

The Polymath program for the bimodal distribution, $E_2(t)$, is shown in Table E13-9.3. The Polymath program for the asymmetric distribution is identical with the exception of the polynomial fit for $E_1(t)$ and is given on the CD-ROM. A comparison of the exit concentration and selectivities of the two RTD distributions is shown in Table E13-9.4.

Living Example Problem

TABLE E13-9.3. POLYMATH PROGRAM FOR MAXIMUM MIXEDNESS MODEL WITH BIMODAL DISTRIBUTION (MULTIPLE REACTIONS)



```
ODE Report (RKF45)

Differential equations as entered by the user
 [1]  d(ca)/d(z) = -(-ra+(ca-cao)*EF)
 [2]  d(cb)/d(z) = -(-rb+(cb-cbo)*EF)
 [3]  d(cc)/d(z) = -(-rc+(cc-cco)*EF)
 [4]  d(F)/d(z) = -E
 [5]  d(cd)/d(z) = -(-rd+(cd-cdo)*EF)
 [6]  d(ce)/d(z) = -(-re+(ce-ceo)*EF)

Explicit equations as entered by the user
 [1]  cbo = 1
 [2]  cao = 1
 [3]  cco = 0
 [4]  cdo = 0
 [5]  ceo = 0
 [6]  lam = 6-z
 [7]  k2 = 1
 [8]  k1 = 1
 [9]  k3 = 1
 [10]  rc = k1*ca*cb
 [11]  re = k3*cb*cd
 [12]  E1 = 0.47219*lam^4-1.30733*lam^3+0.31723*lam^2+0.85688*lam+0.20909
 [13]  E2 = 3.83999*lam^6-58.16185*lam^5+366.2097*lam^4-1224.66963*lam^3+2289.84857*lam^2-2265.62125*lam+925.46463
 [14]  E3 = 0.00410*lam^4-0.07593*lam^3+0.52276*lam^2-1.59457*lam+1.84445
 [15]  rb = -k1*ca*cb-k3*cb*cd
 [16]  ra = -k1*ca*cb-k2*ca
 [17]  rd = k2*ca-k3*cb*cd
 [18]  E = if(lam<=1.82)then(E1)else(if(lam<=2.8)then(E2)else(E3))
 [19]  EF = E/(1-F)
```

TABLE E13-9.4. MAXIMUM MIXEDNESS MODEL RESULTS

Asymmetric Distribution The solution for $E_1(t)$ (1) is:		*Bimodal Distribution* The solution for $E_2(t)$ (2) is:	
C_A = 0.161	C_E = 0.192	C_A = 0.266	C_E = 0.190
C_B = 0.467	X = 83.9%	C_B = 0.535	X = 73.4%
C_C = 0.341	$S_{C/D}$ = 1.11	C_C = 0.275	$S_{C/D}$ = 1.02
C_D = 0.306	$S_{D/E}$ = 1.59	C_D = 0.269	$S_{D/E}$ = 1.41

Solved Problems

Calculations similar to those in Example 13-9 are given in an example on the CD-ROM for the series reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

In addition, the effect of the variance of the RTD on the parallel reactions in Example 13-9 and on the series reaction in the CD-ROM is shown on the CD-ROM.

Closure After completing this chapter the reader will use the tracer concentration time data to calculate the external age distribution function $E(t)$, the cumulative distribution function $F(t)$, the mean residence time, t_m, and the variance, σ^2. The reader will be able to sketch $E(t)$ for ideal reactors, and by comparing $E(t)$ from experiment with $E(t)$ for ideal reactors (PFR, PBR, CSTR, laminar flow reactor) the reader will be able to diagnose problems in real reactors. The reader will also be able to couple RTD data with reaction kinetics to predict the conversion and exit concentrations using the segregation and the maximum mixedness models without using any adjustable parameters. By analyzing the second derivative of the reaction rate with respect to concentration, the reader will be able to determine whether the segregation model or maximum mixedness model will give the greater conversion.

SUMMARY

1. The quantity $E(t)\,dt$ is the fraction of material exiting the reactor that has spent between time t and $t + dt$ in the reactor.
2. The mean residence time

$$t_m = \int_0^\infty tE(t)\,dt = \tau \tag{S13-1}$$

is equal to the space time τ for constant volumetric flow, $v = v_0$.

3. The variance about the mean residence time is

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)\,dt \tag{S13-2}$$

4. The cumulative distribution function $F(t)$ gives the fraction of effluent material that has been in the reactor a time t or less:

$$F(t) = \int_0^t E(t)\,dt$$

$$1 - F(t) = \text{fraction of effluent material that has been in the reactor a time } t \text{ or longer} \tag{S13-3}$$

5. The RTD functions for an ideal reactor are

Plug-flow: $$E(t) = \delta(t - \tau) \tag{S13-4}$$

CSTR: $$E(t) = \frac{e^{-t/\tau}}{\tau} \tag{S13-5}$$

Laminar flow: $$E(t) = 0 \qquad t < \frac{\tau}{2} \tag{S13-6}$$

$$E(t) = \frac{\tau^2}{2t^3} \qquad t \ge \frac{\tau}{2} \tag{S13-7}$$

6. The dimensionless residence time is

$$\Theta = \frac{t}{\tau} \tag{S13-8}$$

$$E(\Theta) = \tau E(t) \tag{S13-9}$$

7. The internal-age distribution, $[I(\alpha)\ d\alpha]$, gives the fraction of material inside the reactor that has been inside between a time α and a time $(\alpha + d\alpha)$.
8. Segregation model: The conversion is

$$\bar{X} = \int_0^\infty X(t)E(t)\ dt \tag{S13-10}$$

   and for multiple reactions

$$\bar{C}_A = \int_0^\infty C_A(t)E(t)\ dt$$

9. Maximum mixedness: Conversion can be calculated by solving the following equations:

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)}(X) \tag{S13-11}$$

   and for multiple reactions

$$\frac{dC_A}{d\lambda} = -r_{A_{net}} + (C_A - C_{A0})\frac{E(\lambda)}{1-F(\lambda)} \tag{S13-12}$$

$$\frac{dC_B}{d\lambda} = -r_{B_{net}} + (C_B - C_{B0})\frac{E(\lambda)}{1-F(\lambda)} \tag{S13-13}$$

   from $\lambda = \lambda_{max}$ to $\lambda = 0$. To use an ODE solver let $z = \lambda_{max} - \lambda$.

CD-ROM MATERIAL

Summary Notes

- **Learning Resources**
  1. *Summary Notes*
  2. *Web Material Links*
     A. The Attainable Region Analysis *www.engin.umich.edu/~cre/Chapters/ARpages/Intro/intro.htm* and *www.wits.ac.za/fac/engineering/promat/aregion*
  4. *Solved Problems*
     A. Example CD13-1 Calculate the exit concentrations for the series reaction

$$A \longrightarrow B \longrightarrow C$$

     B. Example CD13-2 Determination of the effect of variance on the exit concentrations for the series reaction

$$A \longrightarrow B \longrightarrow C$$

Links

Solved Problems

Living Example Problem

- **Living Example Problems**
  1. *Example 13–6 Laminar Flow Reactor*
  2. *Example 13–8 Using Software to Make Maximum Mixedness Model Calculations*
  3. *Example 13–9 RTD and Complex Reactions*
  4. *Example CD13-1* $A \rightarrow B \rightarrow C$ Effect of RTD
  5. *Example CD13-2* $A \rightarrow B \rightarrow C$ Effect of Variance
- **Professional Reference Shelf**

Reference Shelf

13R.1. *Fitting the Tail*

Whenever there are dead zones into which the material diffuses in and out, the C and E curves may exhibit long tails. This section shows how to analytically describe fitting these tails to the curves.

$$E(t) = ae^{-bt}$$

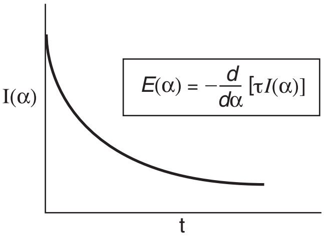
$$b = \text{slope of } \ln E \text{ vs. } t$$

$$a = be^{\mathrm{bt}_1}[1 - F(t_1)]$$

13R.2. *Internal-Age Distribution*

The internal-age distribution currently in the reactor is given by the distribution of ages with respect to how long the molecules have been in the reactor.

The equation for the internal-age distribution is derived and an example is given showing how it is applied to catalyst deactivation in a “fluidized CSTR.”



$$E(\alpha) = -\frac{d}{d\alpha}[\tau I(\alpha)]$$

Example 13R2.1 Mean Catalyst Activity in a Fluidized Bed Reactor.

13R.3. *Comparing* X_{seg} *with* X_{mm}

The derivation of equations using the second derivative criteria

$$\frac{\partial^2(-r_A)}{\partial C_A^2} = ?$$

is carried out.

QUESTIONS AND PROBLEMS

Homework Problems

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

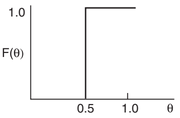
A = ● B = ■ C = ◆ D = ◆◆

P13-1$_A$ Read over the problems of this chapter. Make up an original problem that uses the concepts presented in this chapter. The guidelines are given in Problem P4-1$_A$. RTDs from real reactors can be found in *Ind. Eng. Chem.*, *49*, 1000 (1957); *Ind. Eng. Chem. Process Des. Dev.*, *3*, 381 (1964); *Can. J. Chem. Eng.*, *37*, 107 (1959); *Ind. Eng. Chem.*, *44*, 218 (1952); *Chem. Eng. Sci.*, *3*, 26 (1954); and *Ind. Eng. Chem.*, *53*, 381 (1961).

P13-2$_A$ **What if…**

(a) **Example 13-1.** What fraction of the fluid spends nine minutes or longer in the reactor?

(b) The combinations of ideal reactors are used to model the following real reactors, given $E(\Theta)$, $F(\Theta)$, or $1 - F(\Theta)$.



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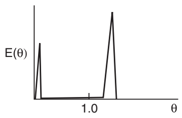

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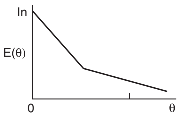

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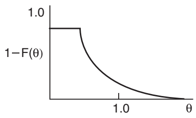

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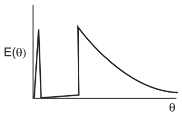

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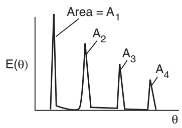

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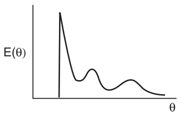

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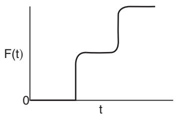

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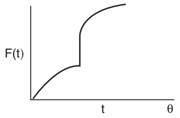

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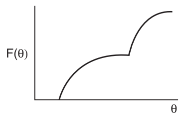


(12)

Suggest a model for each figure.

(c) **Example 13-3.** How would the $E(t)$ change if τ_p as reduced by 50% and τ_s was increased by 50%?

(d) **Example 13-4.** For 75% conversion, what are the relative sizes of the CSTR, PFR, and LFR?

(e) **Example 13-5.** How does the mean conversion compare with the conversion calculated with the same t_m applied to an ideal PFR and CSTR? Can you give examples of $E(t)$ where this calculation would and would not be a good estimate of X?

(f) **Example 13-6.** Load the *Living Example Problem*. How would your results change if $T = 40°\text{C}$? How would your answer change if the reaction was pseudo first order with $kC_{A0} = 4 \times 10^{-3}/\text{s}$? What if the reaction were carried out adiabatically where

$C_{P_A} = C_{P_B} = 20\ cal/mol/K,\ \Delta H^\circ_{Rx} = -10\ kcal/mol$

$k = 0.01\ dm^3/mol/\text{min}$ at 25°C with $E = 8\ kcal/mol$

(g) **Example 13-7.** Load the *Living Example Problem*. How does the X_{seg} and X_{MM} compare with the conversion calculated for a PFR and a CSTR at the mean residence time?

(h) **Example 13-8.** Load the *Living Example Problem*. How would your results change if the reaction was pseudo first order with $k_1 = C_{A0}k = 0.08$ min^{-1}? If the reaction was third order with $kC_{A0}^2 = 0.08$ min^{-1}? If the reaction was half order with $kC_{A0}^{1/2} = 0.08$ min^{-1}? Describe any trends.

(i) **Example 13-9.** Load the *Living Example Problem*. If the activation energies in cal/mol are $E_1 = 5{,}000$, $E_2 = 1{,}000$, and $E_3 = 9{,}000$, how would the selectivities and conversion of A change as the temperature was raised or lowered around 350 K?

(j) **Heat Effects.** Redo *Living Example Problems* 13-7 and 13-8 for the case when the reaction is carried out adiabatically with

(1) Exothermic reaction with

$$T(\text{K}) = T_0 + \left(\frac{-\Delta H_{\text{Rx}}^{\circ}}{C_{\text{P}}}\right)X = 320 + 150X \qquad (13\text{-}2.\text{j}.1)$$

with k given at 320 K and $E = 10{,}000$ cal/mol.

(2) Endothermic reaction with

$$T = 320 - 100X \qquad (13\text{-}2.\text{j}.2)$$

and $E = 45$ kJ/mol. How will your answers change?

(k) you were asked to compare the results from **Example 13-9** for the asymmetric and bimodal distributions in Tables E13-9.2 and E13-9.4. What similarities and differences do you observe? What generalizations can you make?

(l) Repeat (h) above using the RTD in Polymath program E13-8 to predict and compare conversions predicted by the segregation model.

(m) the reaction in **Example 13-5** was half order with $kC_{A0}^{1/2} = 0.08$ min^{-1}? How would your answers change? *Hint:* Modify the Living Example 13-8 program.

(n) you were asked to vary the specific reaction rates k_1 and k_2 in the series reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ given on the Solved Problems CD-ROM? What would you find?

(o) you were asked to vary the isothermal temperature in **Example 13-9** from 300 K, at which the rate constants are given, up to a temperature of 500 K? The activation energies in cal/mol are $E_1 = 5000$, $E_2 = 7000$, and $E_3 = 9000$. How would the selectivity change for each RTD curve?

(p) the reaction in **Example 13-7** were carried out adiabatically with the same parameters as those in Equation [P13-2(j).1]? How would your answers change?

Heat effects

(q) If the reaction in **Examples 13-8** and **13-5** were endothermic and carried out adiabatically with

$$T(K) = 320 - 100X \quad \text{and} \quad E = 45\ \text{kJ/mol} \qquad [\text{P13-2(j).1}]$$

how would your answers change? What generalizations can you make about the effect of temperature on the results (e.g., conversion) predicted from the RTD?

(r) If the reaction in Example 8-12 were carried out in the reactor described by the RTD in Example 13-9 with the exception that RTD is in seconds rather than minutes (i.e., $t_m = 1.26$ s), how would your answers change?

P13-3$_C$ Show that for a first-order reaction

$$A \longrightarrow B$$

the exit concentration maximum mixedness equation

$$\frac{dC_A}{d\lambda} = kC_A + \frac{E(\lambda)}{1-F(\lambda)}(C_A - C_{A0}) \tag{P13-3.1}$$

is the same as the exit concentration given by the segregation model

$$C_A = C_{A0}\int_0^\infty E(t)e^{-kt}\,dt \tag{P13-3.2}$$

[*Hint:* Verify

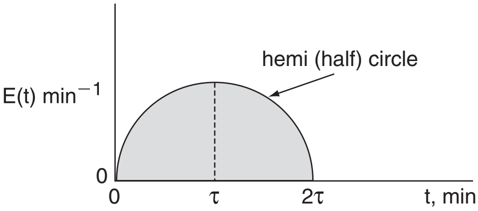
$$C_A(\lambda) = \frac{C_{A0}e^{k\lambda}}{1-F(\lambda)}\int_\lambda^\infty E(t)e^{-kt}\,dt \tag{P13-3.3}$$

is a solution to Equation (P13-3.1).]

P13-4$_C$ The first-order reaction

$$A \longrightarrow B$$

with k = 0.8 min^{-1} is carried out in a real reactor with the following RTD function



For $2\tau \geq t \geq 0$ then $E(t) = \sqrt{\tau^2 - (t-\tau)^2}$ min^{-1}(hemi circle)
For $t > 2\tau$ then $E(t) = 0$

(a) What is the mean residence time?
(b) What is the variance?
(c) What is the conversion predicted by the segregation model?
(d) What is the conversion predicted by the maximum mixedness model?

P13-5$_B$ A step tracer input was used on a real reactor with the following results:

For $t \leq 10$ min, then $C_T = 0$
For $10 \leq t \leq 30$ min, then $C_T = 10$ g/dm^3
For $t \geq 30$ min, then $C_T = 40$ g/dm^3

The second-order reaction A → B with $k = 0.1$ dm^3/mol · min is to be carried out in the real reactor with an entering concentration of A of 1.25 mol/dm^3 at a volumetric flow rate of 10 dm^3/min. Here k is given at 325 K.

(a) What is the mean residence time t_m?
(b) What is the variance σ^2?
(c) What conversions do you expect from an ideal PFR and an ideal CSTR in a real reactor with t_m?

(d) What is the conversion predicted by
  (1) the segregation model?
  (2) the maximum mixedness model?

(e) What conversion is predicted by an ideal laminar flow reactor?

(f) Calculate the conversion using the segregation model assuming $T(\text{K}) = 325 - 500X$ and $E/R = 5000\text{K}$.

P13-6$_B$ The following $E(t)$ curves were obtained from a tracer test on two tubular reactors in which dispersion is believed to occur.

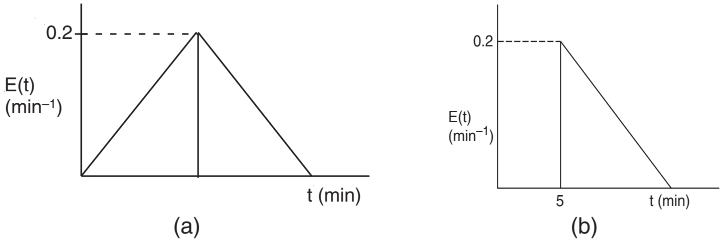


Figure P13-6$_B$ (a) RTD Reactor A; (b) RTD Reactor B.

A second-order reaction

$$A \xrightarrow{k} B \quad \text{with} \quad kC_{A0} = 0.2 \text{ min}^{-1}$$

is to be carried out in this reactor. There is no dispersion occurring either upstream or downstream of the reactor, but there is dispersion inside the reactor. (a) Find the quantities asked for in parts (**a**) through (**e**) in problem P13-5$_B$ for reactor A. (b) Repeat for Reactor B.

P13-7$_B$ The irreversible liquid phase reaction

$$A \xrightarrow{k_1} B$$

is half order in A. The reaction is carried out in a nonideal CSTR, which can be modeled using the segregation model. RTD measurements on the reactor gave values of $\tau = 5$ min and $\sigma = 3$ min. For an entering concentration of pure A of 1.0 mol/dm^3 the mean exit conversion was 10%. Estimate the specific reaction rate constant, k_1. *Hint:* Assume a Gaussian distribution.

P13-8$_B$ The third-order liquid-phase reaction with an entering concentration of 2M

$$A \xrightarrow{k_3} B$$

was carried out in a reactor that has the following RTD

$E(t) = 0$ for $t < 1$ min
$E(t) = 1.0 \text{ min}^{-1}$ for $1 \le t \le 2$ min
$E(t) = 0$ for $t > 2$ min

(a) For isothermal operation, what is the conversion predicted by
  1) a CSTR, a PFR, an LFR, and the segregation model, X_{seg}.
  Hint: Find t_m (i.e., τ) from the data and then use it with $E(t)$ for each of the ideal reactors.
  2) the maximum mixedness model, X_{MM}. Plot X vs. z (or λ) and explain why the curve looks the way it does.

(b) For isothermal operation, at what temperature is the discrepancy between X_{seg} and X_{MM} the greatest in the range $300 \text{ K} < T < 350 \text{ K}$?

(c) Suppose the reaction is carried out adiabatically with an entering temperature of 305 K. Calculate X_{seq}.

Additional Information

$k = 0.3$ dm^6/mol^2/min at 300 K $\quad E/R = 20{,}000$ K

$\Delta H^\circ_{\text{Rx}} = -40{,}000$ cal/mol $\quad C_{P_\text{A}} = C_{P_\text{B}} = 25$ cal/mol/K

P13-9$_\text{A}$ Consider again the nonideal reactor characterized by the RTD data in Example 13-5. The irreversible gas-phase nonelementary reaction

$$\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$$

is first order in A and second order in B and is to be carried out isothermally. Calculate the conversion for:

(a) A PFR, a laminar flow reactor with complete segregation, and a CSTR.
(b) The cases of complete segregation and maximum mixedness.

Also

(c) Plot $I(\alpha)$ and $\Lambda(\lambda)$ as a function of time and then determine the mean age $\bar{\alpha}$ and the mean life expectancy $\bar{\lambda}$.
(d) How would your answers change if the reaction is carried out adiabatically with parameter values given by Equation [P13-2(h).1]?

Additional information:

$C_{\text{A0}} = C_{\text{B0}} = 0.0313$ mol/dm^3, $V = 1000$ dm^3,
$v_0 = 10$ dm^3/s, $k = 175$ dm^6/mol$^2\cdot$s at 320 K.

P13-10$_\text{B}$ An irreversible first-order reaction takes place in a long cylindrical reactor. There is no change in volume, temperature, or viscosity. The use of the simplifying assumption that there is plug flow in the tube leads to an estimated degree of conversion of 86.5%. What would be the actually attained degree of conversion if the real state of flow is laminar, with negligible diffusion?

P13-11$_\text{A}$ Consider a PFR, CSTR, and LFR.

(a) Evaluate the first moment about the mean $m_1 = \int_0^\infty (t-\tau)\ E(t)dt$ for a PFR, a CSTR, and a laminar flow reactor.
(b) Calculate the conversion in each of these ideal reactors for a second-order liquid-phase reaction with Da = 1.0 ($\tau = 2$ min and $kC_{\text{A0}} = 0.5$ min^{-1}).

P13-12$_\text{B}$ For the catalytic reaction

$$\text{A} \xrightarrow[\text{cat}]{} \text{C} + \text{D}$$

the rate law can be written as

$$-r'_\text{A} = \frac{kC_\text{A}}{(1+K_\text{A}C_\text{A})^2}$$

Which will predict the highest conversion, the maximum mixedness model or the segregation model?

Hint: Specify the different ranges of the conversion where one model will dominate over the other.

Additional Information

$C_{A0} = 2\ \text{mol/dm}^3$
$k = 0.01\ \text{dm}^3/\text{mol} \cdot \text{s}$
$K_A = 0.25\ \text{dm}^3/\text{mol}$

P13-13$_D$ Too unlucky! Skip!

P13-14$_C$ The second-order liquid-phase reaction

$$2A \xrightarrow{k_{1A}} B$$

is carried out in a nonideal CSTR. At 300 K the specific reaction rate is 0.5 dm^3/mol·min. In a tracer test, the tracer concentration rose linearly up to 1 mg/dm^3 at 1.0 minutes and then decreased linearly to zero at exactly 2.0 minutes. Pure A enters the reactor at a temperature of 300 K.

(a) Calculate the conversion predicted by the segregation and maximum mixedness models.

(b) Now consider that a second reaction also takes place

$$A + B \xrightarrow{k_{2C}} C, \qquad k_{2C} = 0.12\ \text{dm}^3/\text{mol} \cdot \text{min}$$

Compare the selectivities $\tilde{S}_{B/C}$ predicted by the segregation and maximum mixedness models.

(c) Repeat (a) for adiabatic operation.

Additional information:

$C_{P_A} = 50\ \text{J/mol} \cdot \text{K}$, $C_{P_B} = 100\ \text{J/mol} \cdot \text{K}$, $E = 10\ \text{kcal/mol}$
$\Delta H^\circ_{Rx1A} = -7500\ \text{J/mol}$ $C_{A0} = 2\ \text{mol/dm}^3$

P13-15$_B$ The reactions described in Problem P6-16$_B$ are to be carried out in the reactor whose RTD is described in Problem CDP13-N$_B$.
Determine the exit selectivities

(a) Using the segregation model.

(b) Using the maximum mixedness model.

(c) Compare the selectivities in parts (a) and (b) with those that would be found in an ideal PFR and ideal CSTR in which the space time is equal to the mean residence time.

(d) What would your answers to parts (a) to (c) be if the reactor in Problem P13-7$_B$ were used?

P13-16$_B$ The reactions described in Example 6-10 are to be carried out in the reactor whose RTD is described in Example 13-7 with $C_{A0} = C_{B0} = 0.05\ \text{mol/dm}^3$.

(a) Determine the exit selectivities using the segregation model.

(b) Determine the exit selectivities using the maximum mixedness model.

(c) Compare the selectivities in parts (a) and (b) with those that would be found in an ideal PFR and ideal CSTR in which the space time is equal to the mean residence time.

(d) What would your answers to parts (a) to (c) be if the RTD curve rose from zero at $t = 0$ to a maximum of 50 mg/dm^3 after 10 min, and then fell linearly to zero at the end of 20 min?

P13-17$_B$ The reactions described in Problem P6-12$_B$ are to be carried out in the reactor whose RTD is described in Example 13-9.

(a) Determine the exit selectivities using the segregation model.
(b) Determine the exit selectivities using the maximum mixedness model.
(c) Compare the selectivities in parts (a) and (b) with those that would be found in an ideal PFR and ideal CSTR in which the space time is equal to the mean residence time.

P13-18$_C$ The reactions described in Problem P6-11$_B$ are to be carried out in the reactor whose RTD is described in Problem CDP13-I$_B$ with $C_{A0} = 0.8$ mol/dm^3 and $C_{B0} = 0.6$ mol/dm^3.

(a) Determine the exit selectivities using the segregation model.
(b) Determine the exit selectivities using the maximum mixedness model.
(c) Compare the selectivities in parts (a) and (b) with those that would be found in an ideal PFR and ideal CSTR in which the space time is equal to the mean residence time.
(d) How would your answers to parts (a) and (b) change if the reactor in Problem P13-14$_C$ were used?

P13-19$_B$ The volumetric flow rate through a reactor is 10 dm^3/min. A pulse test gave the following concentration measurements at the outlet:

t (min)	$c \times 10^5$	t (min)	$c \times 10^5$
0	0	15	238
0.4	329	20	136
1.0	622	25	77
2	812	30	44
3	831	35	25
4	785	40	14
5	720	45	8
6	650	50	5
8	523	60	1
10	418		

(a) Plot the external age distribution $E(t)$ as a function of time.
(b) Plot the external age cumulative distribution $F(t)$ as a function of time.
(c) What are the mean residence time t_m and the variance, σ^2?
(d) What fraction of the material spends between 2 and 4 min in the reactor?
(e) What fraction of the material spends longer than 6 min in the reactor?
(f) What fraction of the material spends less than 3 min in the reactor?
(g) Plot the normalized distributions $E(\Theta)$ and $F(\Theta)$ as a function of Θ.
(h) What is the reactor volume?
(i) Plot the internal age distribution $I(t)$ as a function of time.
(j) What is the mean internal age α_m?
(k) Plot the intensity function, $\Lambda(t)$, as a function of time.

Problem P13-19_B will be continued in Chapter 14, P14-13_B.

(l) The activity of a "fluidized" CSTR is maintained constant by feeding fresh catalyst and removing spent catalyst at a constant rate. Using the preceding RTD data, what is the mean catalytic activity if the catalyst decays according to the rate law

$$-\frac{da}{dt} = k_D a^2$$

with

$$k_D = 0.1 \text{ s}^{-1}?$$

(m) What conversion would be achieved in an ideal PFR for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$?

(n) Repeat **(m)** for a laminar flow reactor.

(o) Repeat **(m)** for an ideal CSTR.

(p) What would be the conversion for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$ using the segregation model?

(q) What would be the conversion for a second-order reaction with $kC_{A0} = 0.1 \text{ min}^{-1}$ and $C_{A0} = 1 \text{ mol/dm}^3$ using the maximum mixedness model?

- **Additional Homework Problems**

CDP13-A_C After showing that $E(t)$ for two CSTRs in series having different volumes is

$$E(t) = \frac{1}{\tau(2m-1)}\left\{\exp\left(\frac{-t}{\tau_m}\right) - \exp\left[\frac{-t}{(1-m)\tau}\right]\right\}$$

you are asked to make a number of calculations. [2nd Ed. P13-11]

CDP13-B_B Determine $E(t)$ from data taken from a pulse test in which the pulse is not perfect and the inlet concentration varies with time. [2nd Ed. P13-15]

CDP13-C_B Derive the $E(t)$ curve for a Bingham plastic flowing in a cylindrical tube. [2nd Ed. P13-16]

CDP13-D_B The order of a CSTR and PFR in series is investigated for a third-order reaction. [2nd Ed. P13-10]

CDP13-E_B Review the Murphree pilot plant data when a second-order reaction occurs in the reactor. [1st Ed. P13-15]

CDP13-F_A Calculate the mean waiting time for gasoline at a service station and in a parking garage. [2nd Ed. P13-3]

CDP13-G_B Apply the RTD given by

$$E(t) = \begin{cases} A - B(t_0 - t)^2 & \text{for } 0 \le t \le 2t_0 \\ 0 & \text{for } 0 > 2t_0 \end{cases}$$

to Examples 13-6 through 13-8. [2nd Ed. P13-2_B]

CDP13-H_B The multiple reactions in Problem 6-27 are carried out in a reactor whose RTD is described in Example 13-7.

CDP13-I_B Real RTD data from an industrial packed bed reactor operating poorly. [3rd Ed. P13-5]

CDP13-J_B Real RTD data from distribution in a stirred tank. [3rd Ed. P13-7_B]

CDP13-K_B Triangle RTD with second-order reaction. [3rd Ed. P13-8_B]

CDP13-L_B Derive $E(t)$ for a turbulent flow reactor with 1/7th power law.

CDP13-M_B Good problem—must use numerical techniques. [3rd Ed. P13-12_B]

CDP13-N_B	Internal age distribution for a catalyst. [3rd Ed. P13-13 $_B$]
CDP13-DQEA	U of M, Doctoral Qualifying Exam (DQE), May, 2000
CDP13-DQEB	U of M, Doctoral Qualifying Exam (DQE), April, 1999
CDP13-DQEC	U of M, Doctoral Qualifying Exam (DQE), January, 1999
CDP13-DQED	U of M, Doctoral Qualifying Exam (DQE), January, 1999
CDP13-DQEE	U of M, Doctoral Qualifying Exam (DQE), January, 1998
CDP13-DQEF	U of M, Doctoral Qualifying Exam (DQE), January, 1998
CDP13-ExG	U of M, Graduate Class Final Exam
CDP13-New	New Problems will be inserted from time to time on the web.

SUPPLEMENTARY READING

1. Discussions of the measurement and analysis of residence-time distribution can be found in

Curl, R. L., and M. L. McMillin, "Accuracies in residence time measurements," *AIChE J.*, *12*, 819–822 (1966).

Levenspiel, O., *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999, Chaps. 11–16.

2. An excellent discussion of segregation can be found in

Douglas, J. M., "The effect of mixing on reactor design," *AIChE Symp. Ser.*, *48*, Vol. 60, p. 1 (1964).

3. Also see

Dudukovic, M., and R. Felder, in *CHEMI Modules on Chemical Reaction Engineering*, Vol. 4, ed. B. Crynes and H. S. Fogler. New York: AIChE, 1985.

Nauman, E. B., "Residence time distributions and micromixing," *Chem. Eng. Commun.*, *8*, 53 (1981).

Nauman, E. B., and B. A. Buffham, *Mixing in Continuous Flow Systems*. New York: Wiley, 1983.

Robinson, B. A., and J. W. Tester, *Chem. Eng. Sci.*, *41*(3), 469–483 (1986).

Villermaux, J., "Mixing in chemical reactors," in *Chemical Reaction Engineering—Plenary Lectures*, ACS Symposium Series 226. Washington, D.C.: American Chemical Society, 1982.