14 *Models for Nonideal Reactors*

Success is a journey, not a destination.
Ben Sweetland

Overview Not all tank reactors are perfectly mixed nor do all tubular reactors exhibit plug-flow behavior. In these situations, some means must be used to allow for deviations from ideal behavior. Chapter 13 showed how the RTD was sufficient if the reaction was first order *or* if the fluid was either in a state of complete segregation or maximum mixedness. We use the segregation and maximum mixedness models to bound the conversion when no adjustable parameters are used. For non-first-order reactions in a fluid with good micromixing, more than just the RTD is needed. These situations compose a great majority of reactor analysis problems and cannot be ignored. For example, we may have an existing reactor and want to carry out a new reaction in that reactor. To predict conversions and product distributions for such systems, a model of reactor flow patterns is necessary. To model these patterns, we use combinations and/or modifications of ideal reactors to represent real reactors. With this technique, we classify a model as being either a one-parameter model (e.g., tanks-in-series model or dispersion model) or a two-parameter model (e.g., reactor with bypassing and dead volume). The RTD is then used to evaluate the parameter(s) in the model. After completing this chapter, the reader will be able to apply the tanks-in-series model and the dispersion model to tubular reactors. In addition, the reader will be able to suggest combinations of ideal reactors to model a real reactor.

Use the RTD to evaluate parameters

14.1 Some Guidelines

The overall goal is to use the following equation

$$\boxed{\text{RTD Data} + \text{Kinetics} + \text{Model} = \text{Prediction}}$$

Conflicting goals

The choice of the particular model to be used depends largely on the engineering judgment of the person carrying out the analysis. It is this person's job to choose the model that best combines the conflicting goals of mathematical simplicity and physical realism. There is a certain amount of art in the development of a model for a particular reactor, and the examples presented here can only point toward a direction that an engineer's thinking might follow.

For a given real reactor, it is not uncommon to use all the models discussed previously to predict conversion and then make a comparison. Usually, the real conversion will be *bounded* by the model calculations.

A Model Must
- Fit the data
- Be able to extrapolate theory and experiment
- Have realistic parameters

The following guidelines are suggested when developing models for nonideal reactors:

1. *The model must be mathematically tractable*. The equations used to describe a chemical reactor should be able to be solved without an inordinate expenditure of human or computer time.
2. *The model must realistically describe the characteristics of the nonideal reactor*. The phenomena occurring in the nonideal reactor must be reasonably described physically, chemically, and mathematically.
3. *The model must not have more than two adjustable parameters*. This constraint is used because an expression with more than two adjustable parameters can be fitted to a great variety of experimental data, and the modeling process in this circumstance is nothing more than an exercise in curve fitting. The statement "Give me four adjustable parameters and I can fit an elephant; give me five and I can include his tail!" is one that I have heard from many colleagues. Unless one is into modern art, a substantially larger number of adjustable parameters is necessary to draw a reasonable-looking elephant.[1] A one-parameter model is, of course, superior to a two-parameter model if the one-parameter model is sufficiently realistic. To be fair, however, in complex systems (e.g., internal diffusion and conduction, mass transfer limitations) where other parameters may be measured *independently*, then more than two parameters are quite acceptable.

Table 14-1 gives some guidelines that will help your analysis and model building of nonideal reaction systems.

[1] J. Wei, *CHEMTECH*, *5*, 128 (1975).

TABLE 14-1. A PROCEDURE FOR CHOOSING A MODEL TO PREDICT THE OUTLET CONCENTRATION AND CONVERSION

The Guidelines

1. *Look at the reactor.*
   a. Where are the inlet and outlet streams to and from the reactors? (Is by-passing a possibility?)
   b. Look at the mixing system. How many impellers are there? (Could there be multiple mixing zones in the reactor?)
   c. Look at the configuration. (Is internal recirculation possible? Is the packing of the catalyst particles loose so channeling could occur?)
2. *Look at the tracer data.*
   a. Plot the E(t) and F(t) curves.
   b. Plot and analyze the shapes of the E(Θ) and F(Θ) curves. Is the shape of the curve such that the curve or parts of the curve can be fit by an ideal reactor model? Does the curve have a long tail suggesting a stagnant zone? Does the curve have an early spike indicating bypassing?
   c. Calculate the mean residence time, t_m, and variance, σ^2. How does the t_m determined from the RTD data compare with τ as measured with a yardstick and flow meter? How large is the variance; is it larger or smaller than τ^2?
3. *Choose a model or perhaps two or three models.*
4. *Use the tracer data to determine the model parameters* (e.g., n, D_a, v_b).
5. *Use the CRE algorithm in Chapter 4.* Calculate the exit concentrations and conversion for the model system you have selected.

14.1.1 One-Parameter Models

Here we use a single parameter to account for the nonideality of our reactor. This parameter is most always evaluated by analyzing the RTD determined from a tracer test. Examples of one-parameter models for nonideal CSTRs include a reactor dead volume V_D, where no reaction takes place, or a fraction f of fluid bypassing the reactor, thereby exiting unreacted. Examples of one-parameter models for tubular reactors include the tanks-in-series model and the dispersion model. For the tanks-in-series model, the parameter is the number of tanks, n, and for the dispersion model, it is the dispersion coefficient, D_a. Knowing the parameter values, we then proceed to determine the conversion and/or effluent concentrations for the reactor.

Nonideal tubular reactors

We first consider nonideal tubular reactors. Tubular reactors may be empty, or they may be packed with some material that acts as a catalyst, heat-transfer medium, or means of promoting interphase contact. Until now when analyzing ideal tubular reactors, it usually has been assumed that the fluid moved through the reactor in piston-like flow (PFR), and every atom spends an identical length of time in the reaction environment. Here, the *velocity profile is flat,* and there is no axial mixing. Both of these assumptions are false to some extent in every tubular reactor; frequently, they are sufficiently false to warrant some modification. Most popular tubular reactor models need to have means to allow for failure of the plug-flow model and insignificant axial mixing assumptions; examples include the unpacked laminar flow tubular reactor, the unpacked turbulent flow, and packed-bed reactors. One of two approaches is usually taken to compensate for failure of either or both of the ideal assumptions. One approach involves modeling the nonideal tubular reactor as a series

of identically sized CSTRs. The other approach (the dispersion model) involves a modification of the ideal reactor by imposing axial dispersion on plug flow.

14.1.2 Two-Parameter Models

The premise for the two-parameter model is that we can use a combination of ideal reactors to model the real reactor. For example, consider a packed bed reactor with channeling. Here the response to a pulse tracer input would show two dispersed pulses in the output as shown in Figure 13-10 and Figure 14-1.

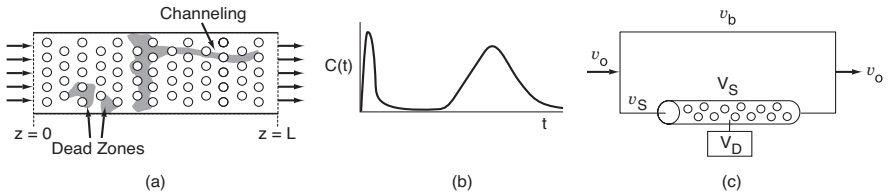


Figure 14-1 (a) Real system; (b) outlet for a pulse input; (c) model system.

Here we could model the real reactor as two ideal PBRs in parallel with the two parameters being the fluid that channels, v_b, and the reactor dead volume, V_D. The real reactor voume is $V = V_D + V_S$ with $v_0 = v_b + v_S$.

14.2 Tanks-in-Series (T-I-S) Model

In this section we discuss the use of the tanks-in-series (T-I-S) model to describe nonideal reactors and calculate conversion. The T-I-S model is a one-parameter model. We will analyze the RTD to determine the number of ideal tanks, n, in series that will give approximately the same RTD as the nonideal reactor. Next we will apply the reaction engineering algorithm developed in Chapters 1 through 4 to calculate conversion. We are first going to develop the RTD equation for three tanks in series (Figure 14-2) and then generalize to n reactors in series to derive an equation that gives the number of tanks in series that best fits the RTD data.

n = ?

In Figure 2-9, we saw how tanks in series could approximate a PFR.

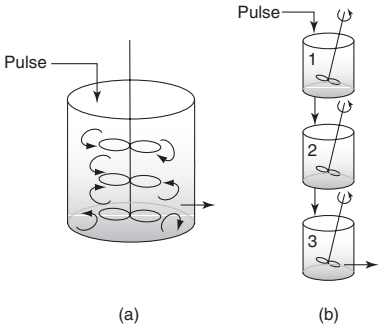


Figure 14-2 Tanks in series: (a) real system, (b) model system.

The RTD will be analyzed from a tracer pulse injected into the first reactor of three equally sized CSTRs in series. Using the definition of the RTD presented in Section 13.2, the fraction of material leaving the system of three reactors (i.e., leaving the third reactor) that has been in the system between time t and $t + \Delta t$ is

$$E(t)\,\Delta t = \frac{vC_3(t)\,\Delta t}{N_0} = \frac{C_3(t)}{\displaystyle\int_0^\infty C_3(t)\,dt}\,\Delta t$$

Then

$$E(t) = \frac{C_3(t)}{\displaystyle\int_0^\infty C_3(t)\,dt} \tag{14-1}$$

In this expression, $C_3(t)$ is the concentration of tracer in the effluent from the third reactor and the other terms are as defined previously.

It is now necessary to obtain the outlet concentration of tracer, $C_3(t)$, as a function of time. As in a single CSTR, a material balance on the first reactor gives

$$V_1 \frac{dC_1}{dt} = -vC_1 \tag{14-2}$$

We perform a tracer balance on each reactor to obtain $C_3(t)$

Integrating gives the expression for the tracer concentration in the effluent from the first reactor:

$$C_1 = C_0 e^{-vt/V_1} = C_0\, e^{-t/\tau_1} \tag{14-3}$$

$$C_0 = N_0/V_1 = \frac{v_0 \displaystyle\int_0^\infty C_3(t)\,dt}{V_1}$$

The volumetric flow rate is constant ($v = v_0$) and all the reactor volumes are identical ($V_1 = V_2 = V_i$); therefore, all the space times of the individual reactors are identical ($\tau_1 = \tau_2 = \tau_i$). Because V_i is the volume of a single reactor in the series, τ_i here is the residence time in *one* of the reactors, *not* in the entire reactor system (i.e., $\tau_i = \tau/n$).

A material balance on the tracer in the second reactor gives

$$V_2 \frac{dC_2}{dt} = vC_1 - vC_2$$

Using Equation (14-3) to substitute for C_1, we obtain the first-order ordinary differential equation

$$\frac{dC_2}{dt} + \frac{C_2}{\tau_i} = \frac{C_0}{\tau_i} e^{-t/\tau_i}$$

This equation is readily solved using an integrating factor e^{t/τ_i} along with the initial condition $C_2 = 0$ at $t = 0$, to give

$$C_2 = \frac{C_0 t}{\tau_i} e^{-t/\tau_i} \tag{14-4}$$

The same procedure used for the third reactor gives the expression for the concentration of tracer in the effluent from the third reactor (and therefore from the reactor system),

$$C_3 = \frac{C_0 t^2}{2\tau_i^2} e^{-t/\tau_i} \tag{14-5}$$

Substituting Equation (14-5) into Equation (14-1), we find that

$$E(t) = \frac{C_3(t)}{\int_0^\infty C_3(t)dt} = \frac{C_0 t^2/(2\tau_i^2) e^{-t/\tau_i}}{\int_0^\infty \frac{C_0 t^2 e^{-t/\tau_i}}{2\tau_i^2} dt}$$

$$= \frac{t^2}{2\tau_i^3} e^{-t/\tau_i} \tag{14-6}$$

Generalizing this method to a series of n CSTRs gives the RTD for n CSTRs in series, $E(t)$:

RTD for equal-size tanks in series

$$\boxed{E(t) = \frac{t^{n-1}}{(n-1)!\tau_i^n} e^{-t/\tau_i}} \tag{14-7}$$

Because the total reactor volume is nV_i, then $\tau_i = \tau/n$, where τ represents the total reactor volume divided by the flow rate, v:

$$E(\Theta) = \tau E(t) = \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta} \tag{14-8}$$

where $\Theta = t/\tau$.

Figure 14-3 illustrates the RTDs of various numbers of CSTRs in series in a two-dimensional plot (a) and in a three-dimensional plot (b). As the number becomes very large, the behavior of the system approaches that of a plug-flow reactor.

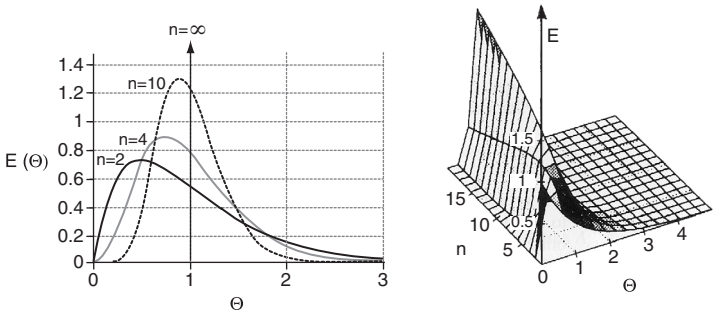


Figure 14-3 Tanks-in-series response to a pulse tracer input for different numbers of tanks.

We can determine the number of tanks in series by calculating the dimensionless variance σ_Θ^2 from a tracer experiment.

$$\sigma_\Theta^2 = \frac{\sigma^2}{\tau^2} = \int_0^\infty (\Theta - 1)^2 E(\Theta)\, d\Theta$$

$$= \int_0^\infty \Theta^2 E(\Theta)\, d\Theta - 2\int_0^\infty \Theta E(\Theta)\, d\Theta + \int_0^\infty E(\Theta)\, d\Theta \qquad (14\text{-}9)$$

$$\boxed{\sigma_\Theta^2 = \int_0^\infty \Theta^2 E(\Theta)\, d\Theta - 1} \qquad (14\text{-}10)$$

$$= \int_0^\infty \Theta^2 \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta}\, d\Theta - 1$$

$$\sigma_\Theta^2 = \frac{n^n}{(n-1)!}\int_0^\infty \Theta^{n+1} e^{-n\Theta}\, d\Theta - 1$$

$$= \frac{n^n}{(n-1)!}\left[\frac{(n+1)!}{n^{n+2}}\right] - 1$$

As the number of tanks increases, the variance decreases.

$$= \frac{1}{n} \qquad (14\text{-}11)$$

The number of tanks in series is

$$\boxed{n = \frac{1}{\sigma_\Theta^2} = \frac{\tau^2}{\sigma^2}} \qquad (14\text{-}12)$$

This expression represents the number of tanks necessary to model the real reactor as n ideal tanks in series. If the number of reactors, n, turns out to be

small, the reactor characteristics turn out to be those of a single CSTR or perhaps two CSTRs in series. At the other extreme, when n turns out to be large, we recall from Chapter 2 the reactor characteristics approach those of a PFR.

If the reaction is first order, we can use Equation (4-11) to calculate the conversion,

$$X = 1 - \frac{1}{(1+\tau_i k)^n} \tag{4-11}$$

where

$$\tau_i = \frac{V}{v_0 n}$$

It is acceptable (and usual) for the value of n calculated from Equation (14-12) to be a noninteger in Equation (4-11) to calculate the conversion. For reactions other than first order, an integer number of reactors must be used and sequential mole balances on each reactor must be carried out. If, for example, n = 2.53, then one could calculate the conversion for two tanks and also for three tanks to bound the conversion. The conversion and effluent concentrations would be solved sequentially using the algorithm developed in Chapter 4. That is, after solving for the effluent from the first tank, it would be used as the input to the second tank and so on as shown in Table 14-2.

TABLE 14-2. TANKS-IN-SERIES SECOND-ORDER REACTION

Two-Reactor System	Three-Reactor System
For two equally sized reactors	For three equally sized reactors
$V = V_1 + V_2$	$V = V_1 + V_2 + V_3$
$V_1 = V_2 = \frac{V}{2}$	$V_1 = V_2 = V_3 = V/3$
$\tau_2 = \frac{V_2}{v_0} = \frac{V/2}{v_0} = \frac{\tau}{2}$	$\tau_1 = \tau_2 = \tau_3 = \frac{V/3}{v_0} = \frac{\tau}{3}$

For a second-order reaction, the combined mole balance, rate law, and stoichiometry for the first reactor gives

$$\tau = \frac{C_{\text{Ain}} - C_{\text{Aout}}}{k_1 C_{\text{Aout}}^2}$$

Solving for C_{Aout}

$$C_{\text{Aout}} = \frac{-1 + \sqrt{1 + 4k\tau C_{\text{Ain}}}}{2k\tau}$$

Two-Reactor System: $\tau_2 = \frac{\tau}{2}$ Three-Reactor System: $\tau_3 = \frac{\tau}{3}$

Solving for exit concentration from reactor 1 for each reactor system gives

$$C_{\text{A1}} = \frac{-1 + \sqrt{1 + 4\tau_2 k C_{\text{A0}}}}{2\tau_2 k} \qquad C'_{A1} = \frac{-1 + \sqrt{1 + 4\tau_3 k C_{\text{A0}}}}{2\tau_3 k}$$

The exit concentration from the second reactor for each reactor system gives

TABLE 14-2. TANKS-IN-SERIES SECOND-ORDER REACTION (CONTINUED)

Two-Reactor System	Three-Reactor System
$C_{A2} = \dfrac{-1+\sqrt{1+4\tau_2 k C_{A1}}}{2\tau_2 k}$	$C'_{A2} = \dfrac{-1+\sqrt{1+4\tau_3 k C'_{A1}}}{2\tau_3 k}$

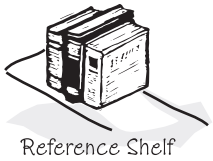
Balancing on the third reactor for the three-reactor system and solving for its outlet concentration, C'_{A3}, gives

$$C'_{A3} = \frac{-1+\sqrt{1+4\tau_3 k C'_{A2}}}{2\tau_3 k}$$

The corresponding conversion for the two- and three-reactor systems are

$$X_2 = \frac{C_{A0} - C_{A2}}{C_{A0}} \qquad X'_3 = \frac{C_{A0} - C'_{A3}}{C_{A0}}$$

For $n = 2.53$, $(X_2 < X < X'_3)$



Tanks-in-Series Versus Segregation for a First-Order Reaction We have already stated that the segregation and maximum mixedness models are equivalent for a first-order reaction. The proof of this statement was left as an exercise in Problem P13-3$_B$. We now show the tanks-in-series model and the segregation models are equivalent for a first-order reaction.

Example 14–1 Equivalency of Models for a First-Order Reaction

Show that $X_{T-I-S} = X_{MM}$ for a first-order reaction

$$A \xrightarrow{k} B$$

Solution

For a first-order reaction, we already showed in Problem P13-3 that

$$\boxed{X_{Seg} = X_{MM}}$$

Therefore we only need to show $X_{Seg} = X_{T\text{-}I\text{-}S}$.
For a first-order reaction in a batch reactor the conversion is

$$X = 1 - e^{-kt} \tag{E14-1.1}$$

Segregation Model

$$\bar{X} = \int_0^\infty X(t)E(t)dt = \int_0^\infty (1 - e^{-kt})E(t)dt \tag{E14-1.2}$$

$$= 1 - \int_0^\infty e^{-kt}E(t)dt \tag{E14-1.3}$$

Using Maclaurin's series expansion gives

$$e^{-kt} = 1 - kt + \frac{k^2t^2}{2} + \text{Error} \tag{E14-1.4}$$

neglecting the error term

$$\overline{X} = 1 - \int_0^\infty \left[1 - kt + \frac{k^2t^2}{2}\right] E(t)dt \tag{E14-1.5}$$

$$\overline{X} = \tau k - \frac{k^2}{2}\int_0^\infty t^2 E(t)dt \tag{E14-1.6}$$

To evaluate the second term, we first recall Equation (E13-2.5) for the variance

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt = \int_0^\infty t^2 E(t)dt - 2\tau\int_0^\infty tE(t)dt + \tau^2\int_0^\infty E(t)dt \tag{E14-1.7}$$

$$\sigma^2 = \int_0^\infty t^2 E(t)dt - 2\tau^2 + \tau^2 \tag{E14-1.8}$$

Rearranging Equation (E14-1.8)

$$\int_0^\infty t^2 E(t)dt = \sigma^2 + \tau^2 \tag{E14-1.9}$$

Combining Equations (E14-1.6) and (E14-1.9), we find the mean conversion for the segregation model for a first-order reaction is

$$\boxed{\overline{X} = \tau k - \frac{k^2}{2}(\sigma^2 + \tau^2)} \tag{E14-1.10}$$

Tanks in Series

Recall from Chapter 4, for n tanks in series for a first-order reaction, the conversion is

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n}k\right)^n} \tag{4-11}$$

Rearranging yields

$$X = 1 - \left(1 + \frac{\tau}{n}k\right)^{-n} \tag{E14-1.11}$$

We now expand in a binomial series

$$X = 1 - \left[1 - n\frac{\tau}{n}k + \frac{n(n+1)}{2}\frac{\tau^2k^2}{n^2} + \text{Error}\right] \tag{E14-1.12}$$

$$= k\tau - \frac{\tau^2k^2}{2} - \frac{\tau^2k^2}{2n} + \text{Error} \tag{E14-1.13}$$

Neglecting the error gives

$$X = k\tau - \frac{k^2}{2}\left[\tau^2 + \frac{\tau^2}{n}\right] \qquad \text{(E14-1.14)}$$

Rearranging Equation (14-12) in the form

$$\frac{\tau^2}{n} = \sigma^2 \qquad (14\text{-}12)$$

and substituting in Equation (E14-1.14) the mean conversion for the T-I-S model is

$$\boxed{X = \tau k - \frac{k^2}{2}(\tau^2 + \sigma^2)} \qquad \text{(E14-1.15)}$$

We see that Equations (E14-1.10) and (E14-1.15) are identical; thus, the conversions are identical, and for a first-order reaction we have

Important Result

$$\boxed{X_{\text{T-I-S}} = X_{\text{Seg}} = X_{\text{MM}}}$$

But this is true only for a first-order reaction.

14.3 Dispersion Model

The dispersion model is also used to describe nonideal tubular reactors. In this model, there is an axial dispersion of the material, which is governed by an analogy to Fick's law of diffusion, superimposed on the flow as shown in Figure 14-4. So in addition to transport by bulk flow, UA_cC, every component in the mixture is transported through any cross section of the reactor at a rate equal to $[-D_a A_c(dC/dz)]$ resulting from molecular and convective diffusion. By convective diffusion (i.e., dispersion) we mean either Aris-Taylor dispersion in laminar flow reactors or turbulent diffusion resulting from turbulent eddies. Radial concentration profiles for plug flow (a) and a representative axial and radial profile for dispersive flow (b) are shown in Figure 14-4. Some molecules will diffuse forward ahead of the molar average velocity while others will lag behind.

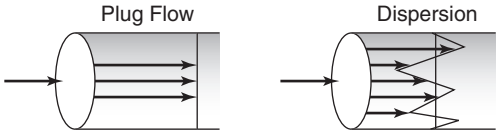


Figure 14-4 Concentration profiles (a) without and (b) with dispersion.

To illustrate how dispersion affects the concentration profile in a tubular reactor we consider the injection of a perfect tracer pulse. Figure 14-5 shows how dispersion causes the pulse to broaden as it moves down the reactor and becomes less concentrated.

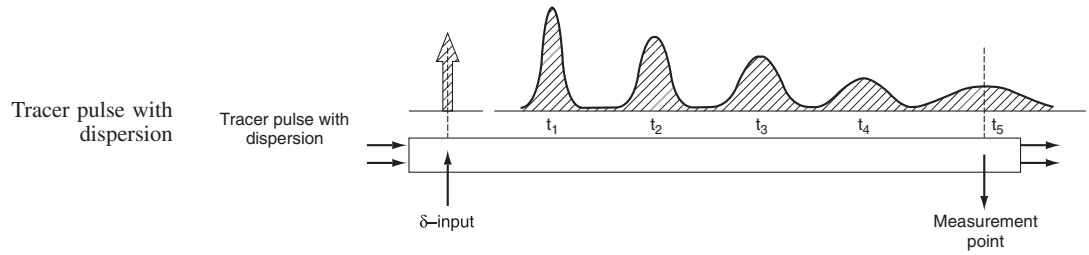


Figure 14-5 Dispersion in a tubular reactor. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

Recall Equation (11-20). The molar flow rate of tracer (F_T) by both convection and dispersion is

$$F_T = \left[- D_a \frac{\partial C_T}{\partial z} + UC_T \right] A_c \tag{11-20}$$

In this expression D_a is the effective dispersion coefficient (m^2/s) and U (m/s) is the superficial velocity. To better understand how the pulse broadens, we refer to the concentration peaks t_2 and t_3 in Figure 14-6. We see that there is a concentration gradient on both sides of the peak causing molecules to diffuse away from the peak and thus broaden the pulse. The pulse broadens as it moves through the reactor.

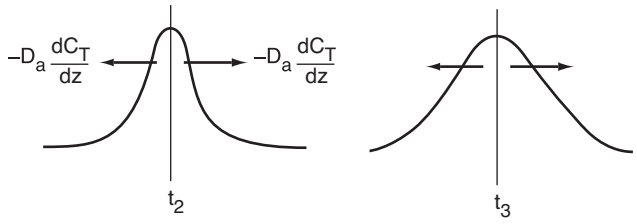


Figure 14-6 Symmetric concentration gradients causing the spreading by dispersion of a pulse input.

Correlations for the dispersion coefficients in both liquid and gas systems may be found in Levenspiel.[2] Some of these correlations are given in Section 14.4.5.

[2] O. Levenspiel, *Chemical Reaction Engineering* (New York: Wiley, 1962), pp. 290–293.

A mole balance on the inert tracer T gives

$$-\frac{\partial F_T}{\partial z} = A_c \frac{\partial C_T}{\partial t}$$

Substituting for F_T and dividing by the cross-sectional area A_c, we have

Pulse tracer balance with dispersion

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (UC_T)}{\partial z} = \frac{\partial C_T}{\partial t} \tag{14-13}$$

Once we know the boundary conditions, the solution to Equation (14-13) will give the outlet tracer concentration–time curves. Consequently, we will have to wait to obtain this solution until we discuss the boundary conditions in Section 14.4.2.

The Plan

We are now going to proceed in the following manner. First, we will write the balance equations for dispersion with reaction. We will discuss the two types of boundary conditions: closed-closed and open-open. We will then obtain an analytical solution for the closed-closed system for the conversion for a first-order reaction in terms of the Peclet number (dispersion coefficient) and the Damköhler number. We then will discuss how the dispersion coefficient can be obtained either from correlations or from the analysis of the RTD curve.

14.4 Flow, Reaction, and Dispersion

Now that we have an intuitive feel for how dispersion affects the transport of molecules in a tubular reactor, we shall consider two types of dispersion in a tubular reactor, *laminar* and *turbulent*.

14.4.1 Balance Equations

A mole balance is taken on a particular component of the mixture (say, species A) over a short length Δz of a tubular reactor of cross section A_c in a manner identical to that in Chapter 1, to arrive at

$$-\frac{1}{A_c}\frac{dF_A}{dz} + r_A = 0 \tag{14-14}$$

Combining Equations (14-14) and the equation for the molar flux F_A, we can rearrange Equation (11-22) in Chapter 11 as

$$\boxed{\frac{D_a}{U}\frac{d^2C_A}{dz^2} - \frac{dC_A}{dz} + \frac{r_A}{U} = 0} \tag{14-15}$$

This equation is a second-order ordinary differential equation. It is nonlinear when r_A is other than zero or first order.

When the reaction rate r_A is first order, $r_A = -kC_A$, then Equation (14-16)

Flow, reaction, and dispersion

$$\boxed{\frac{D_a}{U}\frac{d^2C_A}{dz^2} - \frac{dC_A}{dz} - \frac{kC_A}{U} = 0} \tag{14-16}$$

is amenable to an analytical solution. However, before obtaining a solution, we put our Equation (14-16) describing dispersion and reaction in dimensionless form by letting $\psi = C_A/C_{A0}$ and $\lambda = z/L$:

D_a = Dispersion coefficient

$$\boxed{\frac{1}{\mathrm{Pe}_r}\frac{d^2\psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - \boldsymbol{Da}\cdot\psi = 0} \tag{14-17}$$

Da = Damköhler number

The quantity ***Da*** appearing in Equation (14-17) is called the *Damköhler number* for convection and physically represents the ratio

Damköhler number for a first-order reaction

$$\boldsymbol{Da} = \frac{\text{Rate of consumption of A by reaction}}{\text{Rate of transport of A by convection}} = k\tau \tag{14-18}$$

The other dimensionless term is the *Peclet number,* Pe,

$$\mathrm{Pe} = \frac{\text{Rate of transport by convection}}{\text{Rate of transport by diffusion or dispersion}} = \frac{Ul}{D_a} \tag{14-19}$$

in which l is the characteristic length term. There are two different types of Peclet numbers in common use. We can call Pe_r the reactor Peclet number; it uses the reactor length, L, for the characteristic length, so $\mathrm{Pe}_r \equiv UL/D_a$. It is Pe_r that appears in Equation (14-17). The reactor Peclet number, Pe_r, for mass dispersion is often referred to in reacting systems as the Bodenstein number, Bo, rather than the Peclet number. The other type of Peclet number can be called the fluid Peclet number, Pe_f; it uses the characteristic length that determines the fluid's mechanical behavior. In a packed bed this length is the particle diameter d_p, and $\mathrm{Pe}_f \equiv Ud_p/\phi D_a$. (The term U is the empty tube or superficial velocity. For packed beds we often wish to use the average interstitial velocity, and thus U/ϕ is commonly used for the packed-bed velocity term.) In an empty tube, the fluid behavior is determined by the tube diameter d_t, and $\mathrm{Pe}_f = Ud_t/D_a$. The fluid Peclet number, Pe_f, is given in all correlations relating the Peclet number to the Reynolds number because both are directly related to the fluid mechanical behavior. It is, of course, very simple to convert Pe_f to Pe_r: Multiply by the ratio L/d_p or L/d_t. The reciprocal of Pe_r, D_a/UL, is sometimes called the *vessel dispersion number.*

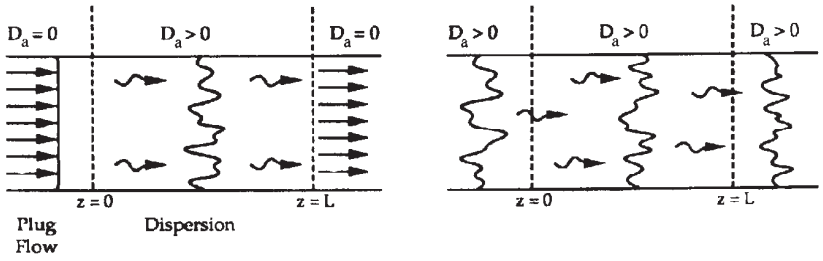
For open tubes $\mathrm{Pe}_r \sim 10^6$, $\mathrm{Pe}_f \sim 10^4$

For packed beds $\mathrm{Pe}_r \sim 10^3$, $\mathrm{Pe}_f \sim 10^1$

14.4.2 Boundary Conditions

There are two cases that we need to consider: boundary conditions for closed vessels and open vessels. In the case of closed-closed vessels, we assume that there is no dispersion or radial variation in concentration either upstream (closed) or downstream (closed) of the reaction section; hence this is a closed-closed vessel. In an open vessel, dispersion occurs both upstream (open) and downstream (open) of the reaction section; hence this is an

open-open vessel. These two cases are shown in Figure 14-7, where fluctuations in concentration due to dispersion are superimposed on the plug-flow velocity profile. A closed-open vessel boundary condition is one in which there is no dispersion in the entrance section but there is dispersion in the reaction and exit sections.

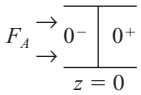


Closed-closed vessel Open-open vessel

Figure 14-7 Types of boundary conditions.

14.4.2A Closed-Closed Vessel Boundary Condition

For a closed-closed vessel, we have plug flow (no dispersion) to the immediate left of the entrance line ($z = 0^-$) (closed) and to the immediate right of the exit $z = L$ ($z = L^+$) (closed). However, between $z = 0^+$ and $z = L^-$, we have dispersion and reaction. The corresponding entrance boundary condition is



At $z = 0$: $$F_A(0^-) = F_A(0^+)$$

Substituting for F_A yields

$$UA_cC_A(0^-) = -A_cD_a\left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + UA_cC_A(0^+)$$

Solving for the entering concentration $C_A(0^-) = C_{A0}$:

Concentration boundary conditions at the entrance

$$\boxed{C_{A0} = \frac{-D_a}{U}\left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + C_A(0^+)} \tag{14-20}$$

At the exit to the reaction section, the concentration is continuous, and there is no gradient in tracer concentration.

Concentration boundary conditions at the exit

At $z = L$: $$\boxed{\begin{aligned} &C_A(L^-) = C_A(L^+) \\ &\frac{\partial C_A}{\partial z} = 0 \end{aligned}} \tag{14-21}$$

These two boundary conditions, Equations (14-20) and (14-21), first stated by Danckwerts,[3] have become known as the famous *Danckwerts boundary conditions*. Bischoff[4] has given a rigorous derivation of them, solving the differential equations governing the dispersion of component A in the entrance and exit sections and taking the limit as D_a in the entrance and exit sections approaches zero. From the solutions he obtained boundary conditions on the reaction section identical with those Danckwerts proposed.

The closed-closed concentration boundary condition at the entrance is shown schematically in Figure 14-8. One should not be uncomfortable with the discontinuity in concentration at $z = 0$ because if you recall for an ideal CSTR the concentration drops immediately on entering from C_{A0} to C_{Aexit}. For the other boundary condition at the exit $z = L$, we see the concentration gradient has gone to zero. At steady state, it can be shown that this Danckwerts boundary condition at $z = L$ also applies to the open-open system at steady state.

Prof. P. V. Danckwerts, Cambridge University, U.K.

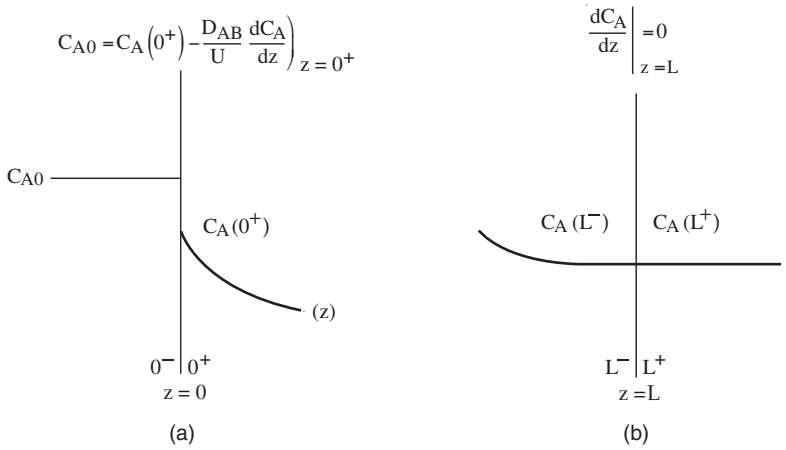


Figure 14-8 Schematic of Danckwerts boundary conditions. (a) Entrance (b) Exit

14.4.2B Open-Open System

For an open-open system there is continuity of flux at the boundaries at z = 0,

$$F_A(0^-) = F_A(0^+)$$

Open-open boundary condition

$$\boxed{-D_a\frac{\partial C_A}{\partial z}\Big)_{z=0^-} + UC_A(0^-) = -D_a\frac{\partial C_A}{\partial z}\Big)_{z=0^+} + UC_A(0^+)} \quad (14\text{-}22)$$

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

[4] K. B. Bischoff, *Chem. Eng. Sci., 16,* 131 (1961).

At $z = L$, we have continuity of concentration and

$$\boxed{\frac{dC_A}{dz} = 0} \tag{14-23}$$

14.4.2C Back to the Solution for a Closed-Closed System

We now shall solve the dispersion reaction balance for a first-order reaction

$$\frac{1}{\mathrm{Pe}_r}\frac{d^2\psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - \boldsymbol{Da}\psi = 0 \tag{14-17}$$

For the closed-closed system, the Danckwerts boundary conditions in dimensionless form are

$$\text{At } \lambda = 0 \text{ then } 1 = -\frac{1}{\mathrm{Pe}_r}\frac{d\psi}{d\lambda}\bigg)_{\lambda = 0^+} + \psi(0^+ \tag{14-24}$$

$$\text{At } \lambda = 1 \text{ then } \frac{d\psi}{d\lambda} = 0 \tag{14-25}$$

At the end of the reactor, where $\lambda = 1$, the solution to Equation (14-17) is

Da = τk
$\mathrm{Pe_r}$ = UL/Da

$$\boxed{\begin{aligned}\psi_L &= \frac{C_{AL}}{C_{A0}} = 1 - X \\ &= \frac{4q\exp(\mathrm{Pe}_r/2)}{(1+q)^2\exp(\mathrm{Pe}_r q/2) - (1-q)^2\exp(-\mathrm{Pe}_r q/2)} \\ &\text{where } q = \sqrt{1 + 4\boldsymbol{Da}/\mathrm{Pe}_r}\end{aligned}} \tag{14-26}$$

This solution was first obtained by Danckwerts[5] and has been published in many places (e.g., Levenspiel[6]). With a slight rearrangement of Equation (14-26), we obtain the conversion as a function of ***Da*** and Pe_r.

$$\boxed{X = 1 - \frac{4q\exp(\mathrm{Pe}_r/2)}{(1+q)^2\exp(\mathrm{Pe}_r q/2) - (1-q)^2\exp(-\mathrm{Pe}_r q/2)}} \tag{14-27}$$

Outside the limited case of a first-order reaction, a numerical solution of the equation is required, and because this is a split-boundary-value problem, an iterative technique is required.

To evaluate the exit concentration given by Equation (14-26) or the conversion given by (14-27), we need to know the Damköhler and Peclet numbers. The Damköhler number for a first-order reaction, $\boldsymbol{Da} = \tau k$, can be found using the techniques in Chapter 5. In the next section, we discuss methods to determine D_a, by finding the Peclet number.

---

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

[6] Levenspiel, *Chemical Reaction Engineering,* 3rd ed. (New York: Wiley, 1999).

14.4.3 Finding D_a and the Peclet Number

Three ways to find D_a

There are three ways we can use to find D_a and hence Pe_r

1. Laminar flow with radial and axial molecular diffusion theory
2. Correlations from the literature for pipes and packed beds
3. Experimental tracer data

At first sight, simple models described by Equation (14-13) appear to have the capability of accounting only for axial mixing effects. It will be shown, however, that this approach can compensate not only for problems caused by axial mixing, *but also for those caused by radial mixing and other nonflat velocity profiles*.[7] These fluctuations in concentration can result from different flow velocities and pathways and from molecular and turbulent diffusion.

14.4.4 Dispersion in a Tubular Reactor with Laminar Flow

In a laminar flow reactor, we know that the axial velocity varies in the radial direction according to the Hagen–Poiseuille equation:

$$u(r) = 2U\left[1 - \left(\frac{r}{R}\right)^2\right]$$

where U is the average velocity. For laminar flow, we saw that the RTD function $E(t)$ was given by

$$E(t) = \begin{cases} 0 & \text{for } t < \dfrac{\tau}{2} \qquad \left(\tau = \dfrac{L}{U}\right) \\ \dfrac{\tau^2}{2t^3} & \text{for } t \geq \dfrac{\tau}{2} \end{cases} \tag{13-47}$$

In arriving at this distribution $E(t)$, it was assumed that there was no transfer of molecules in the radial direction between streamlines. Consequently, with the aid of Equation (13-43), we know that the molecules on the center streamline ($r = 0$) exited the reactor at a time $t = \tau/2$, and molecules traveling on the streamline at $r = 3R/4$ exited the reactor at time

$$t = \frac{L}{u} = \frac{L}{2U[1 - (r/R)^2]} = \frac{\tau}{2[1 - (3/4)^2]}$$
$$= \frac{8}{7} \cdot \tau$$

[7] R. Aris, *Proc. R. Soc. (London), A235*, 67 (1956).

The question now arises: What would happen if some of the molecules traveling on the streamline at r = 3R/4 jumped (i.e., diffused) onto the streamline at r = 0? The answer is that they would exit sooner than if they had stayed on the streamline at r = 3R/4. Analogously, if some of the molecules from the faster streamline at r = 0 jumped (i.e., diffused) on to the streamline at r = 3R/4, they would take a longer time to exit (Figure 14-9). In addition to the molecules diffusing between streamlines, they can also move forward or backward relative to the average fluid velocity by molecular diffusion (Fick's law). With both axial and radial diffusion occurring, the question arises as to what will be the distribution of residence times when molecules are transported between and along streamlines by diffusion. To answer this question we will derive an equation for the axial dispersion coefficient, D_a, that accounts for the axial and radial diffusion mechanisms. In deriving D_a, which is referred to as the Aris–Taylor dispersion coefficient, we closely follow the development given by Brenner and Edwards.[8]

Molecules diffusing between streamlines and back and forth along a streamline

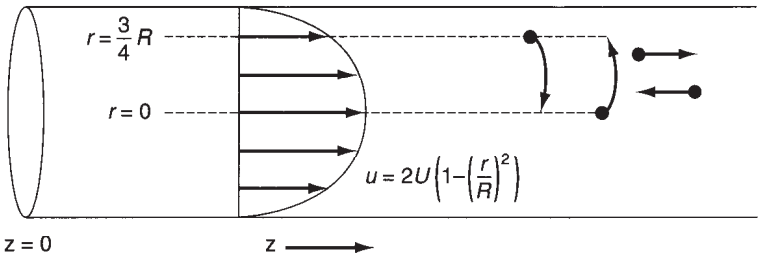


Figure 14-9 Radial diffusion in laminar flow.

The convective–diffusion equation for solute (e.g., tracer) transport in both the axial and radial direction can be obtained by combining Equations (11-3) and (11-15),

$$\frac{\partial c}{\partial t} + u(r)\,\frac{\partial c}{\partial z} = D_{\mathrm{AB}}\left\{\frac{1}{r}\,\frac{\partial\,[r(\partial c/\partial r)]}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right\} \tag{14-28}$$

where c is the solute concentration at a particular r, z, and t.

We are going to change the variable in the axial direction z to z^*, which corresponds to an observer moving with the fluid

$$z^* = z - Ut \tag{14-29}$$

A value of $z^* = 0$ corresponds to an observer moving with the fluid on the center streamline. Using the chain rule, we obtain

[8] H. Brenner and D. A. Edwards, *Macrotransport Processes* (Boston: Butterworth-Heinemann, 1993).

$$\left(\frac{\partial c}{\partial t}\right)_{z^*} + [u(r) - U]\frac{\partial c}{\partial z^*} = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial z^{*2}}\right] \tag{14-30}$$

Because we want to know the concentrations and conversions at the exit to the reactor, we are really only interested in the average axial concentration $\overline{C}$, which is given by

$$\overline{C}(z, t) = \frac{1}{\pi R^2}\int_0^R c(r, z, t)2\pi r\, dr \tag{14-31}$$

Consequently, we are going to solve Equation (14-30) for the solution concentration as a function of r and then substitute the solution c (r, z, t) into Equation (14-31) to find $\overline{C}$ (z, t). All the intermediate steps are given on the CD-ROM R14.1, and the partial differential equation describing the variation of the average axial concentration with time and distance is

$$\frac{\partial \overline{C}}{\partial t} + U\frac{\partial \overline{C}}{\partial z^*} = D^*\frac{\partial^2 \overline{C}}{\partial z^{*2}} \tag{14-32}$$

where D^* is the Aris–Taylor dispersion coefficient:

Aris–Taylor dispersion coefficient

$$\boxed{D^* = D_{AB} + \frac{U^2R^2}{48D_{AB}}} \tag{14-33}$$

That is, for laminar flow in a pipe

$$D_a \equiv D^*$$

Figure 14-10 shows the dispersion coefficient D^* in terms of the ratio $D^*/U(2R) = D^*/Ud_t$ as a function of the product of the Reynolds and Schmidt numbers.

14.4.5 Correlations for D_a

14.4.5A Dispersion for Laminar and Turbulent Flow in Pipes

An estimate of the dispersion coefficient, D_a, can be determined from Figure 14-11. Here d_t is the tube diameter and Sc is the Schmidt number discussed in Chapter 11. The flow is laminar (streamline) below 2,100, and we see the ratio (D_a/Ud_t) increases with increasing Schmidt and Reynolds numbers. Between Reynolds numbers of 2,100 and 30,000, one can put bounds on D_a by calculating the maximum and minimum values at the top and bottom of the shaded region.

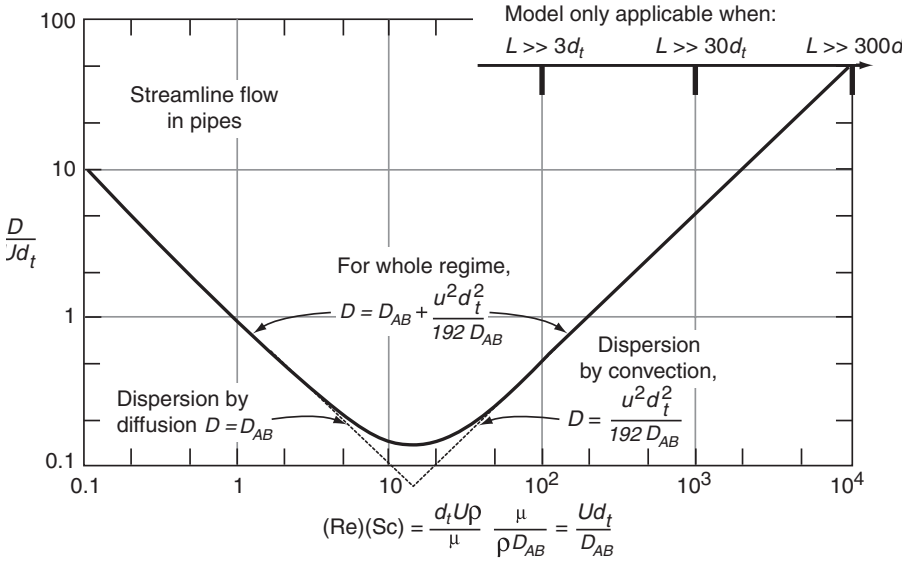


Figure 14-10 Correlation for dispersion for streamline flow in pipes. (From O. Levenspiel, Chemical Reaction Engineering, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [Note: $D \equiv D_a$]

Once the Reynolds number is calculated, D_a can be found.

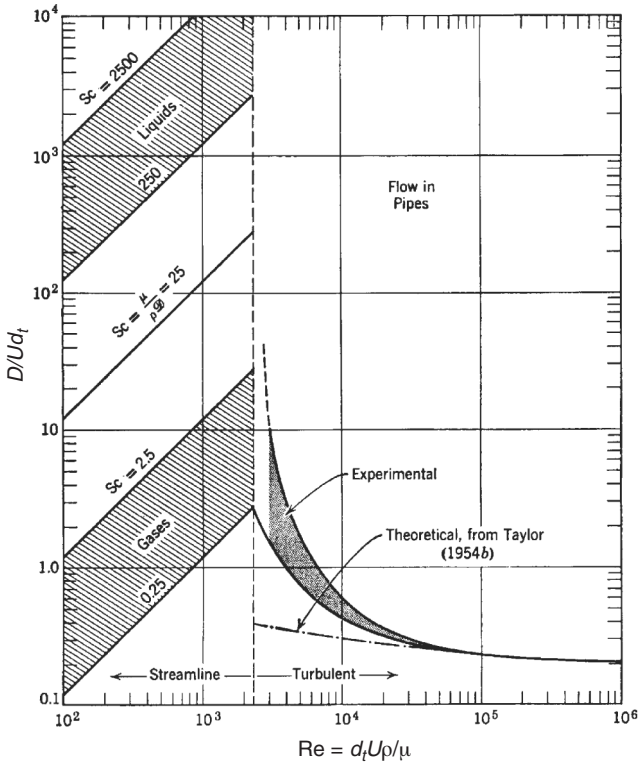


Figure 14-11 Correlation for dispersion of fluids flowing in pipes. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

14.4.5B Dispersion in Packed Beds

For the case of gas–solid catalytic reactions that take place in packed-bed reactors, the dispersion coefficient, D_a, can be estimated by using Figure 14-12. Here d_p is the particle diameter and ε is the porosity.

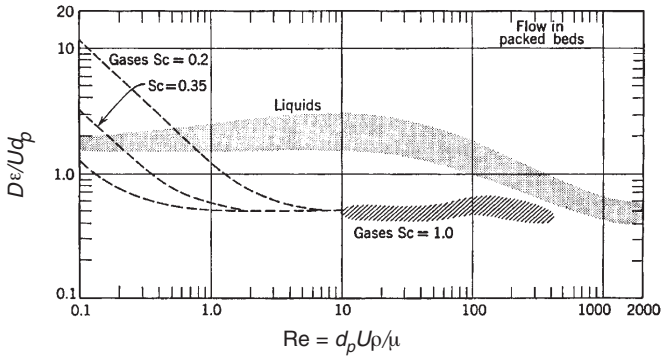


Figure 14-12 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

14.4.6 Experimental Determination of D_a

The dispersion coefficient can be determined from a pulse tracer experiment. Here, we will use t_m and σ^2 to solve for the dispersion coefficient D_a and then the Peclet number, Pe_r. Here the effluent concentration of the reactor is measured as a function of time. From the effluent concentration data, the mean residence time, t_m, and variance, σ^2, are calculated, and these values are then used to determine D_a. To show how this is accomplished, we will write

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (UC_T)}{\partial z} = \frac{\partial C_T}{\partial t} \tag{14-13}$$

in dimensionless form, discuss the different types of boundary conditions at the reactor entrance and exit, solve for the exit concentration as a function of dimensionless time ($\Theta = t/\tau$), and then relate D_a, σ^2, and τ.

14.4.6A The Unsteady-State Tracer Balance

The first step is to put Equation (14-13) in dimensionless form to arrive at the dimensionless group(s) that characterize the process. Let

$$\psi = \frac{C_T}{C_{T0}}, \quad \lambda = \frac{z}{L}, \quad \text{and} \quad \Theta = \frac{tU}{L}$$

For a pulse input, C_{T0} is defined as the mass of tracer injected, M, divided by the vessel volume, V. Then

$$\boxed{\frac{1}{\mathrm{Pe}_r}\frac{\partial^2\psi}{\partial\lambda^2}-\frac{\partial\psi}{\partial\lambda}=\frac{\partial\psi}{\partial\Theta}} \tag{14-34}$$

The initial condition is

Initial condition

$$\text{At } t=0, \quad z>0, \quad C_T(0^+,0)=0, \quad \psi(0^+)=0 \tag{14-35}$$

The mass of tracer injected, M is

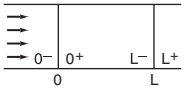
$$M = UA_c\int_0^\infty C_T(0^-, t)\,dt$$

14.4.6B Solution for a Closed-Closed System

In dimensionless form, the Danckwerts boundary conditions are

$$\text{At } \lambda=0: \qquad \left(-\frac{1}{\mathrm{Pe}_r}\frac{\partial\psi}{\partial\lambda}\right)_{\lambda=0^+}+\psi(0^+)=\frac{C_T(0^-,t)}{C_{T0}}=1 \tag{14-36}$$

$$\text{At } \lambda=1: \qquad \frac{\partial\psi}{\partial\lambda}=0 \tag{14-37}$$



Equation (14-34) has been solved numerically for a pulse injection, and the resulting dimensionless effluent tracer concentration, ψ_{exit}, is shown as a function of the dimensionless time Θ in Figure 14-13 for various Peclet numbers. Although analytical solutions for ψ can be found, the result is an infinite series. The corresponding equations for the mean residence time, t_m, and the variance, σ^2, are[9]

$$\boxed{t_m=\tau} \tag{14-38}$$

and

$$\frac{\sigma^2}{t_m^2}=\frac{1}{\tau^2}\int_0^\infty (t-\tau)^2E(t)\,dt$$

which can be used with the solution to Equation (14-34) to obtain

[9] See K. Bischoff and O. Levenspiel, *Adv. Chem. Eng.*, *4*, 95 (1963).

Effects of dispersion on the effluent tracer concentration

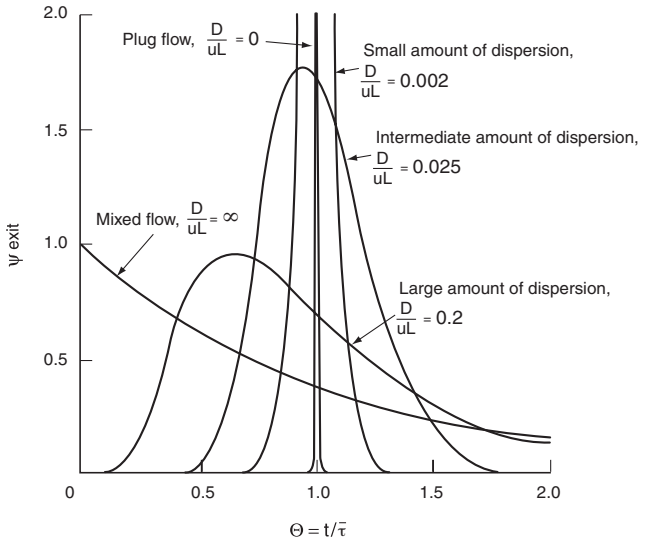


Figure 14-13 *C* curves in closed vessels for various extents of back-mixing as predicted by the dispersion model. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$][10]

Calculating Pe_r using t_m and σ^2 determined from RTD data for a closed-closed system

$$\boxed{\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}\left(1 - e^{-Pe_r}\right)} \tag{14-39}$$

Consequently, we see that the Peclet number, Pe_r (and hence D_a), can be found experimentally by determining t_m and σ^2 from the RTD data and then solving Equation (14-39) for Pe_r.

14.4.6C Open-Open Vessel Boundary Conditions

When a tracer is injected into a packed bed at a location more than two or three particle diameters downstream from the entrance and measured some distance upstream from the exit, the open-open vessel boundary conditions apply. For an open-open system, an analytical solution to Equation (14-13) can be obtained for a pulse tracer input.

For an open-open system, the boundary conditions at the entrance are

$$F_T(0^-, t) = F_T(0^+, t)$$

[10]O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. (New York: Wiley, 1972), p. 277.

Then for the case when the dispersion coefficient is the same in the entrance and reaction sections:

$$-D_a\left(\frac{\partial C_T}{\partial z}\right)_{z=0^-} + UC_T(0^-,t) = -D_a\left(\frac{\partial C_T}{\partial z}\right)_{z=0^+} + UC_T(0^+,t) \quad (14\text{-}40)$$

Because there are no discontinuities across the boundary at $z = 0$

$$C_T(0^-,t) = C_T(0^+,t) \quad (14\text{-}41)$$

At the exit

Open at the exit

$$-D_a\left(\frac{\partial C_T}{\partial z}\right)_{z=L^-} + UC_T(L^-,t) = -D_a\left(\frac{\partial C_T}{\partial z}\right)_{z=L^+} + UC_T(L^+,t) \quad (14\text{-}42)$$

$$C_T(L^-,t) = C_T(L^+,t) \quad (14\text{-}43)$$

There are a number of perturbations of these boundary conditions that can be applied. The dispersion coefficient can take on different values in each of the three regions ($z < 0$, $0 \le z \le L$, and $z > L$), and the tracer can also be injected at some point z_1 rather than at the boundary, $z = 0$. These cases and others can be found in the supplementary readings cited at the end of the chapter. We shall consider the case when there is no variation in the dispersion coefficient for all z and an impulse of tracer is injected at $z = 0$ at $t = 0$.

For long tubes ($Pe_r > 100$) in which the concentration gradient at $\pm\infty$ will be zero, the solution to Equation (14-34) at the exit is[11]

Valid for $Pe_r > 100$

$$\psi(1,\Theta) = \frac{C_T(L,t)}{C_{T0}} = \frac{1}{2\sqrt{\pi\Theta/Pe_r}}\exp\left[\frac{-(1-\Theta)^2}{4\Theta/Pe_r}\right] \quad (14\text{-}44)$$

The mean residence time for an open-open system is

Calculate τ for an open-open system

$$\boxed{t_m = \left(1 + \frac{2}{Pe_r}\right)\tau} \quad (14\text{-}45)$$

where τ is based on the volume between z = 0 and z = L (i.e., reactor volume measured with a yardstick). We note that the mean residence time for an open system is greater than that for a closed system. The reason is that the molecules can diffuse back into the reactor after they exit. The variance for an open-open system is

Calculate Pe_r for an open–open system.

$$\boxed{\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}} \quad (14\text{-}46)$$

[11]W. Jost, *Diffusion in Solids, Liquids and Gases* (New York: Academic Press, 1960), pp. 17, 47.

We now consider two cases for which we can use Equations (14-39) and (14-46) to determine the system parameters:

Case 1. The space time τ is *known*. That is, V and v_0 are measured independently. Here we can determine the Peclet number by determining t_m and σ^2 from the concentration–time data and then using Equation (14-46) to calculate Pe_r. We can also calculate t_m and then use Equation (14-45) as a check, but this is usually less accurate.

Case 2. The space time τ is *unknown*. This situation arises when there are dead or stagnant pockets that exist in the reactor along with the dispersion effects. To analyze this situation we first calculate t_m and σ^2 from the data as in case 1. Then use Equation (14-45) to eliminate τ^2 from Equation (14-46) to arrive at

$$\boxed{\frac{\sigma^2}{t_m^2} = \frac{2Pe_r + 8}{Pe_r^2 + 4Pe_r + 4}} \tag{14-47}$$

Finding the effective reactor voume

We now can solve for the Peclet number in terms of our experimentally determined variables σ^2 and t_m^2. Knowing Pe_r, we can solve Equation (14-45) for τ, and hence V. The dead volume is the difference between the measured volume (i.e., with a yardstick) and the effective volume calculated from the RTD.

14.4.7 Sloppy Tracer Inputs

It is not always possible to inject a tracer pulse cleanly as an input to a system because it takes a finite time to inject the tracer. When the injection does not approach a perfect pulse input (Figure 14-14), the differences in the variances between the input and output tracer measurements are used to calculate the Peclet number:

$$\Delta\sigma^2 = \sigma_{in}^2 - \sigma_{out}^2$$

where σ_{in}^2 is the variance of the tracer measured at some point upstream (near the entrance) and σ_{out}^2 is the variance measured at some point downstream (near the exit).

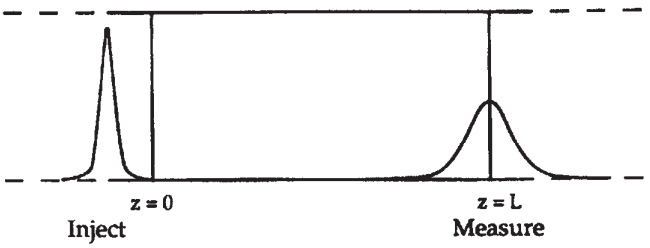


Figure 14-14 Imperfect tracer input.

For an open-open system, it has been shown[12] that the Peclet number can be calculated from the equation

$$\boxed{\frac{\Delta\sigma^2}{t_m^2} = \frac{2}{\mathrm{Pe}_r}} \tag{14-48}$$

Now let's put all the material in Section 14.4 together to determine the conversion in a tubular reactor for a first-order reaction.

Example 14–2 Conversion Using Dispersion and Tanks-in-Series Models

The first-order reaction

$$\mathrm{A} \longrightarrow \mathrm{B}$$

is carried out in a 10-cm-diameter tubular reactor 6.36 m in length. The specific reaction rate is 0.25 min^{-1}. The results of a tracer test carried out on this reactor are shown in Table E14-2.1.

TABLE E14-2.1. EFFLUENT TRACER CONCENTRATION AS A FUNCTION OF TIME

t (min)	0	1	2	3	4	5	6	7	8	9	10	12	14
C (mg/L)	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0

Calculate the conversion using (a) the closed vessel dispersion model, (b) PFR, (c) the tanks-in-series model, and (d) a single CSTR.

Solution

(a) We will use Equation (14-27) to calculate the conversion

$$X = 1 - \frac{4q\,\exp(\mathrm{Pe}_r/2)}{(1+q)^2\,\exp(\mathrm{Pe}_r q/2) - (1-q)^2\,\exp(-\mathrm{Pe}_r q/2)} \tag{14-27}$$

where $q = \sqrt{1 + 4\boldsymbol{Da}/\mathrm{Pe}_r}$ $\boldsymbol{Da} = \tau k$, and $\mathrm{Pe}_r = UL/D_a$. We can calculate Pe_r from Equation (14-39):

$$\frac{\sigma^2}{\tau^2} = \frac{2}{\mathrm{Pe}_r} - \frac{2}{\mathrm{Pe}_r^2}\left(1 - e^{-\mathrm{Pe}_r}\right) \tag{14-39}$$

First calculate t_m and σ^2 from RTD data.

However, we must find τ^2 and σ^2 from the tracer concentration data first.

$$\tau = \int_0^\infty tE(t)\,dt = \frac{V}{v} \tag{E14-2.1}$$

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)\,dt = \int_0^\infty t^2 E(t)\,dt - \tau^2 \tag{E14-2.2}$$

[12]R. Aris, *Chem. Eng. Sci., 9,* 266 (1959).

Consider the data listed in Table E14-2.2.

TABLE E14-2.2. CALCULATIONS TO DETERMINE t_m AND σ^2

t (min)	0	1	2	3	4	5	6	7	8	9	10	12	14
$C(t)$ (mol/dm^3)	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
$E(t)$ (min^{-1})	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0
$tE(t)$	0	0.02	0.2	0.48	0.8	0.80	0.72	0.56	0.48	0.40	0.3	0.14	0
$t^2E(t)$ (min)	0	0.02	0.4	1.44	3.2	4.0	4.32	3.92	3.84	3.60	3.0	1.68	0

Here again spreadsheets can be used to calculate τ^2 and σ^2.

To find $E(t)$ and then t_m, we first find the area under the C curve, which is

$$\int_0^\infty C(t)\,dt = 50\ \text{g}\cdot\text{min}$$

Then

$$\tau = t_m = \int_0^\infty tE(t)\,dt = 5.15\ \text{min}$$

Calculating the first term on the right-hand side of Equation (E14-2.2), we find

$$\begin{aligned}\int_0^\infty t^2E(t)\,dt = (\tfrac{1}{3})[1(0) + 4(0.02) + 2(0.4) + 4(1.44) + 2(3.2) + 4(4.0)\\ + 2(4.32) + 4(3.92) + 2(3.84) + 4(3.6) + 1(3.0)]\\ + (\tfrac{2}{3})[3.0 + 4(1.68) + 0]\\ = 32.63\ \text{min}^2\end{aligned}$$

Substituting these values into Equation (E14-2.2), we obtain the variance, σ^2.

$$\sigma^2 = 32.63 - (5.15)^2 = 6.10\ \text{min}^2$$

Most people, including the author, would use Polymath or Excel to form Table E14-2.2 and to calculate t_m and σ^2. Dispersion in a closed vessel is represented by

$$\frac{\sigma^2}{\tau^2} = \frac{2}{\text{Pe}_r^2}(\text{Pe}_r - 1 + e^{-\text{Pe}_r}) \tag{14-39}$$

Calculate Pe_r from t_m and σ^2.

$$= \frac{6.1}{(5.15)^2} = 0.23 = \frac{2}{\text{Pe}_r^2}(\text{Pe}_r - 1 + e^{-\text{Pe}_r})$$

Solving for Pe_r either by trial and error or using Polymath, we obtain

$$\boxed{\text{Pe}_r = 7.5}$$

Next, calculate ***Da***, q, and X.

Next we calculate ***Da*** to be

$$\boxed{\textbf{\textit{Da}} = \tau k = (5.15\ \text{min})(0.25\ \text{min}^{-1}) = 1.29}$$

Using the equations for q and X gives

$$q = \sqrt{1 + \frac{4\boldsymbol{Da}}{\text{Pe}_r}} = \sqrt{1 + \frac{4(1.29)}{7.5}} = 1.30$$

Then

$$\frac{\text{Pe}_r q}{2} = \frac{(7.5)(1.3)}{2} = 4.87$$

Substitution into Equation (14-40) yields

Dispersion Model

$$X = 1 - \frac{4(1.30)\, e^{(7.5/2)}}{(2.3)^2 \exp(4.87) - (-0.3)^2 \exp(-4.87)}$$

$\boxed{X = 0.68}$ 68% conversion for the dispersion model

When dispersion effects are present in this tubular reactor, 68% conversion is achieved.

(b) If the reactor were operating ideally as a plug-flow reactor, the conversion would be

PFR

$$\boxed{X = 1 - e^{-\tau k} = 1 - e^{-\text{Da}} = 1 - e^{-1.29} = 0.725}$$

That is, 72.5% conversion would be achieved in an ideal plug-flow reactor.

Tanks-in-series model

(c) Conversion using the tanks-in-series model: We recall Equation (14-12) to calculate the number of tanks in series:

$$n = \frac{\tau^2}{\sigma^2} = \frac{(5.15)^2}{6.1} = 4.35$$

To calculate the conversion, we recall Equation (4-11). For a first-order reaction for n tanks in series, the conversion is

$$\boxed{X = 1 - \frac{1}{(1 + \tau_t k)^n} = 1 - \frac{1}{[1 + (\tau/n)\, k]^n} = 1 - \frac{1}{(1 + 1.29/4.35)^{4.35}}}$$

$\boxed{X = \textbf{67.7\% for the tanks-in-series model}}$

(d) For a single CSTR,

CSTR

$$X = \frac{\tau k}{1 + \tau k} = \frac{1.29}{2.29} = 0.563$$

So 56.3% conversion would be achieved in a single ideal tank.

Summary:

Summary

$$\boxed{\begin{aligned} \text{PFR: } X &= 72.5\% \\ \text{Dispersion: } X &= 68.0\% \\ \text{Tanks in series: } X &= 67.7\% \\ \text{Single CSTR: } X &= 56.3\% \end{aligned}}$$

In this example, correction for finite dispersion, whether by a dispersion model or a tanks-in-series model, is significant when compared with a PFR.

14.5 Tanks-in-Series Model Versus Dispersion Model

We have seen that we can apply both of these one-parameter models to tubular reactors using the variance of the RTD. For first-order reactions, the two models can be applied with equal ease. However, the tanks-in-series model is mathematically easier to use to obtain the effluent concentration and conversion for reaction orders other than one and for multiple reactions. However, we need to ask what would be the accuracy of using the tanks-in-series model over the dispersion model. These two models are equivalent when the Peclet–Bodenstein number is related to the number of tanks in series, n, by the equation[13]

$$\text{Bo} = 2(n - 1) \tag{14-49}$$

Equivalency between models of tanks-in-series and dispersion

or

$$n = \frac{\text{Bo}}{2} + 1 \tag{14-50}$$

where Bo = UL/D_a, where U is the superficial velocity, L the reactor length, and D_a the dispersion coefficient.

For the conditions in Example 14-2, we see that the number of tanks calculated from the Bodenstein number, Bo (i.e., Pe_r), Equation (14-50), is 4.75, which is very close to the value of 4.35 calculated from Equation (14-12). Consequently, for reactions other than first order, one would solve successively for the exit concentration and conversion from each tank in series for both a battery of four tanks in series and of five tanks in series in order to bound the expected values.

In addition to the one-parameter models of tanks-in-series and dispersion, many other one-parameter models exist when a combination of ideal reactors is used to model the real reactor as shown in Section 13.5 for reactors with bypassing and dead volume. Another example of a one-parameter model would be to model the real reactor as a PFR and a CSTR in series with the one parameter being the fraction of the total volume that behaves as a CSTR. We can dream up many other situations that would alter the behavior of ideal reactors in a way that adequately describes a real reactor. However, it may be that one parameter is not sufficient to yield an adequate comparison between theory and practice. We explore these situations with combinations of ideal reactors in the section on two-parameter models.

The reaction rate parameters are usually known (i.e., ***Da***), but the Peclet number is usually not known because it depends on the flow and the vessel. Consequently, we need to find Pe_r using one of the three techniques discussed earlier in the chapter.

[13]K. Elgeti, *Chem. Eng. Sci., 51,* 5077 (1996).

14.6 Numerical Solutions to Flows with Dispersion and Reaction

We now consider dispersion and reaction. We first write our mole balance on species A by recalling Equation (14-28) and including the rate of formation of *A*, r_A. At steady state we obtain

$$D_{AB}\left[\frac{1}{r}\frac{\partial\left(r\dfrac{\partial C_A}{\partial r}\right)}{\partial r}+\frac{\partial^2 C_A}{\partial z^2}\right]-u(r)\frac{\partial C_A}{\partial z}+r_A=0 \tag{14-51}$$

Analytical solutions to dispersion with reaction can only be obtained for isothermal zero- and first-order reactions. We are now going to use COMSOL to solve the flow with reaction and dispersion with reaction. A COMSOL CD-ROM is included with the text.

We are going to compare two solutions: one which uses the Aris–Taylor approach and one in which we numerically solve for both the axial and radial concentration using COMSOL.

Case A. Aris–Taylor Analysis for Laminar Flow

For the case of an nth-order reaction, Equation (14-15) is

$$\frac{D_a}{U}\frac{d^2C_A}{dz^2}-\frac{dC_A}{dz}-\frac{kC_A^n}{U}=0 \tag{14-52}$$

If we use the Aris–Taylor analysis, we can use Equation (14-15) with a caveat that $\overline{\psi}=\overline{C}_A/C_{A0}$ where $\overline{C}_A$ is the average concentration from $r = 0$ to $r = R$ as given by

$$\frac{1}{\mathrm{Pe}_r}\frac{d^2\overline{\psi}}{d\lambda^2}-\frac{d\overline{\psi}}{d\lambda}-\boldsymbol{Da}\overline{\psi}^n=0 \tag{14-53}$$

where

$$\mathrm{Pe}_r=\frac{UL}{D_a}\ \text{and}\ \boldsymbol{Da}=\tau k C_{A0}^{n-1}$$

For the closed-closed boundary conditions we have

$$\text{At}\quad \lambda=0:\quad -\frac{1}{\mathrm{Pe}_r}\frac{d\overline{\psi}}{d\lambda}\bigg|_{\lambda=0^+}+\overline{\psi}(0^+)=1 \tag{14-54}$$

Danckwerts boundary conditions

$$\text{At}\quad \lambda=1:\quad \frac{d\overline{\psi}}{d\lambda}=0$$

For the open-open boundary conditions we have

$$\text{At} \quad \lambda = 0: \quad \overline{\psi}(0^-) - \frac{1}{\text{Pe}_r}\frac{d\overline{\psi}}{d\lambda}\bigg|_{\lambda=0^-} = \overline{\psi}(0^+) - \frac{1}{\text{Pe}_r}\frac{d\overline{\psi}}{d\lambda}\bigg|_{\lambda=0^+} \tag{14-55}$$

$$\text{At} \quad \lambda = 1: \quad \frac{d\overline{\psi}}{d\lambda} = 0$$

Equation (14-53) is a nonlinear second order ODE that is solved on the COMSOL CD-ROM.

Case B. Full Numerical Solution

To obtain profiles, $C_A(r,z)$, we now solve Equation (14-51)

$$D_{AB}\left[\frac{1}{r}\frac{\partial\left(r\dfrac{\partial C_A}{\partial r}\right)}{\partial r} + \frac{\partial^2 C_A}{\partial z^2}\right] - u(r)\frac{\partial C_A}{\partial z} + r_A = 0 \tag{14-51}$$

First we will put the equations in dimensionless form by letting $\psi = C_A/C_{A0}$, $\lambda = z/L$, and $\phi = r/R$. Following our earlier transformation of variables, Equation (14-51) becomes

$$\left(\frac{L}{R}\right)\frac{1}{\text{Pe}_r}\left[\frac{1}{\phi}\frac{\partial\left(\phi\dfrac{\partial\psi}{\partial\phi}\right)}{\partial\phi}\right] + \frac{1}{\text{Pe}_r}\frac{d^2\psi}{d\lambda^2} - 2(1-\phi^2)\frac{d\psi}{d\lambda} - \boldsymbol{Da}\psi^n = 0 \tag{14-56}$$

Example 14–3 Dispersion with Reaction

(a) First, use COMSOL to solve the dispersion part of Example 14-2 again. How does the COMSOL result compare with the solution to Example 14-2?

(b) Repeat (a) for a second-order reaction with k = 0.5 dm³/mol • min.

(c) Repeat (a) but assume laminar flow and consider radial gradients in concentration. Use D_{AB} for both the radial and axial diffusion coefficients. Plot the axial and radial profiles. Compare your results with part (a).

Additional information:

C_{A0} = 0.5 mol/dm³, $U_0 = L/\tau$ = 1.24 m/min, $D_a = U_0 L/\text{Pe}_r$ = 1.05 m²/min. D_{AB} = 7.6E-5 m²/min.

Note: For part (a), the two-dimensional model with no radial gradients (plug flow) becomes a one-dimensional model. The inlet boundary condition for part (a) and part (b) is a closed-closed vessel (flux[$z = 0^-$] = flux[$z = 0^+$] or $U_z \cdot C_{A0}$ = flux) at the inlet boundary. In COMSOL format it is: $-N_i \cdot n$ = U0*CA0. The boundary condition for laminar flow in COMSOL format for part (c) is: $-N_i \cdot n$ = 2*U0*(1–(r/Ra)$_2$)*CA0.

The different types of COMSOL Boundary Conditions are given in Problem P14-19$_c$

Solution

(a) Equation (14-52) was used in the COMSOL program along with the rate law

$$r_A = -kC_A = -kC_{A0}\,\psi$$

We see that we get the same results as the analytical solution in Example 14-2. With the Aris–Taylor analysis the two-dimensional profile becomes a one-dimensional plug flow velocity profile. Figure E14-3.1(a) shows a uniform concentration surface and shows the plug flow behavior of the reactor. Figure E14-3.1(b) shows the corresponding cross-section plots at the inlet, half axial location, and outlet. The average outlet conversion is 67.9%.

The average outlet concentration at an axial distance z is found by integrating across the radius as shown below

$$C_A(z) = \int_0^R \frac{2\pi r C_A(r,z)dr}{\pi R^2}$$

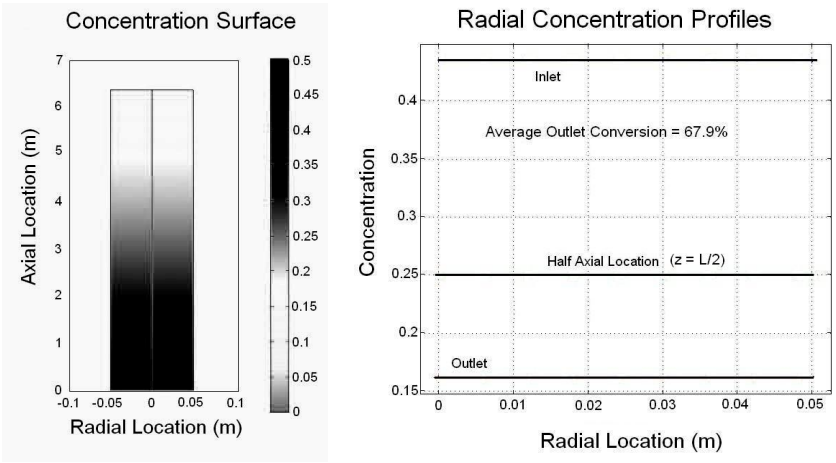
Be sure to view documentation on COMSOL CD-ROM to see COMSOL tutorial with screen shots

From the average concentrations at the inlet and outlet we can calculate the average conversion as

$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

Load enclosed COMSOL CD

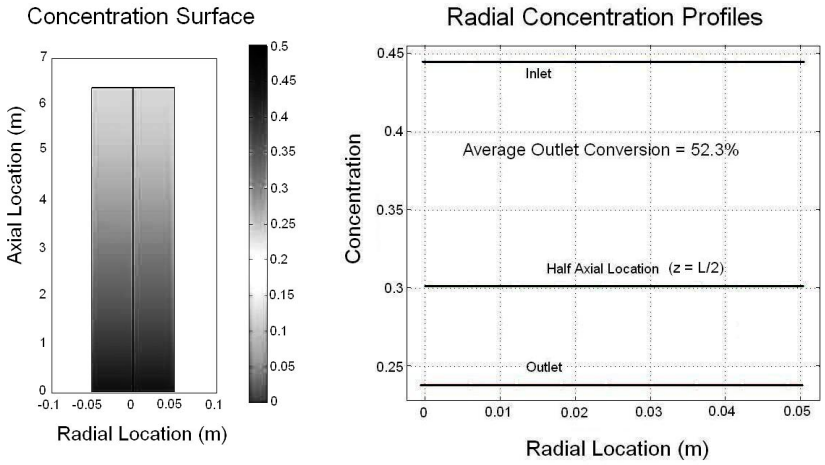
Living Example Problem



(a) (b)

Figure E14-3.1 COMSOL results for a plug flow reactor with first-order reaction. (Concentrations in mol/dm^3.)

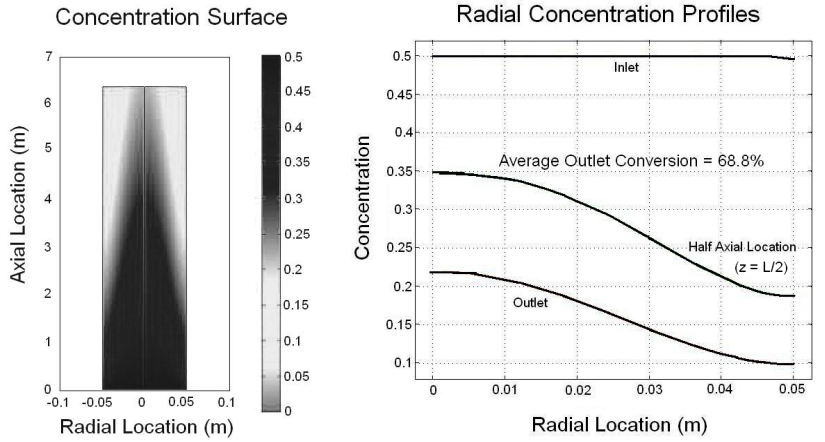
(b) Now we expand our results to consider the case when the reaction is second order ($-r_A = kC_A^2 = kC_{A0}^2\,\psi^2$) with $k = 0.5$ dm^3/mol·min and $C_{A0} = 0.5$ mol/dm^3. Let's assume the radial dispersion coefficient is equal to the molecular diffusivity. Keeping everything else constant, the average outlet conversion is 52.3%. However, because the flow inside the reactor is modeled as plug flow the concentration profiles are still flat, as shown in Figure E14-3.2.



(a) (b)

Figure E14-3.2 COMSOL results for a plug flow reactor with second-order reaction. (Concentrations in mol/dm^3.)

(c) Now, we will change the flow assumption from plug flow to laminar flow and solve Equation (14-51) for a first-order reaction.



(a) (b)

Figure E14-3.3 COMSOL output for laminar flow in the reactor. (Concentrations in mol/dm^3.)

The average outlet conversion becomes 68.8%, not much different from the one in part (a) in agreement with the Aris–Taylor analysis. However, due to the laminar flow assumption in the reactor, the radial concentration profiles are very different throughout the reactor.

(d) As a homework exercise, repeat part (c) for the second-order reaction given in part (b).

14.7 Two-Parameter Models—Modeling Real Reactors with Combinations of Ideal Reactors

Creativity and engineering judgment are necessary for model formulation

We now will see how a real reactor might be modeled by one of two different combinations of ideal reactors. These are but two of an almost unlimited number of combinations that could be made. However, if we limit the number of adjustable parameters to two (e.g., bypass flow rate, v_b, and dead volume, V_D), the situation becomes much more tractable. After reviewing the steps in Table 14-1, choose a model and determine if it is reasonable by qualitatively comparing it with the RTD, and if it is, determine the model parameters. Usually, the simplest means of obtaining the necessary data is some form of tracer test. These tests have been described in Chapter 13, together with their uses in determining the RTD of a reactor system. Tracer tests can be used to determine the RTD, which can then be used in a similar manner to determine the suitability of the model and the value of its parameters.

A tracer experiment is used to evaluate the model parameters.

In determining the suitability of a particular reactor model and the parameter values from tracer tests, it may not be necessary to calculate the RTD function $E(t)$. The model parameters (e.g., V_D) may be acquired directly from measurements of effluent concentration in a tracer test. The theoretical prediction of the particular tracer test in the chosen model system is compared with the tracer measurements from the real reactor. The parameters in the model are chosen so as to obtain the closest possible agreement between the model and experiment. If the agreement is then sufficiently close, the model is deemed reasonable. If not, another model must be chosen.

The quality of the agreement necessary to fulfill the criterion "sufficiently close" again depends on creativity in developing the model and on engineering judgment. The most extreme demands are that the maximum error in the prediction not exceed the estimated error in the tracer test and that there be no observable trends with time in the difference between prediction (the model) and observation (the real reactor). To illustrate how the modeling is carried out, we will now consider two different models for a CSTR.

14.7.1 Real CSTR Modeled Using Bypassing and Dead Space

A real CSTR is believed to be modeled as a combination of an ideal CSTR of volume V_s, a dead zone of volume V_d, and a bypass with a volumetric flow rate v_b (Figure 14-15). We have used a tracer experiment to evaluate the parameters of the model V_s and v_s. Because the total volume and volumetric flow rate are known, once V_s and v_s are found, v_b and V_d can readily be calculated.

14.7.1A Solving the Model System for C_A and X

We shall calculate the conversion for this model for the first-order reaction

$$A \longrightarrow B$$

The model system

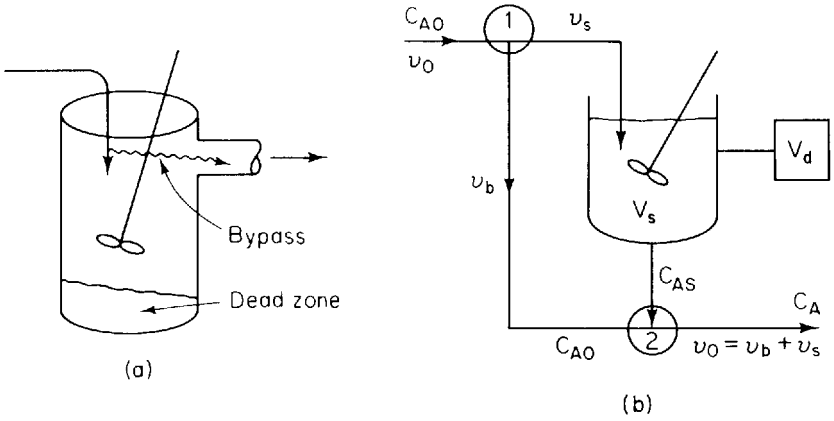


Figure 14-15 (a) Real system; (b) model system.

The bypass stream and effluent stream from the reaction volume are mixed at point 2. From a balance on species A around this point,

Balance at junction

$$[\text{In}] = [\text{Out}]$$

$$[C_{A0}V_b + C_{As}V_s] = [C_A(V_b + V_s)] \tag{14-57}$$

We can solve for the concentration of A leaving the reactor,

$$C_A = \frac{v_b C_{A0} + C_{As} v_s}{v_b + v_s} = \frac{v_b C_{A0} + C_{As} v_s}{v_0}$$

Let $\alpha = V_s/V$ and $\beta = v_b/v_0$. Then

$$\boxed{C_A = \beta C_{A0} + (1 - \beta) C_{As}} \tag{14-58}$$

For a first-order reaction, a mole balance on V_s gives

Mole balance on CSTR

$$v_s C_{A0} - v_s C_{As} - kC_{As}V_s = 0 \tag{14-59}$$

or, in terms of α and β,

$$\boxed{C_{As} = \frac{C_{A0}(1-\beta)v_0}{(1-\beta)v_0 + \alpha V k}} \tag{14-60}$$

Substituting Equation (14-60) into (14-58) gives the effluent concentration of species A:

Conversion as a function of model parameters

$$\boxed{\frac{C_A}{C_{A0}} = 1 - X = \beta + \frac{(1-\beta)^2}{(1-\beta) + \alpha\tau k}} \tag{14-61}$$

We have used the ideal reactor system shown in Figure 14-15 to predict the conversion in the real reactor. The model has two parameters, α and β. If these parameters are known, we can readily predict the conversion. In the following section, we shall see how we can use tracer experiments and RTD data to evaluate the model parameters.

14.7.1B Using a Tracer to Determine the Model Parameters in CSTR-with-Dead-Space-and-Bypass Model

In Section 14.7.1A, we used the system shown in Figure 14-16, with bypass flow rate v_b and dead volume V_d, to model our real reactor system. We shall inject our tracer, T, as a positive-step input. The unsteady-state balance on the nonreacting tracer T in the reactor volume V_s is

$$\text{In} - \text{out} = \text{accumulation}$$

Tracer balance for step input

$$\boxed{v_s C_{T0} - v_s C_{Ts} = \frac{dN_{Ts}}{dt} = V_s \frac{dC_{Ts}}{dt}} \tag{14-62}$$

Model system

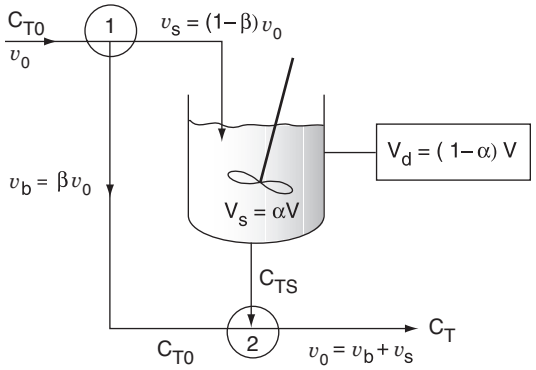


Figure 14-16 Model system: CSTR with dead volume and bypassing.

The conditions for the positive-step input are

$$\text{At } t < 0 \quad C_T = 0$$

$$\text{At } t \geq 0 \quad C_T = C_{T0}$$

The junction balance

A balance around junction point 2 gives

$$\boxed{C_T = \frac{v_b C_{T0} + C_{Ts} v_s}{v_0}} \tag{14-63}$$

As before,

$$V_s = \alpha V$$

$$v_b = \beta v_0$$

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

Integrating Equation (14-62) and substituting in terms of α and β gives

$$\frac{C_{Ts}}{C_{T0}} = 1 - \exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\tau}\right)\right] \tag{14-64}$$

Combining Equations (14-63) and (14-64), the effluent tracer concentration is

$$\frac{C_T}{C_{T0}} = 1 - (1-\beta)\exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\tau}\right)\right] \tag{14-65}$$

We now need to rearrange this equation to extract the model parameters, α and β, either by regression (Polymath/MATLAB/Excel) or from the proper plot of the effluent tracer concentration as a function of time. Rearranging yields

Evaluating the model parameters

$$\boxed{\ln\frac{C_{T0}}{C_{T0}-C_T} = \ln\frac{1}{1-\beta} + \left(\frac{1-\beta}{\alpha}\right)\frac{t}{\tau}} \tag{14-66}$$

Consequently, we plot $\ln[C_{T0}/(C_{T0} - C_T)]$ as a function of t. If our model is correct, a straight line should result with a slope of $(1 - \beta)/\tau\alpha$ and an intercept of $\ln[1/(1 - \beta)]$.

Example 14–4 CSTR with Dead Space and Bypass

The elementary reaction

$$A + B \longrightarrow C + D$$

is to be carried out in the CSTR shown schematically in Figure 14-15. There is both bypassing and a stagnant region in this reactor. The tracer output for this reactor is shown in Table E14-4.1. The measured reactor volume is 1.0 m^3 and the flow rate to the reactor is 0.1 m^3/min. The reaction rate constant is 0.28 m^3/kmol·min. The feed is equimolar in A and B with an entering concentration of A equal to 2.0 kmol/m^3. Calculate the conversion that can be expected in this reactor (Figure E14-4.1).

TABLE E14-4.1 TRACER DATA FOR STEP INPUT

C_T (mg/dm^3)	1000	1333	1500	1666	1750	1800
t (min)	4	8	10	14	16	18

The entering tracer concentration is C_{T0} = 2000 mg/dm^3.

Two-parameter model

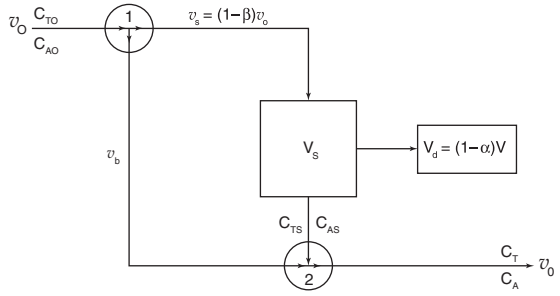


Figure E14-4.1 Schematic of real reactor modeled with dead space (V_d) and bypass (v_b).

Solution

Recalling Equation (14-66)

$$ln\frac{C_{T0}}{C_{T0}-C_T} = ln\frac{1}{1-\beta}+\frac{(1-\beta)}{\alpha}\frac{t}{\tau} \tag{14-66}$$

Equation (14-66) suggests that we construct Table E14-4.2 from Table E14-4.1 and plot $C_{T0}/(C_{T0} - C_T)$ as a function of time on semilog paper. Using this table we get Figure E14-4.2.

TABLE E14-4.2. PROCESSED DATA

t (min)	4	8	10	14	16	18
$\frac{C_{T0}}{C_{T0}-C_T}$	2	3	4	6	8	10

We can find α and β from either a semilog plot as shown in Figure E14-4.2 or by regression using Polymath, MATLAB, or Excel.

Evaluating the parameters α and β

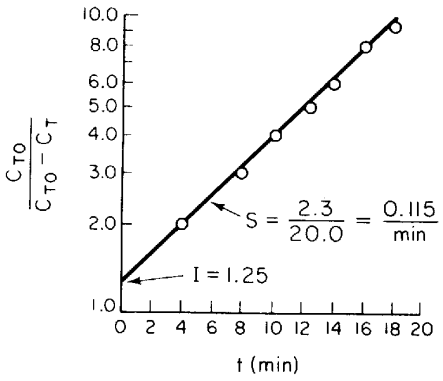


Figure E14-4.2 Response to a step input**.**

The volumetric flow rate to the well-mixed portion of the reactor, v_s, can be determined from the intercept, I:

$$\frac{1}{1-\beta} = I = 1.25$$

$$\boxed{\beta = \frac{v_b}{v_0} = 0.2}$$

The volume of the well-mixed region, V_s, can be calculated from the slope:

$$\frac{1-\beta}{\alpha\tau} = S = 0.115 \text{ min}^{-1}$$

$$\alpha\tau = \frac{1-0.2}{0.115} = 7 \text{ min}$$

$$\tau = \frac{V}{V_0} = \frac{1\ \text{m}^3}{(0.1\ \text{m}^3/\text{min})} = 10\ \text{min}$$

$$\boxed{\alpha = \frac{7\ \text{min}}{\tau} = 0.7}$$

We now proceed to determine the conversion corresponding to these model parameters.

1. **Balance on reactor volume V_s:**

$$[\text{In}] - \text{Out} + \text{Generation} = \text{Accumulation}$$

$$V_s C_{A0} - V_s C_{As} + r_{As} V_s = 0 \tag{E14-4.1}$$

2. **Rate law:**

$$-r_{AS} = kC_{As}C_{Bs}$$

Equimolar feed $\therefore C_{As} = C_{Bs}$

$$-r_{As} = kC_{As}^2 \tag{E14-4.2}$$

3. **Combining** Equations (E14-4.1) and (E14-4.2) gives

$$v_s C_{A0} - v_s C_{As} - kC_{As}^2 V_s = 0 \tag{E14-4.3}$$

Rearranging, we have

$$\tau_s k C_{As}^2 + C_{As} - C_{A0} = 0 \tag{E14-4.4}$$

The *Duck Tape Council* would like to point out the new wrinkle: **The Junction Balance.**

Solving for C_{As} yields

$$\boxed{C_{As} = \frac{-1 + \sqrt{1 + 4\tau_s k C_{A0}}}{2\tau_s k}} \tag{E14-4.5}$$

4. **Balance around junction** point 2:

$$[\text{In}] = [\text{Out}]$$

$$[v_b C_{A0} + v_s C_{As}] = [v_0 C_A] \tag{E14-4.6}$$

Rearranging Equation (E14-4.6) gives us

$$\boxed{C_A = \frac{v_0 - v_s}{v_0} C_{A0} + \frac{v_s}{v_0} C_{As}} \tag{E14-4.7}$$

5. Parameter evaluation:

$$v_s = 0.8\,v_0 = (0.8)(0.1\ \text{m}^3/\text{min}) = 0.08\ \text{m}^3/\text{min}$$

$$V_s = (\alpha\tau)\,v_0 = (7.0\ \text{min})(0.1\ \text{m}^3/\text{min}) = 0.7\ \text{m}^3$$

$$\tau_s = \frac{V_s}{v_s} = 8.7\ \text{min}$$

$$C_{As} = \frac{\sqrt{1+4\tau_s k C_{A0}}-1}{2\tau_s k} \tag{E14-4.8}$$

$$= \frac{\sqrt{1+(4)(8.7\ \text{min})(0.28\ \text{m}^3/\text{kmol}\cdot\text{min})(2\ \text{kmol}/\text{m}^3)}-1}{(2)(8.7\ \text{min})(0.28\ \text{m}^3/\text{kmol}\cdot\text{min})}$$

$$= 0.724\ \text{kmol}/\text{m}^3$$

Substituting into Equation (E14-4.7) yields

$$C_A = \frac{0.1-0.08}{0.1}(2) + (0.8)(0.724) = 0.979$$

Finding the conversion

$$X = 1 - \frac{0.979}{2.0} = 0.51$$

If the real reactor were acting as an ideal CSTR, the conversion would be

$$\boxed{C_A = \frac{\sqrt{1+4\tau k C_{A0}}-1}{2\tau k}} \tag{E14-4.9}$$

$$C_A = \frac{\sqrt{1+4(10)(0.28)(2)}-1}{2(10)(0.28)} = 0.685$$

$$\boxed{X = 1 - \frac{C_A}{C_{A0}} = 1 - \frac{0.685}{2.0} = 0.66} \tag{E14-4.10}$$

$X_{\text{model}} = 0.51$
$X_{\text{Ideal}} = 0.66$

Other Models. In Section 14.7.1 it was shown how we formulated a model consisting of ideal reactors to represent a real reactor. First, we solved for the exit concentration and conversion for our model system in terms of two parameters α and β. We next evaluated these parameters from data of tracer concentration as a function of time. Finally, we substituted these parameter values into the mole balance, rate law, and stoichiometric equations to predict the conversion in our real reactor.

To reinforce this concept, we will use one more example.

14.7.2 Real CSTR Modeled as Two CSTRs with Interchange

In this particular model there is a highly agitated region in the vicinity of the impeller; outside this region, there is a region with less agitation (Figure 14-17). There is considerable material transfer between the two regions. Both inlet and outlet flow channels connect to the highly agitated region. We shall

model the highly agitated region as one CSTR, the quieter region as another CSTR, with material transfer between the two.

The model system

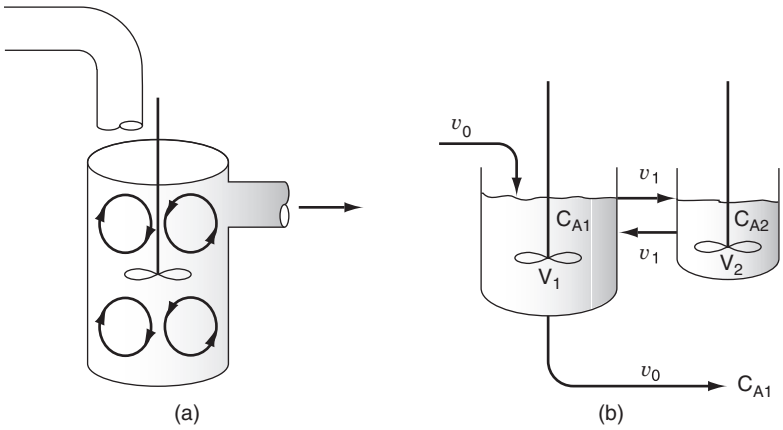


Figure 14-17 (a) Real reaction system; (b) model reaction system.

14.7.2A Solving the Model System for C_A and X

Let β represent that fraction of the total flow that is exchanged between reactors 1 and 2, that is,

$$v_1 = \beta v_0$$

and let α represent that fraction of the total volume V occupied by the highly agitated region:

Two parameters: α and β

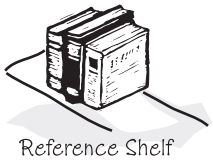
$$V_1 = \alpha V$$

Then

$$V_2 = (1 - \alpha)V$$

The space time is

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



As shown on the CD-ROM 14R.2, for a first-order reaction, the exit concentration and conversion are

$$C_{A1} = \frac{C_{A0}}{1 + \beta + \alpha\tau k - \{\beta^2/[\beta + (1 - \alpha)\tau k]\}} \tag{14-67}$$

and

Conversion for two-CSTR model

$$X = 1 - \frac{C_{A1}}{C_{A0}} = \frac{(\beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2}{(1 + \beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2} \tag{14-68}$$

where C_{A1} is the reactor concentration exiting the first reactor in Figure 14-17(b).

14.7.2B Using a Tracer to Determine the Model Parameters in a CSTR with an Exchange Volume

The problem now is to evaluate the parameters α and β using the RTD data. A mole balance on a tracer pulse injected at $t = 0$ for each of the tanks is

$$\text{Accumulation} = \text{Rate in} - \text{Rate out}$$

Unsteady-state balance of inert tracer

$$\text{Reactor 1:} \qquad V_1 \frac{dC_{T1}}{dt} = v_1 C_{T2} - (v_0 C_{T1} + v_1 C_{T1}) \tag{14-69}$$

$$\text{Reactor 2:} \qquad V_2 \frac{dC_{T2}}{dt} = v_1 C_{T1} - v_1 C_{T2} \tag{14-70}$$

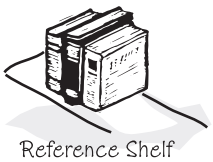
C_{T1} and C_{T2} are the tracer concentrations in reactors 1 and 2, respectively, with initial conditions $C_{T10} = N_{T0}/V_1$ and $C_{T20} = 0$.

Substituting in terms of α, β, and τ, we arrive at two coupled differential equations describing the unsteady behavior of the tracer that must be solved simultaneously.

See Appendix A.3 for method of solution

$$\tau\alpha \frac{dC_{T1}}{dt} = \beta C_{T2} - (1+\beta) C_{T1} \tag{14-71}$$

$$\tau(1-\alpha) \frac{dC_{T2}}{dt} = \beta C_{T1} - \beta C_{T2} \tag{14-72}$$



Analytical solutions to Equations (14-71) and (14-72) are given in the CD-ROM, in Appendix A.3 and in Equation (14-73), below. However, for more complicated systems, analytical solutions to evaluate the system parameters may not be possible.

$$\left(\frac{C_{T1}}{C_{T10}}\right)_{\text{pulse}} = \frac{(\alpha m_1 + \beta + 1)\, e^{m_2 t/\tau} - (\alpha m_2 + \beta + 1)\, e^{m_1 t/\tau}}{\alpha (m_1 - m_2)} \tag{14-73}$$

where

$$m_1,\ m_2 = \left[\frac{1 - \alpha + \beta}{2\alpha(1-\alpha)}\right]\left[-1 \pm \sqrt{1 - \frac{4\alpha\beta(1-\alpha)}{(1-\alpha+\beta^2)}}\right]$$

By regression on Equation (14-73) and the data in Table E14-4.2 or by an appropriate semilog plot of C_{T1}/C_{T10} versus time, one can evaluate the model parameters α and β.

14.8 Use of Software Packages to Determine the Model Parameters

If analytical solutions to the model equations are not available to obtain the parameters from RTD data, one could use ODE solvers. Here, the RTD data would first be fit to a polynomial to the effluent concentration–time data and then compared with the model predictions for different parameter values.

Example 14–5 CSTR with Bypass and Dead Volume

(a) Determine parameters α and β that can be used to model two CSTRs with interchange using the tracer concentration data listed in Table E14-5.1.

TABLE E14-5.1. RTD DATA

t (min)	0.0	20	40	60	80	120	160	200	240
C_{Te} (g/m^3)	2000	1050	520	280	160	61	29	16.4	10.0

(b) Determine the conversion of a first-order reaction with $k = 0.03\ \text{min}^{-1}$ and $\tau = 40$ min.

Solution

First we will use Polymath to fit the RTD to a polynomial. Because of the steepness of the curve, we shall use two polynomials.

For $t \leq 80$ min,

$$C_{Te} = 2000 - 59.6t + 0.642t^2 - 0.00146t^3 - 1.04 \times 10^{-5}t^4 \quad \text{(E14-5.1)}$$

For $t > 80$,

$$C_{Te} = 921 - 17.3t + 0.129t^2 - 0.000438t^3 - 5.6 \times 10^{-7}t^4 \quad \text{(E14-5.2)}$$

where C_{Te} is the exit concentration of tracer determined experimentally. Next we would enter the tracer mole (mass) balances Equations (14-71) and (14-72) into an ODE solver. The Polymath program is shown in Table E14-5.2. Finally, we vary the parameters α and β and then compare the calculated effluent concentration C_{T1} with the experimental effluent tracer concentration C_{Te}. After a few trials we converge on the values $\alpha = 0.8$ and $\beta = 0.1$. We see from Figure E14-5.1 and Table E14-5.3 that the agreement between the RTD data and the calculated data are quite good, indicating the validity of our values of α and β. The graphical solution to this problem is given on the CD-ROM and in the 2nd Edition. We now substitute these values in Equation (14-68), and as shown in the CD-ROM, the corresponding conversion is 51% for the model system of two CSTRs with interchange:

Trial and error using software packages

$$\boxed{X = 1 - \frac{C_{A1}}{C_{A0}} = \frac{(\beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2}{(1 + \beta + \alpha\tau k)[\beta + (1-\alpha)\tau k] - \beta^2}} \quad \text{(14-68)}$$

$$\tau k = (40 \text{ min})(0.03 \text{ min}^{-1}) = 1.2$$

$$X = \frac{[0.1 + (0.8)(1.2)][0.1 + (1 - 0.8)(1.2)] - (0.1)^2}{[1 + 0.1 + (0.8)(1.2)][0.1 + (1 - 0.8)(1.2) - (0.1)^2]}$$

$$X = 0.51$$

Comparing models, we find

$$(X_{\text{model}} = 0.51) < (X_{\text{CSTR}} = 0.55) < (X_{\text{PFR}} = 0.7)$$

TABLE E14-5.2. POLYMATH PROGRAM: TWO CSTRS WITH INTERCHANGE

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(CT1)/d(t) = (beta*CT2-(1+beta)*CT1)/alpha/tau
[2] d(CT2)/d(t) = (beta*CT1-beta*CT2)/(1-alpha)/tau

Explicit equations as entered by the user
[1] beta = 0.1
[2] alpha = 0.8
[3] tau = 40
[4] CTe1 = 2000-59.6*t+0.64*t^2-0.00146*t^3-1.047*10^(-5)*t^4
[5] CTe2 = 921-17.3*t+0.129*t^2-0.000438*t^3+5.6*10^(-7)*t^4
[6] t1 = t-80
[7] CTe = if(t<80)then(CTe1)else(CTe2)

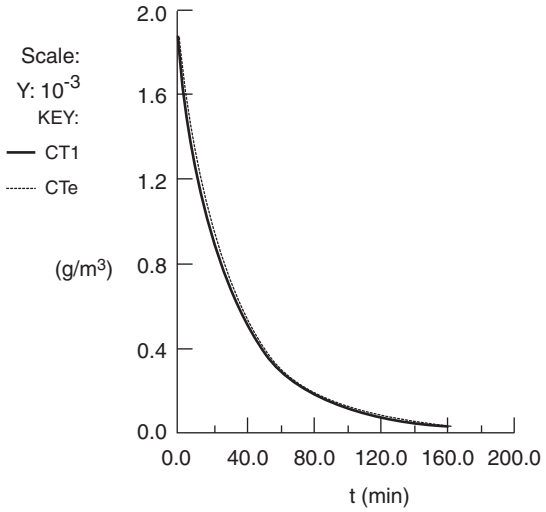


Figure E14-5.1 Comparison of model and experimental exit tracer concentrations.

TABLE E14-5.3. COMPARING MODEL (CT1) WITH EXPERIMENT (CTe)

t	CT1	CTe
0	2000	2000
10	1421.1968	1466.4353
20	1014.8151	1050.6448
30	728.9637	740.0993
40	527.4236	519.7568
50	384.9088	372.0625
60	283.7609	276.9488
70	211.6439	211.8353
80	159.9355	161.2816
100	95.43456	99
120	60.6222	61.8576
140	40.92093	40.6576
160	29.10943	28.3536

Two CSTRs with interchange

14.9 Other Models of Nonideal Reactors Using CSTRs and PFRs

Several reactor models have been discussed in the preceding pages. All are based on the physical observation that in almost all agitated tank reactors, there is a well-mixed zone in the vicinity of the agitator. This zone is usually represented by a CSTR. The region outside this well-mixed zone may then be modeled in various fashions. We have already considered the simplest models, which have the main CSTR combined with a dead-space volume; if some short-circuiting of the feed to the outlet is suspected, a bypass stream can be added. The next step is to look at all possible combinations that we can use to model a nonideal reactor using only CSTRs, PFRs, dead volume, and bypassing. The rate of transfer between the two reactors is one of the model parameters. The positions of the inlet and outlet to the model reactor system depend on the physical layout of the real reactor.

Figure 14-18(a) describes a real PFR or PBR with channeling that is modeled as two PFRs/PBRs in parallel. The two parameters are the fraction of flow to the reactors [i.e., β and $(1 - \beta)$] and the fractional volume [i.e., α and $(1 - \alpha)$] of each reactor. Figure 14-18(b) describes a real PFR/PBR that has a backmix region and is modeled as a PFR/PBR in parallel with a CSTR. Figures 14-19(a) and (b) show a real CSTR modeled as two CSTRs with interchange. In one case, the fluid exits from the top CSTR (a) and in the other case the fluid exits from the bottom CSTR. The parameter β represents the interchange volumetric flow rate and α the fractional volume of the top reactor, where the fluid exits the reaction system. We note that the reactor in model 14-19(b) was found to describe extremely well a real reactor used in the production of terephthalic acid.[14] A number of other combinations of ideal reactions can be found in Levenspiel.[15]

A case history for terephthalic acid

[14]Proc. Indian Inst. Chem. Eng. Golden Jubilee, a Congress, Delhi, 1997, p. 323.

[15]Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed. (New York: Wiley, 1999), pp. 284–292.

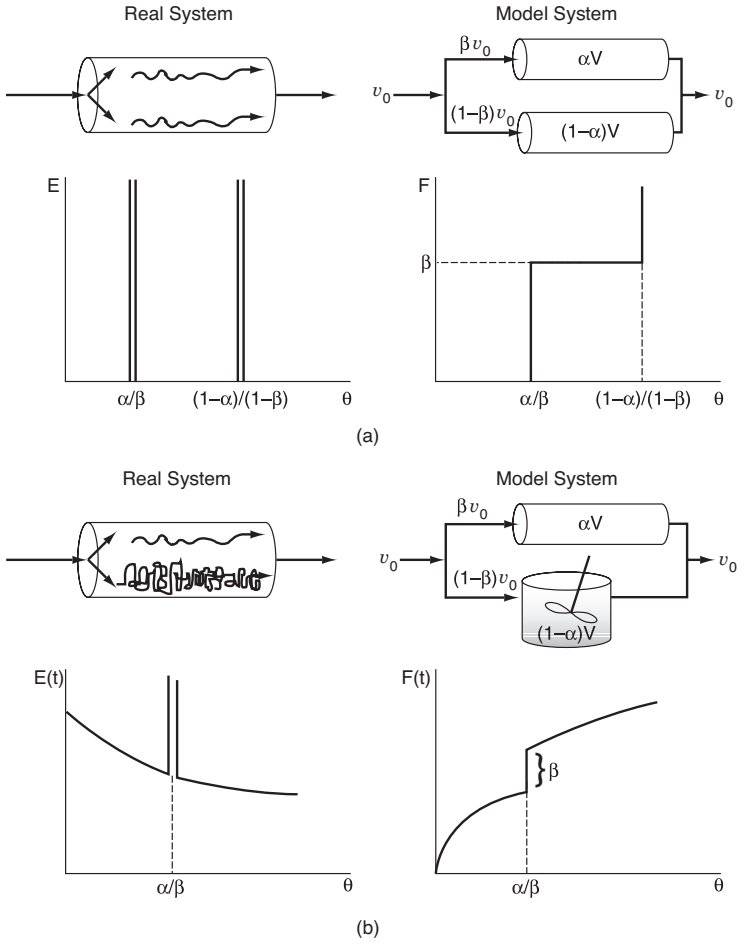


Figure 14-18 Combinations of ideal reactors used to model real tubular reactors. (a) two ideal PFRs in parallel (b) ideal PFR and ideal CSTR in parallel.

14.10 Applications to Pharmacokinetic Modeling

The use of combinations of ideal reactors to model metabolism and drug distribution in the human body is becoming commonplace. For example, one of the simplest models for drug adsorption and elimination is similar to that shown in Figure 14-19(a). The drug is injected intravenously into a central compartment containing the blood (the top reactor). The blood distributes the drug back and forth to the tissue compartment (the bottom reactor) before being eliminated (top reactor). This model will give the familiar linear semi-log plot found in pharmacokinetics textbooks. As can be seen in the figure for *Professional Reference Shelf* R7.5 on pharmacokinetics on page 453, there are two different slopes, one for the drug distribution phase and one for the elmination phase. More elaborate models using combinations of ideal reactors to model a real system are described in section 7.5 where alcohol metabolism is discussed.

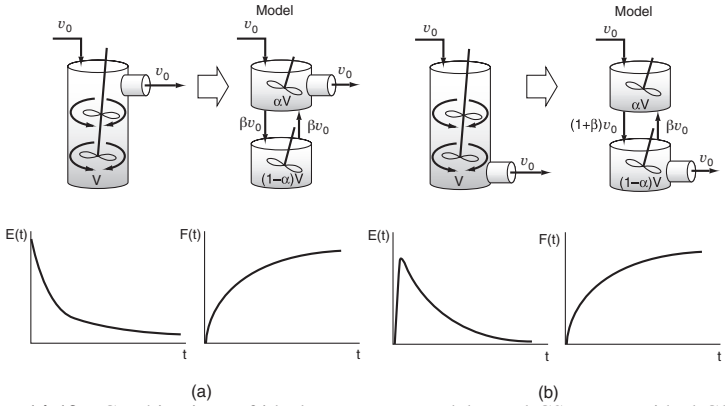


Figure 14-19 Combinations of ideal reactors to model a real CSTR. Two ideal CSTRs with interchange (a) exit from the top of the CSTR (b) exit from the bottom of the CSTR.

Closure

RTD Data + Kinetics + Model = Prediction

In this chapter, models were developed for existing reactors to obtain a more precise estimate of the exit conversion and concentration than estimates of the examples given by the zero-order parameter models of segregation and maximum mixedness. After completing this chapter, the reader will use the RTD data and kinetic rate law and reactor model to make predictions of the conversion and exit concentrations using the tank-in-series and dispersion one-parameter models. In addition, the reader should be able to create combinations of ideal reactors that mimic the RTD data and to solve for the exit conversions and concentrations. The choice of a proper model is almost pure art *requiring creativity and engineering judgment*. The flow pattern of the model must possess the most important characteristics of that in the real reactor. Standard models are available that have been used with some success, and these can be used as starting points. Models of real reactors usually consist of combinations of PFRs, perfectly mixed CSTRs, and dead spaces in a configuration that matches the flow patterns in the reactor. For tubular reactors, the simple dispersion model has proven most popular.

The parameters in the model, which with rare exception should not exceed two in number, are obtained from the RTD data. Once the parameters are evaluated, the conversion in the model, and thus in the real reactor, can be calculated. For typical tank-reactor models, this is the conversion in a series–parallel reactor system. For the dispersion model, the second-order differential equation must be solved, usually numerically. Analytical solutions exist for first-order reactions, but as pointed out previously, no model has to be assumed for the first-order system if the RTD is available.

Correlations exist for the amount of dispersion that might be expected in common packed-bed reactors, so these systems can be designed using the dispersion model without obtaining or estimating the RTD. This situation is perhaps the only one where an RTD is not necessary for designing a nonideal reactor.

SUMMARY

The models

1. The models for predicting conversion from RTD data are:
   a. Zero adjustable parameters
      (1) Segregation model
      (2) Maximum mixedness model
   b. One adjustable parameter
      (1) Tanks-in-series model
      (2) Dispersion model
   c. Two adjustable parameters: real reactor modeled as combinations of ideal reactors
2. Tanks-in-series model: Use RTD data to estimate the number of tanks in series,

$$n = \frac{\tau^2}{\sigma^2} \tag{S14-1}$$

For a first-order reaction

$$X = 1 - \frac{1}{(1 + \tau_i k)^n}$$

3. Dispersion model: For a first-order reaction, use the Danckwerts boundary conditions

$$X = 1 - \frac{4q \exp(\mathrm{Pe}_r/2)}{(1+q)^2 \exp(\mathrm{Pe}_r q/2) - (1-q)^2 \exp(-\mathrm{Pe}_r q/2)} \tag{S14-2}$$

where

$$q = \sqrt{1 + \frac{4\boldsymbol{Da}}{\mathrm{Pe}_r}} \tag{S14-3}$$

$$\boldsymbol{Da} = \tau k \qquad \mathrm{Pe}_r = \frac{UL}{D_a} \qquad \mathrm{Pe}_f = \frac{Ud_p}{D_a \varepsilon} \tag{S14-4}$$

4. Determine D_a
   a. For laminar flow the dispersion coefficient is

$$D^* = D_{\mathrm{AB}} + \frac{U^2 R^2}{48 D_{\mathrm{AB}}} \tag{S14-5}$$

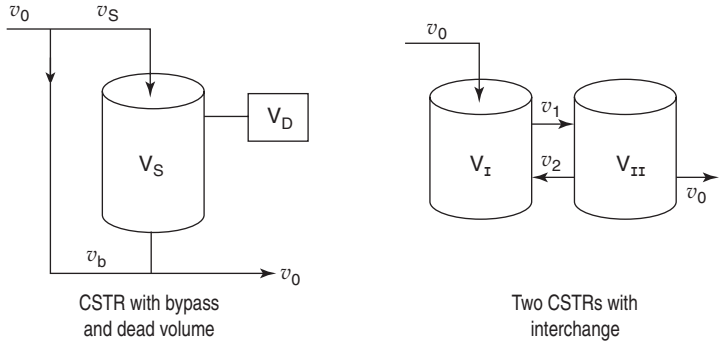
   b. Correlations. Use Figures 14-10 through 14-12.
   c. Experiment in RTD analysis to find t_m and σ^2.
   For a closed-closed system use Equation (S14-6) to calculate Pe_r from the RTD data:

$$\frac{\sigma^2}{\tau^2} = \frac{2}{\mathrm{Pe}_r} - \frac{2}{\mathrm{Pe}_r^2}\left(1 - e^{-\mathrm{Pe}_r}\right) \tag{S14-6}$$

For an open-open system, use

$$\boxed{\frac{\sigma^2}{t_m^2} = \frac{2\text{Pe}_r + 8}{\text{Pe}_r^2 + 4\text{Pe}_r + 4}} \tag{14-47}$$

5. If a real reactor is modeled as a combination of ideal reactors, the model should have at most two parameters.



6. The RTD is used to extract model parameters.
7. Comparison of conversions for a PFR and CSTR with the zero-parameter and two-parameter models. X_{seg} symbolizes the conversion obtained from the segregation model and X_{mm} that from the maximum mixedness model for reaction orders greater than one.

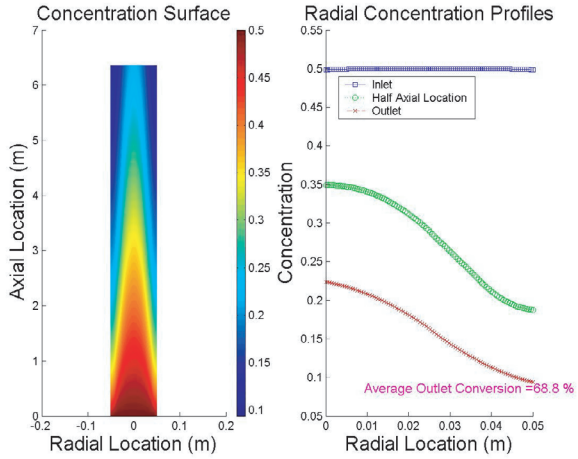
$$\boxed{\begin{array}{c} X_{\text{PFR}} > X_{\text{seg}} > X_{\text{mm}} > X_{\text{CSTR}} \\ X_{\text{PFR}} > X_{\text{model}} \qquad \text{with } X_{\text{model}} < X_{\text{CSTR}} \quad \text{or} \quad X_{\text{model}} > X_{\text{CSTR}} \end{array}}$$

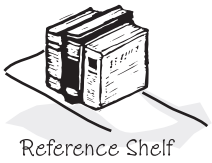
Cautions: For rate laws with unusual concentration functionalities or for nonisothermal operation, these bounds may not be accurate for certain types of rate laws.

CD-ROM MATERIAL

- **Learning Resources**
  1. *Summary Notes*
  2. *Web Material*
     COMSOL CD-ROM
- **Living Example Problems**
  1. *Example 14-3 Dispersion with Reaction—COMSOL*
  2. *Example 14-5 CSTR with Bypass and Dead Volume*

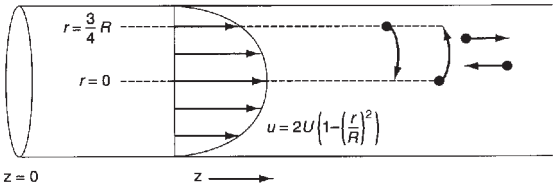
COMSOL results





- **Professional Reference Shelf**

R14.1 *Derivation of Equation for Taylor–Aris Dispersion*

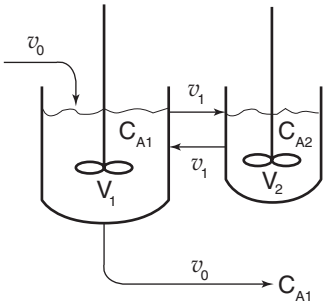


$$\frac{\partial \overline{C}}{\partial t} + U\frac{\partial \overline{C}}{\partial z^*} = D^*\frac{\partial^2 \overline{C}}{\partial z^{*2}}$$

$$D^* = D_{AB} + \frac{U^2R^2}{48D_{AB}}$$

R14.2 *Real Reactor Modeled as two Ideal CSTRs with Exchange Volume*

Example R14-1 Two CSTRs with interchange.

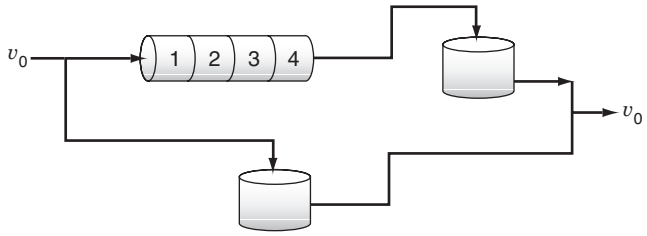


QUESTIONS AND PROBLEMS

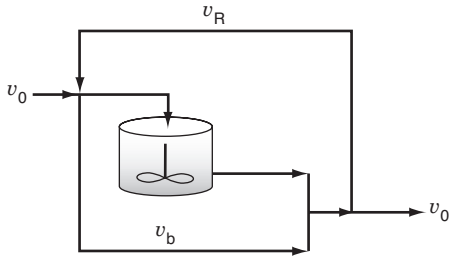
The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

A = ● B = ■ C = ◆ D = ◆◆

P14-1$_B$ Make up and solve an original problem. The guidelines are given in Problem P4-1$_A$. However, make up a problem in reverse by first choosing a model system such as a CSTR in parallel with a CSTR and PFR [with the PFR modeled as four small CSTRs in series; Figure P14-1$_B$(a)] or a CSTR with recycle and bypass [Figure P14-1$_B$(b)]. Write tracer mass balances and use an ODE solver to predict the effluent concentrations. In fact, you could build up an arsenal of tracer curves for different model systems to compare against real reactor RTD data. In this way you could deduce which model best describes the real reactor.



(a)



(b)

Figure P14-1.1 Model systems.

P14-2$_B$ **(a) Example 14-1.** How large would the error term be in Equation E14-1.4 if $\tau k = 0.1$? $\tau k = 1$? $\tau k = 10$?

(b) Example 14-2. Vary D_a, k, U, and L. To what parameters or groups of parameters (e.g., kL^2/D_a) would the conversion be most sensitive? What if the first-order reaction were carried out in tubular reactors of different diameters, but with the space time, τ, remaining constant? The diameters would range from a diameter of 0.1 dm to a diameter of 1 m for kinematic viscosity $\upsilon = \mu/\rho = 0.01$ cm^2/s, $U = 0.1$ cm/s, and $D_{AB} = 10^{-5}$ cm^2/s. How would your conversion change? Is there a diameter that would maximize or minimize conversion in this range?

(c) **Example 14-3.** (1) Load the reaction and dispersion program from the COMSOL CD-ROM. Vary the Damköhler number for a second-order reaction using the Aris–Taylor approximation (part (b) in Example 14-3). (2) Vary the Peclet and Damköhler numbers for a second-order reaction in laminar flow. What values of the Peclet number affect the conversion significantly?

(d) **Example 14-4.** How would your answers change if the slope was 4 min^{-1} and the intercept was 2 in Figure E14-4.2?

(e) **Example 14-5.** Load the *Living Example Polymath Program*. Vary α and β and describe what you find. What would be the conversion if $\alpha = 0.75$ and $\beta = 0.15$?

(f) **What if** you were asked to design a tubular vessel that would minimize dispersion? What would be your guidelines? How would you maximize the dispersion? How would your design change for a packed bed?

(g) **What if** someone suggested you could use the solution to the flow-dispersion-reactor equation, Equation (14-27), for a second-order equation by linearizing the rate law by lettering $-r_A = kC_A^2 \cong (kC_{A0}/2)\ C_A = k'C_A$? Under what circumstances might this be a good approximation? Would you divide C_{A0} by something other than 2? What do you think of linearizing other non-first-order reactions and using Equation (14-27)? How could you test your results to learn if the approximation is justified?

(h) **What if** you were asked to explain why physically the shapes of the curves in Figure 14-3 look the way they do, what would you say? What if the first pulse in Figure 14.1(b) broke through at $\Theta = 0.5$ and the second pulse broke through at $\Theta = 1.5$ in a tubular reactor in which a second-order liquid-phase reaction

$$2A \longrightarrow B + C$$

was occurring? What would the conversion be if $\tau = 5$ min, $C_{A0} = 2$ mol/dm^3, and $k = 0.1$ dm^3/mol·min?

P14-3$_B$ The second-order liquid-phase reaction

$$A \longrightarrow B + C$$

is to be carried out isothermally. The entering concentration of A is 1.0 mol/dm^3. The specific reaction rate is 1.0 dm^3/mol·min. A number of used reactors (shown below) are available, each of which has been characterized by an RTD. There are two crimson and white reactors and three maize and blue reactors available.

Reactor	σ*(min)*	τ*(min)*	*Cost*
Maize and blue	2	2	$25,000
Green and white	4	4	50,000
Scarlet and gray	3.05	4	50,000
Orange and blue	2.31	4	50,000
Purple and white	5.17	4	50,000
Silver and black	2.5	4	50,000
Crimson and white	2.5	2	25,000

(a) You have $50,000 available to spend. What is the greatest conversion you can achieve with the available money and reactors?

(b) How would your answer to (a) change if you had $75,000 available to spend?

(c) From which cities do you think the various used reactors came from?

P14-4$_B$ The elementary liquid-phase reaction

$$A \xrightarrow{k_1} B, \qquad k_1 = 1.0\ \text{min}^{-1}$$

is carried out in a packed bed reactor in which dispersion is present. What is the conversion?

Additional information

Porosity = 50% Reactor length = 0.1 m
Particle size = 0.1 cm Mean velocity = 1 cm/s
Kinematic viscosity = 0.01 cm^2/s

P14-5$_A$ A gas-phase reaction is being carried out in a 5-cm-diameter tubular reactor that is 2 m in length. The velocity inside the pipe is 2 cm/s. As a very first approximation, the gas properties can be taken as those of air (kinematic viscosity = 0.01 cm^2/s), and the diffusivities of the reacting species are approximately 0.005 cm^2/s.

(a) How many tanks in series would you suggest to model this reactor?

(b) If the second-order reaction A + B $\longrightarrow$ C + D is carried out for the case of equal molar feed and with C_{A0} = 0.01 mol/dm^3, what conversion can be expected at a temperature for which k = 25 dm^3/mol·s?

(c) How would your answers to parts (a) and (b) change if the fluid velocity were reduced to 0.1 cm/s? Increased to 1 m/s?

(d) How would your answers to parts (a) and (b) change if the superficial velocity was 4 cm/s through a packed bed of 0.2-cm-diameter spheres?

(e) How would your answers to parts (a) to (d) change if the fluid were a liquid with properties similar to water instead of a gas, and the diffusivity was 5×10^{-6} cm^2/s?

P14-6$_A$ Use the data in Example 13-2 to make the following determinations. (The volumetric feed rate to this reactor was 60 dm^3/min.)

(a) Calculate the Peclet numbers for both open and closed systems.

(b) For an open system, determine the space-time τ and then calculate the % dead volume in a reactor for which the manufacturer's specifications give a volume of 420 dm^3.

(c) Using the dispersion and tanks-in-series models, calculate the conversion for a closed vessel for the first-order isomerization

$$A \longrightarrow B$$

with k = 0.18 min^{-1}.

(d) Compare your results in part (c) with the conversion calculated from the tanks-in-series model, a PFR, and a CSTR.

P14-7$_A$ A tubular reactor has been sized to obtain 98% conversion and to process 0.03 m^3/s. The reaction is a first-order irreversible isomerization. The reactor is 3 m long, with a cross-sectional area of 25 dm^2. After being built, a pulse tracer test on the reactor gave the following data: t_m = 10 s and σ^2 = 65 s^2. What conversion can be expected in the real reactor?

P14-8$_B$ The following $E(t)$ curve was obtained from a tracer test on a reactor.

$$\begin{aligned} E(t) &= 0.25t && 0 < t < 2 \\ &= 1 - 0.25t && 2 < t < 4 \\ &= 0 && t > 4 \end{aligned}$$

t in minutes, and E(t) in min^{-1}.

The conversion predicted by the tanks-in-series model for the isothermal elementary reaction

$$A \longrightarrow B$$

was 50% at 300 K.

(a) If the temperature is to be raised 10°C (E = 25,000 cal/mol) and the reaction carried out isothermally, what will be the conversion predicted by the maximum mixedness model? The T-I-S model?

(b) The elementary reactions

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

$$A \xrightarrow{k_3} D$$

$k_1 = k_2 = k_3 = 0.1 \text{ min}^{-1}$ at 300 K, $C_{A0} = 1 \text{ mol/dm}^3$

were carried out isothermally at 300 K in the same reactor. What is the concentration of B in the exit stream predicted by the maximum mixedness model?

(c) For the multiple reactions given in part (b), what is the conversion of A predicted by the dispersion model in an isothermal closed-closed system?

P14-9$_B$ Revisit Problem P13-4$_C$ where the RTD function is a hemicircle. What is the conversion predicted by

(a) the tanks-in-series model?

(b) the dispersion model?

P14-10$_B$ Revisit Problem P13-5$_B$.

(a) What combination of ideal reactors would you use to model the RTD?

(b) What are the model parameters?

(c) What is the conversion predicted for your model?

P14-11$_B$ Revisit Problem P13-6$_B$.

(a) What conversion is predicted by the tanks-in-series model?

(b) What is the Peclet number?

(c) What conversion is predicted by the dispersion model?

P14-12$_C$ Consider a real tubular reactor in which dispersion is occurring.

(a) For small deviations from plug flow, show that the conversion for a first-order reaction is given approximately as

$$X = 1 - \exp\left[-\tau k + \frac{(\tau k)^2}{\text{Pe}_r}\right] \tag{P14.1}$$

(b) Show that to achieve the same conversion, the relationship between the volume of a plug-flow reactor, V_P, and volume of a real reactor, V, in which dispersion occurs is

$$\frac{V_P}{V} = 1 - \frac{(k\tau)}{\text{Pe}} = 1 - \frac{kD_e}{U^2} \tag{P14.2}$$

(c) For a Peclet number of 0.1 based on the PFR length, how much bigger than a PFR must the real reactor be to achieve the 99% conversion predicted by the PFR?

(d) For an *n*th-order reaction, the ratio of exit concentration for reactors of the same length has been suggested as

$$\frac{C_A}{C_{A_{plug}}} = 1 + \frac{n}{Pe}(\tau k C_{A0}^{n-1}) \ln \frac{C_{A0}}{C_{A_{plu}}} \qquad \text{(P14.3)}$$

What do you think of this suggestion?

(e) What is the effect of dispersion on zero-order reactions?

P14-13$_B$ Let's continue Problem P13-19$_B$.

(a) 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?

(b) 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?

(c) If the reactor is modeled as tanks in series, how many tanks are needed to represent this reactor? What is the conversion for a first-order reaction with $k = 0.1\ \text{min}^{-1}$?

(d) If the reactor is modeled by a dispersion model, what are the Peclet numbers for an open system and for a closed system? What is the conversion for a first-order reaction with $k = 0.1\ \text{min}^{-1}$ for each case?

(e) Use the dispersion model to estimate the conversion for a second-order reaction with $k = 0.1\ \text{dm}^3/\text{mol}\cdot\text{s}$ and $C_{A0} = 1\ \text{mol/dm}^3$.

(f) It is suspected that the reactor might be behaving as shown in Figure P14-13$_B$, with *perhaps (?)* $V_1 = V_2$. What is the "backflow" from the second to the first vessel, as a multiple of v_0?

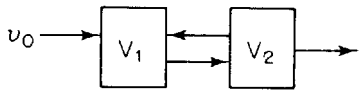


Figure P14-13$_B$ Proposed model system

(g) If the model above is correct, what would be the conversion for a second-order reaction with $k = 0.1\ \text{dm}^3/\text{mol}\cdot\text{min}$ if $C_{A0} = 1.0\ \text{mol/dm}^3$?

(h) Prepare a table comparing the conversion predicted by each of the models described above.

(i) How would your answer to part (a) change if the reaction were carried out adiabatically with the parameter values given in Problem P13-2$_A$(j)?

Application Pending for Problem Hall of Fame

P14-14$_D$ It is proposed to use the elementary reactions

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

$$C + B \xrightarrow{k_2} X + Y$$

to characterize mixing in a real reactor by monitoring the product distribution at different temperatures. The ratio of specific reaction rates (k_2/k_1) at temperatures T_1, T_2, T_3, and T_4 is 5.0, 2.0, 0.5, and 0.1, respectively. The corresponding values of $\tau k_1 C_{A0}$ are 0.2, 2, 20, and 200.

(a) Calculate the product distribution for the CSTR and PFR in series described in Example 13-3 for $\tau_{CSTR} = \tau_{PFR} = 0.5\tau$.

(b) Compare the product distribution at two temperatures using the RTD shown in Examples 13-1 and 13-2 for the complete segregation model and the maximum mixedness model.

(c) Explain how you could use the product distribution as a function of temperature (and perhaps flow rate) to characterize your reactor. For example, could you use the test reactions to determine whether the early mixing scheme or the late mixing scheme in Example 13-3 is more representative of a real reactor? Recall that both schemes have the same RTD.

(d) How should the reactions be carried out (i.e., at high or low temperatures) for the product distribution to best characterize the micromixing in the reactor?

P14-15$_B$ A second-order reaction is to be carried out in a real reactor which gives the following outlet concentration for a step input.

For $0 \le t < 10$ min then $C_T = 10\ (1-e^{-.1t})$

For 10 min $\le t$ then $C_T = 5+10\ (1-e^{-.1t})$

(a) What model do you propose and what are your model parameters, α and β?

(b) What conversion can be expected in the real reactor?

(c) How would your model change and conversion change if your outlet tracer concentration was

For $t \le 10$ min, then $C_T = 0$

For $t \ge 10$ min, then $C_T = 5+10\ (1-e^{-0.2(t-10)})$

$v_0 = 1$ dm^3/min, $k = 0.1$ dm^3/mol · min, $C_{A0} = 1.25$ mol/dm^3

P14-16$_B$ Suggest combinations of ideal reactors to model real reactors given in Problem 13-2$_A$(b) for either $E(\theta)$,$E(t)$, $F(\theta)$, $F(t)$, or $(1 - F(\theta))$.

P14-17$_B$ Below are two COMSOL simulations for a laminar flow reactor with heat effects: Run 1 and Run 2. The figures below show the cross-section plot of concentration for species A at the middle of the reactor. Run 2 shows a minimum on the cross-section plot. This minimum could be the result of (circle all that apply and explain your reasoning for each suggestion (a) through (e))

(a) the thermal conductivity of reaction mixture decreases

(b) overall heat transfer coefficient increases

(c) overall heat transfer coefficient decreases

(d) the coolant flow rate increases

(e) the coolant flow rate decreases

Hint: Explore "Nonisothermal Reactor II" on the COMSOL CD-ROM.

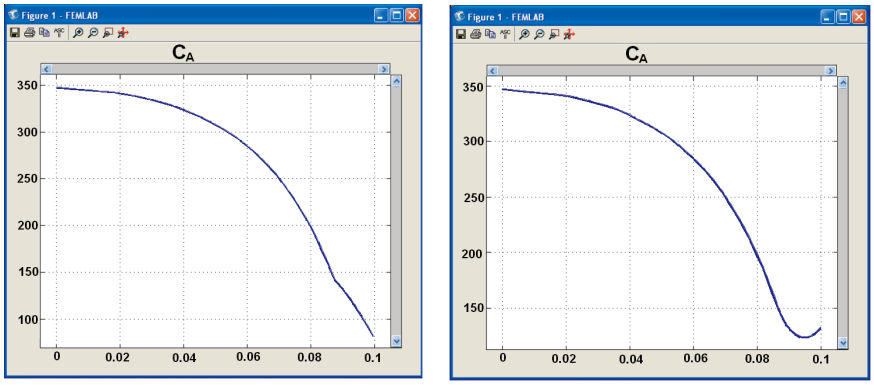


Figure P14-17$_B$ COMSOL screen shots

P14-18$_B$ Load the laminar flow with dispersion example on the COMSOL CD-ROM. Keep ***Da*** and L/R constant and vary the reaction order n, ($0.5 \le n \le 5$) for different Peclet numbers. Are there any combinations of n and Pe where dispersion is more important or less important on the exit concentration? What generalizations can you make? *Hint:* for n < 1 use $r_A = -k \cdot (Abs(C_A^n))$

COMSOL Problem

P14-19$_C$ Revisit the COMSOL Example 14-3 for laminar flow with dispersion.

(a) Plot the radial concentration profiles for $z/L = 0.5$ and 1.0 for a second-order reaction with $C_{A0} = 0.5$ mol/dm^3 and $kC_{A0} = 0.7$ min^{-1} using both the closed-vessel and the laminar flow open-vessel boundary conditions at the inlet. Is the average outlet conversion for the open-vessel boundary condition lower than that which uses the closed-vessel boundary condition? In what situation, if any, will the two boundary conditions result in significantly different outlet concentrations? Vary Pe and ***Da*** and describe what you find, i.e., $C_{A0} = 0.5$ mol/dm^3.

(b) Repeat (a) for both a third order with $kC_{A0}^2 = 0.7\ \text{min}^{-1}$ and a half-order reaction with $k = 0.495\ (\text{mol/dm}^3)^{1/2}\ \text{min}^{-1}$. Compare the radial conversion profiles for a first-, a second-, a third-, and a half-order reaction at different locations down the reactor.

Note in COMSOL:

Open-vessel Boundary (Laminar Flow): –Ni·n = 2*U0*(1-(r/Ra).^2)*CA0

Closed-vessel Boundary: –Ni·n = U0*CA0

Concentration Boundary Condition CA = CA0

Symmetry/Insulation Condition n·N = 0

P14-20$_B$ The F curves for two tubular reactors are shown here, for a closed–closed system.

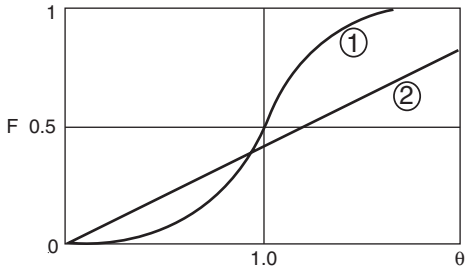


Figure P14-20$_B$ F Curves

(a) Which curve has the higher Peclet number? Explain.

(b) Which curve has the higher dispersion coefficient? Explain.

(c) If this F curve is for the tanks-in-series model applied to two different reactors, which curve has the largest number of T-I-S (1) or (2)?

U of M, ChE528 Fall 2000 Exam II

P14-21$_B$ Consider the following system used to model a real reactor:

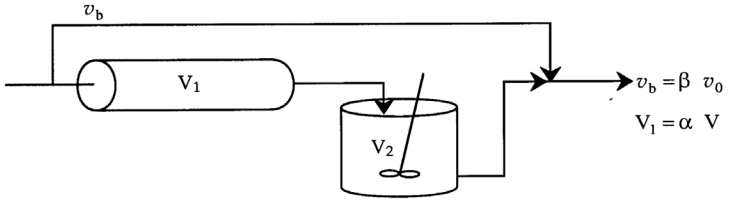


Figure P14-21$_B$ Model system

Describe how you would evaluate the parameters α and β.

(a) Draw the F and E curves for this system of ideal reactors used to model a real reactor using $\beta = 0.2$ and $\alpha = 0.4$. Identify the numerical values of the points on the F curve (e.g., t_1) as they relate to τ.

(b) If the reaction A $\rightarrow$ B is second order with $kC_{A0} = 0.5\ \text{min}^{-1}$, what is the conversion assuming the space time for the real reactor is 2 min?

U of M, ChE528 Fall 2000 Final Exam

P14-26$_B$ There is a 2 m^3 reactor in storage that is to be used to carry out the liquid-phase second-order reaction

$$A + B \longrightarrow C$$

A and B are to be fed in equal molar amounts at a volumetric rate of 1 m^3/min. The entering concentration of A is 2 molar, and the specific reaction rate is 1.5 m^3/kmol • min. A tracer experiment was carried out and reported in terms of F as a function of time in minutes.

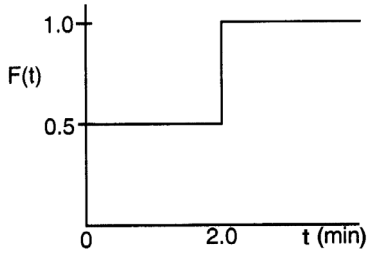


Figure P14-22$_B$ F curve for a nonideal reactor

Suggest a two-parameter model consistent with the data; evaluate the model parameters and the expected conversion.

U of M, ChE528 Fall 2001 Final Exam

P14-23$_B$ The following E curve was obtained from a tracer test:

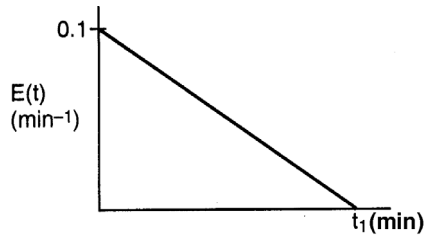


Figure P14-23 E curve for a nonideal reactor

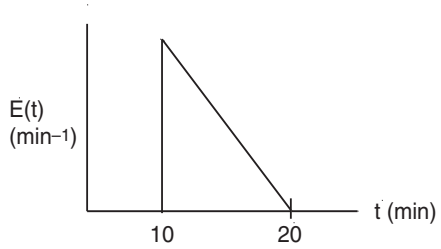
(a) What is the mean residence time?

(b) What is the Peclet number for a closed-closed system?

(c) How many tanks in series are necessary to model this non-ideal reactor?

U of M, Doctoral Qualifying Exam (DQE), May 2001

P14-24$_B$ The A first-order reaction is to be carried out in the reactor with $k = 0.1$ min^{-1}.



P14-25$_B$ Fill in the following table with the conversion predicted by each type of model/reactor.

Ideal PFR	Ideal CSTR	Ideal laminar flow reactor	Segregation	Maximum mixedness	Dispersion	Tanks in series

P14-26$_B$ The following outlet concentration trajectory was obtained from a step input to a nonideal reactor. The entering concentration was 10 millimolar of tracer.

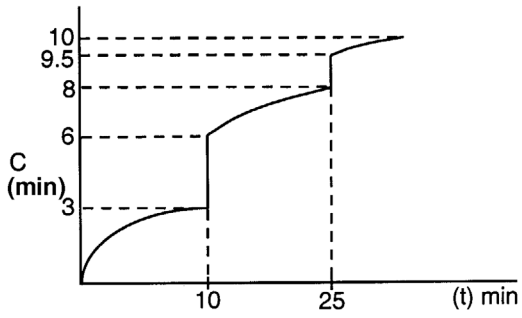


Figure P14-26$_B$ C curve for a nonideal reactor

Suggest a model using a collection of ideal reactors to model the nonideal reactor.

U of M, Doctoral Qualifying Exam (DQE), May 2001

- **Additional Homework Problems**

CDP14-A$_C$ A real reactor is modeled as a combination of ideal PFRs and CSTRs. [2nd Ed. P14-5]

CDP14-B$_B$ A real batch reactor is modeled as a combination of two ideal reactors. [2nd Ed. P14-13]

CDP14-C$_C$ Develop a model for a real reactor for RTD obtained from a step input. [2nd Ed. P14-10]

CDP14-D$_B$ Calculate D_a and X from sloppy tracer data. [2nd Ed. P14-6$_A$]

CDP14-E$_B$ Use RTD data from Oak Ridge National Laboratory to calculate the conversion from the tanks-in-series and the dispersion models. [2nd Ed. P14-7$_B$]

CDP14-F$_B$ RTD data from a slurry reactor. [3rd Ed. P14-8]

CDP14-G_C RTD data to calculate conversion for a second-order reaction for all models. [3rd Ed. P14-9]
CDP14-H_B RTD data from barge spill on Mississippi River. [3rd Ed. P14-10]
CDP14-I_B RTD data to calculate conversion using all models. [3rd Ed. P14-11]
CDP14-J_B Apply two-parameter model to multiple reactions. [3rd Ed. P14-15]
CDP14-New New problems will be inserted from time to time on the web.

SUPPLEMENTARY READING

1. Excellent discussions of maximum mixedness can be found in

   DOUGLAS, J. M., "The effect of mixing on reactor design," *AIChE Symp. Ser. 48*, Vol. 60, p. 1 (1964).

   ZWIETERING, TH. N., *Chem. Eng. Sci.*, *11*, 1 (1959).

2. Modeling real reactors with a combination of ideal reactors is discussed together with axial dispersion in

   LEVENSPIEL, O., *Chemical Reaction Engineering*, 3rd ed. New York: Wiley, 1999.

   WEN, C. Y., and L. T. FAN, *Models for Flow Systems and Chemical Reactors*. New York: Marcel Dekker, 1975.

3. Mixing and its effects on chemical reactor design have been receiving increasingly sophisticated treatment. See, for example:

   BISCHOFF, K. B., "Mixing and contacting in chemical reactors," *Ind. Eng. Chem.*, *58*(11), 18 (1966).

   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.

   PATTERSON, G. K., "Applications of turbulence fundamentals to reactor modeling and scaleup," *Chem. Eng. Commun.*, *8*, 25 (1981).

4. See also

   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.

5. Dispersion. A discussion of the boundary conditions for closed-closed, open-open, closed-open, and open-closed vessels can be found in

   ARIS, R., *Chem. Eng. Sci.*, *9*, 266 (1959).

   LEVENSPIEL, O., and K. B. BISCHOFF, *Adv. in Chem. Eng.*, *4*, 95 (1963).

   NAUMAN, E. B., *Chem. Eng. Commun.*, *8*, 53 (1981).

This is not the end.
It is not even the beginning of the end.
But it is, perhaps, the end of the beginning.

Winston Churchill
November 10, 1942