

Isothermal 4 Reactor Design

Why, a four-year-old child could understand this.
Someone get me a four-year-old child.

Groucho Marx



Tying everything
together

Overview. Chapters 1 and 2 discussed mole balances on *reactors* and the manipulation of these balances to predict reactor sizes. Chapter 3 discussed *reactions*. In Chapter 4, we combine *reactions* and *reactors* as we bring all the material in the preceding three chapters together to arrive at a logical structure for the design of various types of reactors. By using this structure, one should be able to solve reactor engineering problems by reasoning rather than by memorizing numerous equations together with the various restrictions and conditions under which each equation applies (i.e., whether there is a change in the total number of moles, etc.). In perhaps no other area of engineering is mere formula plugging more hazardous; the number of physical situations that can arise appears infinite, and the chances of a simple formula being sufficient for the adequate design of a real reactor are vanishingly small.

We divide the chapter into two parts: Part 1 “Mole Balances in Terms of Conversion,” and Part 2 “Mole Balances in Terms of Concentration, C_i , and Molar Flow Rates, F_i .” In Part 1, we will concentrate on batch reactors, CSTRs, and PFRs where conversion is the preferred measure of a reaction’s progress for single reactions. In Part 2, we will analyze membrane reactors, the startup of a CSTR, and semibatch reactors, which are most easily analyzed using concentration and molar flow rates as the variables rather than conversion. We will again use mole balances in terms of these variables (C_i , F_i) for multiple reactors in Chapter 6.

This chapter focuses attention on reactions that are operated isothermally. We begin the chapter by studying a liquid-phase reaction to form ethylene glycol in a batch reactor. Here, we determine the specific reaction rate constant that will be used to design an industrial CSTR to produce ethylene glycol. After illustrating the design of a CSTR from batch data, we carry out the design of a PFR for the gas-phase pyrolysis reaction to form ethylene. This section is followed by the design of a packed bed reactor with pressure drop to form ethylene oxide from the partial oxidation of ethylene. When we put all these reactions and reactors together, we will see we have designed a chemical plant to produce 200 million pounds per year of ethylene glycol. We close the chapter by analyzing some of the newer reactors such as microreactors, membrane reactors, and, on the CD-ROM, reactive distillation semibatch reactors.

PART 1 Mole Balances in Terms of Conversion

4.1 Design Structure for Isothermal Reactors

Logic
vs.
Memorization

One of the primary goals of this chapter is to solve chemical reaction engineering (CRE) problems by using logic rather than memorizing which equation applies where. It is the author's experience that following this structure, shown in Figure 4-1, will lead to a greater understanding of isothermal reactor design. We begin by applying our general mole balance equation (level ①) to a specific reactor to arrive at the design equation for that reactor (level ②). If the feed conditions are specified (e.g., N_{A0} or F_{A0}), all that is required to evaluate the design equation is the rate of reaction as a function of conversion at the same conditions as those at which the reactor is to be operated (e.g., temperature and pressure). When $-r_A = f(X)$ is known or given, one can go directly from level ③ to level ⑨ to determine either the batch time or reactor volume necessary to achieve the specified conversion.

Use the algorithm
rather than memo-
rizing equations.

If the rate of reaction is not given explicitly as a function of conversion, we must proceed to level ④ where the rate law must be determined by either finding it in books or journals or by determining it experimentally in the laboratory. Techniques for obtaining and analyzing rate data to determine the reaction order and rate constant are presented in Chapter 5. After the rate law has been established, one has only to use stoichiometry (level ⑤) together with the conditions of the system (e.g., constant volume, temperature) to express concentration as a function of conversion.

For liquid-phase reactions and for gas-phase reactions with no pressure drop ($P = P_0$), one can combine the information in levels ④ and ⑤, to express the rate of reaction as a function of conversion and arrive at level ⑥. It is now possible to determine either the time or reactor volume necessary to achieve the desired conversion by substituting the relationship linking conversion and rate of reaction into the appropriate design equation (level ⑨).

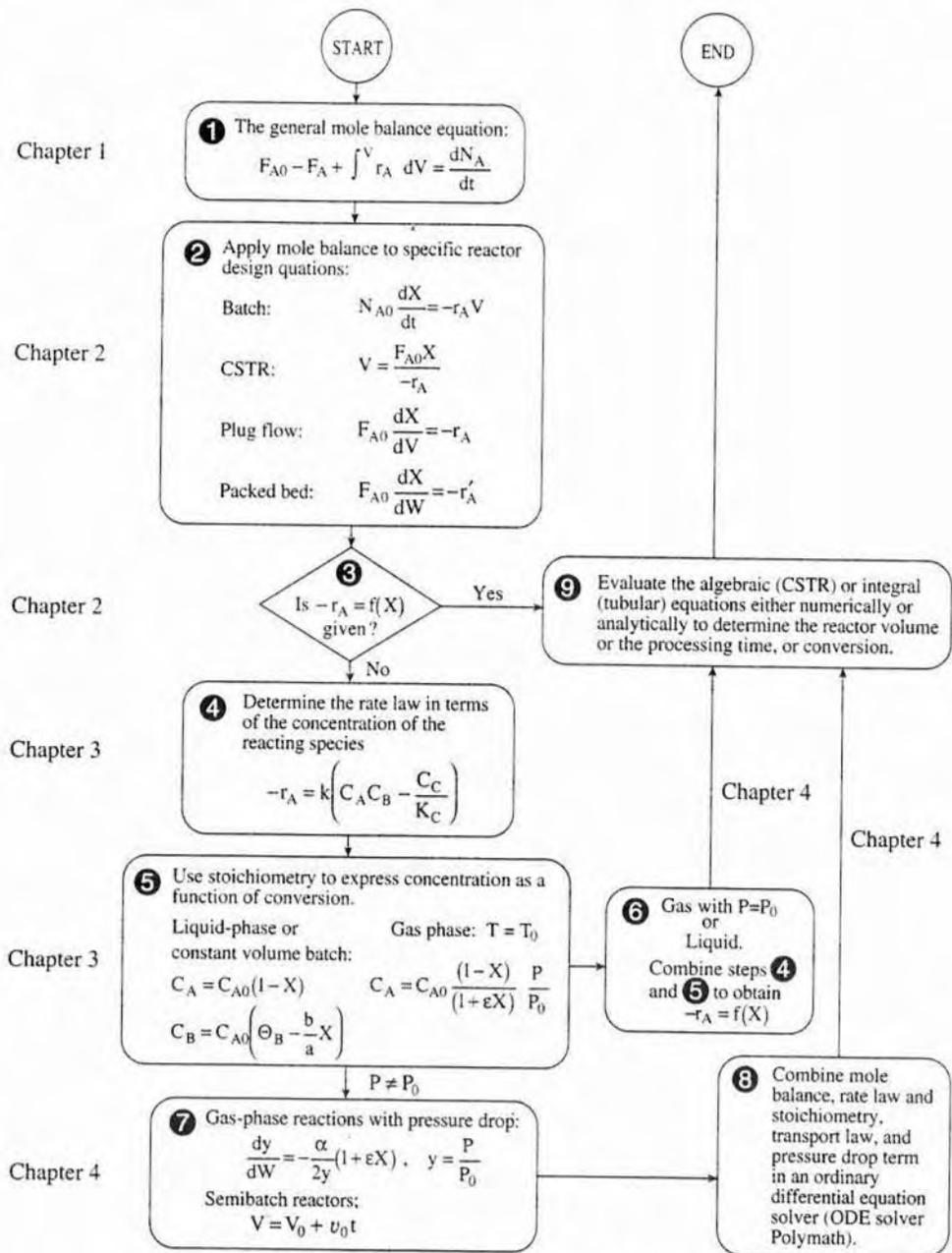


Figure 4-1 Isothermal reaction design algorithm for conversion.

For gas-phase reactions in packed beds where there is a pressure drop, we need to proceed to level ⑦ to evaluate the pressure ratio (P/P_0) in the concentration term using the Ergun equation (Section 4.5). In level ⑧, we combine the equations for pressure drop in level ⑦ with the information in levels ④ and ⑤, to proceed to level ⑨ where the equations are then evaluated in the appropriate manner (i.e., analytically using a table of integrals, or numerically using an ODE solver). Although this structure emphasizes the determination of a reaction time or reactor volume for a specified conversion, it can also readily be used for other types of reactor calculations, such as determining the conversion for a specified volume. Different manipulations can be performed in level ⑨ to answer the different types of questions mentioned here.

The structure shown in Figure 4-1 allows one to develop a few basic concepts and then to arrange the parameters (equations) associated with each concept in a variety of ways. Without such a structure, one is faced with the possibility of choosing or perhaps memorizing the correct equation from a *multitude of equations* that can arise for a variety of different combinations of reactions, reactors, and sets of conditions. The challenge is to put everything together in an orderly and logical fashion so that we can proceed to arrive at the correct equation for a given situation.

The Algorithm

1. Mole balance
2. Rate law
3. Stoichiometry
4. Combine
5. Evaluate

Fortunately, by using an algorithm to formulate CRE problems, which happens to be analogous to the algorithm for ordering dinner from a fixed-price menu in a fine French restaurant, we can eliminate virtually all memorization. In both of these algorithms, we must make choices in each category. For example, in ordering from a French menu, we begin by choosing one dish from the *appetizers* listed. Step 1 in the analog in CRE is to begin by choosing the appropriate mole balance for one of the three types of reactors shown. In Step 2 we choose the rate law (*entrée*), and in Step 3 we specify whether the reaction is gas or liquid phase (*cheese* or *dessert*). Finally, in Step 4 we combine Steps 1, 2, and 3 and either obtain an analytical solution or solve the equations using an ODE solver. (See the complete French menu on the CD-ROM).

We now will apply this algorithm to a specific situation. Suppose that we have, as shown in Figure 4-2, mole balances for three reactors, three rate laws, and the equations for concentrations for both liquid and gas phases. In Figure 4-2 we see how the algorithm is used to formulate the equation to calculate the *PFR reactor volume for a first-order gas-phase reaction*. The pathway to arrive at this equation is shown by the ovals connected to the dark lines through the algorithm. The dashed lines and the boxes represent other pathways for solutions to other situations. The algorithm for the pathway shown is

1. **Mole balance**, choose species A reacting in a PFR
2. **Rate law**, choose the irreversible first-order reaction
3. **Stoichiometry**, choose the gas-phase concentration
4. **Combine** Steps 1, 2, and 3 to arrive at Equation A
5. **Evaluate**. The combine step can be evaluated either
 - a. Analytically (Appendix A1)
 - b. Graphically (Chapter 2)

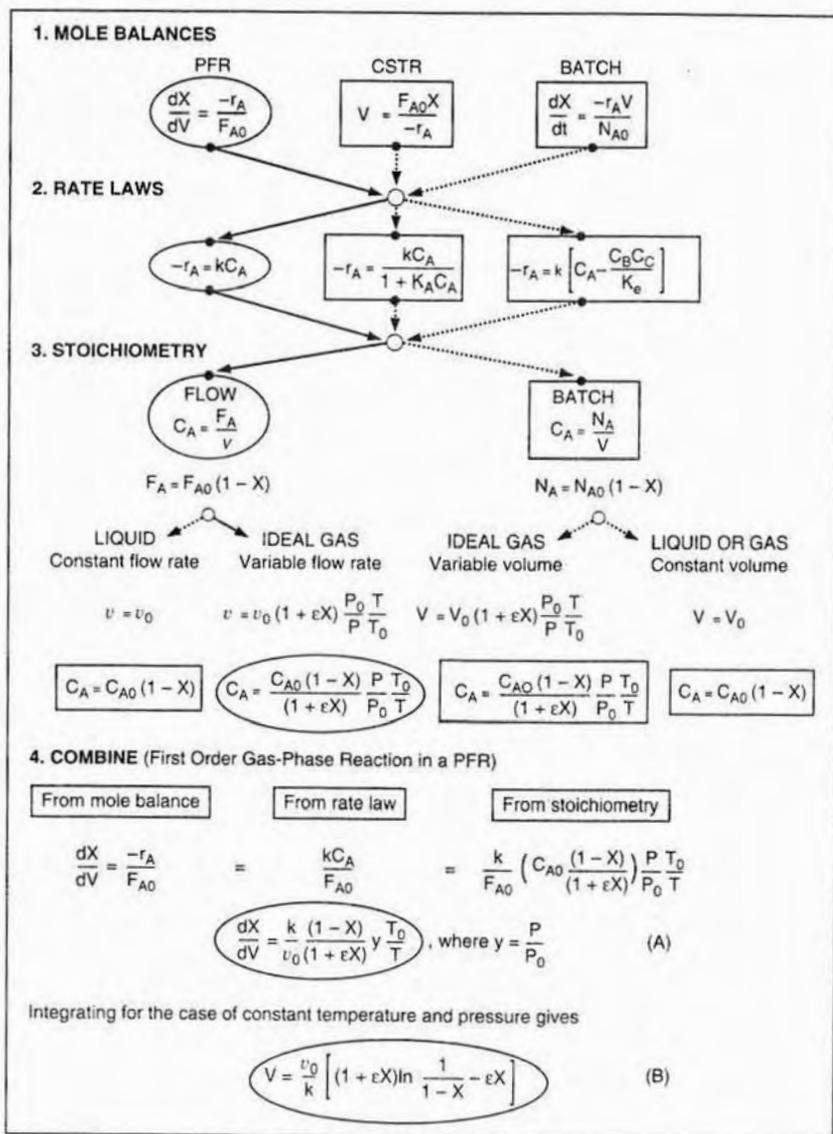


Figure 4-2 Algorithm for isothermal reactors.

Substitute parameter values in steps 1–4 only if they are zero.

We can solve the equations in the **combine** step either

1. Analytically (Appendix A1)
2. Graphically (Chapter 2)
3. Numerically (Appendix A4)
4. Using Software (Polymath).

- c. Numerically (Appendix A4), or
- d. Using software (Polymath)

In Figure 4-2 we chose to integrate Equation A for constant temperature and pressure to find the volume necessary to achieve a specified conversion (or calculate the conversion that can be achieved in a specified reactor volume). Unless the parameter values are zero, we typically don't substitute numerical values for parameters in the combine step until the very end.

For the case of isothermal operation with no pressure drop, we were able to obtain an analytical solution, given by equation B, which gives the reactor volume necessary to achieve a conversion X for a first-order gas-phase reaction carried out isothermally in a PFR. However, in the majority of situations, analytical solutions to the ordinary differential equations appearing in the combine step are not possible. Consequently, we include Polymath, or some other ODE solver such as MATLAB, in our menu in that it makes obtaining solutions to the differential equations much more palatable.

4.2 Scale-Up of Liquid-Phase Batch Reactor Data to the Design of a CSTR

One of the jobs in which chemical engineers are involved is the scale-up of laboratory experiments to pilot-plant operation or to full-scale production. In the past, a pilot plant would be designed based on laboratory data. However, owing to the high cost of a pilot-plant study, this step is beginning to be surpassed in many instances by designing a full-scale plant from the operation of a laboratory-bench-scale unit called a *microplant*. To make this jump successfully requires a thorough understanding of the chemical kinetics and transport limitations. In this section we show how to analyze a laboratory-scale batch reactor in which a liquid-phase reaction of known order is being carried out. After determining the specific reaction rate, k , from a batch experiment, we use it in the design of a full-scale flow reactor.

4.2.1 Batch Operation

In modeling a batch reactor, we have assumed that there is no inflow or outflow of material and that the reactor is well mixed. For most liquid-phase reactions, the density change with reaction is usually small and can be neglected (i.e., $V = V_0$). In addition, for *gas-phase* reactions in which the batch reactor volume remains constant, we also have $V = V_0$. Consequently, for constant-volume ($V = V_0$) (e.g., closed metal vessels) batch reactors the mole balance

$$\frac{1}{V} \left(\frac{dN_A}{dt} \right) = r_A \quad (4-1)$$

can be written in terms of concentration.

$$\frac{1}{V} \frac{dN_A}{dt} = \frac{1}{V_0} \frac{dN_A}{dt} = \frac{d(N_A/V_0)}{dt} = \frac{dC_A}{dt} = r_A \quad (4-2)$$

Generally, when analyzing laboratory experiments, it is best to process the data in terms of the measured variable. Because concentration is the measured variable for most liquid-phase reactions, the general mole balance equation applied to reactions in which there is no volume change becomes

Used to analyze
batch reaction data

$$-\frac{dC_A}{dt} = -r_A$$

This is the form we will use in analyzing reaction rate data in Chapter 5.

Let's calculate the time necessary to achieve a given conversion X for the irreversible second-order reaction



The **mole balance** on a constant-volume, $V = V_0$, batch reactor is

Mole balance
$$N_{A0} \frac{dX}{dt} = -r_A V_0 \quad (2-6)$$

The **rate law** is

Rate law
$$-r_A = kC_A^2 \quad (4-3)$$

From **stoichiometry** for a constant-volume batch reactor, we obtain

Stoichiometry
$$C_A = C_{A0}(1 - X) \quad (3-29)$$

The **mole balance**, **rate law**, and **stoichiometry** are **combined** to obtain

Combine
$$\frac{dX}{dt} = kC_{A0}(1 - X)^2 \quad (4-4)$$

To **evaluate**, we rearrange and integrate

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

Initially, if $t = 0$, then $X = 0$. If the reaction is carried out isothermally, k will be constant; we can integrate this equation (see Appendix A.1 for a table of Integrals used in CRE applications) to obtain

Evaluate
$$\int_0^t dt = \frac{1}{kC_{A0}} \int_0^X \frac{dX}{(1 - X)^2}$$

Second-order,
isothermal,
constant-volume
batch reaction

$$t = \frac{1}{kC_{A0}} \left(\frac{X}{1-X} \right) \quad (4-5)$$

This time is the reaction time t (i.e., t_R) needed to achieve a conversion X for a second-order reaction in a batch reactor. It is important to have a grasp of the order of magnitudes of batch reaction times, t_R , to achieve a given conversion, say 90%, for different values of the product of specific reaction rate, k , and initial concentration, C_{A0} . Table 4-1 shows the algorithm to find the batch reaction times, t_R , for both first- and a second-order reactions carried out isothermally. We can obtain these estimates of t_R by considering the first- and second-order irreversible reactions of the form



TABLE 4-1. ALGORITHM TO ESTIMATE REACTION TIMES

Mole balance	$\frac{dX}{dt_R} = \frac{-r_A}{N_{A0}} V$	
Rate law	First-Order $-r_A = kC_A$	Second-Order $-r_A = kC_A^2$
Stoichiometry ($V = V_0$)	$C_A = \frac{N_A}{V_0} = C_{A0}(1-X)$	
Combine	$\frac{dX}{dt_R} = k(1-X)$	$\frac{dX}{dt_R} = kC_{A0}(1-X)^2$
Evaluate (Integrate)	$t_R = \frac{1}{k} \ln \frac{1}{1-X}$	$t_R = \frac{X}{kC_{A0}(1-X)}$

For first-order reactions the reaction time to reach 90% conversion (i.e., $X = 0.9$) in a constant-volume batch reactor scales as

$$t_R = \frac{1}{k} \ln \frac{1}{1-X} = \frac{1}{k} \ln \frac{1}{1-0.9} = \frac{2.3}{k}$$

If $k = 10^{-4} \text{ s}^{-1}$,

$$t_R = \frac{2.3}{10^{-4} \text{ s}^{-1}} = 23,000 \text{ s} = 6.4 \text{ h}$$

The time necessary to achieve 90% conversion in a batch reactor for an irreversible first-order reaction in which the specific reaction rate is (10^{-4} s^{-1}) is 6.4 h.

For second-order reactions, we have

$$t_R = \frac{1}{kC_{A0}} \frac{X}{1-X} = \frac{0.9}{kC_{A0}(1-0.9)} = \frac{9}{kC_{A0}}$$

If $kC_{A0} = 10^{-3} \text{ s}^{-1}$,

$$t_R = \frac{9}{10^{-3} \text{ s}^{-1}} = 9000 \text{ s} = 2.5 \text{ h}$$

We note that if 99% conversion had been required for this value of kC_{A0} , the reaction time, t_R , would jump to 27.5 h.

Table 4-2 gives the *order of magnitude* of time to achieve 90% conversion for first- and second-order irreversible batch reactions.



Estimating Reaction Times

TABLE 4-2. BATCH REACTION TIMES

Reaction Time t_R	First-Order k (s^{-1})	Second-Order kC_{A0} (s^{-1})
Hours	10^{-4}	10^{-3}
Minutes	10^{-2}	10^{-1}
Seconds	1	10
Milliseconds	1000	10,000

Flow reactors would be used for reactions with *characteristic reaction times*, t_R , of minutes or less.

The times in Table 4-2 are the reaction time to achieve 90% conversion (i.e., to reduce the concentration from C_{A0} to $0.1 C_{A0}$). The total cycle time in any batch operation is considerably longer than the reaction time, t_R , as one must account for the time necessary to fill (t_f) and heat (t_c) the reactor together with the time necessary to clean the reactor between batches, t_e . In some cases, the reaction time calculated from Equation (4-5) may be only a small fraction of the total cycle time, t_t .

$$t_t = t_f + t_e + t_c + t_R$$

Typical cycle times for a batch polymerization process are shown in Table 4-3. Batch polymerization reaction times may vary between 5 and 60 hours. Clearly, decreasing the reaction time with a 60-hour reaction is a critical problem. As the reaction time is reduced (e.g., 2.5 h for a second-order reaction with $kC_{A0} = 10^3 s^{-1}$), it becomes important to use large lines and pumps to achieve rapid transfers and to utilize efficient sequencing to minimize the cycle time.

TABLE 4-3. TYPICAL CYCLE TIME FOR A BATCH POLYMERIZATION PROCESS

Activity	Time (h)
1. Charge feed to the reactor and agitate, t_f	1.5–3.0
2. Heat to reaction temperature, t_c	0.2–2.0
3. Carry out reaction, t_R	(varies)
4. Empty and clean reactor, t_e	0.5–1.0
Total time excluding reaction	3.0–6.0

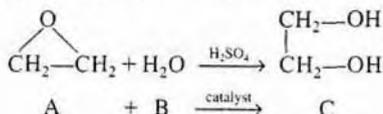
Batch operation times

Usually one has to optimize the reaction time with the processing times listed in Table 4-3 to produce the maximum number of batches (i.e., pounds of product) in a day. See Problems P4-6(f) and P4-7(c).

In the next four examples, we will describe the various reactors needed to produce 200 million pounds per year of ethylene glycol from a feedstock of ethane. We begin by finding the rate constant, k , for the hydrolysis of ethylene oxide to form ethylene glycol.

Example 4-1 Determining k from Batch Data

It is desired to design a CSTR to produce 200 million pounds of ethylene glycol per year by hydrolyzing ethylene oxide. However, before the design can be carried out, it is necessary to perform and analyze a batch reactor experiment to determine the specific reaction rate constant, k . Because the reaction will be carried out isothermally, the specific reaction rate will need to be determined only at the reaction temperature of the CSTR. At high temperatures there is a significant by-product formation, while at temperatures below 40°C the reaction does not proceed at a significant rate; consequently, a temperature of 55°C has been chosen. Because water is usually present in excess, its concentration may be considered constant during the course of the reaction. The reaction is first-order in ethylene oxide.



In the laboratory experiment, 500 mL of a 2 M solution (2 kmol/m³) of ethylene oxide in water was mixed with 500 mL of water containing 0.9 wt % sulfuric acid, which is a catalyst. The temperature was maintained at 55°C. The concentration of ethylene glycol was recorded as a function of time (Table E4-1.1).

Using the data in Table E4-1.1, determine the specific reaction rate at 55°C.

TABLE E4-1.1. CONCENTRATION-TIME DATA

Time (min)	Concentration of Ethylene Glycol (kmol/m ³) ^a
0.0	0.000
0.5	0.145
1.0	0.270
1.5	0.376
2.0	0.467
3.0	0.610
4.0	0.715
6.0	0.848
10.0	0.995

^a1 kmol/m³ = 1 mol/dm³ = 1 mol/L.

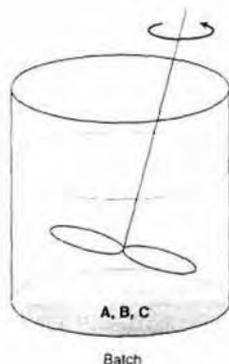
Analysis

In this example we use the problem-solving algorithm (A through G) that is given in the CD-ROM and on the web www.engin.umich.edu/~problemsolving. You may wish to follow this algorithm in solving the other examples in this chapter and the problems given at the end of the chapter. However, to conserve space it will not be repeated for other example problems.

A. *Problem statement.* Determine the specific reaction rate, k_A .

Check 10 types of homework problems on the CD-ROM for more solved examples using this algorithm.

B. Sketch:



C. Identify:

C1. Relevant theories

Mole balance: $\frac{dN_A}{dt} = r_A V$

Rate law: $-r_A = k_A C_A$

C2. Variables

Dependent: concentrations, C_A , C_B , and C_C

Independent: time, t

C3. Knowns and unknowns

Knowns: concentration of ethylene glycol as a function of time

Unknowns:

1. Concentration of ethylene oxide as a function of time, $C_A = ?$
2. Specific reaction rate, $k_A = ?$
3. Reactor volume, $V = ?$

C4. Inputs and outputs: reactant fed all at once to a batch reactor

C5. Missing information: None; does not appear that other sources need to be sought.

D. Assumptions and approximations:

Assumptions

1. Well mixed
2. All reactants enter at the same time
3. No side reactions
4. Negligible filling time
5. Isothermal operation

Approximations

1. Water in excess so that its concentration is essentially constant, (i.e., $C_B \cong C_{B0}$).

E. Specification. The problem is neither overspecified nor underspecified

Check 10 types of homework problems on the CD-ROM for more solved examples using this algorithm.



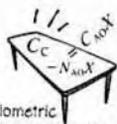
Solved Problems



Following the Algorithm



Mole Balance

Stoichiometric
Table for Constant VolumeCombining
mole balance,
rate law, and
stoichiometry

F. *Related material.* This problem uses the mole balances developed in Chapter 1 for a batch reactor and the stoichiometry and rate laws developed in Chapter 3.

G. *Use an algorithm.* For an isothermal reaction, use the chemical reaction engineering algorithm shown in Figures 4-1 and 4-2.

Solution

1. A **mole balance** on a batch reactor that is well-mixed is

$$\frac{1}{V} \frac{dN_A}{dt} = r_A \quad (\text{E4-1.1})$$

2. The **rate law** is

$$-r_A = kC_A \quad (\text{E4-1.2})$$

Because water is present in such excess, the concentration of water at any time t is virtually the same as the initial concentration and the rate law is independent of the concentration of H_2O . ($C_B \cong C_{B0}$.)

3. **Stoichiometry.** Liquid phase, no volume change, $V = V_0$ (Table E4-1.2):

TABLE E4-1.2. STOICHIOMETRIC TABLE

Species	Symbol	Initial	Change	Remaining	Concentration
$\text{CH}_2\text{CH}_2\text{O}$	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1 - X)$	$C_A = C_{A0}(1 - X)$
H_2O	B	$\Theta_B N_{A0}$	$-N_{A0}X$	$N_B = N_{A0}(\Theta_B - X)$	$C_B = C_{A0}(\Theta_B - X)$ $C_B \approx C_{A0}\Theta_B = C_{B0}$
$(\text{CH}_2\text{OH})_2$	C	0	$N_{A0}X$	$N_C = N_{A0}X$	$C_C = C_{A0}X$
		N_{T0}		$N_T = N_{T0} - N_{A0}X$	

Recall Θ_B is the initial number of moles of A to B (i.e., $\Theta_B = \frac{N_{B0}}{N_{A0}}$).

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0}$$

$$\frac{1}{V_0} \left(\frac{dN_A}{dt} \right) = \frac{d(N_A/V_0)}{dt} = \frac{dC_A}{dt}$$

4. **Combining** the rate law and the mole balance, we have

$$-\frac{dC_A}{dt} = kC_A \quad (\text{E4-1.3})$$

5. **Evaluate.** For isothermal operation, k is constant, so we can integrate this equation (E4-1.3)

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k dt = k \int_0^t dt$$

using the initial condition that when $t = 0$, then $C_A = C_{A0}$. The initial concentration of A after mixing the two volumes together is 1.0 kmol/m^3 (1 mol/L).

Integrating yields

$$\ln \frac{C_{A0}}{C_A} = kt \quad (\text{E4-1.4})$$

The concentration of ethylene oxide at any time t is

$$C_A = C_{A0}e^{-kt} \quad (\text{E4-1.5})$$

The concentration of ethylene glycol at any time t can be obtained from the reaction stoichiometry:



$$N_C = N_{A0}X = N_{A0} - N_A$$

For liquid-phase reactions $V = V_0$,

$$C_C = \frac{N_C}{V} = \frac{N_C}{V_0} = C_{A0} - C_A = C_{A0}(1 - e^{-kt}) \quad (\text{E4-1.6})$$

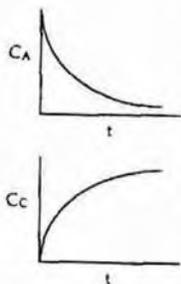
Rearranging and taking the logarithm of both sides yields

$$\ln \frac{C_{A0} - C_C}{C_{A0}} = -kt \quad (\text{E4-1.7})$$

We see that a plot of $\ln[(C_{A0} - C_C)/C_{A0}]$ as a function of t will be a straight line with a slope $-k$. Using Table E4-1.1, we can construct Table E4-1.3 and use Excel to plot $\ln(C_{A0} - C_C)/C_{A0}$ as a function of t .

TABLE E4-1.3. PROCESSED DATA

t (min)	C_C (kmol/m ³)	$\frac{C_{A0} - C_C}{C_{A0}}$	$\ln\left(\frac{C_{A0} - C_C}{C_{A0}}\right)$
0.0	0.000	1.000	0.0000
0.5	0.145	0.855	-0.1570
1.0	0.270	0.730	-0.3150
1.5	0.376	0.624	-0.4720
2.0	0.467	0.533	-0.6290
3.0	0.610	0.390	-0.9420
4.0	0.715	0.285	-1.2550
6.0	0.848	0.152	-1.8840
10.0	0.957	0.043	-3.1470



Evaluating the specific reaction rate from batch reactor concentration-time data

From the slope of a plot of $\ln[(C_{A0} - C_C)/C_{A0}]$ versus t , we can find k as shown in the Excel Figure E4-4.1.

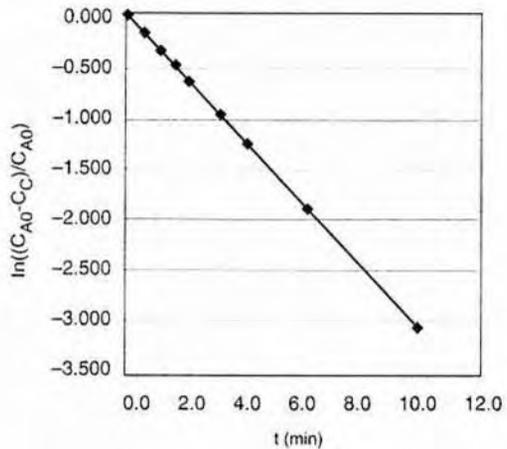


Figure E4-1.1 Excel plot of data.

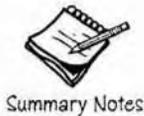
$$\text{Slope} = -k = -0.311 \text{ min}^{-1}$$

$$k = 0.311 \text{ min}^{-1}$$

The rate law becomes

$$-r_A = 0.311 \text{ min}^{-1} C_A$$

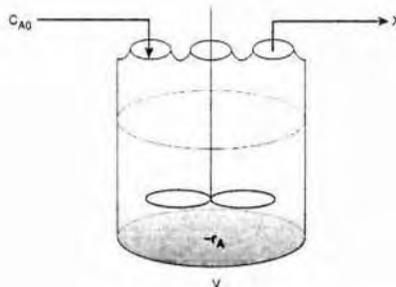
The rate law can now be used in the design of an industrial CSTR. For those who prefer to find k using semilog graph paper, this type of analysis is given in Chapter 3. Summary Notes on the CD-ROM. An Excel tutorial is also given in the Summary Notes for Chapter 3.



Summary Notes

4.3 Design of Continuous Stirred Tank Reactors (CSTRs)

Continuous stirred tank reactors (CSTRs), such as the one shown here schematically, are typically used for liquid-phase reactions.



In Chapter 2, we derived the following design equation for a CSTR:

Mole balance

$$V = \frac{F_{A0}X}{(-r_A)_{\text{exit}}} \quad (2-13)$$

which gives the volume V necessary to achieve a conversion X . As we saw in Chapter 2, the space time, τ , is a characteristic time of a reactor. To obtain the space time, τ , as a function of conversion we first substitute for $F_{A0} = v_0 C_{A0}$ in Equation (2-13)

$$V = \frac{v_0 C_{A0} X}{-r_A} \quad (4-6)$$

and then divide by v_0 to obtain the space time, τ , to achieve a conversion X in a CSTR

$$\tau = \frac{V}{v_0} = \frac{C_{A0} X}{-r_A} \quad (4-7)$$

This equation applies to a single CSTR or to the first reactor of CSTRs connected in series.

4.3.1 A Single CSTR

Let's consider a first-order irreversible reaction for which the rate law is

Rate law

$$-r_A = kC_A$$

For liquid-phase reactions, there is no volume change during the course of the reaction, so we can use Equation (3-29) to relate concentration and conversion,

Stoichiometry

$$C_A = C_{A0}(1 - X) \quad (3-29)$$

We can combine mole balance Equation (4-7), the rate law and concentration, Equation (3-29) to obtain

Combine

$$\tau = \frac{1}{k} \left(\frac{X}{1 - X} \right)$$

CSTR Relationship
between space time
and conversion for a
first-order liquid-
phase reaction

Rearranging

$$X = \frac{\tau k}{1 + \tau k} \quad (4-8)$$

We could also combine Equations (3-29) and (4-8) to find the exit reactor concentration of A, C_A .

$$C_A = \frac{C_{A0}}{1 + \tau k} \quad (4-9)$$

For a first-order reaction, the product τk is often referred to as the reaction **Damköhler number**, Da , which is a dimensionless number that can give us a quick estimate of the degree of conversion that can be achieved in continuous-flow reactors. The Damköhler number is the ratio of the rate of reaction of A to the rate of convective transport of A at the entrance to the reactor.

$$Da = \frac{-r_{A0}V}{F_{A0}}$$

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{\text{Rate of reaction at entrance}}{\text{Entering flow rate of A}} = \frac{\text{"A reaction rate"}}{\text{"A convection rate"}}$$

The Damköhler number for a first-order irreversible reaction is

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{kC_{A0}V}{v_0C_{A0}} = \tau k$$

For a second-order irreversible reaction, the Damköhler number is

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{kC_{A0}^2V}{v_0C_{A0}} = \tau k C_{A0}$$

It is important to know what values of the Damköhler number, Da , give high and low conversion in continuous-flow reactors. A value of $Da = 0.1$ or less will usually give less than 10% conversion and a value of $Da = 10.0$ or greater will usually give greater than 90% conversion; that is, the rule of thumb is

$$0.1 \leq Da \leq 10$$



if $Da < 0.1$, then $X < 0.1$

if $Da > 10$, then $X > 0.9$

Equation (4-8) for a first-order liquid-phase reaction in a CSTR can also be written in terms of the Damköhler

$$X = \frac{Da}{1 + Da}$$

4.3.2 CSTRs in Series

A first-order reaction with no change in the volumetric flow rate ($v = v_0$) is to be carried out in two CSTRs placed in series (Figure 4-3).

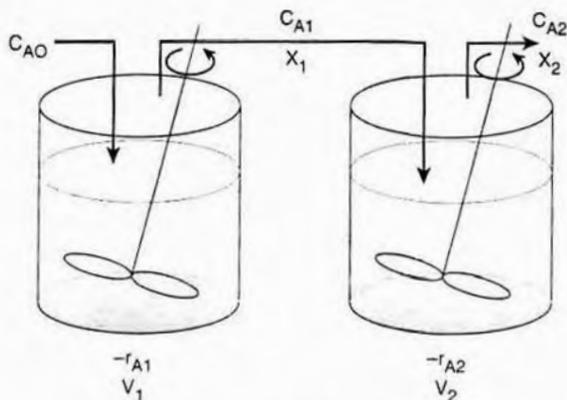


Figure 4-3 Two CSTRs in series.

The effluent concentration of reactant A from the first CSTR can be found using Equation (4-9)

$$C_{A1} = \frac{C_{A0}}{1 + \tau_1 k_1}$$

with $\tau_1 = V_1/u_0$. From a mole balance on reactor 2,

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{u_0(C_{A1} - C_{A2})}{k_2 C_{A2}}$$

Solving for C_{A2} , the concentration exiting the second reactor, we obtain

$$C_{A2} = \frac{C_{A1}}{1 + \tau_2 k_2} = \frac{C_{A0}}{(1 + \tau_2 k_2)(1 + \tau_1 k_1)}$$

First-order reaction

If both reactors are of equal size ($\tau_1 = \tau_2 = \tau$) and operate at the same temperature ($k_1 = k_2 = k$), then

$$C_{A2} = \frac{C_{A0}}{(1 + \tau k)^2}$$

If instead of two CSTRs in series we had n equal-sized CSTRs connected in series ($\tau_1 = \tau_2 = \dots = \tau_n = \tau_i = (V_i/u_0)$) operating at the same temperature ($k_1 = k_2 = \dots = k_n = k$), the concentration leaving the last reactor would be

$$C_{An} = \frac{C_{A0}}{(1 + \tau k)^n} = \frac{C_{A0}}{(1 + Da)^n} \quad (4-10)$$

Substituting for C_{An} in terms of conversion

$$C_{A0}(1 - X) = \frac{C_{A0}}{(1 + Da)^n}$$

and rearranging, the conversion for these n tank reactors in series will be

Conversion as a function of the number of tanks in series

$$X = 1 - \frac{1}{(1 + Da)^n} \equiv 1 - \frac{1}{(1 + \tau k)^n} \quad (4-1)$$

A plot of the conversion as a function of the number of reactors in series for first-order reaction is shown in Figure 4-4 for various values of the Damköhler

CSTRs in series

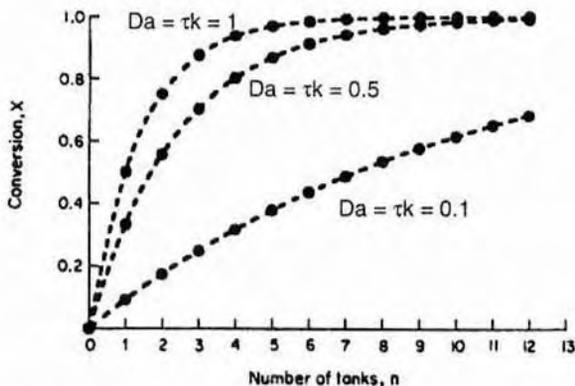


Figure 4-4 Conversion as a function of the number of tanks in series for different Damköhler numbers for a first-order reaction.

Economics

number τk . Observe from Figure 4-4 that when the product of the space time and the specific reaction rate is relatively large, say, $Da \geq 1$, approximately 90% conversion is achieved in two or three reactors; thus the cost of adding subsequent reactors might not be justified. When the product τk is small, $Da \sim 0.1$, the conversion continues to increase significantly with each reactor added.

The rate of disappearance of A in the n th reactor is

$$-r_{An} = kC_{An} = k \frac{C_{A0}}{(1 + \tau k)^n}$$

4.3.3 CSTRs in Parallel

We now consider the case in which equal-sized reactors are placed in parallel rather than in series, and the feed is distributed equally among each of the reactors (Figure 4-5). The balance on any reactor, say i , gives

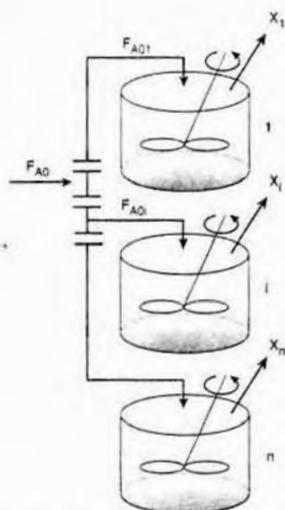


Figure 4-5 CSTRs in parallel.

the individual reactor volume

$$V_i = F_{A0i} \left(\frac{X_i}{-r_{Ai}} \right) \quad (4-12)$$

Since the reactors are of equal size, operate at the same temperature, and have identical feed rates, the conversion will be the same for each reactor:

$$X_1 = X_2 = \dots = X_n = X$$

as will be the rate of reaction in each reactor

$$-r_{A1} = -r_{A2} = \dots = -r_{An} = -r_A$$

The volume of each individual reactor, V_i , is related to the total volume, V , of all the reactors by the equation

$$V_i = \frac{V}{n}$$

A similar relationship exists for the total molar flow rate, which is equally divided:

$$F_{A0i} = \frac{F_{A0}}{n}$$

Substituting these values into Equation (4-12) yields

$$\frac{V}{n} = \frac{F_{A0}}{n} \left(\frac{X_i}{-r_{Ai}} \right)$$

or

Conversion for tanks in parallel. Is this result surprising?

$$V = \frac{F_{A0}X_i}{-r_{Ai}} = \frac{F_{A0}X}{-r_A} \quad (4-13)$$

This result shows that the conversion achieved in any one of the reactors in parallel is identical to what would be achieved if the reactant were fed in one stream to one large reactor of volume V !

4.3.4 A Second-Order Reaction in a CSTR

For a second-order liquid-phase reaction being carried out in a CSTR, the **combination** of the **rate law** and the **design equation** yields

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}X}{kC_A^2} \quad (4-14)$$

Using our stoichiometric table for constant density $v = v_0$, $C_A = C_{A0}(1 - X)$, and $F_{A0}X = v_0 C_{A0}X$, then

$$V = \frac{v_0 C_{A0} X}{k C_A^2 (1 - X)^2}$$

Dividing by v_0 ,

$$\tau = \frac{V}{v_0} = \frac{X}{k C_{A0} (1 - X)^2} \quad (4-15)$$

We solve Equation (4-15) for the conversion X :

Conversion for a second-order liquid-phase reaction in a CSTR

$$\begin{aligned} X &= \frac{(1 + 2\tau k C_{A0}) - \sqrt{(1 + 2\tau k C_{A0})^2 - (2\tau k C_{A0})^2}}{2\tau k C_{A0}} \\ &= \frac{(1 + 2\tau k C_{A0}) - \sqrt{1 + 4\tau k C_{A0}}}{2\tau k C_{A0}} \end{aligned} \quad (4-16)$$

$$X = \frac{(1 + 2Da) - \sqrt{1 + 4Da}}{2Da}$$

The minus sign must be chosen in the quadratic equation because X cannot be greater than 1. Conversion is plotted as a function of the Damköhler parameter, $\tau k C_{A0}$, in Figure 4-6. Observe from this figure that at high conversions (say 67%) a 10-fold increase in the reactor volume (or increase in the specific reaction rate by raising the temperature) will increase the conversion only to 88%. This observation is a consequence of the fact that the CSTR operates under the condition of the lowest value of the reactant concentration (i.e., the exit concentration), and consequently the smallest value of the rate of reaction.

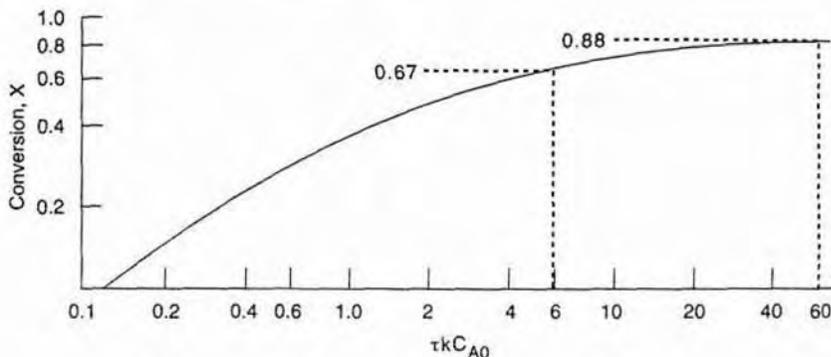


Figure 4-6 Conversion as a function of the Damköhler number ($\tau k C_{A0}$) for a second-order reaction in a CSTR.

Example 4-2 Producing 200 Million Pounds per Year in a CSTR

Close to 12.2 billion metric tons of ethylene glycol (EG) were produced in 2000, which ranked it the twenty-sixth most produced chemical in the nation that year on a total pound basis. About one-half of the ethylene glycol is used for *antifreeze* while the other half is used in the manufacture of polyesters. In the polyester category, 88% was used for fibers and 12% for the manufacture of bottles and films. The 2004 selling price for ethylene glycol was \$0.28 per pound.

It is desired to produce 200 million pounds per year of EG. The reactor is to be operated isothermally. A 1 lb mol/ft³ solution of ethylene oxide (EO) in water is fed to the reactor (shown in Figure E4-2.1) together with an equal volumetric solution of water containing 0.9 wt % of the catalyst H₂SO₄. The specific reaction rate constant is 0.311 min⁻¹, as determined in Example 4-1. Practical guidelines for reactor scale-up were recently given by Mukesh¹ and by Warsteel².

- If 80% conversion is to be achieved, determine the necessary CSTR volume.
- If two 800-gal reactors were arranged in parallel, what is the corresponding conversion?
- If two 800-gal reactors were arranged in series, what is the corresponding conversion?

Solution

Assumption: Ethylene glycol (EG) is the only reaction product formed.

Uses and
economics



Scale-Up
of
Batch Reactor
Data

¹ D. Mukesh, *Chemical Engineering*, 46 (January 2002); www.CHE.com.

² J. Warsteel, *Chemical Engineering Progress*, (June 2000).

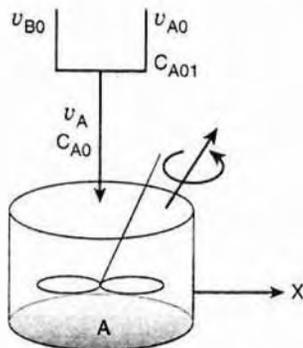
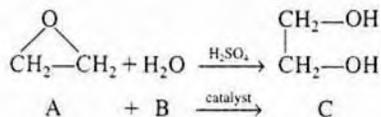


Figure E4-2.1 Single CSTR.

The specified Ethylene Glycol (EG) production rate in lb mol/min is

$$F_C = 2 \times 10^8 \frac{\text{lb}}{\text{yr}} \times \frac{1 \text{ yr}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ lb mol}}{62 \text{ lb}} = 6.137 \frac{\text{lb mol}}{\text{min}}$$

From the reaction stoichiometry

$$F_C = F_{A0}X$$

we find the required molar flow rate of ethylene oxide to be

$$F_{A0} = \frac{F_C}{X} = \frac{6.137}{0.8} = 7.67 \frac{\text{lb mol}}{\text{min}} \quad (58.0 \text{ g mol/s})$$

(a) We now calculate the single CSTR volume to achieve 80% conversion using the CRE algorithm.

1. Design equation:

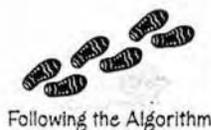
$$V = \frac{F_{A0}X}{-r_A} \quad (\text{E4-2.1})$$

2. Rate law:

$$-r_A = kC_A \quad (\text{E4-2.2})$$

3. Stoichiometry. Liquid phase ($v = v_0$):

$$C_A = \frac{F_A}{v_0} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X) \quad (\text{E4-2.3})$$



Following the Algorithm

4. Combining:

$$V = \frac{F_{A0} X}{k C_{A0} (1 - X)} = \frac{v_0 X}{k (1 - X)} \quad (\text{E4-2.4})$$

5. Evaluate:

The entering volumetric flow rate of stream A, with $C_{A01} = 1 \text{ lb mol/ft}^3$ before mixing, is

$$v_{A0} = \frac{F_{A0}}{C_{A01}} = \frac{7.67 \text{ lb mol/min}}{1 \text{ lb mol/ft}^3} = 7.67 \frac{\text{ft}^3}{\text{min}}$$

From the problem statement $v_{B0} = v_{A0}$

$$F_{B0} = v_{B0} C_{B01} = \left(7.67 \frac{\text{ft}^3}{\text{min}}\right) \cdot \left(62.4 \frac{\text{lb}}{\text{ft}^3} \times \frac{1 \text{ lb mol}}{18 \text{ lb}}\right) = 26.6 \frac{\text{lb mol}}{\text{min}}$$

The total entering volumetric flow rate of liquid is

$$v_0 = v_{A0} + v_{B0} = 15.34 \frac{\text{ft}^3}{\text{min}} \quad (7.24 \text{ dm}^3/\text{s})$$

Substituting in Equation (E4-2.4), recalling that $k = 0.311 \text{ min}^{-1}$, yields

$$\begin{aligned} V &= \frac{v_0 X}{k(1-X)} = 15.34 \frac{\text{ft}^3}{\text{min}} \frac{0.8}{(0.311 \text{ min}^{-1})(1-0.8)} = 197.3 \text{ ft}^3 \\ &= 1480 \text{ gal } (5.6 \text{ m}^3) \end{aligned}$$

A tank 5 ft in diameter and approximately 10 ft tall is necessary to achieve 80% conversion.

(b) **CSTRs in parallel.** For two 800-gal CSTRs arranged in parallel (as shown in Figure E4-2.2) with $7.67 \text{ ft}^3/\text{min}$ ($v_0/2$) fed to each reactor, the conversion achieved can be calculated by rearranging Equation (E4-2.4)

$$\frac{V}{v_0} k = \tau k = \frac{X}{1 - X}$$

to obtain

$$X = \frac{\tau k}{1 + \tau k} \quad (\text{E4-2.5})$$

where

$$\tau = \frac{V}{v_0/2} = \left(800 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}}\right) \times \frac{1}{7.67 \text{ ft}^3/\text{min}} = 13.94 \text{ min}$$

The *Damköhler number* is

$$Da = \tau k = 13.94 \text{ min} \times \frac{0.311}{\text{min}} = 4.34$$

Substituting into Equation (E4-2.5) gives us

