



# *Mole Balances* 1

The first step to knowledge  
is to know that we are ignorant.

Socrates (470–399 B.C.)

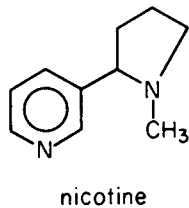
Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals. It is primarily a knowledge of chemical kinetics and reactor design that distinguishes the chemical engineer from other engineers. The selection of a reaction system that operates in the safest and most efficient manner can be the key to the economic success or failure of a chemical plant. For example, if a reaction system produced a large amount of undesirable product, subsequent purification and separation of the desired product could make the entire process economically unfeasible. The chemical kinetic principles learned here, in addition to the production of chemicals, can be applied in areas such as living systems, waste treatment, and air and water pollution. Some of the examples and problems used to illustrate the principles of chemical reaction engineering are: the use of wetlands to remove toxic chemicals from rivers, increasing the octane number of gasoline, the production of anti-freeze starting from ethane, the manufacture of computer chips, and the application of enzyme kinetics to improve an artificial kidney.

This book focuses on a variety of chemical reaction engineering topics. It is concerned with the rate at which chemical reactions take place, together with the mechanism and rate-limiting steps that control the reaction process. The sizing of chemical reactors to achieve production goals is an important segment. How materials behave within reactors, both chemically and physically, is significant to the designer of a chemical process, as is how the data from chemical reactors should be recorded, processed, and interpreted.

Before entering into discussions of the conditions that affect chemical reaction rates and reactor design, it is necessary to account for the various chemical species entering and leaving a reaction system. This accounting process is achieved through overall mole balances on individual species in the



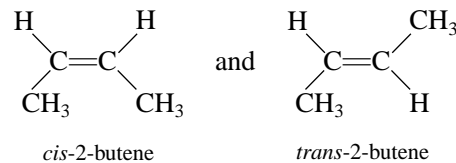
reacting system. In this chapter we develop a general mole balance that can be applied to any species (usually a chemical compound) entering, leaving, and/or remaining within the reaction system volume. After defining the rate of reaction,  $-r_A$ , and discussing the earlier difficulties of properly defining the chemical reaction rate, in this chapter we show how the general balance equation may be used to develop a preliminary form of the design equations of the most common industrial reactors: batch, continuous-stirred tank (CSTR), and tubular. In developing these equations, the assumptions pertaining to the modeling of each type of reactor are delineated. Finally, a brief summary and series of short review questions are given at the end of the chapter.



### 1.1 Definition of the Rate of Reaction, $-r_A$

We begin our study by performing mole balances on each chemical species in the system. Here, the term *chemical species* refers to any chemical compound or element with a given identity. The identity of a chemical species is determined by the *kind*, *number*, and *configuration* of that species' atoms. For example, the species nicotine (a bad tobacco alkaloid) is made up of a fixed number of specific elements in a definite molecular arrangement or configuration. The structure shown illustrates the kind, number, and configuration of the species nicotine (responsible for "nicotine fits") on a molecular level.

Even though two chemical compounds have exactly the same number of atoms of each element, they could still be different species because of different configurations. For example, 2-butene has four carbon atoms and eight hydrogen atoms; however, the atoms in this compound can form two different arrangements.



As a consequence of the different configurations, these two isomers display different chemical and physical properties. Therefore, we consider them as two different species even though each has the same number of atoms of each element.

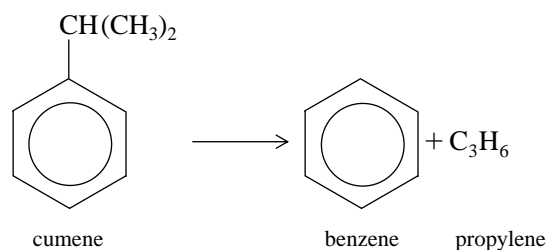
When has a  
chemical reaction  
taken place?

We say that a *chemical reaction* has taken place when a detectable number of molecules of one or more species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and/or by a change in structure or configuration of these atoms. In this classical approach to chemical change, it is assumed that the total mass is neither created nor destroyed when a chemical reaction occurs. The mass referred to is the total collective mass of all the different species in the system. However, when considering the individual species involved in a particular reaction, we do speak of the rate of disappearance of mass of a particular species. The rate of disappearance of a species, say species A, is the number of A molecules that

Sec. 1.1 Definition of the Rate of Reaction,  $-r_A$ 

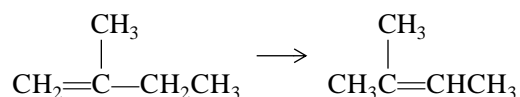
lose their chemical identity per unit time per unit volume through the breaking and subsequent re-forming of chemical bonds during the course of the reaction. In order for a particular species to “appear” in the system, some prescribed fraction of another species must lose its chemical identity.

There are three basic ways a species may lose its chemical identity. One way is by *decomposition*, in which a molecule is broken down into smaller molecules, atoms, or atom fragments. For example, if benzene and propylene are formed from a cumene molecule,



the cumene molecule has lost its identity (i.e., disappeared) by breaking its bonds to form these molecules. A second way that a molecule may lose its species identity is through *combination* with another molecule or atom. In the example above, the propylene molecule would lose its species identity if the reaction were carried out in the reverse direction so that it combined with benzene to form cumene.

The third way a species may lose its identity is through *isomerization*, such as the reaction

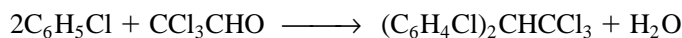


A species can lose its identity by decomposition, combination, or isomerization

Here, although the molecule neither adds other molecules to itself nor breaks into smaller molecules, it still loses its identity through a change in configuration.

To summarize this point, we say that a given number of molecules (e.g., mole) of a particular chemical species have reacted or disappeared when the molecules have lost their chemical identity.

The rate at which a given chemical reaction proceeds can be expressed in several ways. It can be expressed either as the rate of disappearance of reactants *or* the rate of formation of products. For example, the insecticide DDT (dichlorodiphenyltrichloroethane) is produced from chlorobenzene and chloral in the presence of fuming sulfuric acid.



What is  $-r_A$ ?  
 $r_A$ ?

Letting the symbol A represent the chemical chloral, the numerical value of the **rate of reaction**,  $-r_A$ , is defined as *the number of moles of chloral reacting (disappearing) per unit time per unit volume* ( $\text{mol}/\text{dm}^3 \cdot \text{s}$ ). In the next chapter we delineate the prescribed relationship between the rate of formation of one

species,  $r_j$  (e.g., DDT), and the rate of disappearance of another species,  $-r_i$  (e.g., chlorobezene), in a chemical reaction.

In heterogeneous reaction systems, the rate of reaction is usually expressed in measures other than volume, such as reaction surface area or catalyst weight. Thus for a gas–solid catalytic reaction, the dimensions of this rate,  $-r'_A$ , are the number of moles of A reacted per unit time per unit mass of catalyst (mol/s·g catalyst). Most of the introductory discussions on chemical reaction engineering in this book focus on homogeneous systems.

The mathematical definition of a chemical reaction rate has been a source of confusion in chemical and chemical engineering literature for many years. The origin of this confusion stems from laboratory bench-scale experiments that were carried out to obtain chemical reaction rate data. These early experiments were batch-type, in which the reaction vessel was closed and rigid; consequently, the ensuing reaction took place at constant volume. The reactants were mixed together at time  $t = 0$  and the concentration of one of the reactants,  $C_A$ , was measured at various times  $t$ . The rate of reaction was determined from the slope of a plot of  $C_A$  as a function of time. Letting  $r_A$  be the rate of formation of A per unit volume (e.g., g mol/s·dm<sup>3</sup>), the investigators then defined and reported the chemical reaction rate as

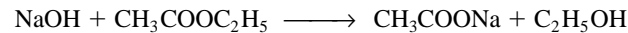
$$r_A = \frac{dC_A}{dt} \quad (1-1)$$

However, this definition was for a *constant-volume batch reactor*.

As a result of the limitations and restrictions given, Equation (1-1) is a rather limited and confusing definition of the chemical reaction rate. For amplification of this point, consider the following steady-flow system in which the saponification of ethyl acetate is carried out.

#### **Example 1-1 Is Sodium Hydroxide Reacting?**

Sodium hydroxide and ethyl acetate are continuously fed to a rapidly stirred tank in which they react to form sodium acetate and ethanol:



(Figure E1-1.1). The product stream, containing sodium acetate and ethanol, together with the unreacted sodium hydroxide and ethyl acetate, is continuously withdrawn from the tank at a rate equal to the total feed rate. The contents of the tank in which this reaction is taking place may be considered to be perfectly mixed. Because the system is operated at steady state, if we were to withdraw liquid samples at some location in the tank at various times and analyze them chemically, we would find that the concentrations of the individual species in the different samples were identical. That is, the concentration of the sample taken at 1 P.M. is the same as that of the sample taken at 3 P.M. Because the species concentrations are constant and therefore do not change with time,

$$\frac{dC_A}{dt} = 0 \quad (\text{E1-1.1})$$

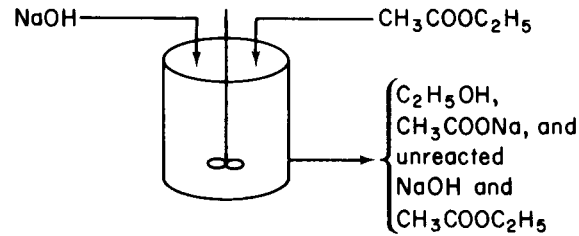


Figure E1-1.1 Well mixed reaction vessel.

where  $A \equiv \text{NaOH}$ . Substitution of Equation (E1-1.1) into Equation (1-1) leads to

$$r_A = 0 \quad (\text{E1-1.2})$$

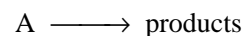
which is incorrect because  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{COONa}$  are being formed from  $\text{NaOH}$  and  $\text{CH}_3\text{COOC}_2\text{H}_5$  at a finite rate. Consequently, the rate of reaction as defined by Equation (1-1) cannot apply to a flow system and is incorrect if it is defined in this manner.

Definition of  $r_j$

By now you should be convinced that Equation (1-1) is not the definition of the chemical reaction rate. We shall simply say that  $r_j$  is the rate of formation of species  $j$  per unit volume. It is the number of moles of species  $j$  generated per unit volume per unit time. The rate equation for  $r_j$  is solely a function of the properties of the reacting materials [e.g., species concentration (i.e. activities), temperature, pressure, or type of catalyst, if any] at a point in the system and is independent of the type of system (i.e., batch or continuous flow) in which the reaction is carried out. However, since the properties of the reacting materials can vary with position in a chemical reactor,  $r_j$  can in turn be a function of position and can vary from point to point in the system.

What is  $-r_A$   
a function of?

The chemical reaction rate is an intensive quantity and depends on temperature and concentration. The reaction rate equation (i.e., the rate law) is essentially an algebraic equation involving concentration, not a differential equation.<sup>1</sup> For example, the algebraic form of the rate law  $-r_A$  for the reaction



may be a linear function of concentration,

$$-r_A = kC_A$$

or it may be some other algebraic function of concentration, such as

<sup>1</sup> For further elaboration on this point, see *Chem. Eng. Sci.*, 25, 337 (1970); B. L. Crynes and H. S. Fogler, eds., *AIChE Modular Instruction Series E: Kinetics*, Vol. 1 (New York: AIChE, 1981), p. 1; and R. L. Kabel, "Rates," *Chem. Eng. Commun.*, 9, 15 (1981).

$$-r_A = kC_A^2 \quad (1-2)$$

or

The rate law is an algebraic equation

$$-r_A = \frac{k_1 C_A}{1 + k_2 C_A}$$

For a given reaction, the particular concentration dependence that the rate law follows (i.e.,  $-r_A = kC_A$  or  $-r_A = kC_A^2$  or ...) must be determined from experimental observation. Equation (1-2) states that the rate of disappearance of A is equal to a rate constant  $k$  times the square of the concentration of A. By convention,  $r_A$  is the rate of formation of A; consequently,  $-r_A$  is the rate of disappearance of A. Throughout this book the phrase *rate of generation* means exactly the same as the phrase *rate of formation*, and these phrases are used interchangeably.

### 1.2 The General Mole Balance Equation

To perform a mole balance on any system, the system boundaries must first be specified. The volume enclosed by these boundaries will be referred to as the *system volume*. We shall perform a mole balance on species  $j$  in a system volume, where species  $j$  represents the particular chemical species of interest, such as water or NaOH (Figure 1-1).

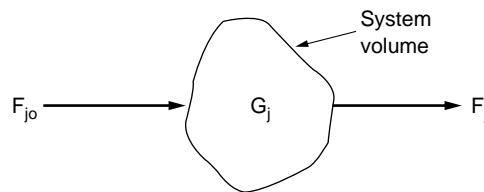


Figure 1-1 Balance on system volume.

A mole balance on species  $j$  at any instant in time,  $t$ , yields the following equation:

$$\begin{array}{r}
 \left[ \begin{array}{l} \text{rate of flow} \\ \text{of } j \text{ into} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] + \left[ \begin{array}{l} \text{rate of generation} \\ \text{of } j \text{ by chemical} \\ \text{reaction within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] - \left[ \begin{array}{l} \text{rate of flow} \\ \text{of } j \text{ out of} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] = \left[ \begin{array}{l} \text{rate of} \\ \text{accumulation} \\ \text{of } j \text{ within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] \\
 \text{Mole balance} \quad \text{in} \quad + \quad \text{generation} \quad - \quad \text{out} \quad = \quad \text{accumulation} \\
 F_{j0} \quad + \quad G_j \quad - \quad F_j \quad = \quad \frac{dN_j}{dt} \quad (1-3)
 \end{array}$$

where  $N_j$  represents the number of moles of species  $j$  in the system at time  $t$ . If all the system variables (e.g., temperature, catalytic activity, concentration of

the chemical species) are spatially uniform throughout the system volume, the rate of generation of species  $j$ ,  $G_j$ , is just the product of the reaction volume,  $V$ , and the rate of formation of species  $j$ ,  $r_j$ .

$$G_j = r_j \cdot V$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{time} \cdot \text{volume}} \cdot \text{volume}$$

Suppose now that the rate of formation of species  $j$  for the reaction varies with the position in the system volume. That is, it has a value  $r_{j1}$  at location 1, which is surrounded by a small volume,  $\Delta V_1$ , within which the rate is uniform: similarly, the reaction rate has a value  $r_{j2}$  at location 2 and an associated volume,  $\Delta V_2$  (Figure 1-2). The rate of generation,  $\Delta G_{j1}$ , in terms of  $r_{j1}$  and

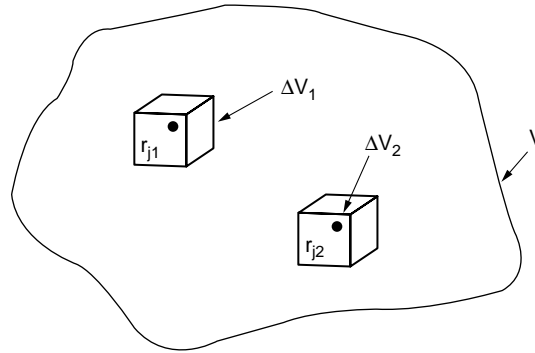


Figure 1-2 Dividing up the system volume  $V$ .

subvolume  $\Delta V_1$  is

$$\Delta G_{j1} = r_{j1} \Delta V_1$$

Similar expressions can be written for  $\Delta G_{j2}$  and the other system subvolumes  $\Delta V_i$ . The total rate of generation within the system volume is the sum of all the rates of generation in each of the subvolumes. If the total system volume is divided into  $M$  subvolumes, the total rate of generation is

$$G_j = \sum_{i=1}^M \Delta G_{ji} = \sum_{i=1}^M r_{ji} \Delta V_i$$

By taking the appropriate limits (i.e., let  $M \rightarrow \infty$  and  $\Delta V \rightarrow 0$ ) and making use of the definition of an integral, we can rewrite the foregoing equation in the form

$$G_j = \int^V r_j dV$$



From this equation we see that  $r_j$  will be an indirect function of position, since the properties of the reacting materials (e.g., concentration, temperature) can have different values at different locations in the reactor.

We now replace  $G_j$  in Equation (1-3),

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

by its integral form to yield a form of the general mole balance equation for any chemical species  $j$  that is entering, leaving, reacting, and/or accumulating within any system volume  $V$ .

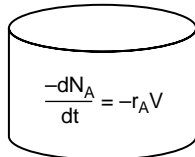
This is a basic equation for chemical reaction engineering

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

From this general mole balance equation we can develop the design equations for the various types of industrial reactors: batch, semibatch, and continuous-flow. Upon evaluation of these equations we can determine the time (batch) or reactor volume (continuous-flow) necessary to convert a specified amount of the reactants to products.

### 1.3 Batch Reactors

A batch reactor has neither inflow nor outflow of reactants or products while the reaction is being carried out;  $F_{j0} = F_j = 0$ . The resulting general mole balance on species  $j$  is



$$\frac{dN_j}{dt} = \int^V r_j dV$$

If the reaction mixture is perfectly mixed so that there is no variation in the rate of reaction throughout the reactor volume, we can take  $r_j$  out of the integral and write the mole balance in the form

$$\frac{dN_j}{dt} = r_j V \quad (1-5)$$

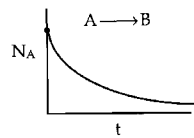
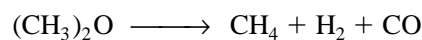


Figure 1-3 shows two different types of batch reactors used for gas-phase reactions. Reactor A is a constant-volume (variable-pressure) reactor and Reactor B is a constant-pressure (variable-volume) reactor. At time  $t = 0$ , the reactants are injected into the reactor and the reaction is initiated. To see clearly the different forms the mole balance will take for each type of reactor, consider the following examples, in which the gas-phase decomposition of dimethyl ether is taking place to form methane, hydrogen, and carbon monoxide:





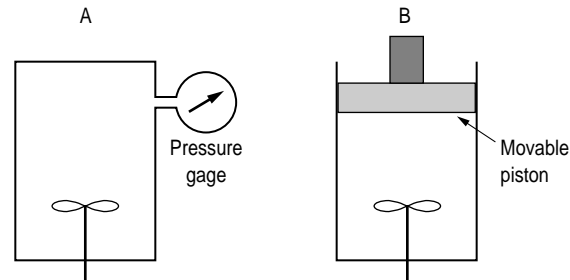


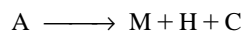
Figure 1-3 Batch reactors for gas-phase reactions.

**Example 1-2 Constant Volume or Constant Pressure:  
Does It Make a Difference?**

Write the mole balance for dimethyl ether in terms of the reactor volume, concentration, and rate of formation of dimethyl ether for both a constant-pressure and a constant-volume batch reactor.

*Solution*

To reduce the number of subscripts, we write the reaction symbolically as



where A is dimethyl ether, M is methane, H is hydrogen, and C is carbon monoxide. For both batch reactors, the mole balance on A is

$$\frac{1}{V} \frac{dN_A}{dt} = r_A \quad (1-5)$$

In writing the mole balance for dimethyl ether for a batch reactor, the only assumption made is that there are no spatial variations in  $r_A$ .

**Constant-volume batch reactor.** The reactor is perfectly mixed so that the concentration of the reacting species is spatially uniform. Because the volume is constant we can take  $V$  inside the differential and write the mole balance in terms of the concentration of A:

$$\frac{1}{V} \frac{dN_A}{dt} = \frac{d(N_A/V)}{dt} = \frac{dC_A}{dt} = r_A \quad (E1-2.1)$$

**Constant-pressure batch reactor.** To write the mole balance for this reactor in terms of concentration, we again use the fact that

$$N_A = C_A V$$

$$\frac{1}{V} \frac{dN_A}{dt} = \frac{1}{V} \frac{d(C_A V)}{dt} = \frac{dC_A}{dt} + \frac{C_A}{V} \frac{dV}{dt} = r_A \quad (E1-2.2)$$

$$r_A = \frac{dC_A}{dt} + \frac{C_A}{V} \frac{dV}{dt} \quad (E1-2.3)$$

The difference between equations (E1-2.1) and (E1-2.3) for the two different types of reactors is apparent.

## 1.4 Continuous-Flow Reactors

### 1.4.1 Continuous-Stirred Tank Reactor

A type of reactor used very commonly in industrial processing is a stirred tank operated continuously (Figure 1-4). It is referred to as the *continuous-stirred tank reactor* (CSTR) or *backmix reactor*. The CSTR is normally run at steady state and is usually operated so as to be quite well mixed. As a result of the latter quality, the CSTR is generally modeled as having no spatial variations in concentration, temperature, or reaction rate throughout the vessel. Since the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. Thus the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. In systems where mixing is highly nonideal, the well-mixed model is inadequate and we must resort to other modeling techniques, such as residence-time distributions, to obtain meaningful results. This topic is discussed in Chapters 13 and 14.

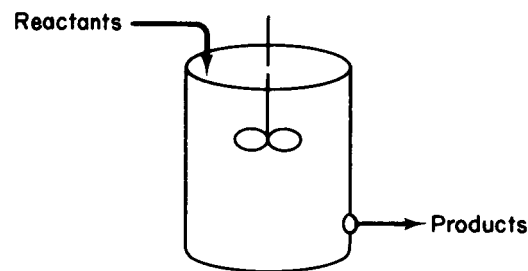


Figure 1-4 Continuous-stirred tank reactor.

When the general mole balance equation

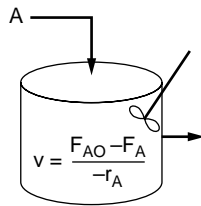
$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

is applied to a CSTR operated at steady state (i.e., conditions do not change with time),

$$\frac{dN_j}{dt} = 0$$

in which there are no spatial variations in the rate of reaction,

$$\int^V r_j dV = Vr_j$$



it takes the familiar form known as the *design equation* for a CSTR:

$$V = \frac{F_{j0} - F_j}{-r_j} \quad (1-6)$$

The CSTR design equation gives the reactor volume necessary to reduce the entering flow rate of species,  $j$ ,  $F_{j0}$ , to the exit flow rate  $F_j$ . We note that the CSTR is modeled such that the conditions in the exit stream (e.g., concentration, temperature) are identical to those in the tank. The molar flow rate  $F_j$  is just the product of the concentration of species  $j$  and the volumetric flow rate  $v$ :

$$F_j = C_j \cdot v \quad (1-7)$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{volume}}{\text{time}}$$

#### 1.4.2 Tubular Reactor

In addition to the CSTR and batch reactors, another type of reactor commonly used in industry is the *tubular reactor*. It consists of a cylindrical pipe and is normally operated at steady state, as is the CSTR. For the purposes of the material presented here, we consider systems in which the flow is highly turbulent and the flow field may be modeled by that of plug flow. That is, there is no radial variation in concentration and the reactor is referred to as a plug-flow reactor (PFR). (The laminar flow reactor is discussed in Chapter 13.)

In the tubular reactor, the reactants are continually consumed as they flow down the length of the reactor. In modeling the tubular reactor, we assume that the concentration varies continuously in the axial direction through the reactor. Consequently, the reaction rate, which is a function of concentration for all but zero-order reactions, will also vary axially. The general mole balance equation is given by Equation (1-4):

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

To develop the PFR design equation we shall divide (conceptually) the reactor into a number of subvolumes so that within each subvolume  $\Delta V$ , the reaction rate may be considered spatially uniform (Figure 1-5). We now focus our attention on the subvolume that is located a distance  $y$  from the entrance of the reactor. We let  $F_j(y)$  represent the molar flow rate of species  $j$  into volume  $\Delta V$  at  $y$  and  $F_j(y + \Delta y)$  the molar flow of species  $j$  out of the volume at the location  $(y + \Delta y)$ . In a spatially uniform subvolume  $\Delta V$ ,

$$\int^{\Delta V} r_j dV = r_j \Delta V$$

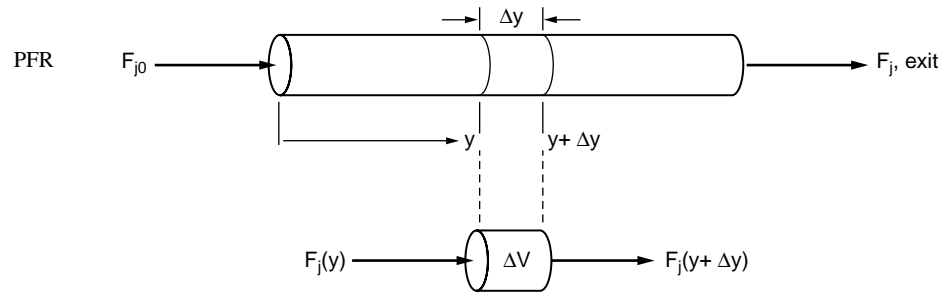


Figure 1-5 Tubular reactor.

For a tubular reactor operated at steady state,

$$\frac{dN_j}{dt} = 0$$

Equation (1-4) becomes

$$F_j(y) - F_j(y + \Delta y) + r_j \Delta V = 0 \quad (1-8)$$

In this expression  $r_j$  is an indirect function of  $y$ . That is,  $r_j$  is a function of reactant concentration, which is a function of the position  $y$  down the reactor. The volume  $\Delta V$  is the product of the cross-sectional area  $A$  of the reactor and the reactor length  $\Delta y$ .

$$\Delta V = A \Delta y$$

We now substitute in Equation (1-8) for  $\Delta V$  and then divide by  $\Delta y$  to obtain

$$-\left[ \frac{F_j(y + \Delta y) - F_j(y)}{\Delta y} \right] = -Ar_j$$

The term in brackets resembles the definition of the derivative

$$\lim_{\Delta x \rightarrow 0} \left[ \frac{f(x + \Delta x) - f(x)}{\Delta x} \right] = \frac{df}{dx}$$

Taking the limit as  $\Delta y$  approaches zero, we obtain

$$-\frac{dF_j}{dy} = -Ar_j$$

or dividing by  $-1$ , we have

$$\frac{dF_j}{dy} = Ar_j \quad (1-9)$$





It is usually most convenient to have the reactor volume  $V$  rather than the reactor length  $y$  as the independent variable. Accordingly, we shall change variables using the relation  $dV = A dy$  to obtain one form of the design equation for a tubular reactor:

$$\frac{dF_j}{dV} = r_j \quad (1-10)$$

We also note that for a reactor in which the cross-sectional area  $A$  varies along the length of the reactor, the design equation remains unchanged. This equation can be generalized for the reactor shown in Figure 1-6, in a manner simi-

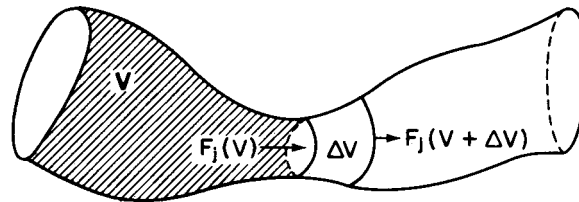


Figure 1-6

lar to that presented above, by utilizing the volume coordinate  $V$  rather than a linear coordinate  $y$ . After passing through volume  $V$ , species  $j$  enters subvolume  $\Delta V$  at volume  $V$  at a molar flow rate  $F_j(V)$ . Species  $j$  leaves subvolume  $\Delta V$  at volume  $(V + \Delta V)$ , at a molar flow rate  $F_j(V + \Delta V)$ . As before,  $\Delta V$  is chosen small enough so that there is no spatial variation of reaction rate within the subvolume:

$$G_j = \int^{\Delta V} r_j dV = r_j \Delta V \quad (1-11)$$

After accounting for steady-state operation in Equation (1-4), it is combined with Equation (1-11) to yield

$$F_j(V) - F_j(V + \Delta V) + r_j \Delta V = 0$$

Rearranging gives

$$\frac{F_j(V + \Delta V) - F_j(V)}{\Delta V} = r_j$$

and taking the limit as  $\Delta V \rightarrow 0$ , we again obtain Equation (1-10):

Tubular reactor

$$\frac{dF_j}{dV} = r_j$$

(1-10)

Consequently, we see that Equation (1-10) applies equally well to our model of tubular reactors of variable and constant cross-sectional area, although it is



doubtful that one would find a reactor of the shape shown in Figure 1-6, unless designed by Pablo Picasso. The conclusion drawn from the application of the design equation is an important one: The extent of reaction achieved in a plug-flow tubular reactor (PFR) does not depend on its shape, only on its total volume.

### 1.4.3 Packed-Bed Reactor

The principal difference between reactor design calculations involving homogeneous reactions and those involving fluid–solid heterogeneous reactions is that for the latter, the reaction rate is based on mass of solid catalyst,  $W$ , rather than on reactor volume,  $V$ . For a fluid–solid heterogeneous system, the rate of reaction of a substance A is defined as

$$-r'_A = \text{g mol A reacted/s} \cdot \text{g catalyst}$$

The mass of solid is used because the amount of the catalyst is what is important to the rate of reaction. The reactor volume that contains the catalyst is of secondary significance.

In the three idealized types of reactors just discussed [the perfectly mixed batch reactor, the plug-flow tubular reactor, and the perfectly mixed continuous-stirred tank reactor (CSTR)], the design equations (i.e., mole balances) were developed based on reactor volume. The derivation of the design equation for a packed-bed catalytic reactor will be carried out in a manner analogous to the development of the tubular design equation. To accomplish this derivation, we simply replace the volume coordinate in Equation (1-8) with the catalyst weight coordinate  $W$  (Figure 1-7). As with the PFR, the PBR is assumed to have

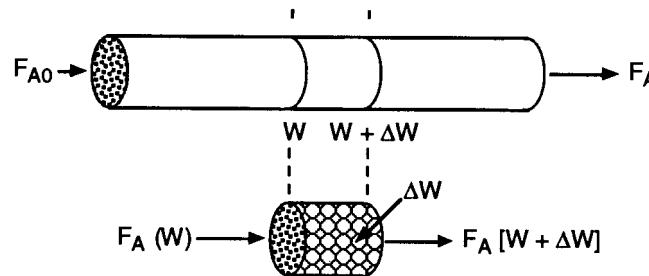


Figure 1-7 Packed-bed reactor schematic.

no radial gradients in concentration, temperature, or reaction rate. The generalized mole balance on species A over catalyst weight  $\Delta W$  results in the equation

$$\begin{array}{rcccc} \text{in} & - & \text{out} & + & \text{generation} & = & \text{accumulation} \\ F_A(W) & - & F_A(W + \Delta W) & + & r'_A \Delta W & = & 0 \end{array} \quad (1-12)$$

The dimensions of the generation term in Equation (1-12) are

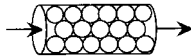
$$(r'_A) \Delta W \equiv \frac{\text{moles A}}{(\text{time})(\text{mass of catalyst})} \cdot (\text{mass of catalyst}) \equiv \frac{\text{moles A}}{\text{time}}$$



which are, as expected, the same dimension of the molar flow rate  $F_A$ . After dividing by  $\Delta W$  and taking the limit as  $\Delta W \rightarrow 0$ , we arrive at the differential form of the mole balance for a packed-bed reactor:

Use differential form of design equation for catalyst decay and pressure drop

$$\frac{dF_A}{dW} = r'_A \quad (1-13)$$



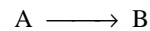
When pressure drop through the reactor (see Section 4.4) and catalyst decay (see Section 10.7) are neglected, the integral form of the packed-catalyst-bed design equation can be used to calculate the catalyst weight.

$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} \quad (1-14)$$

To obtain some insight into things to come, consider the following example of how one can use the tubular reactor design equation (1-10).

### Example 1-3 How Large Is It?

The first-order reaction



is carried out in a tubular reactor in which the volumetric flow rate,  $v$ , is constant. Derive an equation relating the reactor volume to the entering and exiting concentrations of A, the rate constant  $k$ , and the volumetric flow rate  $v$ . Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm<sup>3</sup>/min (i.e., liters/min) and the specific reaction rate,  $k$ , is 0.23 min<sup>-1</sup>.

#### Solution

For a tubular reactor, the mole balance on species A ( $j = A$ ) was shown to be

$$\frac{dF_A}{dV} = r_A \quad (1-10)$$

For a first-order reaction, the rate law (discussed in Chapter 3) is

$$-r_A = kC_A \quad (E1-3.1)$$

Since the volumetric flow rate,  $v_0$ , is constant,

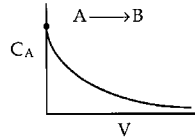
Reactor sizing

$$\frac{dF_A}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \quad (E1-3.2)$$

Substituting for  $r_A$  in Equation (E1-3.1) yields

$$-\frac{v_0 dC_A}{dV} = -r_A = kC_A \quad (E1-3.3)$$





Rearranging gives

$$-\frac{v_0}{k} \left( \frac{dC_A}{C_A} \right) = dV$$

Using the conditions at the entrance of the reactor that when  $V = 0$ , then  $C_A = C_{A0}$ ,

$$-\frac{v_0}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V dV \quad (\text{E1-3.4})$$

This equation gives

$$V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A} \quad (\text{E1-3.5})$$

Substituting  $C_{A0}$ ,  $C_A$ ,  $v_0$ , and  $k$  in Equation (E1-3.5), we have

$$V = \frac{10 \text{ dm}^3/\text{min}}{0.23 \text{ min}^{-1}} \ln \frac{C_{A0}}{0.1 C_{A0}} = \frac{10 \text{ dm}^3}{0.23} \ln 10 = 100 \text{ dm}^3 \text{ (i.e., 100 L; 0.1 m}^3\text{)}$$

We see that a reactor volume of  $0.1 \text{ m}^3$  is necessary to convert 90% of species A entering into product B.

In the remainder of this chapter we look at slightly more detailed drawings of some typical industrial reactors and point out a few of the advantages and disadvantages of each.<sup>2</sup>

## 1.5 Industrial Reactors

When is a batch reactor used?

A batch reactor is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations. The reactor can be charged (i.e., filled) through the holes at the top (Figure 1-8). The batch reactor has the advantage of high conversions that can be obtained by leaving the reactant in the reactor for long periods of time, but it also has the disadvantages of high labor costs per batch and the difficulty of large-scale production.

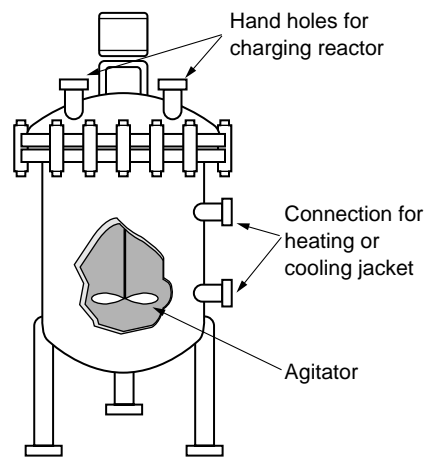
**Liquid-Phase Reactions.** Although a semibatch reactor (Figure 1-9) has essentially the same disadvantages as the batch reactor, it has the advantages of good temperature control and the capability of minimizing unwanted side reactions through the maintenance of a low concentration of one of the reactants. The semibatch reactor is also used for two-phase reactions in which a gas is usually bubbled continuously through the liquid.

What are the advantages and disadvantages of a CSTR?

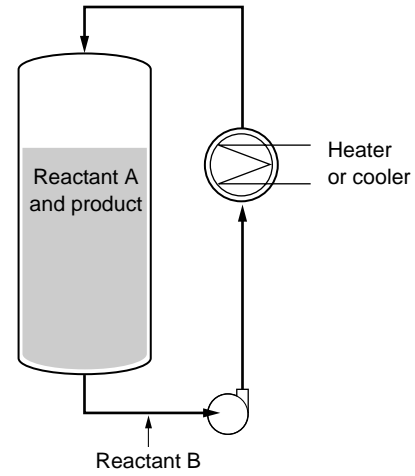
A continuous-stirred tank reactor (CSTR) is used when intense agitation is required. A photo showing a cutaway view of a Pfaudler CSTR/batch reactor is presented in Figure 1-10. Table 1-1 gives the typical sizes (along with that of

<sup>2</sup> *Chem. Eng.*, 63(10), 211 (1956). See also *AIChE Modular Instruction Series E*, Vol. 5 (1984).

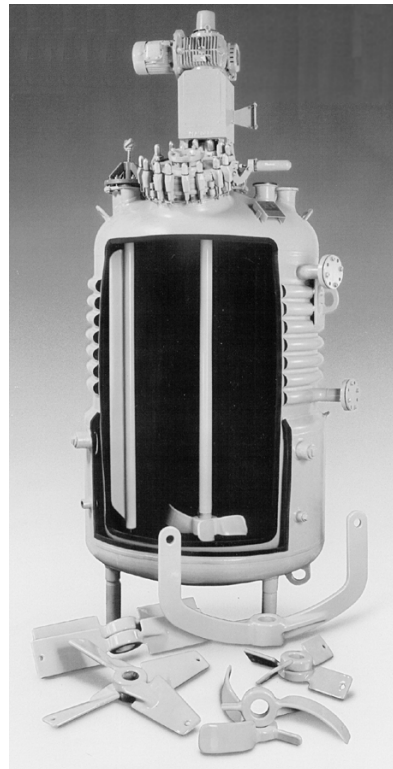




**Figure 1-8** Simple batch homogeneous reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]



**Figure 1-9** Semibatch reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]



**Figure 1-10** CSTR/batch reactor. (Courtesy of Pfaudler, Inc.)



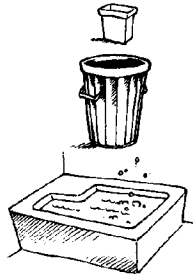
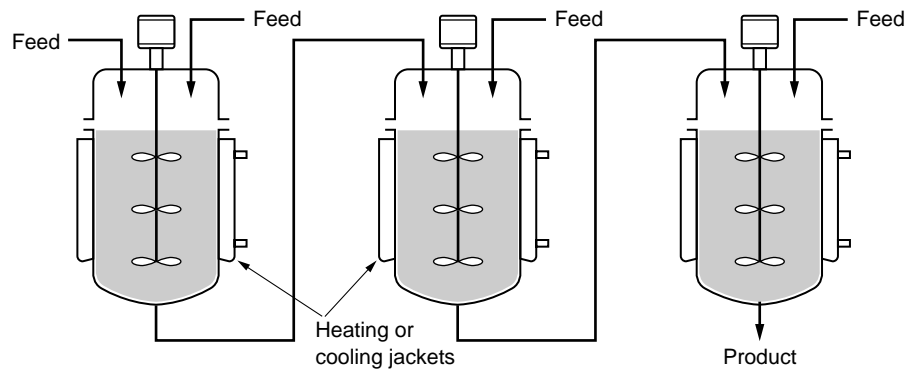


TABLE 1-1. REPRESENTATIVE PFAUDLER CSTR/BATCH REACTOR SIZES AND 1996 PRICES

Volume	Price	Volume	Price
5 Gallons (wastebasket)	\$27,000	1000 Gallons (2 Jacuzzis)	\$80,000
50 Gallons (garbage can)	\$35,000	4000 Gallons (8 Jacuzzis)	\$143,000
500 Gallons (Jacuzzi)	\$67,000	8000 Gallons (gasoline tanker)	\$253,000



**Figure 1-11** Battery of stirred tanks. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

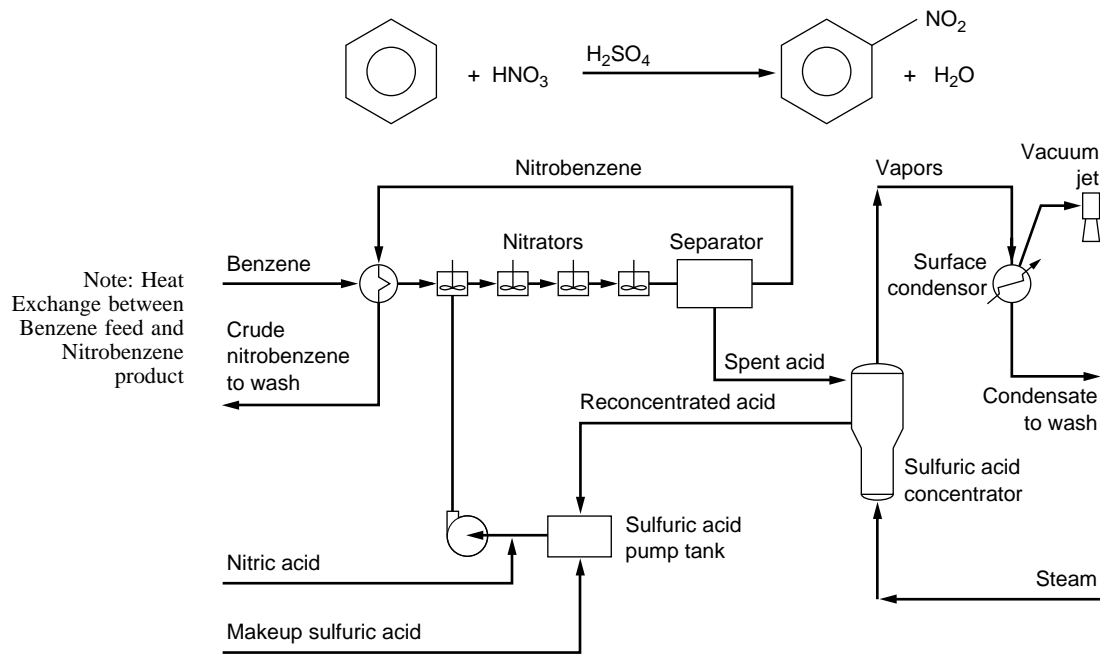
the comparable size of a familiar object) and costs for batch and CSTR reactors. All reactors are glass lined and the prices include heating/cooling jacket, motor, mixer, and baffles. The reactors can be operated at temperatures between 20 and 450°F and at pressures up to 100 psi.

The CSTR can either be used by itself or, in the manner shown in Figure 1-11, as part of a series or battery of CSTRs. It is relatively easy to maintain good temperature control with a CSTR. There is, however, the disadvantage that the conversion of reactant per volume of reactor is the smallest of the flow reactors. Consequently, very large reactors are necessary to obtain high conversions.

If you are not able to afford to purchase a new reactor, it may be possible to find a used reactor that may fit your needs. Previously owned reactors are much less expensive and can be purchased from equipment clearinghouses such as Universal Process Equipment or Loeb Equipment Supply.

**Example 1-4 Liquid-Phase Industrial Process Flowsheet**

A battery of three CSTRs similar to those in Figure 1-10 are shown in the plant flowsheet (Figure E1-4.1) for the commercial production of nitrobenzene. In 1995, 1.65 billion pounds of nitrobenzene were produced.



**Figure E1-4.1** Flowsheet for the production of nitrobenzene. [Adapted from *Process Technology and Flowsheet*, Vol. II, reprints from *Chemical Engineering* (New York: McGraw-Hill, 1983), p. 125.]

In 1980 the operating requirements (per ton of nitrobenzene) were as follows (utilities and feedstock requirements have been minimized by recycling sulfuric acid):

Raw materials	
Benzene	0.64 ton
Nitric acid (100%)	0.515 ton
Sulfuric acid (100%)	0.0033 ton
Caustic soda	0.004 ton
Utilities	
Cooling water	14,200 gal
Steam	800 lb
Electricity	20 kWh
Compressed air	180 Scf/m



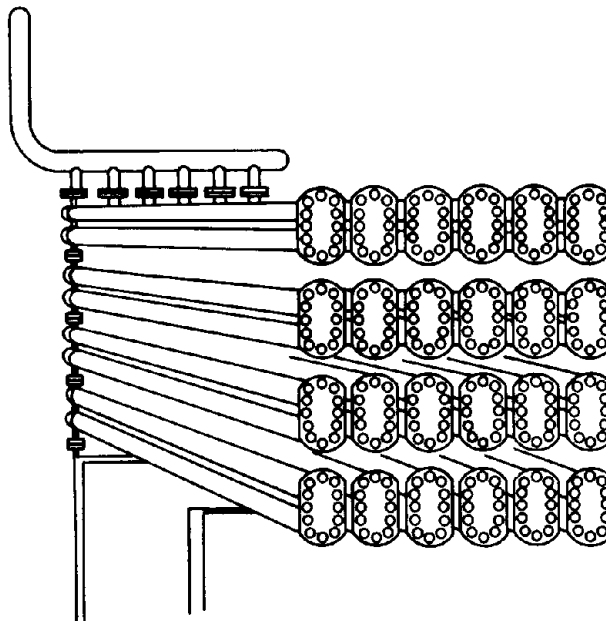
The feed consists of 3 to 7%  $\text{HNO}_3$ , 59 to 67%  $\text{H}_2\text{SO}_4$ , and 28 to 37% water. Sulfuric acid is necessary to adsorb the water and energy generated by the heat of reaction. The plant, which produces 15,000 lb nitrobenzene/h, requires one or two operators per shift together with a plant supervisor and part-time foreman. This exothermic reaction is carried out essentially adiabatically, so that the temperature of the feed stream rises from  $90^\circ\text{C}$  to  $135^\circ\text{C}$  at the exit. One observes that the nitrobenzene stream from the separator is used to heat the benzene feed. However, care must be taken so that the temperature never exceeds  $190^\circ\text{C}$ , where secondary reactions could result in an explosion. One of the safety precautions is the installation of relief valves that will rupture before the temperature approaches  $190^\circ\text{C}$ , thereby allowing a boil-off of water and benzene, which would drop the reactor temperature.

What are the advantages and disadvantages of a PFR?

CSTR: liquids  
PFR: gases

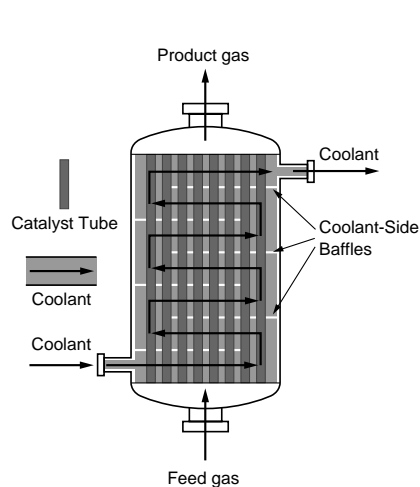
**Gas-Phase Reactions.** The tubular reactor [i.e., plug-flow reactor (PFR)] is relatively easy to maintain (no moving parts), and it usually produces the highest conversion per reactor volume of any of the flow reactors. The disadvantage of the tubular reactor is that it is difficult to control temperature within the reactor, and hot spots can occur when the reaction is exothermic. The tubular reactor is commonly found either in the form of one long tube or as one of a number of shorter reactors arranged in a tube bank as shown in Figure 1-12. Most homogeneous liquid-phase flow reactors are CSTRs, whereas most homogeneous gas-phase flow reactors are tubular.

The costs of PFR and PBR (without catalyst) are similar to the costs of heat exchangers and thus can be found in *Plant Design and Economics for*

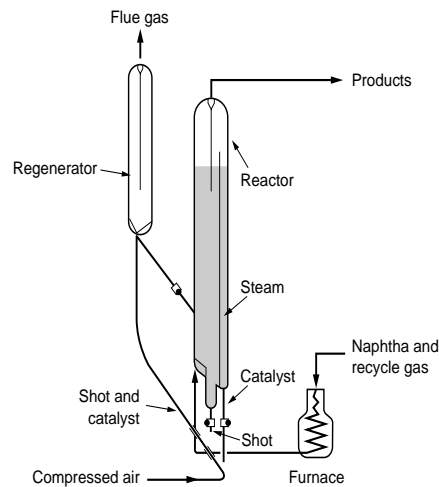


**Figure 1-12** Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]





**Figure 1-13** Longitudinal catalytic packed-bed reactor. [From Cropley, American Institute of Chemical Engineers, 86(2), 34 (1990). Reproduced with permission of the American Institute of Chemical Engineers, Copyright © 1990 AIChE. All rights reserved.]



**Figure 1-14** Fluidized-bed catalytic reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]



*Chemical Engineers*, 4th ed., by M. S. Peters and K. D. Timmerhaus (New York: McGraw-Hill, 1991). From Figure 15-12 of this book, one can get an estimate of the purchase cost per foot of \$1 for a 1-in. pipe and \$2 per foot for a 2-in. pipe for single tubes and approximately \$20 to \$50 per square foot of surface area for fixed-tube sheet exchangers.

A packed-bed (also called a fixed-bed) reactor is essentially a tubular reactor that is packed with solid catalyst particles (Figure 1-13). This heterogeneous reaction system is used most frequently to catalyze gas reactions. This reactor has the same difficulties with temperature control as other tubular reactors, and in addition, the catalyst is usually troublesome to replace. On occasion, channeling of the gas flow occurs, resulting in ineffective use of parts of the reactor bed. The advantage of the packed-bed reactor is that for most reactions it gives the highest conversion per weight of catalyst of any catalytic reactor.

Another type of catalytic reactor in common use is the fluidized-bed (Figure 1-14). The fluidized-bed reactor is analogous to the CSTR in that its contents, though heterogeneous, are well mixed, resulting in an even temperature distribution throughout the bed. The fluidized-bed reactor cannot be modeled as either a CSTR or a tubular reactor (PFR), but requires a model of its own. The temperature is relatively uniform throughout, thus avoiding hot spots. This type of reactor can handle large amounts of feed and solids and has good temperature control; consequently, it is used in a large number of applications. The advantages of the ease of catalyst replacement or regeneration are



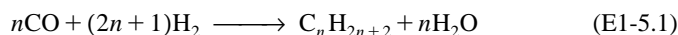
sometimes offset by the high cost of the reactor and catalyst regeneration equipment.

**Example 1-5 Gas-Phase Industrial Reactor/Process**

Synthesis gas contains a mixture of carbon monoxide and hydrogen and can be obtained from the combustion of coal or natural gas. This gas can be used to produce synthetic crude by the Fischer–Tropsch reaction. Describe two industrial reactors used to convert synthesis gas to a mixture of hydrocarbons by the Fischer–Tropsch process.

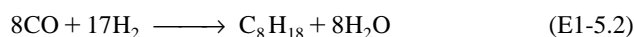
*Solution*

**Reactions.** The Fischer–Tropsch reaction converts synthesis gas into a mixture of alkanes and alkenes over a solid catalyst usually containing iron. The basic reaction for paraffin formation is as follows

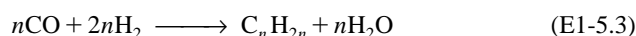


Making Gasoline

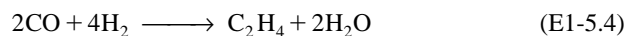
For example, when octane, a component of gasoline, is formed, Equation (E1-5.1) becomes



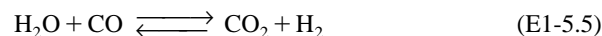
Similarly, for the formation of olefins,



For ethylene formation, Equation (E1-5.3) becomes



The other type of main reaction that occurs in this process is the water-gas-shift reaction



In addition to the simultaneous formation of paraffins and olefins, side reactions also take place to produce small quantities of acids and nonacids (e.g., ethanol).

**Reactors.** Two types of reactors will be discussed, a *straight-through transport reactor*, which is also referred to as a *riser* or *circulating fluidized bed*, and a *packed-bed reactor* (PBR), which is also referred to as a *fixed-bed reactor*.

**Riser.** Because the catalyst used in the process decays rapidly at high temperatures (e.g., 350°C), a *straight-through transport reactor* (STTR) (Chapter 10) is used. This type of reactor is also called a *riser* and/or a *circulating bed*. A schematic diagram is shown in Figure E1-5.1. Here the catalyst particles are fed to the bottom of the reactor and are shot up through the reactor together with the entering reactant gas mixture and then separated from the gas in a settling hopper. The volumetric gas feed rate of  $3 \times 10^5 \text{ m}^3/\text{h}$  is roughly equivalent to feeding the volume of gas contained in the University of Michigan football stadium to the reactor each hour.

A schematic and photo of an industrial *straight-through transport reactor* used at Sasol are shown in Figure E1-5.2 together with the composition of the feed and product streams. The products that are condensed out of the product stream

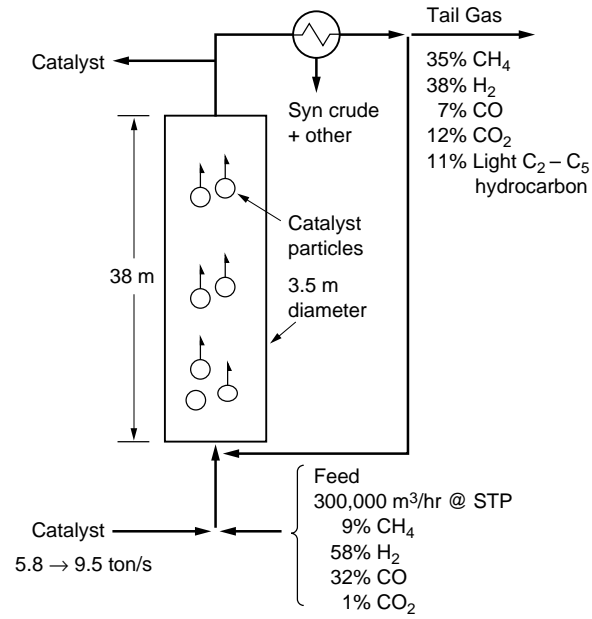


Figure E1-5.1 Schematic of Sasol Fischer-Tropsch process.

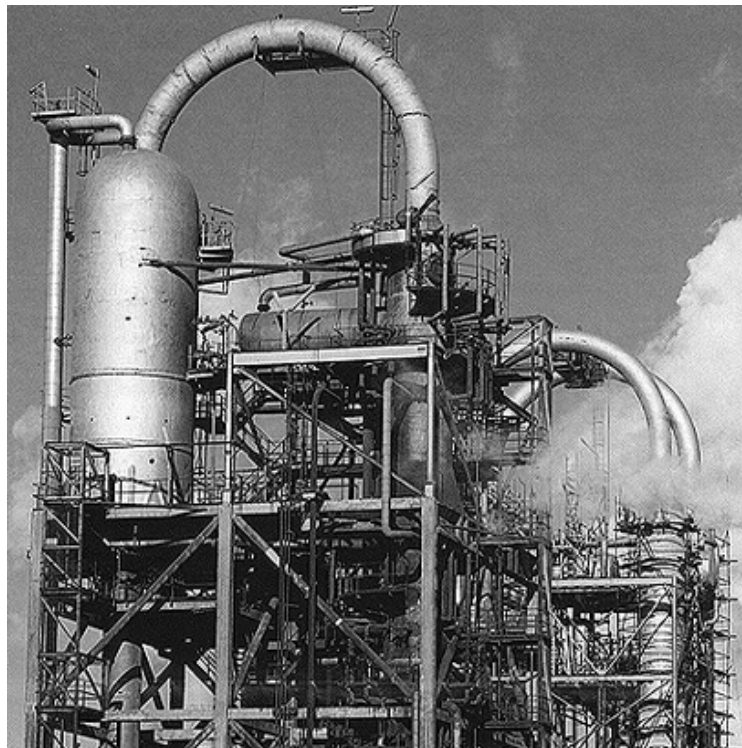
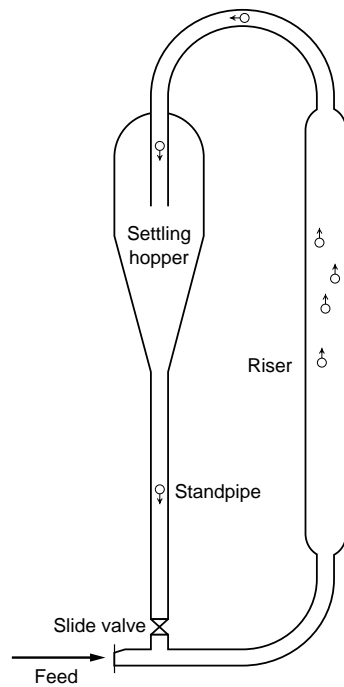
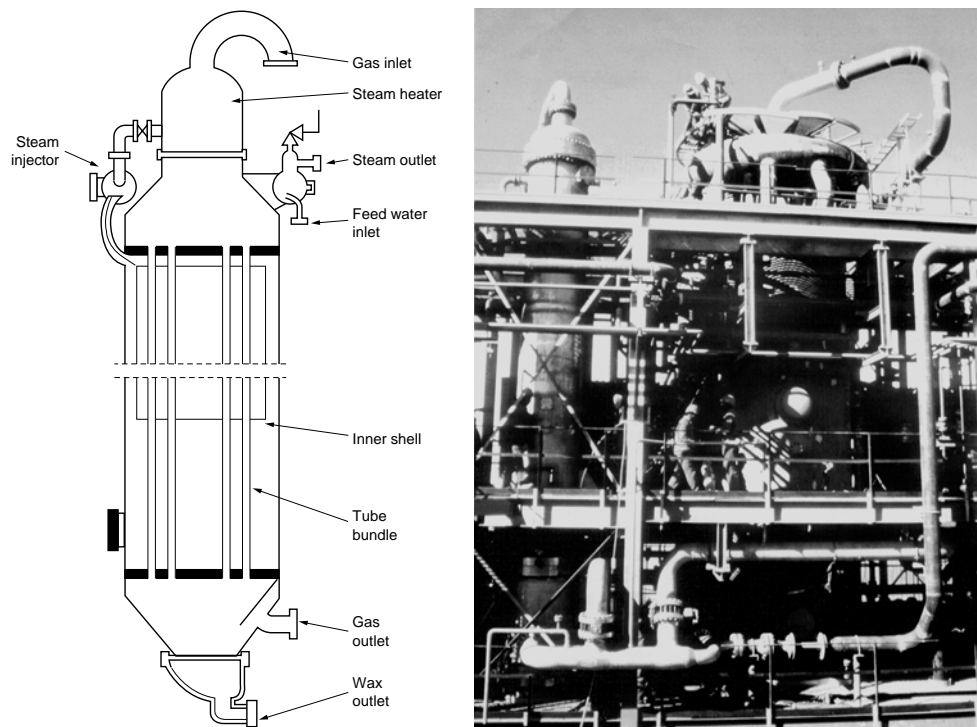


Figure E1-5.2 The reactor is 3.5 m in diameter and 38 m tall. (Schematic and photo courtesy of Sasol/Sastech PT Limited.)

before the stream is recycled include Synoil (a synthetic crude), water, methyl ethyl ketone (MEK), alcohols, acids, and aldehydes. The reactor is operated at 25 atm and 350°C and at any one time contains 150 tons of catalyst. The catalyst feed rate is 6 to 9.5 tons/s, and the gas recycle ratio is 2:1.

**Packed Bed.** The packed-bed reactor used at the Sasol plant to carry out Fischer–Tropsch synthesis reaction is shown in Figure E1-5.3. Synthesis gas is fed at a rate of 30,000 m<sup>3</sup>/h (STP) at 240°C and 27 atm to the packed-bed reactor. The reactor contains 2050 tubes, each of which is 5.0 cm in diameter and 12 m in length. The iron-based catalyst that fills these tubes usually contains K<sub>2</sub>O and SiO<sub>2</sub> and has a specific area on the order of 200 m<sup>2</sup>/g. The reaction products are light hydrocarbons along with a wax that is used in candles and printing inks. Approximately 50% conversion of the reactant is achieved in the reactor.

Use to produce wax  
for candles and  
printing inks.



**Figure E1-5.3** Packed-bed reactor. (Schematic and photograph courtesy of Sasol/Sastech PT Limited.)

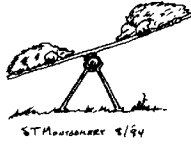
The aim of the preceding discussion on commercial reactors is to give a more detailed picture of each of the major types of industrial reactors: batch, semibatch, CSTR, tubular, fixed-bed (packed-bed), and fluidized-bed. Many variations and modifications of these commercial reactors are in current use; for further elaboration, refer to the detailed discussion of industrial reactors given by Walas.<sup>3</sup>

<sup>3</sup> S. M. Walas, *Reaction Kinetics for Chemical Engineers* (New York: McGraw-Hill, 1959), Chap. 11.





## SUMMARY




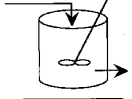

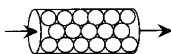
1. A mole balance on species  $j$ , which enters, leaves, reacts, and accumulates in a system volume  $V$ , is

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt} \quad (S1-1)$$

2. The kinetic rate law for  $r_j$  is:
- Solely a function of properties of reacting materials [e.g., concentration (activities), temperature, pressure, catalyst or solvent (if any)].
  - An intensive quantity.
  - An algebraic equation, not a differential equation.

For homogeneous catalytic systems, typical units of  $-r_j$  may be gram moles per second per liter; for heterogeneous systems, typical units of  $r_j'$  may be gram moles per second per gram of catalyst. By convention,  $-r_A$  is the rate of disappearance of species A and  $r_A$  is the rate of formation of species A.

3. Mole balances on four common reactors are as follows:

Reactor	Mole Balance	Comment
	$\frac{dN_j}{dt} = r_j V$	No spatial variation
	$V = \frac{F_{j0} - F_j}{-r_j}$	No spatial variation, steady state
	$\frac{dF_j}{dV} = r_j$	Steady state
	$\frac{dF_j}{dW} = r_j'$	Steady state

## QUESTIONS AND PROBLEMS

I wish I had an answer for that, because I'm getting tired of answering that question.

Yogi Berra, New York Yankees  
*Sports Illustrated*, June 11, 1984

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

A = ● B = ■ C = ◆ D = ◆◆

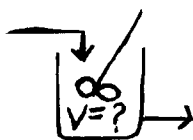
In each of the questions and problems below, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style* (New York: Macmillan, 1979) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace* (Glenview, Ill.: Scott, Foresman, 1989) to enhance the quality of your sentences.



**P1-1<sub>A</sub>** After reading each page, ask yourself a question. Make a list of the most important things that you learned in this chapter.

**P1-2<sub>A</sub>** **What if:**

- the benzene feed stream in Example 1-4 were not preheated by the product stream? What would be the consequences?
- you needed the cost of a 6000-gallon and a 15,000-gallon Pfaudler reactor? What would they be?
- the exit concentration of A in Example 1-3 were specified at 0.1% of the entering concentration?
- the volume of the movable piston in Example 1-2 varied in a manner similar to a car cylinder,  $V = V_0 + V_1 \sin \omega t$ ?
- only one operator showed up to run the nitrobenzene plant, what would be some of your first concerns?



**P1-3<sub>B</sub>** Calculate the volume of a CSTR for the conditions used to calculate the plug-flow reactor volume in Example 1-3.

**P1-4<sub>A</sub>** Calculate the time to reduce the number of moles of A to 1% of its initial value in a constant-volume batch reactor for the reaction and data in Example 1-3.

**P1-5<sub>A</sub>** What assumptions were made in the derivation of the design equation for:

- the batch reactor?
- the CSTR?
- the plug-flow reactor (PFR)?
- the packed-bed reactor (PBR)?
- State in words the meanings of  $-r_A$ ,  $-r'_A$ , and  $r'_A$ . Is the reaction rate  $-r_A$  an extensive quantity? Explain.

**P1-6<sub>A</sub>** What is the difference between the rate of reaction for a homogeneous system,  $-r_A$ , and the rate of reaction for a heterogeneous system,  $-r'_A$ ? Use the mole balance to derive an equation analogous to Equation (1-6) for a fluidized CSTR containing catalyst particles in terms of the catalyst weight,  $W$ , and other appropriate terms.

**P1-7<sub>A</sub>** How can you convert the general mole balance equation for a given species, Equation (1-4), to a general mass balance equation for that species?

**P1-8<sub>A</sub>** The United States produces 24% of the world's chemical products. According to the yearly "Facts and Figures" issue of *Chemical and Engineering News* (*C&E News*, June 24, 1996), the following were the 10 most produced chemicals in 1995:

Chemical	Billions of Pounds	Chemical	Billions of Pounds
1. H <sub>2</sub> SO <sub>4</sub>	95.36	6. NH <sub>3</sub>	35.60
2. N <sub>2</sub>	68.04	7. H <sub>3</sub> PO <sub>4</sub>	26.19
3. O <sub>2</sub>	53.48	8. NaOH	26.19
4. C <sub>2</sub> H <sub>4</sub>	46.97	9. C <sub>3</sub> H <sub>6</sub>	25.69
5. CaO	41.23	10. Cl <sub>2</sub>	25.09

- (a) What were the 10 most produced chemicals for the year that just ended? Were there any significant changes from the 1995 statistics?

The same issue of *C&E News* gives the following chemical companies as the top 10 in total sales in 1995. (Also see <http://www.chemweek.com>)



<i>Company</i>	<i>Sales (billions of dollars)</i>
1. Dow	19.73
2. Dupont	18.43
3. Exxon	11.73
4. Hoechst Celanese	7.39
5. Monsanto	7.25
6. General Electric	6.63
7. Mobil	6.15
8. Union Carbide	5.89
9. Amoco	5.66
10. Occidental Petroleum	5.41

- (b) What 10 companies were tops in sales for the year just ended? Did any significant changes occur compared to the 1995 statistics?
- (c) Why do you think  $H_2SO_4$  is the most produced chemical? What are some of its uses?
- (d) What is the current annual production rate (lb/yr) of ethylene, ethylene oxide, and benzene?
- (e) Why do you suspect there are so few organic chemicals in the top 10?

**P1-9<sub>A</sub>** Referring to the text material and the additional references on commercial reactors given at the end of this chapter, fill in the following table:

<i>Type of Reactor</i>	<i>Characteristics</i>	<i>Kinds of Phases Present</i>	<i>Use</i>	<i>Advantages</i>	<i>Disadvantages</i>
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

**P1-10<sub>B</sub>** Schematic diagrams of the Los Angeles basin are shown in Figure P1-10. The basin floor covers approximately 700 square miles ( $2 \times 10^{10} \text{ ft}^2$ ) and is almost completely surrounded by mountain ranges. If one assumes an inversion height in the basin of 2000 ft, the corresponding volume of air in the basin is  $4 \times 10^{13} \text{ ft}^3$ . We shall use this system volume to model the accumulation and depletion of air pollutants. As a very rough first approximation, we shall treat the Los Angeles basin as a well-mixed container (analogous to a CSTR) in which there are no spatial variations in pollutant concentrations. Consider only the pollutant carbon monoxide and assume that the source of CO is from automobile exhaust and that, on the average, there are 400,000 cars operating in the basin at any one time. Each car gives off roughly 3000 standard cubic feet of exhaust each hour containing 2 mol % carbon monoxide.



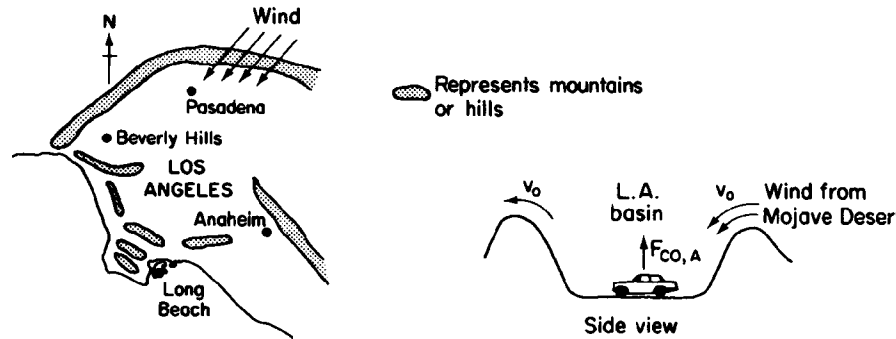


Figure P1-10



We shall perform an unsteady-state mole balance on CO as it is depleted from the basin area by a Santa Ana wind. Santa Ana winds are high-velocity winds that originate in the Mojave Desert just to the northeast of Los Angeles. This clean desert air flows into the basin through a corridor assumed to be 20 miles wide and 2000 ft high (inversion height) replacing the polluted air, which flows out to sea or toward the south. The concentration of CO in the Santa Ana wind entering the basin is 0.08 ppm ( $2.04 \times 10^{-10}$  lb mol/ft<sup>3</sup>).

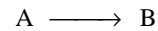
- (a) How many pound moles of gas are in the system volume we have chosen for the Los Angeles basin if the temperature is 75°F and the pressure is 1 atm? (Values of the ideal gas constant may be found in Appendix B.)
- (b) What is the rate,  $F_{CO,A}$ , at which all autos emit carbon monoxide into the basin (lb mol CO/h)?
- (c) What is the volumetric flow rate (ft<sup>3</sup>/h) of a 15-mph wind through the corridor 20 miles wide and 2000 ft high? (*Ans.*:  $1.67 \times 10^{13}$  ft<sup>3</sup>/h.)
- (d) At what rate,  $F_{CO,S}$ , does the Santa Ana wind bring carbon monoxide into the basin (lb mol/h)?
- (e) Assuming that the volumetric flow rates entering and leaving the basin are identical,  $v = v_0$ , show that the unsteady mole balance on CO within the basin becomes

$$F_{CO,A} + F_{CO,S} - v_0 C_{CO} = V \frac{dC_{CO}}{dt} \quad (\text{P1-10.1})$$

- (f) Verify that the solution to Equation (P1-10.1) is

$$t = \frac{V}{v_0} \ln \frac{F_{CO,A} + F_{CO,S} - v_0 C_{CO,0}}{F_{CO,A} + F_{CO,S} - v_0 C_{CO}} \quad (\text{P1-10.2})$$

- (g) If the initial concentration of carbon monoxide in the basin before the Santa Ana wind starts to blow is 8 ppm ( $2.04 \times 10^{-8}$  lb mol/ft<sup>3</sup>), calculate the time required for the carbon monoxide to reach a level of 2 ppm.
- (h) Repeat parts (b) through (g) for another pollutant, NO. The concentration of NO in the auto exhaust is 1500 ppm ( $3.84 \times 10^{-6}$  lb mol/ft<sup>3</sup>), and the initial NO concentration in the basin is 0.5 ppm. If there is no NO in the Santa Ana wind, calculate the time for the NO concentration to reach 0.1 ppm. What is the lowest concentration of NO that could be reached?

**P1-11<sub>A</sub>** The reaction

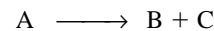
is to be carried out isothermally in a continuous-flow reactor. Calculate both the CSTR and PFR reactor volumes necessary to consume 99% of A (i.e.,  $C_A = 0.01C_{A0}$ ) when the entering molar flow rate is 5 mol/h, assuming the reaction rate  $-r_A$  is:

(a)  $-r_A = k$  with  $k = 0.05 \frac{\text{mol}}{\text{h} \cdot \text{dm}^3}$  (Ans.:  $V = 99 \text{ dm}^3$ )

(b)  $-r_A = kC_A$  with  $k = 0.0001 \text{ s}^{-1}$

(c)  $-r_A = kC_A^2$  with  $k = 3 \frac{\text{dm}^3}{\text{mol} \cdot \text{h}}$  (Ans.:  $V_{\text{CSTR}} = 66,000 \text{ dm}^3$ )

The entering volumetric flow rate is  $10 \text{ dm}^3/\text{h}$ . [Note:  $F_A = C_A v$ . For a constant volumetric flow rate  $v = v_0$ , then  $F_A = C_A v_0$ . Also,  $C_{A0} = F_{A0}/v_0 = (5 \text{ mol/h})/(10 \text{ dm}^3/\text{h}) = 0.5 \text{ mol/dm}^3$ .]

**P1-12<sub>C</sub>** The gas-phase reaction

is carried out isothermally in a  $20\text{-dm}^3$  constant-volume batch reactor. Twenty moles of pure A is initially placed in the reactor. The reactor is well mixed.

(a) If the reaction is first order:

$$-r_A = kC_A \quad \text{with } k = 0.865 \text{ min}^{-1}$$

calculate the time necessary to reduce the number of moles of A in the reactor to 0.2 mol. (Note:  $N_A = C_A V$ ). (Ans.:  $t = 5.3 \text{ min}$ )

(b) If the reaction is second order:

$$-r_A = kC_A^2 \quad \text{with } k = \frac{2 \text{ dm}^3}{\text{mol} \cdot \text{min}}$$

calculate the time necessary to consume 19.0 mol of A.

(c) If the temperature is  $127^\circ\text{C}$ , what is the initial total pressure? What is the final total pressure assuming the reaction goes to completion?

**P1-13<sub>A</sub>** (a) How many cubic feet (at STP) enter the packed-bed reactor described in Example 1-5 every second? How long does a molecule spend, on the average, in the reactor? [Hint: What is the gas velocity in each tube assuming a 30% porosity (volume of gas/volume of reactor) for the packed bed?]

(b) Estimate the time that a catalyst particle and a gas-phase molecule spend in the Sasol straight-through transport reactor (STTR). What is the bulk density of the catalyst ( $\text{kg cat}/\text{m}^3$ ) in the STTR?

**P1-14<sub>A</sub>** Write a one-paragraph summary of a journal article on chemical kinetics or reaction engineering. The article must have been published within the last five years.<sup>4</sup> What did you learn from this article? Why is the article important?

**P1-15<sub>A</sub>** (a) What journals, books, or papers give you costs of industrial (not laboratory, e.g., Fisher catalog) chemicals and catalysts?

(b) List various journals, books, or other sources where you will find details about the construction and safety of industrial reactors.

<sup>4</sup> See the Supplementary Reading list at the end of the chapter, particularly item 4.





**P1-16<sub>C</sub>** What are typical operating conditions (temperature, pressure) of a catalytic cracking reactor used in petroleum refining?

**P1-17<sub>A</sub>** View the photos and schematics on the CD-ROM under Elements of Chemical Reaction Engineering—Chapter 1. Look at the quicktime videos. Write a paragraph describing two or more of the reactors. What similarities and differences do you observe between the reactors on the Web and in the text?

**P1-18<sub>A</sub>** Vary the parameters  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$ . Discuss which parameters can or cannot be larger than others. Write a paragraph describing what you find.



- (a) There are initially 500 rabbits ( $x$ ) and 200 foxes ( $y$ ) on Farmer Oat's property. Use POLYMATH or MATLAB to plot the concentration of foxes and rabbits as a function of time for a period of up to 500 days. The predator-prey relationships are given by the following set of coupled ordinary differential equations:

$$\frac{dx}{dt} = k_1x - k_2x \cdot y$$

$$\frac{dy}{dt} = k_3x \cdot y - k_4y$$

Constant for growth of rabbits  $k_1 = 0.02 \text{ day}^{-1}$

Constant for death of rabbits  $k_2 = 0.00004/(\text{day} \times \text{no. of foxes})$

Constant for growth of foxes after eating rabbits  $k_3 = 0.0004/(\text{day} \times \text{no. of rabbits})$

Constant for death of foxes  $k_4 = 0.04 \text{ day}^{-1}$

What do your results look like for the case of  $k_3 = 0.00004/(\text{day} \times \text{no. of rabbits})$  and  $t_{\text{final}} = 800$  days? Also plot the number of foxes versus the number of rabbits. Explain why the curves look the way they do.

- (b) Use POLYMATH or MATLAB to solve the following set of nonlinear algebraic equations:

$$x^3y - 4y^2 + 3x = 1$$

$$6y^2 - 9xy = 5$$

with initial guesses of  $x = 2$ ,  $y = 2$ . Try to become familiar with the edit keys in POLYMATH MatLab. See CD-ROM for instructions.

**P1-19<sub>A</sub>** (a) Surf the World Wide Web and make a list of the links that are relevant to chemical reaction engineering. Pick the five most relevant links and write two or three sentences about each.

- (b) Check the reaction engineering 3rd ed. web site (<http://www.engin.umich.edu/~cre>) to learn what material has been added and any typographical errors that have been found in the first printing.

**P1-20<sub>A</sub>** Surf the CD-ROM included with the text.

- (a) Approximately how many additional solved example problems are there?  
 (b) List at least one video clip.  
 (c) In what lectures are activation energy discussed?  
 (d) What photos are in the Wetlands Module?

After Reading Each Page in  
This Book, Ask Yourself a Question  
About What You Read



## CD-ROM MATERIAL



- **Learning Resources**

1. *Summary Notes for Lectures 1 and 2*
2. *Web Modules*
  - A. Problem Solving Algorithm for Closed-Ended Problems
  - B. Hints for Getting Unstuck on a Problem
3. *Interactive Computer Modules*
  - A. Quiz Show I
4. *Solved Problems*
  - A. CDP1-A<sub>B</sub> Batch Reactor Calculations: A Hint of Things to Come

- **Professional Reference Shelf**

1. *Photographs of Real Reactors*

- **Additional Homework Problems**

- CDP1-A<sub>A</sub>** Calculate the time to consume 80% of species A in a constant-volume batch reactor for a first- and a second-order reaction. (**Includes Solution**)
- CDP1-B<sub>A</sub>** Derive the differential mole balance equation for a foam reactor. [2nd Ed. P1-10<sub>B</sub>]

## SUPPLEMENTARY READING

1. For further elaboration of the development of the general balance equation, see
  - DIXON, D. C., *Chem. Eng. Sci.*, 25, 337 (1970).
  - FELDER, R. M., and R. W. ROUSSEAU, *Elementary Principles of Chemical Processes*, 2nd ed. New York: Wiley, 1986, Chap. 4.
  - HIMMELBLAU, D. M., *Basic Principles and Calculations in Chemical Engineering*, 6th ed. Upper Saddle River, N.J.: Prentice Hall, 1996, Chaps. 2 and 6.
  - HOLLAND, C. D., and R. G. ANTHONY, *Fundamentals of Chemical Reaction Engineering*, 2nd ed. Upper Saddle River, N.J.: Prentice Hall, 1989, Chap. 1.
2. A detailed explanation of a number of topics in this chapter can be found in
  - CRYNES, B. L., and H. S. FOGLER, eds., *AIChE Modular Instruction Series E: Kinetics*, Vols. 1 and 2. New York: AIChE, 1981.
3. An excellent description of the various types of commercial reactors used in industry is found in Chapter 11 of
  - WALAS, S. M., *Reaction Kinetics for Chemical Engineers*. New York: McGraw-Hill, 1959.

A somewhat different discussion of the usage, advantages, and limitations of various reactor types can be found in

  - DENBIGH, K. G., and J. C. R. TURNER, *Chemical Reactor Theory*, 2nd ed. Cambridge: Cambridge University Press, 1971, pp. 1–10.
4. A discussion of some of the most important industrial processes is presented by
  - MEYERS, R.A., *Handbook of Chemical Production Processes*. New York: McGraw-Hill, 1986.



See also

MCKETTA, J. J., ed., *Encyclopedia of Chemical Processes and Design*. New York: Marcel Dekker, 1976.

A similar book, which describes a larger number of processes, is

SHREVE, R. N., and J. A. BRINK, JR., *Chemical Process Industries*, 4th ed. New York: McGraw-Hill, 1977.

5. The following journals may be useful in obtaining information on chemical reaction engineering: *International Journal of Chemical Kinetics*, *Journal of Catalysis*, *Journal of Applied Catalysis*, *AIChE Journal*, *Chemical Engineering Science*, *Canadian Journal of Chemical Engineering*, *Chemical Engineering Communications*, *Journal of Physical Chemistry*, and *Industrial and Engineering Chemistry Research*.
6. The price of chemicals can be found in such journals as the *Chemical Marketing Reporter*, *Chemical Weekly*, and *Chemical Engineering News*.

