

# ESSENTIALS OF CHEMICAL REACTION ENGINEERING

SECOND EDITION

H. SCOTT FOGLER



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PHYSICAL AND CHEMICAL ENGINEERING SCIENCES



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# *Mole Balances* 1

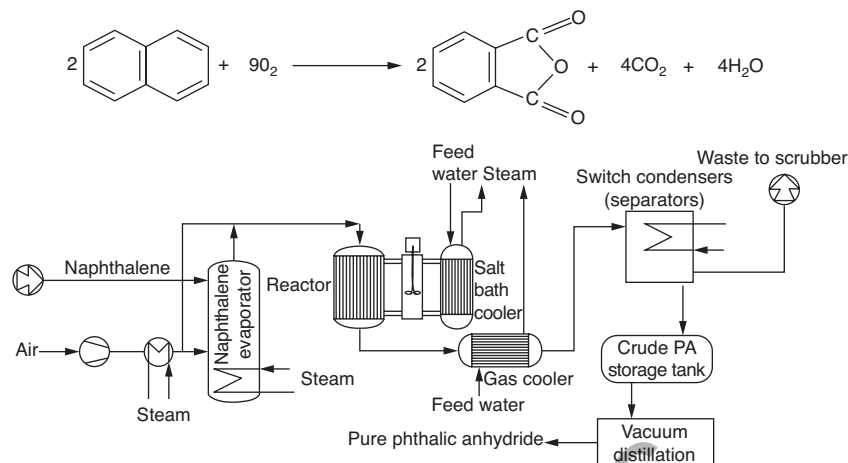
The first step to knowledge  
is to know that we are ignorant.

—Socrates (470–399 B.C.)

## **The Wide Wild World of Chemical Reaction Engineering**

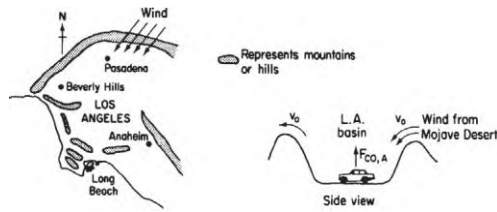
How is a chemical  
engineer different  
from other  
engineers?

Chemical kinetics is the study of chemical reaction rates and reaction mechanisms. The study of chemical reaction engineering (CRE) combines the study of chemical kinetics with the reactors in which the reactions occur. Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals, such as the manufacture of phthalic anhydride shown in Figure 1-1. 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 produces a large amount of undesirable product, subsequent purification and separation of the desired product could make the entire process economically unfeasible.

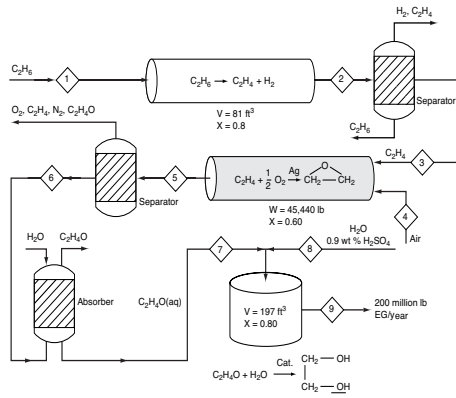


**Figure 1-1** Manufacture of phthalic anhydride.

The chemical reaction engineering (CRE) principles learned here can also be applied in many areas, such as waste treatment, microelectronics, nanoparticles, and living systems, in addition to the more traditional areas of the manufacture of chemicals and pharmaceuticals. Some of the examples that illustrate the wide application of CRE principles in this book are shown in Figure 1-2. These examples include modeling smog in the Los Angeles (L.A.) basin (Chapter 1), the digestive system of a hippopotamus (Chapter 2 on the CRE Web site, [www.umich.edu/~elements/5e/index.html](http://www.umich.edu/~elements/5e/index.html)), and molecular CRE (Chapter 3). Also shown are the manufacture of ethylene glycol (antifreeze), where three of the most common types of industrial reactors are used (Chapters 5 and 6), and the use of wetlands to degrade toxic chemicals (Chapter 7 on the CRE Web site). Other examples shown are the solid-liquid kinetics of acid-rock interactions to improve oil recovery (Chapter 7); pharmacokinetics of cobra bites (Chapter 8 Web Module); free-radical scavengers used in the design of motor oils (Chapter 9); enzyme kinetics (Chapter 9) and drug delivery pharmacokinetics (Chapter 9 on the CRE Web site); heat effects, runaway reactions, and plant safety (Chapters 11 through 13); and increasing the octane number of gasoline and the manufacture of computer chips (Chapter 10).



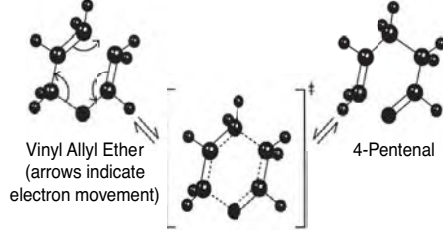
Smog (Ch. 1 on CRE Web site)



Chemical Plant for Ethylene Glycol (Ch. 5)

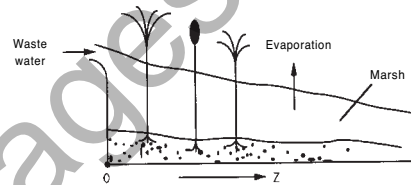


Hippo Digestion (Ch. 2 on CRE Web site)



Transition State (dashed lines show transition state electron delocalization)

Molecular CRE (Ch. 3 on CRE Web site)



Wetlands Remediation of Pollutants (Ch. 7 on CRE Web site)

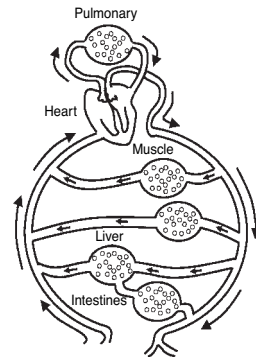


Pharmacokinetics of Cobra Bites  
Multiple Reactions in a Batch (Body) Reactor

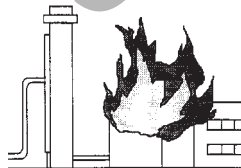
Cobra Bites (Ch. 8 on the CRE Web site)



Effective Lubricant Design Scavenging Free Radicals  
Lubricant Design (Ch. 9)

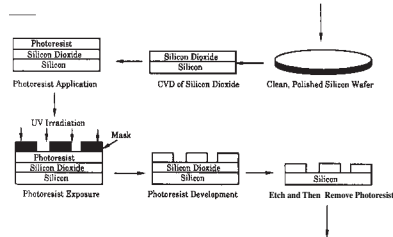


Pharmacokinetics (Ch. 9 on CRE Web site)



Nitroaniline Plant Explosion Exothermic Reactions That Run Away  
Plant Safety (Ch.11 to Ch.13)

(<http://www.umich.edu/~safeche/index.html>)



Microelectronic Fabrication Steps (Ch. 10)

Figure 1-2 The wide world of CRE applications.

**Overview.** This chapter develops the first building block of chemical reaction engineering, *mole balances*, which will be used continually throughout the text. After completing this chapter, the reader will be able to:

- Describe and define the rate of reaction
- Derive the general mole balance equation
- Apply the general mole balance equation to the four most common types of industrial reactors

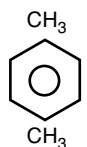
Before entering into discussions of the conditions that affect chemical reaction rate mechanisms and reactor design, it is necessary to account for the various chemical species entering and leaving a reaction system. This accounting process is achieved through overall mole balances on individual species 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,  $-r_A$ , 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 (<http://encyclopedia.che.engin.umich.edu/Pages/Reactors/menu.html>).

- Batch Reactor (BR)
- Continuous-Stirred Tank Reactor (CSTR)
- Plug-Flow Reactor (PFR)
- Packed-Bed Reactor (PBR)

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.

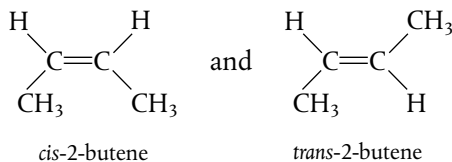
## 1.1 The Rate of Reaction, $-r_A$

The rate of reaction tells us how fast a number of moles of one chemical species are being consumed to form another chemical species. The term *chemical species* refers to any chemical component 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 para-xylene is made up of a fixed number of specific atoms in a definite molecular arrangement or configuration. The structure shown illustrates the kind, number, and configuration of atoms on a molecular level. Even though two chemical compounds have exactly the same kind and 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.



p-xylene

Identify
- Kind
- Number
- Configuration



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?

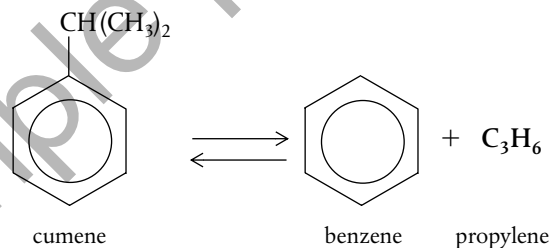
Definition of Rate of Reaction

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 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.

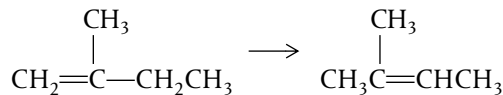
There are three basic ways a species may lose its chemical identity: decomposition, combination, and isomerization. In *decomposition*, the molecule loses its identity by being broken down into smaller molecules, atoms, or atom fragments. For example, if benzene and propylene are formed from a cumene molecule,

A species can lose its identity by

- Decomposition
- Combination
- Isomerization



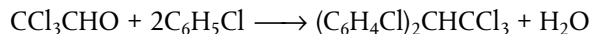
the cumene molecule has lost its identity (i.e., disappeared) by breaking its bonds to form these molecules. A second way that a molecule may lose its chemical identity is through *combination* with another molecule or atom. In the above reaction, the propylene molecule would lose its chemical identity 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 chemical identity is through *isomerization*, such as the reaction



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 (i.e., moles) 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. To illustrate, consider the reaction of chloral with chlorobenzene to produce the banned insecticide DDT (dichlorodiphenyl-trichloroethane) in the presence of fuming sulfuric acid.



Letting the symbol A represent chloral, B be chlorobenzene, C be DDT, and D be  $\text{H}_2\text{O}$ , we obtain



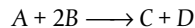
The numerical value of the rate of disappearance of reactant A,  $-r_A$ , is a positive number.

What is  $-r_A$ ?

The rate of reaction,  $-r_A$ , is the number of moles of A (e.g., chloral) reacting (disappearing) per unit time per unit volume ( $\text{mol}/\text{dm}^3\cdot\text{s}$ ).

### Example 1-1 Rates of Disappearance and Formation

Chloral is being consumed at a rate of 10 moles per second per  $\text{m}^3$  when reacting with chlorobenzene to form DDT and water in the reaction described above. In symbol form, the reaction is written as

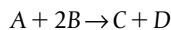


Write the rates of disappearance and formation (i.e., generation) for each species in this reaction.

#### Solution

- (a) *Chloral*[A]: The rate of reaction of chloral [A] ( $-r_A$ ) is given as  $10 \text{ mol}/\text{m}^3\cdot\text{s}$   
 Rate of disappearance of A =  $-r_A = 10 \text{ mol}/\text{m}^3\cdot\text{s}$   
 Rate of formation of A =  $r_A = -10 \text{ mol}/\text{m}^3\cdot\text{s}$
- (b) *Chlorobenzene*[B]: For every mole of chloral that disappears, two moles of chlorobenzene [B] also disappear.  
 Rate of disappearance of B =  $-r_B = 20 \text{ mol}/\text{m}^3\cdot\text{s}$   
 Rate of formation of B =  $r_B = -20 \text{ mol}/\text{m}^3\cdot\text{s}$
- (c) *DDT*[C]: For every mole of chloral that disappears, one mole of DDT[C] appears.  
 Rate of formation of C =  $r_C = 10 \text{ mol}/\text{m}^3\cdot\text{s}$   
 Rate of disappearance of C =  $-r_C = -10 \text{ mol}/\text{m}^3\cdot\text{s}$
- (d) *Water*[D]: Same relationship to chloral as the relationship to DDT  
 Rate of formation of D =  $r_D = 10 \text{ mol}/\text{m}^3\cdot\text{s}$   
 Rate of disappearance of D =  $-r_D = -10 \text{ mol}/\text{m}^3\cdot\text{s}$

$$\begin{aligned} -r_A &= 10 \text{ mol A}/\text{m}^3\cdot\text{s} \\ r_A &= -10 \text{ mol A}/\text{m}^3\cdot\text{s} \\ \text{Equation (3-1) page 73} \\ \text{Then} \\ \frac{r_A}{-1} &= \frac{r_B}{-2} = \frac{r_C}{1} = \frac{r_D}{1} \\ r_B &= 2(r_A) = -20 \text{ mol B}/\text{m}^3\cdot\text{s} \\ -r_B &= 20 \text{ mol B}/\text{m}^3\cdot\text{s} \\ r_C &= -r_A = 10 \text{ mol C}/\text{m}^3\cdot\text{s} \\ r_D &= -r_A = 10 \text{ mol D}/\text{m}^3\cdot\text{s} \end{aligned}$$



The convention

$-r_A = 10 \text{ mol A/m}^3\cdot\text{s}$
$r_A = -10 \text{ mol A/m}^3\cdot\text{s}$
$-r_B = 20 \text{ mol B/m}^3\cdot\text{s}$
$r_B = -20 \text{ mol B/m}^3\cdot\text{s}$
$r_C = 10 \text{ mol C/m}^3\cdot\text{s}$

**Analysis:** The purpose of this example is to better understand the convention for the rate of reaction. The symbol  $r_j$  is the rate of formation (generation) of species  $j$ . If species  $j$  is a reactant, the numerical value of  $r_j$  will be a negative number. If species  $j$  is a product, then  $r_j$  will be a positive number. The rate of reaction,  $-r_A$ , is the rate of disappearance of reactant A and must be a positive number. A mnemonic relationship to help remember how to obtain relative rates of reaction of A to B, etc., is given by Equation (3-1) on page 73.

In Chapter 3, we will delineate the prescribed relationship between the rate of formation of one species,  $r_j$  (e.g., DDT [C]), and the rate of disappearance of another species,  $-r_i$  (e.g., chlorobenzene [B]), in a chemical reaction.

Heterogeneous reactions involve more than one phase. In heterogeneous reaction systems, the rate of reaction is usually expressed in measures other than volume, such as reaction surface area or catalyst weight. For a gas-solid catalytic reaction, the gas molecules must interact with the solid catalyst surface for the reaction to take place, as described in Chapter 10.

What is  $-r'_A$ ? The dimensions of this heterogeneous reaction rate,  $-r'_A$  (prime), are the number of moles of A reacting per unit time per unit mass of catalyst (mol/s-g catalyst).

Definition of  $r_j$  Most of the introductory discussions on chemical reaction engineering in this book focus on homogeneous systems, in which case we 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.

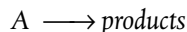
We can say four things about the reaction rate  $r_j$ . The reaction rate law for  $r_j$  is

The rate law does not depend on the type of reactor used!!

- **The rate of formation of species  $j$  (mole/time/volume)**
- **An algebraic equation**
- **Independent of the type of reactor (e.g., batch or continuous flow) in which the reaction is carried out**
- **Solely a function of the properties of the reacting materials and reaction conditions (e.g., species concentration, temperature, pressure, or type of catalyst, if any) at a point in the system**

What is  $-r_A$  a function of? However, because the properties and reaction conditions of the reacting materials may 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.

The chemical reaction 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 for  $-r_A$  for the reaction



may be a linear function of concentration,

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

or it may be some other algebraic function of concentration, such as Equation 3-6 shown in Chapter 3

<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*, 1, 1 (New York: AIChE, 1981); 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.

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

The convention

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  $k$  (which is a function of temperature) times the square of the concentration of A. As noted earlier, 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 is 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 1-3).

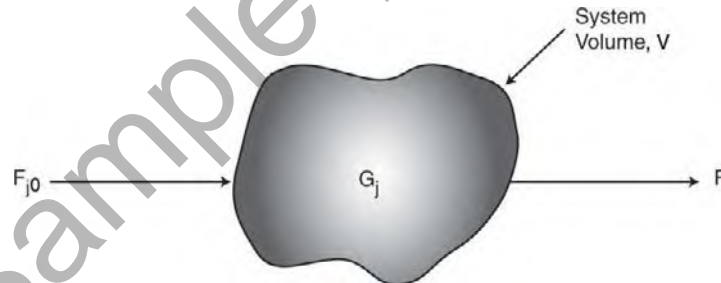


Figure 1-3 Mole balance on species  $j$  in a system volume,  $V$ .

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

$$\left[ \begin{array}{c} \text{Rate of flow} \\ \text{of } j \text{ into} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] - \left[ \begin{array}{c} \text{Rate of flow} \\ \text{of } j \text{ out of} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] + \left[ \begin{array}{c} \text{Rate of generation} \\ \text{of } j \text{ by chemical} \\ \text{reaction within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] = \left[ \begin{array}{c} \text{Rate of} \\ \text{accumulation} \\ \text{of } j \text{ within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right]$$

Mole balance

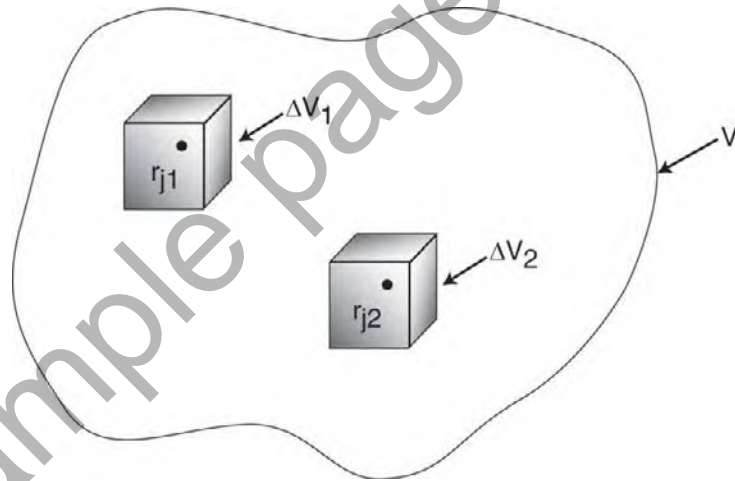
$$\begin{array}{cccccc} \mathbf{In} & - & \mathbf{Out} & + & \mathbf{Generation} & = & \mathbf{Accumulation} \\ F_{j0} & - & F_j & + & G_j & = & \frac{dN_j}{dt} \end{array} \quad (1-3)$$

In this equation,  $N_j$  represents the number of moles of species  $j$  in the system at time  $t$ . If all the system variables (e.g., temperature, catalytic activity, and 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  $j$ ,  $r_j$ .

$$G_j = r_j \cdot V$$

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

Now suppose that the rate of formation of species  $j$  for the reaction varies with 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,  $\Delta V_2$ , and so on (Figure 1-4).



**Figure 1-4** Dividing up the system volume,  $V$ .

The rate of generation,  $\Delta G_{j1}$ , in terms of  $r_{j1}$  and 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 and reaction conditions (e.g., concentration, temperature) can have different values at different locations in the reactor volume.

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

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt} \quad (1-3)$$

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 into products.

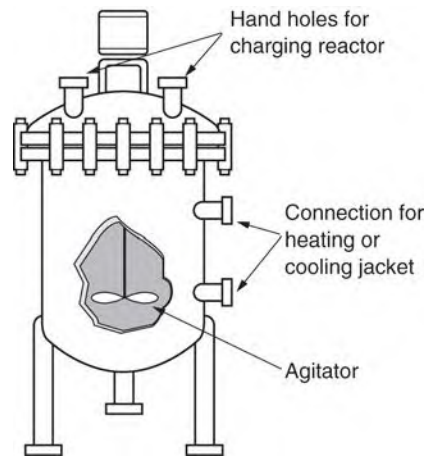
### 1.3 Batch Reactors (BRs)

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 (see Figure 1-5(a)). 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, the variability of products from batch to batch, and the difficulty of large-scale production (see Industrial Reactor Photos in *Professional Reference Shelf* [PRS] on the CRE Web sites, [www.umich.edu/~elements/5e/index.html](http://www.umich.edu/~elements/5e/index.html)). Also see <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/menu.html>.



Reference Shelf



**Figure 1-5(a)** Simple batch homogeneous batch reactor (BR). [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]



**Figure 1-5(b)** Batch reactor mixing patterns. Further descriptions and photos of the batch reactors can be found in both the *Visual Encyclopedia of Equipment* and in the *Professional Reference Shelf* on the CRE Web site.

Also see <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/Batch/Batch.html>.

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 (Figure 1-5(b)) so that there is no variation in the rate of reaction throughout the reactor volume, we can take  $r_j$  out of the integral, integrate, and write the mole balance in the form

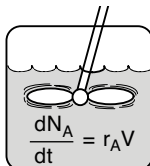
Perfect mixing

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

Let's consider the isomerization of species A in a batch reactor



As the reaction proceeds, the number of moles of A decreases and the number of moles of B increases, as shown in Figure 1-6.



Batch Reactor

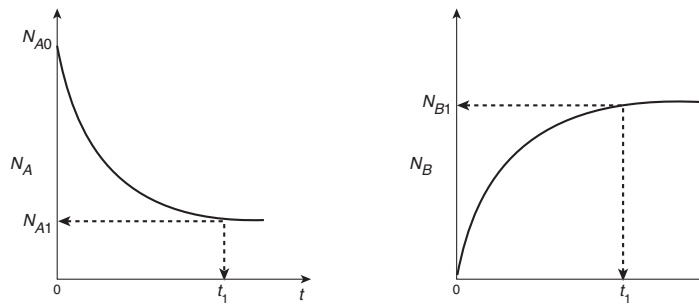


Figure 1-6 Mole-time trajectories.

We might ask what time,  $t_1$ , is necessary to reduce the initial number of moles from  $N_{A0}$  to a final desired number  $N_{A1}$ . Applying Equation (1-5) to the isomerization

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

rearranging,

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

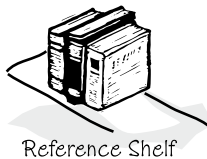
and integrating with limits that at  $t = 0$ , then  $N_A = N_{A0}$ , and at  $t = t_1$ , then  $N_A = N_{A1}$ , we obtain

$$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V} \quad (1-6)$$

This equation is the integral form of the mole balance on a batch reactor. It gives the time,  $t_1$ , necessary to reduce the number of moles from  $N_{A0}$  to  $N_{A1}$  and also to form  $N_{B1}$  moles of B.

## 1.4 Continuous-Flow Reactors

Continuous-flow reactors are almost always operated at steady state. We will consider three types: the *continuous-stirred tank reactor* (CSTR), the *plug-flow reactor* (PFR), and the *packed-bed reactor* (PBR). Detailed physical descriptions of these reactors can be found in both the *Professional Reference Shelf* (PRS) for Chapter 1 and in the *Visual Encyclopedia of Equipment*, <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/CSTR/CSTR.html>, and on the CRE Web site.



Reference Shelf

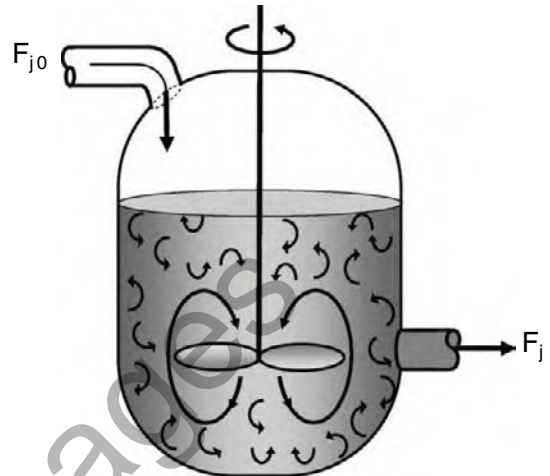
### 1.4.1 Continuous-Stirred Tank Reactor (CSTR)

A type of reactor commonly used in industrial processing is the stirred tank operated continuously (Figure 1-7). It is referred to as the *continuous-stirred tank reactor* (CSTR) or *vat*, or *backmix reactor*, and is primarily used for

What is a CSTR used for?



**Figure 1-7(a)** CSTR/batch reactor. (Photo courtesy of Pfaudler, Inc.)



**Figure 1-7(b)** CSTR mixing patterns.

Also see <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/CSTR/CSTR.html>.

*liquid-phase reactions*. It is normally operated **at steady state** and is assumed to be **perfectly mixed**; consequently, there is no time dependence or position dependence of the temperature, concentration, or reaction rate inside the CSTR. That is, every variable is the same at every point inside the reactor. Because 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 of nonideal mixing is discussed on the Web site in PDF Chapters 16, 17, and 18 on nonideal reactors.

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),

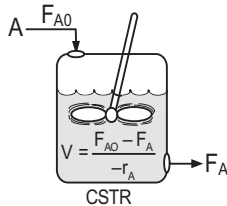
$$\frac{dN_j}{dt} = 0$$

in which there are no spatial variations in the rate of reaction (i.e., perfect mixing),

The ideal CSTR is assumed to be perfectly mixed.

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

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



$$V = \frac{F_{j0} - F_j}{-r_j} \quad (1-7)$$

The CSTR design equation gives the reactor volume  $V$  necessary to reduce the entering molar flow rate of species  $j$  from  $F_{j0}$  to the exit molar flow rate  $F_j$ , when species  $j$  is disappearing at a rate of  $-r_j$ . We note that the CSTR is modeled such that the conditions in the exit stream (e.g., concentration and 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  $v$

$$F_j = C_j \cdot v$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{volume}}{\text{time}} \quad (1-8)$$

Similarly, for the entrance molar flow rate we have  $F_{j0} = C_{j0} \cdot v_0$ . Consequently, we can substitute for  $F_{j0}$  and  $F_j$  into Equation (1-7) to write a balance on species A as

$$V = \frac{v_0 C_{A0} - v C_A}{-r_A} \quad (1-9)$$

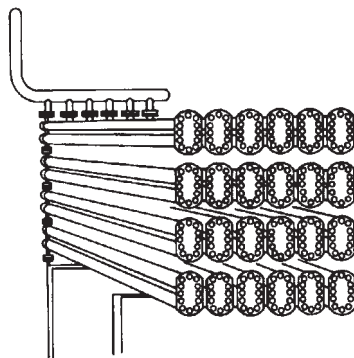
The ideal CSTR mole balance equation is an algebraic equation, not a differential equation.

### 1.4.2 Tubular Reactor

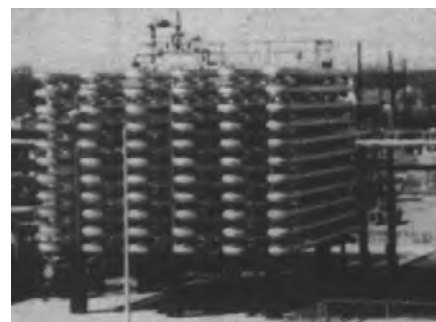
When is a tubular reactor most often used?

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. Tubular reactors are used most often for *gas-phase reactions*. A schematic and a photograph of industrial tubular reactors are shown in Figure 1-8.

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 (cf. Equation 3-2), will *also* vary axially. For the purposes of the material presented here, we consider systems in which the flow field may be modeled by that of a plug-flow profile (e.g., uniform velocity



**Figure 1-8(a)** Tubular reactor schematic. 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.]

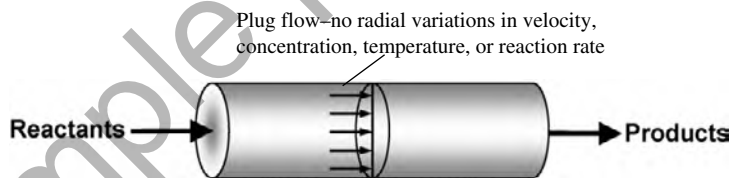


**Figure 1-8(b)** Tubular reactor photo. Tubular reactor for production of Dimersol G. (Photo courtesy of Editions Techniq Institut Français du Pétrole.)

Also see <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/PFR/PFR.html>.

as in turbulent flow), as shown in Figure 1-9. That is, there is no radial variation in reaction rate, and the reactor is referred to as a *plug-flow reactor* (PFR). (The laminar-flow reactor is discussed in PDF Chapters 16 through 18 and on the Web site, along with a discussion of nonideal reactors.)

Also see PRS and  
Visual Encyclopedia of  
Equipment.



**Figure 1-9** Plug-flow tubular reactor.

The general mole balance equation is given by Equation (1-4)

$$F_{j0} - F_j + \int_0^V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

The equation we will use to design PFRs at steady state can be developed in two ways: (1) directly from Equation (1-4) by differentiating with respect to volume  $V$ , and then rearranging the result or (2) from a mole balance on species  $j$  in a differential segment of the reactor volume  $\Delta V$ . Let's choose the second way to arrive at the differential form of the PFR mole balance. The differential volume,  $\Delta V$ , shown in Figure 1-10, will be chosen sufficiently small such that there are no spatial variations in reaction rate within this volume. Thus the generation term,  $\Delta G_j$ , is

$$\Delta G_j = \int_0^{\Delta V} r_j dV = r_j \Delta V$$



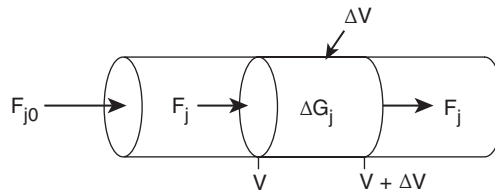


Figure 1-10 Mole balance on species  $j$  in volume  $\Delta V$ .

$\begin{bmatrix} \text{Molar flow} \\ \text{rate of species } j \\ \text{In at } V \\ \text{moles/time} \end{bmatrix}$	-	$\begin{bmatrix} \text{Molar flow} \\ \text{rate of species } j \\ \text{Out at } (V + \Delta V) \\ \text{moles/time} \end{bmatrix}$	+	$\begin{bmatrix} \text{Molar rate of} \\ \text{Generation} \\ \text{of species } j \\ \text{within } \Delta V \\ \text{moles/time} \end{bmatrix}$	=	$\begin{bmatrix} \text{Molar rate of} \\ \text{Accumulation} \\ \text{of species } j \\ \text{within } \Delta V \\ \text{moles/time} \end{bmatrix}$
<b>In</b>		<b>Out</b>		<b>Generation</b>		<b>Accumulation</b>
$F_{j _V}$		$F_{j _{V+\Delta V}}$		$+ r_j \Delta V$		$= 0$ (1-10)

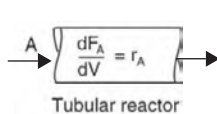
Dividing by  $\Delta V$  and rearranging

$$\left[ \frac{F_{j|_{V+\Delta V}} - F_{j|_V}}{\Delta V} \right] = r_j$$

the term in brackets resembles the definition of a derivative

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

Taking the limit as  $\Delta V$  approaches zero, we obtain the differential form of steady state mole balance on a PFR



$$\frac{dF_j}{dV} = r_j \quad (1-11)$$

We could have made the cylindrical reactor on which we carried out our mole balance an irregularly shaped reactor, such as the one shown in Figure 1-11 for reactant species A. However, we see that by applying Equation (1-10), the result would yield the same equation (i.e., Equation (1-11)). For species A, the mole balance is

$$\frac{dF_A}{dV} = r_A \quad (1-12)$$

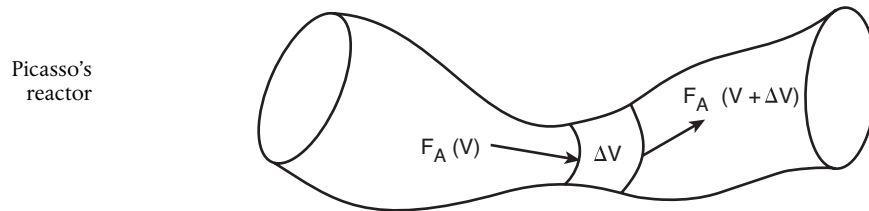


Figure 1-11 Pablo Picasso's reactor.

Consequently, we see that Equation (1-11) 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 1-11 unless it were designed by Pablo Picasso or one of his followers.

The conclusion drawn from the application of the design equation to Picasso's reactor is an important one: the degree of completion of a reaction achieved in an ideal plug-flow reactor (PFR) does not depend on its shape, only on its total volume.

Again consider the isomerization  $A \rightarrow B$ , this time in a PFR. As the reactants proceed down the reactor, A is consumed by chemical reaction and B is produced. Consequently, the molar flow rate  $F_A$  decreases, while  $F_B$  increases as the reactor volume  $V$  increases, as shown in Figure 1-12.

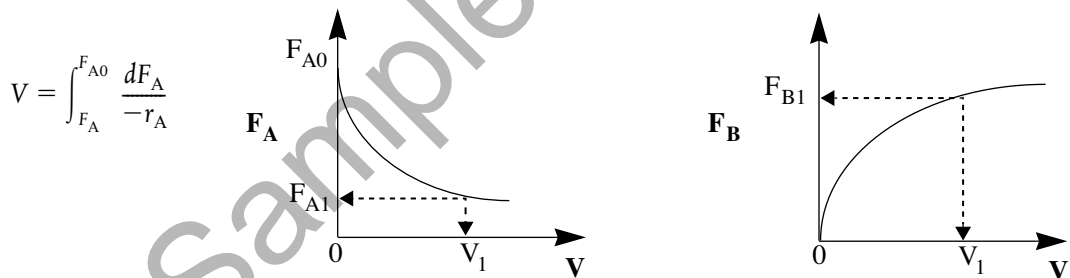


Figure 1-12 Profiles of molar flow rates in a PFR.

We now ask, "What is the reactor volume  $V_1$  necessary to reduce the entering molar flow rate of A from  $F_{A0}$  to  $F_{A1}$ ?" Rearranging Equation (1-12) in the form

$$dV = \frac{dF_A}{r_A}$$

and integrating with limits at  $V = 0$ , then  $F_A = F_{A0}$ , and at  $V = V_1$ , then  $F_A = F_{A1}$

$$V_1 = \int_{F_{A0}}^{F_{A1}} \frac{dF_A}{r_A} = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A} \quad (1-13)$$

$V_1$  is the volume necessary to reduce the entering molar flow rate  $F_{A0}$  to some specified value  $F_{A1}$  and also the volume necessary to produce a molar flow rate of B of  $F_{B1}$ .

### 1.4.3 Packed-Bed Reactor (PBR)

The principal difference between reactor design calculations involving homogeneous reactions and those involving fluid-solid heterogeneous reactions is that for the latter, the reaction takes place on the surface of the catalyst (see Figure 10-5). The greater the mass of a given catalyst, the greater the reactive surface area. Consequently, 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 species A is defined as

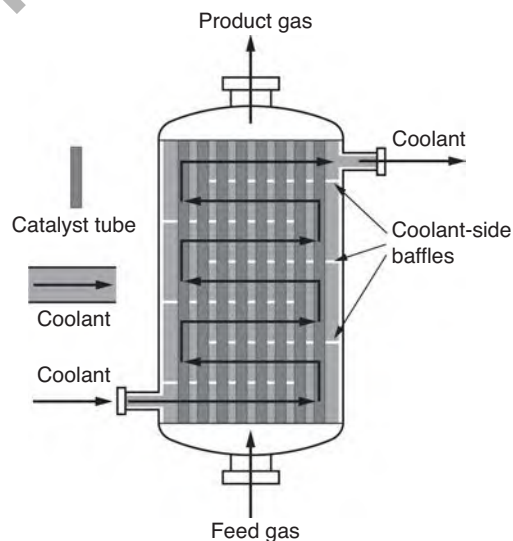
$$-r'_A = \text{mol A reacted} / (\text{time} \times \text{mass of catalyst})$$

The mass of solid catalyst is used because the amount of catalyst is what is important to the rate of product formation. We note that by multiplying the heterogeneous reaction rate,  $-r'_A$ , by the bulk catalyst density,  $\rho_b$   $\left(\frac{\text{mass}}{\text{volume}}\right)$ , we can obtain the homogeneous reaction rate,  $-r_A$

$$-r_A = \rho_b (-r'_A)$$

$$\left(\frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}\right) = \left(\frac{\text{g}}{\text{dm}^3}\right) \left(\frac{\text{mol}}{\text{g} \cdot \text{s}}\right)$$

The reactor volume that contains the catalyst is of secondary significance. Figure 1-13 shows a schematic of an industrial catalytic reactor with vertical tubes packed with solid catalyst.



**Figure 1-13** Longitudinal catalytic packed-bed reactor. [From Cropley, *American Institute of Chemical Engineers*, 86(2), 34 (1990).

Also see <http://encyclopedia.che.engin.umich.edu/Pages/Reactors/PBR/PBR.html>.

PBR  
Mole Balance

In the three idealized types of reactors just discussed (the perfectly mixed batch reactor [BR], the plug-flow tubular reactor [PFR]), 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 (PBR) 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 (1-10) with the catalyst mass (i.e., weight) coordinate  $W$  (Figure 1-14).

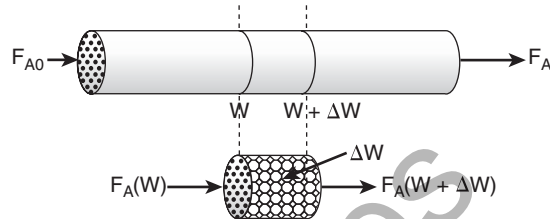


Figure 1-14 Packed-bed reactor schematic.

As with the PFR, the PBR is assumed to have 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

$$\begin{array}{rcccc} \text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\ F_{A|W} & - & F_{A|(W+\Delta W)} & + & r'_A \Delta W & = & 0 \end{array} \quad (1-14)$$

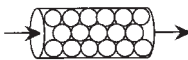
The dimensions of the generation term in Equation (1-14) are

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

which are, as expected, the same dimensions 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 the differential form of design equation for catalyst decay and pressure drop.

$$\boxed{\frac{dF_A}{dW} = r'_A} \quad (1-15)$$



When pressure drop through the reactor (see Section 5.5) and catalyst decay (see Section 10.7 in Chapter 10) are neglected, the integral form of the packed-catalyst-bed design equation can be used to calculate the catalyst weight

You can use the integral form **only** when there is no  $\Delta P$  and no catalyst decay.

$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r'_A} \quad (1-16)$$

$W$  is the catalyst weight necessary to reduce the entering molar flow rate of species A,  $F_{A0}$ , down to a molar flow rate  $F_A$ .