

Mole Balances 1

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

Socrates (470–399 B.C.)

The Wide Wide Wild World of Chemical Reaction Engineering

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.

How is a chemical
engineer different
from other
engineers?

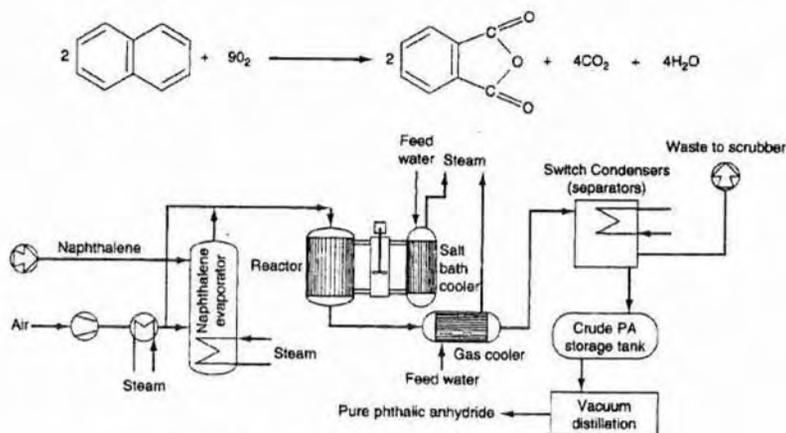
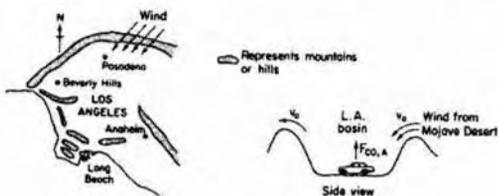
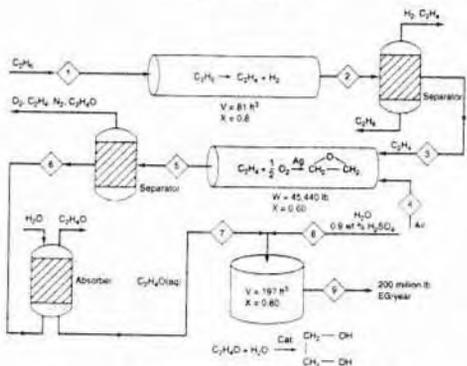


Figure 1-1 Manufacture of phthalic anhydride.

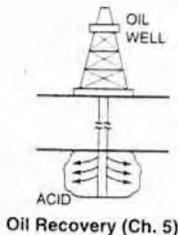
The Chemical Reaction Engineering (CRE) principles learned here can also be applied in areas such as waste treatment, microelectronics, nanoparticles and living systems in addition to the more traditional areas of the manufacture of chemicals and pharmaceuticals. Some of the examples that illustrate the wide application of CRE principles are shown in Figure 1-2. These examples include modeling smog in the L.A. basin (Chapter 1), the digestive system of a hippopotamus (Chapter 2), and molecular CRE (Chapter 3). Also shown is the manufacture of ethylene glycol (antifreeze), where three of the most common types of industrial reactors are used (Chapter 4). The CD-ROM describes the use of wetlands to degrade toxic chemicals (Chapter 4). Other examples shown are the solid-liquid kinetics of acid-rock interactions to improve oil recovery (Chapter 5); pharmacokinetics of cobra bites and of drug delivery (Chapter 6); free radical scavengers used in the design of motor oils (Chapter 7), enzyme kinetics, and pharmacokinetics (Chapter 7); heat effects, runaway reactions, and plant safety (Chapters 8 and 9); increasing the octane number of gasoline (Chapter 10); and the manufacture of computer chips (Chapter 12).



Smog (Ch. 1, Ch. 7)



Chemical Plant for Ethylene Glycol (Ch. 4)

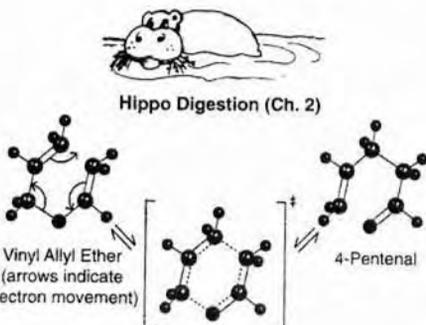


Oil Recovery (Ch. 5)



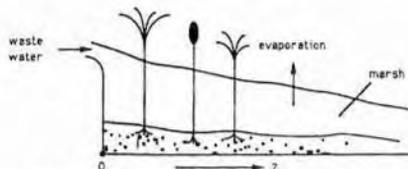
Effective Lubricant Design Scavenging Free Radicals Lubricant Design (Ch. 7)

Pharmacokinetics of Cobra Bites Multiple Reactions in a Batch (Body) Reactor Cobra Bites (Ch. 6)

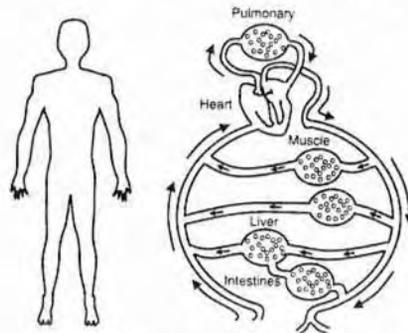


Hippo Digestion (Ch. 2)

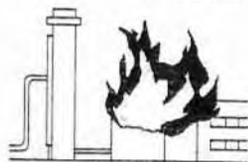
Transition State (dashed lines show transition state electron delocalization) Molecular CRE (Ch. 3)



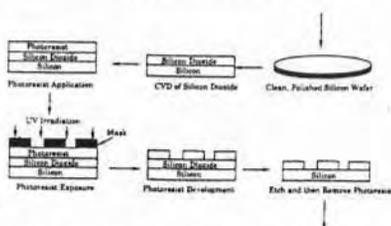
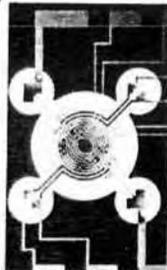
Wetlands Remediation of Pollutants (Ch. 4)



Pharmacokinetics (Ch. 7)



Nitroaniline Plant Explosion Exothermic Reactions That Run Away Plant Safety (Ch.8, Ch.9)



Microelectronic Fabrication Steps (Ch. 10, Ch. 12)

Figure 1-2 The wide world of applications of CRE.

Overview—Chapter 1. This chapter develops the first building block of chemical reaction engineering, mole balances, that 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, and apply the general mole balance equation to the four most common types of industrial reactors.

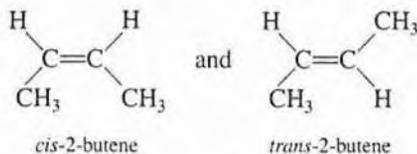
Before entering into discussions of the conditions that affect chemical reaction rate mechanisms and reactor design, it is necessary to account for the various chemical species entering and leaving a reaction system. This accounting process is achieved through overall mole balances on individual species 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, $-r_A$, and discussing the earlier difficulties of properly defining the chemical reaction rate, 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), tubular (PFR), and packed bed (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 nicotine (a bad tobacco alkaloid) 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 in 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.

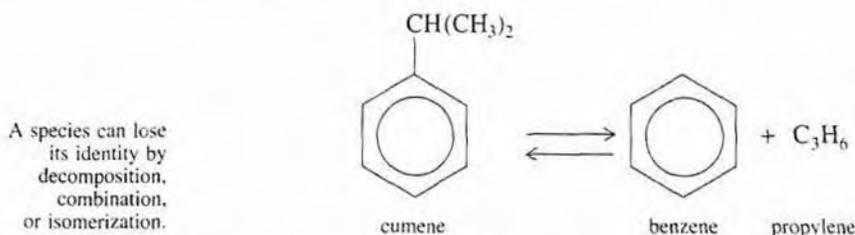


As a consequence of the different configurations, these two isomers display different chemical and physical properties. Therefore, we consider them as two different species even though each has the same number of atoms of each element.

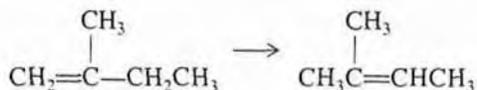
When has a chemical reaction taken place?

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 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,



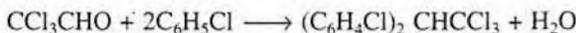
the cumene molecule has lost its identity (i.e., disappeared) by breaking its bonds to form these molecules. A second way that a molecule may lose its species identity is through *combination* with another molecule or atom. In the example above, the propylene molecule would lose its species identity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



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



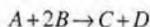
Letting the symbol A represent chloral, B be chlorobenzene, C be DDT, and D be H_2O we obtain



The numerical value of the rate of disappearance of reactant A, $-r_A$, is a positive number (e.g., $-r_A = 4 \text{ mol A/dm}^3\cdot\text{s}$).

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 ($\text{mol/dm}^3\cdot\text{s}$).



The convention

$$\begin{aligned} -r_A &= 4 \text{ mol A/dm}^3\cdot\text{s} \\ r_A &= -4 \text{ mol A/dm}^3\cdot\text{s} \\ -r_B &= 8 \text{ mol B/dm}^3\cdot\text{s} \\ r_B &= -8 \text{ mol B/dm}^3\cdot\text{s} \\ r_C &= 4 \text{ mol C/dm}^3\cdot\text{s} \end{aligned}$$

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 (e.g., $r_A = -4 \text{ moles A/dm}^3\cdot\text{s}$). If species j is a product, then r_j will be a positive number (e.g., $r_C = 4 \text{ moles C/dm}^3\cdot\text{s}$). In Chapter 3, we will delineate the prescribed relationship between the rate of formation of one species, r_j (e.g., $\text{DDT}[C]$), and the rate of disappearance of another species, $-r_i$ (e.g., $\text{chlorobenzene}[B]$), 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.

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 ($\text{mol/s}\cdot\text{g catalyst}$).

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 deter-

mined 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., mol/s-dm³), the investigators then defined and reported the chemical reaction rate as

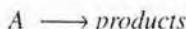
$$r_A = \frac{dC_A}{dt} \quad (1-1)$$

However this "definition" is wrong! It is simply a mole balance that is only valid for a constant volume batch system. Equation (1-1) will not apply to any continuous-flow reactor operated at steady state, such as the tank (CSTR) reactor where the concentration does not vary from day to day (i.e., the concentration is not a function of time). For amplification on this point, see the section "Is Sodium Hydroxide Reacting?" in the Summary Notes for Chapter 1 on the CD-ROM or on the web.

In conclusion, 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 (i.e., rate law) for r_j is an algebraic equation that is 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. The rate equation is independent of the type of reactor (e.g., batch or continuous flow) in which the reaction is carried out. 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.¹ For example, the algebraic form of the rate law for $-r_A$ for the reaction



may be a linear function of concentration,

$$-r_A = kC_A$$

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

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

or

¹ 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).



Summary Notes

Definition of r_j

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

What is $-r_A$ a function of?

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. 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).

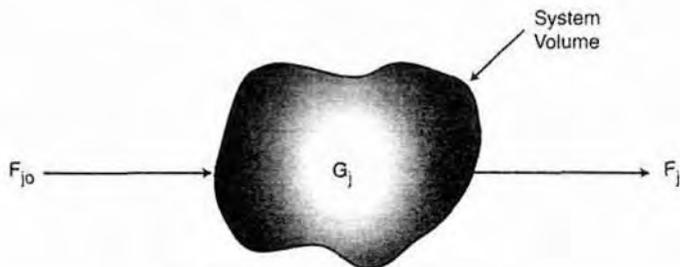


Figure 1-3 Balance on system volume.

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	In		Out		+ Generation		= Accumulation
	F_{j0}	-	F_j		$+ G_j$	=	$\frac{dN_j}{dt}$ (1-3)

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, ΔV_1 , within which the rate is uniform: similarly, the reaction rate has a value r_{j2} at location 2 and an associated volume, ΔV_2 (Figure 1-4).

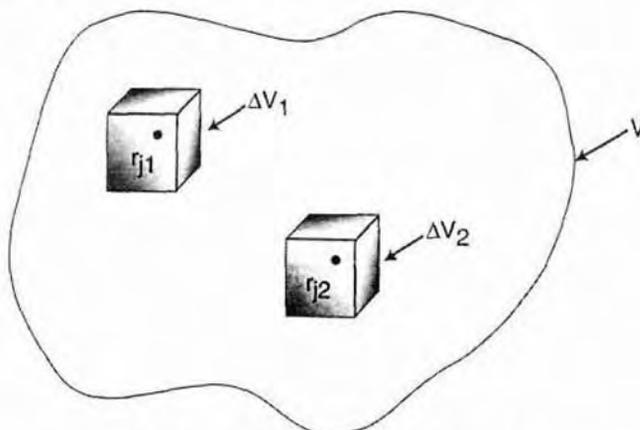


Figure 1-4 Dividing up the system volume, V .

The rate of generation, ΔG_{j1} , in terms of r_{j1} and subvolume ΔV_1 , is

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

Similar expressions can be written for ΔG_{j2} and the other system subvolumes, ΔV_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.

We now replace G_j in Equation (1-3)

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

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

When is a batch reactor used?



Reference Shelf

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 1-5[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 Professional Reference Shelf [PRS]).

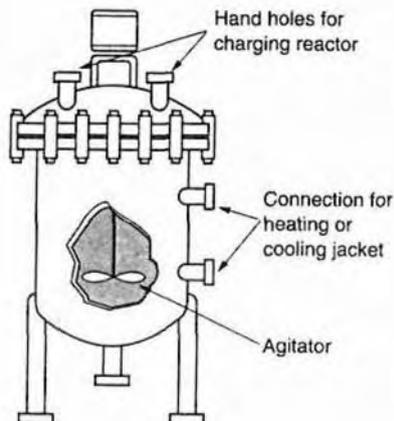


Figure 1-5(a) Simple batch homogeneous reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

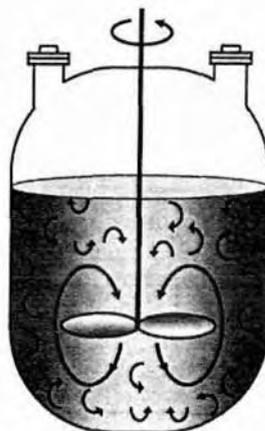


Figure 1-5(b) Batch reactor mixing patterns. Further descriptions and photos of the batch reactors can be found in both the *Visual Encyclopedia of Equipment* and in the *Professional Reference Shelf* on the CD-ROM.

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

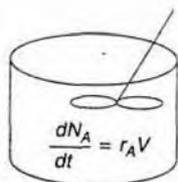
$$\boxed{\frac{dN_j}{dt} = r_j V} \quad (1-5)$$

Perfect mixing

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.



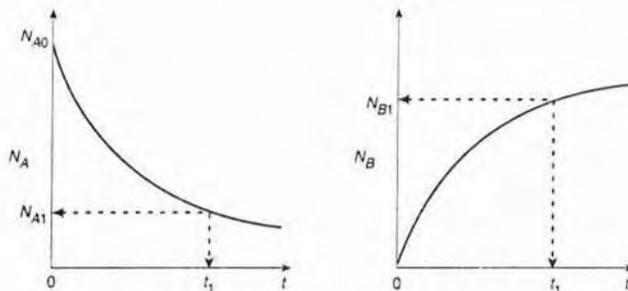


Figure 1-6 Mole-time trajectories.

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 descriptions of these reactors can be found in both the Professional Reference Shelf (PRS) for Chapter 1 and in the *Visual Encyclopedia of Equipment* on the CD-ROM.

1.4.1 Continuous-Stirred Tank Reactor

A type of reactor used commonly 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 used primarily for liquid

What is a CSTR used for?

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, the concentration, or the 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 in Chapters 13 and 14.

What reaction systems use a CSTR?

The ideal CSTR is assumed to be perfectly mixed.

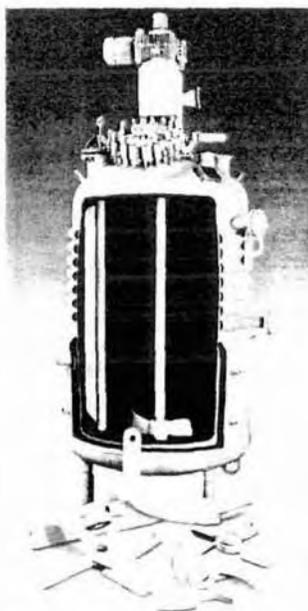


Figure 1-7(a) CSTR/batch reactor. [Courtesy of Pfaudler, Inc.]

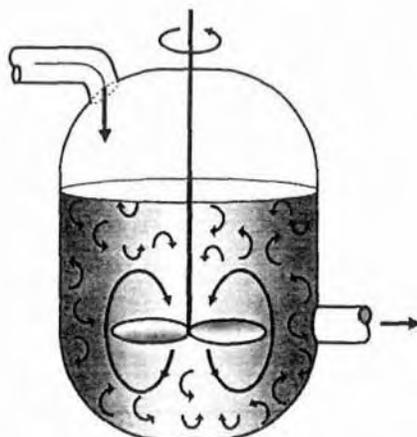


Figure 1-7(b) CSTR mixing patterns. Also see the *Visual Encyclopedia of Equipment* on the CD-ROM.

When the general mole balance equation

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

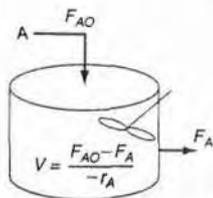
is applied to a CSTR operated at steady state (i.e., conditions do not change with time),

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

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

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

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 flow rate of species j , from F_{j0} to the exit 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, 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 :

$$F_j = C_j \cdot v$$

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

Consequently, we could combine Equations (1-7) and (1-8) to write a balance on species A as

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

1.4.2 Tubular Reactor

When is 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, 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 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 Chapter 13.)

Also see PRS and
Visual Encyclopedia of Equipment.

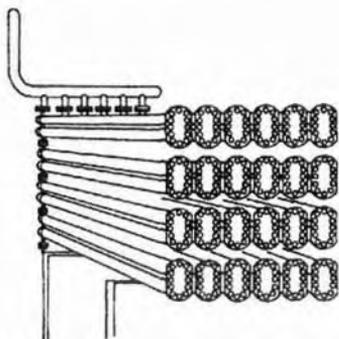


Figure 1-8(a) Tubular reactor schematic. Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

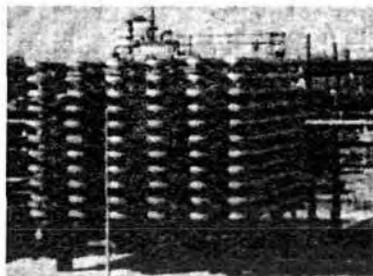


Figure 1-8(b) Tubular reactor photo. Tubular reactor for production of Dimersol G. [Photo Courtesy of Editions Techniq Institute Francois du Petrol].

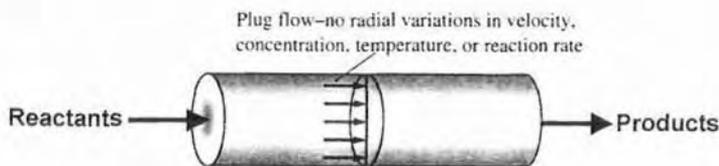


Figure 1-9 Plug-flow tubular reactor.

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

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

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 , or (2) from a mole balance on species j in a differential segment of the reactor volume ΔV . Let's choose the second way to arrive at the differential form of the PFR mole balance. The differential volume, ΔV , 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, ΔG_j , is

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

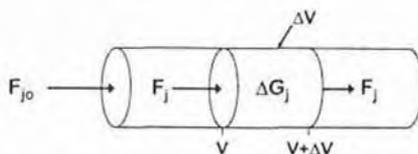


Figure 1-10 Mole balance on species j in volume ΔV .

$$\begin{array}{r}
 \left[\begin{array}{c} \text{Molar flow} \\ \text{rate of species } j \\ \text{In at } V \end{array} \right] - \left[\begin{array}{c} \text{Molar flow} \\ \text{rate of species } j \\ \text{Out at } (V+\Delta V) \end{array} \right] + \left[\begin{array}{c} \text{Molar rate of} \\ \text{Generation} \\ \text{of species } j \\ \text{within } \Delta V \end{array} \right] = \left[\begin{array}{c} \text{Molar rate of} \\ \text{Accumulation} \\ \text{of species } j \\ \text{within } \Delta V \end{array} \right] \\
 \text{In} \quad - \quad \text{Out} \quad + \quad \text{Generation} = \text{Accumulation} \\
 F_{j|V} \quad - \quad F_{j|V+\Delta V} \quad + \quad r_j \Delta V = 0 \quad (1-10)
 \end{array}$$

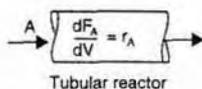
Dividing by ΔV and rearranging

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

the term in brackets resembles the definition of 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 ΔV approaches zero, we obtain the differential form of steady state mole balance on a PFR.



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

We could have made the cylindrical reactor on which we carried out our mole balance an irregular shape reactor, such as the one shown in Figure 1-11 for reactant species A.

Picasso's reactor

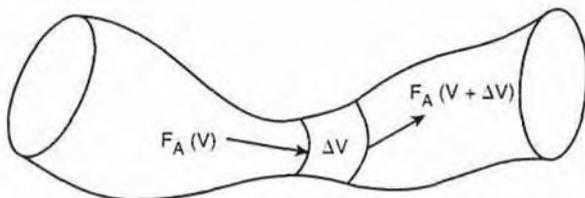


Figure 1-11 Pablo Picasso's reactor.

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

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

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 Figure 1-11 unless it were designed by Pablo Picasso. 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 of A decreases and that of B increases, as shown in Figure 1-12.

$$V = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r_A}$$

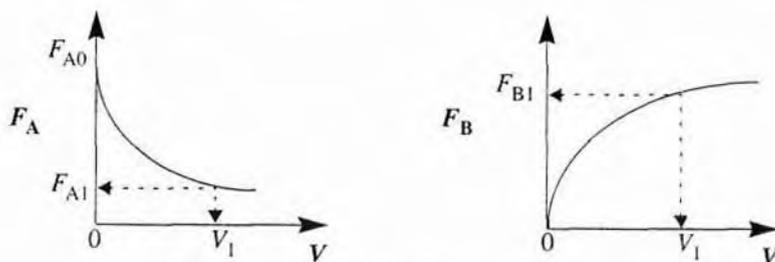


Figure 1-12 Profiles of molar flow rates in a PFR.

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

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. 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 substance A is defined as

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

The mass of solid catalyst is used because the amount of the catalyst is what is important to the rate of product formation. 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 catalyst.

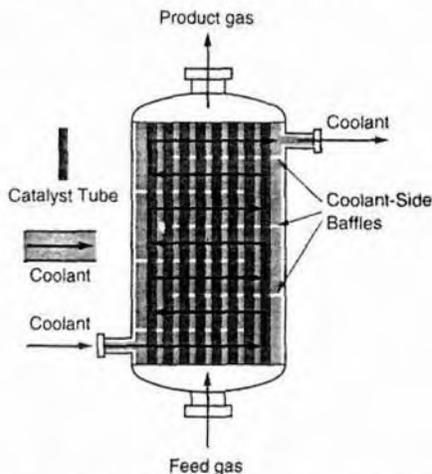


Figure 1-13 Longitudinal catalytic packed-bed reactor. [From Cropley, American Institute of Chemical Engineers, 86(2), 34 (1990). Reproduced with permission of the American Institute of Chemical Engineers, Copyright © 1990 AIChE. All rights reserved.]

In the three idealized types of reactors just discussed (the perfectly mixed batch reactor, 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 weight coordinate W (Figure 1-14).

PBR
Mole Balance

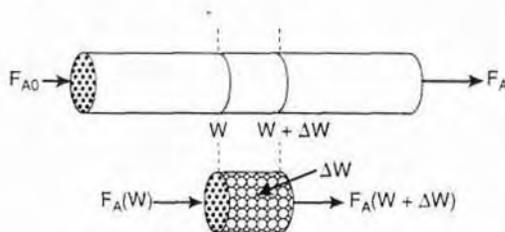


Figure 1-14 Packed-bed reactor schematic.