

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

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.

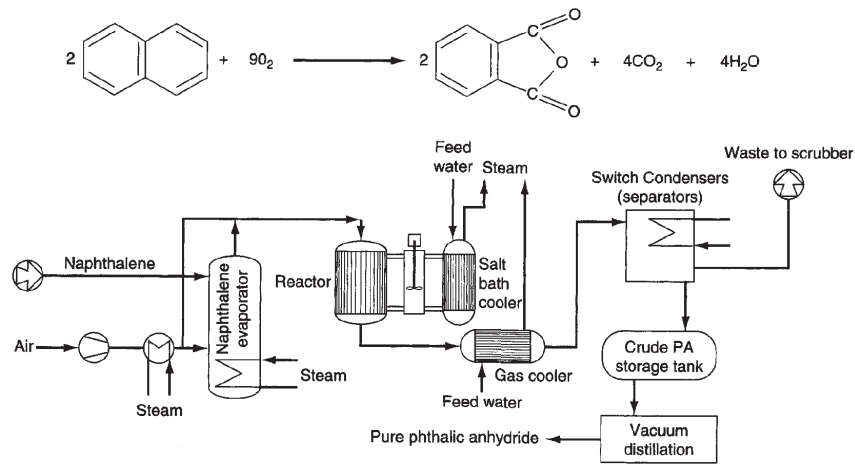
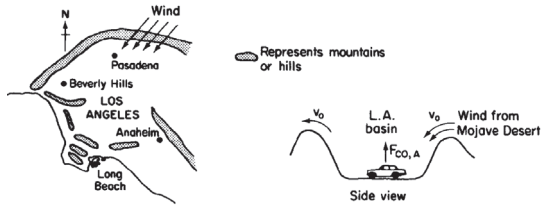


Figure 1-1 Manufacture of phthalic anhydride.

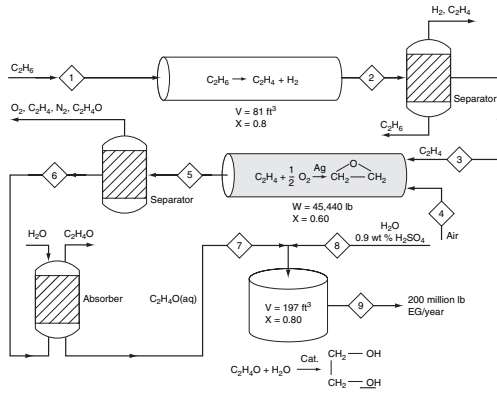
The Chemical Reaction Engineering (CRE) principles learned here can also be applied in areas such as waste treatment, microelectronics, nanoparticles and living systems in addition to the more traditional areas of the manufacture of chemicals and pharmaceuticals. Some of the examples that illustrate 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).



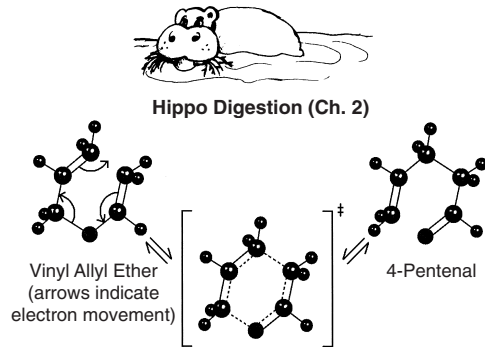
Sec. 1.1 The Rate of Reaction, $-r_A$



Smog (Ch. 1, Ch. 7)



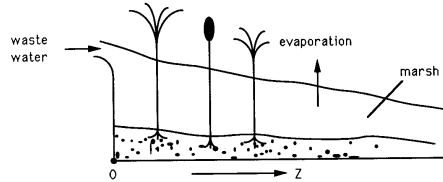
Chemical Plant for Ethylene Glycol (Ch. 4)



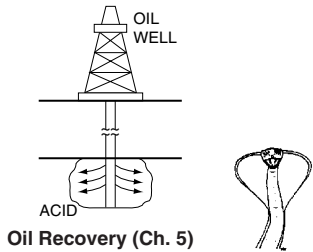
Hippo Digestion (Ch. 2)

Transition State (dashed lines show transition state electron delocalization)

Molecular CRE (Ch. 3)



Wetlands Remediation of Pollutants (Ch. 4)

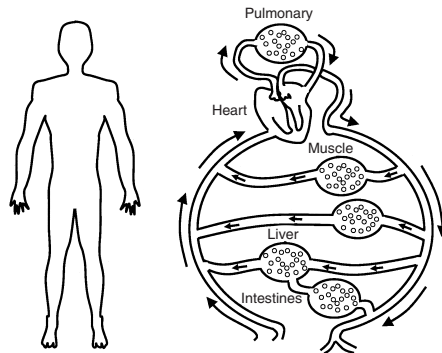


Oil Recovery (Ch. 5)

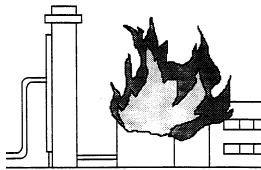


Lubricant Design (Ch. 7)

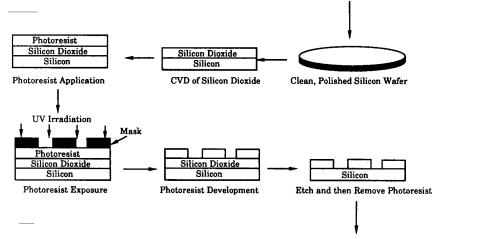
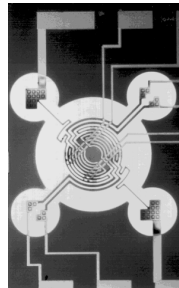
Pharmacokinetics of Cobra Bites Multiple Reactions in a Batch (Body) Reactor Cobra Bites (Ch. 6)



Pharmacokinetics (Ch. 7)



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



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

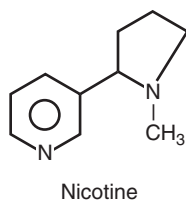
Figure 1-2 The wide world of applications of CRE.

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.

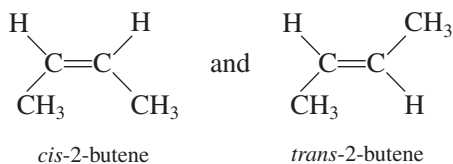
Before entering into discussions of the conditions that affect chemical reaction rate mechanisms and reactor design, it is necessary to account for the various chemical species entering and leaving a reaction system. This accounting process is achieved through overall mole balances on individual species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



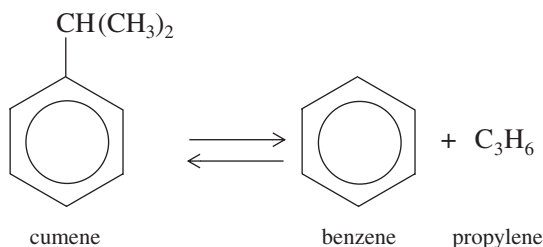
As a consequence of the different configurations, these two isomers display different chemical and physical properties. Therefore, we consider them as two different species even though each has the same number of atoms of each element.

When has a chemical reaction taken place?

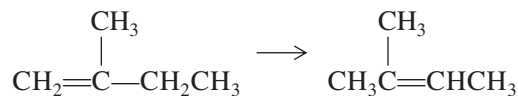
We say that a *chemical reaction* has taken place when a detectable number of molecules of one or more species have lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and/or by a change in structure or configuration of these atoms. In this classical 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,

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



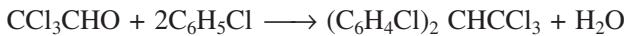
the cumene molecule has lost its identity (i.e., disappeared) by breaking its bonds to form these molecules. A second way that a molecule may lose its species identity is through *combination* with another molecule or atom. In the example above, the propylene molecule would lose its species identity 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 chloral and chlorobenzene to produce the insecticide DDT (dichlorodiphenyl-trichloroethane) in the presence of fuming sulfuric acid.



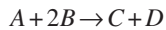
Letting the symbol A represent chloral, B be chlorobenzene, C be DDT, and D be H_2O we obtain



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., $\text{DDT}[\text{C}]$), and the rate of disappearance of another species, $-r_i$ (e.g., $\text{chlorobenzene}[\text{B}]$), 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

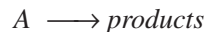
$$r_A = \frac{dC_A}{dt} \quad (1-1)$$

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).

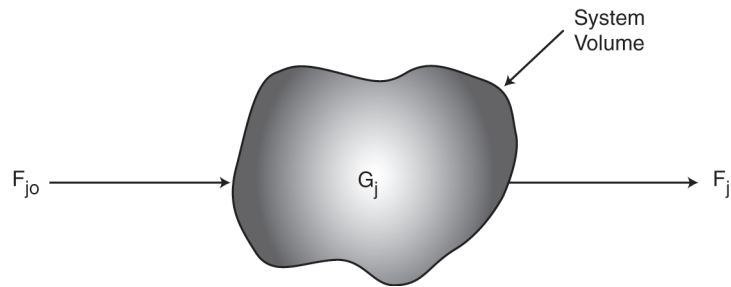


Figure 1-3 Balance on system volume.

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).

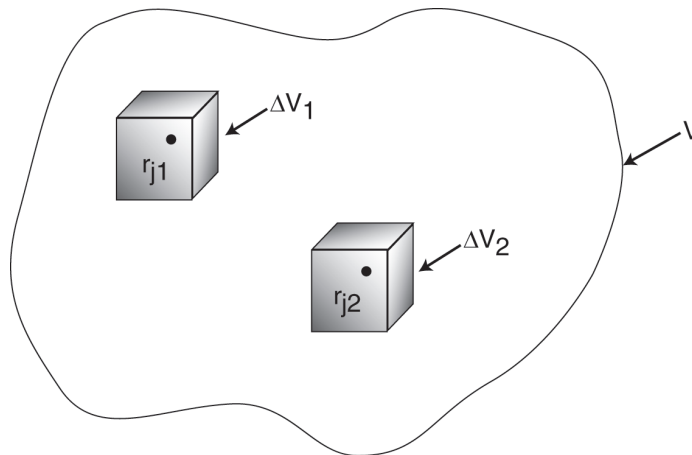


Figure 1-4 Dividing up the system volume, V .

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 .

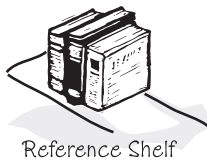
This is a basic equation for chemical reaction engineering.

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

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?



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]).

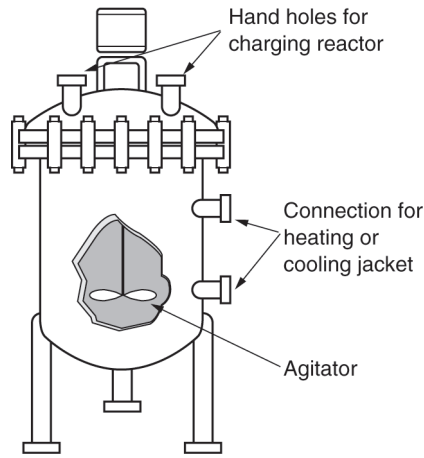


Figure 1-5(a) Simple batch homogeneous reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

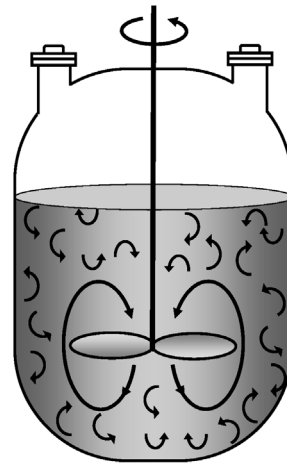
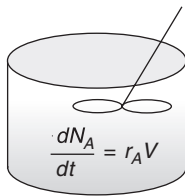


Figure 1-5(b) Batch reactor mixing patterns. Further descriptions and photos of the batch reactors can be found in both the *Visual Encyclopedia of Equipment* and in the *Professional Reference Shelf* on the CD-ROM.



Perfect mixing

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

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

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

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

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.

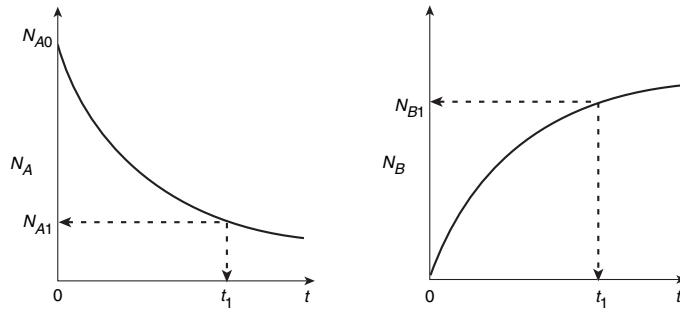


Figure 1-6 Mole-time trajectories.

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

What is a CSTR used for?

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

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.

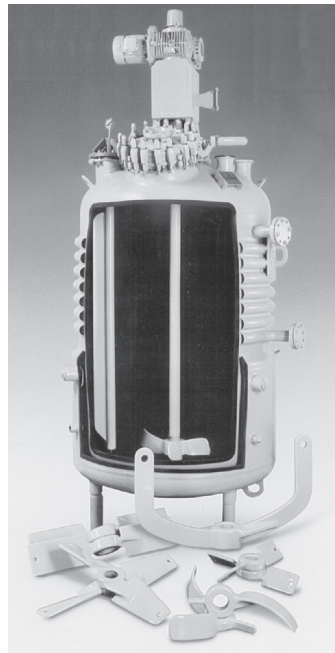


Figure 1-7(a) CSTR/batch reactor. [Courtesy of Pfaunder, Inc.]

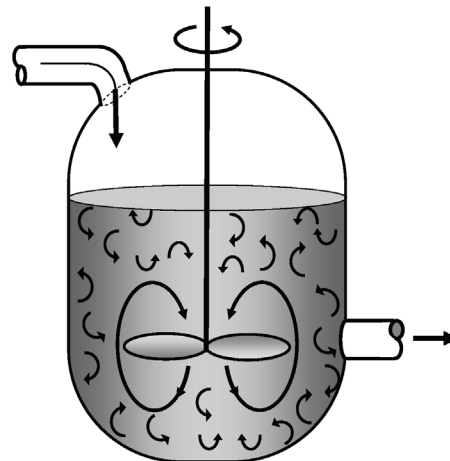


Figure 1-7(b) CSTR mixing patterns. Also see the *Visual Encyclopedia of Equipment* on the CD-ROM.

When the general mole balance equation

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

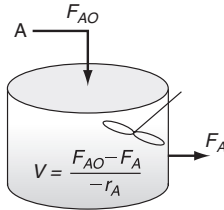
is applied to a CSTR operated at steady state (i.e., conditions do not change with time),

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

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:



$$V = \frac{F_{j0} - F_j}{-r_j} \tag{1-7}$$

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 :

$$F_j = C_j \cdot v$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{volume}}{\text{time}} \tag{1-8}$$

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

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

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.

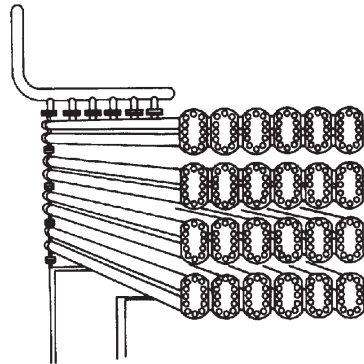


Figure 1-8(a) Tubular reactor schematic. Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

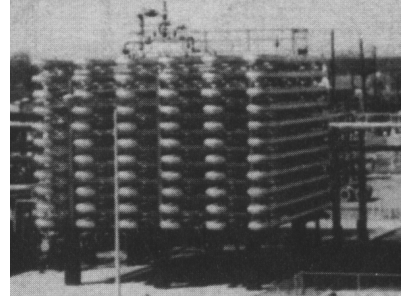


Figure 1-8(b) Tubular reactor photo. Tubular reactor for production of Dimersol G. [Photo Courtesy of Editions Techniq Institute Francois du Petrol].

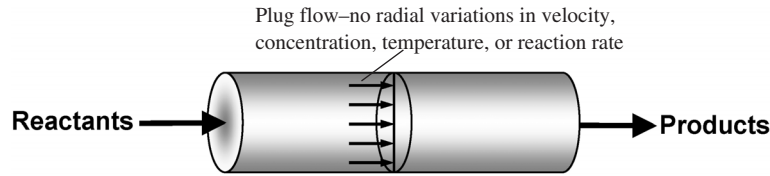


Figure 1-9 Plug-flow tubular reactor.

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

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

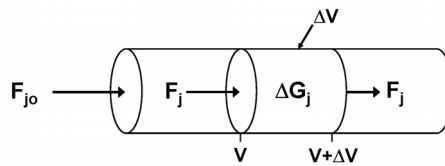


Figure 1-10 Mole balance on species j in volume ΔV .

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

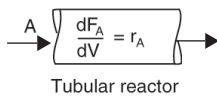
Dividing by ΔV and rearranging

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

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

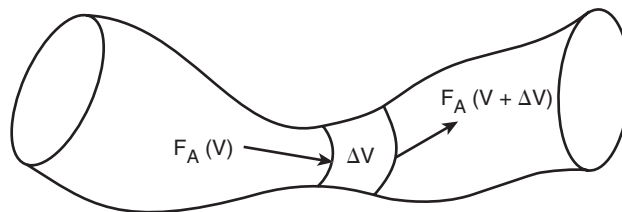


Figure 1-11 Pablo Picasso's reactor.

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.

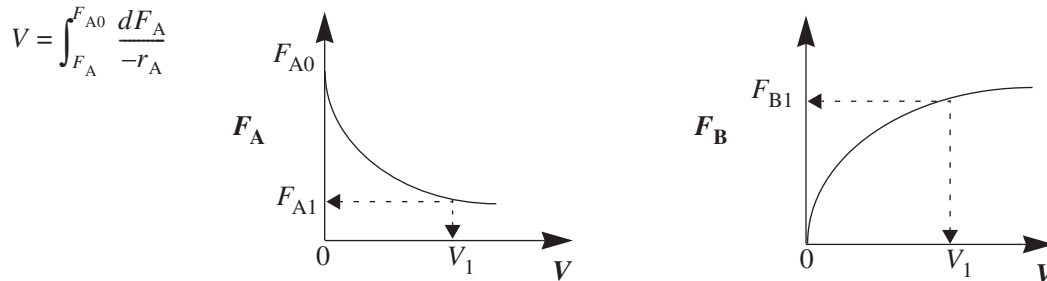


Figure 1-12 Profiles of molar flow rates in a PFR.

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.

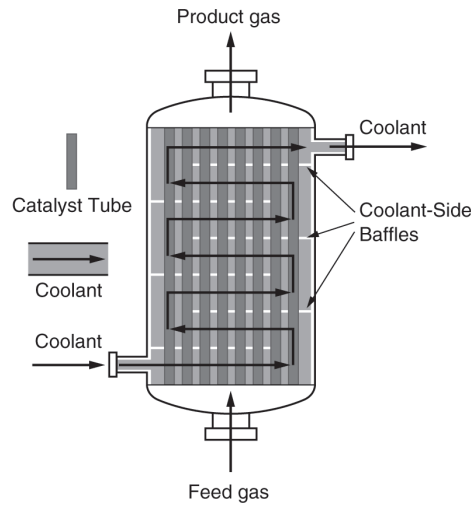


Figure 1-13 Longitudinal catalytic packed-bed reactor. [From Cropley, American Institute of Chemical Engineers, 86(2), 34 (1990). Reproduced with permission of the American Institute of Chemical Engineers, Copyright © 1990 AIChE. All rights reserved.]

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

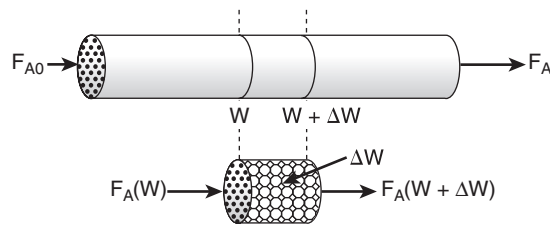


Figure 1-14 Packed-bed reactor schematic.

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 ΔW results in the equation

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

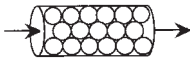
The dimensions of the generation term in Equation (1-14) are

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

which are, as expected, the same dimensions of the molar flow rate F_A . After dividing by ΔW 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.

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



When pressure drop through the reactor (see Section 4.5) 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.

Use integral form only for no ΔP and no catalyst decay.

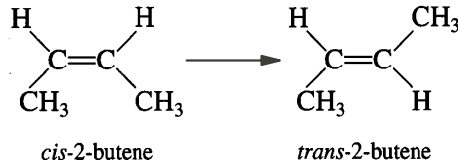
$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r'_A} \quad (1-16)$$

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

For some insight into things to come, consider the following example of how one can use the tubular reactor design Equation (1-11).

Example 1-1 How Large Is It?

Consider the liquid phase *cis* – *trans* isomerization of 2-butene



which we will write symbolically as

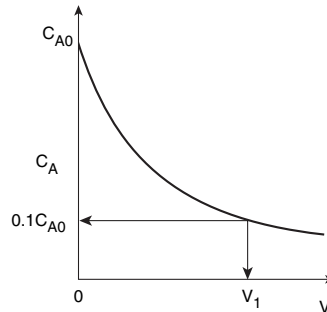


The first order ($-r_A = kC_A$) reaction is carried out in a tubular reactor in which the volumetric flow rate, v , is constant, i.e., $v = v_0$.

1. Sketch the concentration profile.
2. 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 .
3. Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm³/min (i.e., liters/min) and the specific reaction rate, k , is 0.23 min⁻¹.

Solution

1. Species A is consumed as we move down the reactor, and as a result, both the molar flow rate of A and the concentration of A will decrease as we move. Because the volumetric flow rate is constant, $v = v_0$, one can use Equation (1-8) to obtain the concentration of A, $C_A = F_A/v_0$, and then by comparison with Figure 1-12 plot the concentration of A as a function of reactor volume as shown in Figure E1-1.1.

**Figure E1-1.1** Concentration profile.

2. Derive an equation relating V , v_0 , k , C_{A0} , and C_A .

For a tubular reactor, the mole balance on species A ($j = A$) was shown to be given by Equation (1-11). Then for species A ($j = A$) results

$$\frac{dF_A}{dV} = r_A \quad (1-11)$$

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

$$-r_A = kC_A \quad (E1-1.1)$$

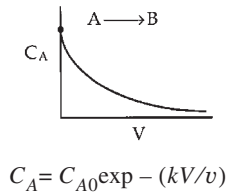
Because the volumetric flow rate, v , is constant ($v = v_0$), as it is for most liquid-phase reactions,

$$\frac{dF_A}{dV} = \frac{d(C_A v)}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \quad (E1-1.2)$$

Multiplying both sides of Equation (E1-1.2) by minus one and then substituting Equation (E1-1.1) yields

$$-\frac{v_0 dC_A}{dV} = -r_A = kC_A \quad (E1-1.3)$$

Reactor sizing



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 $C_A = C_{A0}$,

$$-\frac{v_0}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V dV \quad (\text{E1-1.4})$$

Carrying out the integration of Equation (E1-1.4) gives

$$V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A} \quad (\text{E1-1.5})$$

3. We want to find the volume, V_1 , at which $C_A = \frac{1}{10} C_{A0}$ for $k = 0.23 \text{ min}^{-1}$ and $v_0 = 10 \text{ dm}^3/\text{min}$.

Substituting C_{A0} , C_A , v_0 , and k in Equation (E1-1.5), 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 m^3 is necessary to convert 90% of species A entering into product B for the parameters given.

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.²

1.5 Industrial Reactors

When is a batch reactor used?



Be sure to view actual photographs of industrial reactors on the CD-ROM and on the Web site. There are also links to view reactors on different web sites. The CD-ROM also includes a portion of the *Visual Encyclopedia of Equipment—Chemical Reactors* developed by Dr. Susan Montgomery and her students at University of Michigan.

[1] Liquid-Phase Reactions. Semibatch reactors and CSTRs are used primarily for liquid-phase reactions. A semibatch reactor (Figure 1-15) has essentially the same disadvantages as the batch reactor. However, it has the advantages of temperature control by regulation of the feed rate 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 usually is bubbled continuously through the liquid.

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

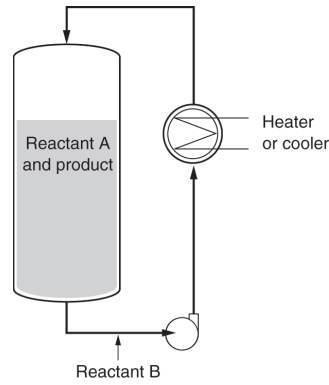


Figure 1-15(a) Semibatch reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

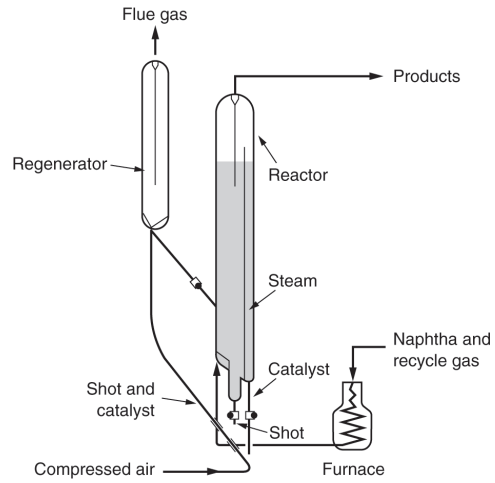


Figure 1-15(b) Fluidized-bed catalytic reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

What are the advantages and disadvantages of a CSTR?

A CSTR is used when intense agitation is required. Figure 1-7(a) showed a cutaway view of a Pfaudler CSTR/batch reactor. Table 1-1 gives the typical sizes (along with that of 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.

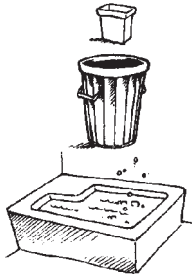
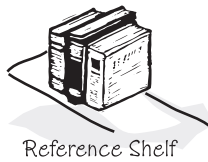


TABLE 1-1. REPRESENTATIVE PFAUDLER CSTR/BATCH REACTOR SIZES AND 2004 PRICES

Volume	Price	Volume	Price
5 Gallons (wastebasket)	\$29,000	1000 Gallons (2 Jacuzzis)	\$85,000
50 Gallons (garbage can)	\$38,000	4000 Gallons (8 Jacuzzis)	\$150,000
500 Gallons (Jacuzzi)	\$70,000	8000 Gallons (gasoline tanker)	\$280,000

The CSTR can either be used by itself or, in the manner shown in Figure 1-16, as part of a series or battery of CSTRs. It is relatively easy to maintain good temperature control with a CSTR because it is well mixed. 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 neces-



sary to obtain high conversions. An industrial flow sheet for the manufacture of nitrobenzene from benzene using a cascade of CSTRs is shown and described in the Professional Reference Shelf for Chapter 1 on the CD-ROM.

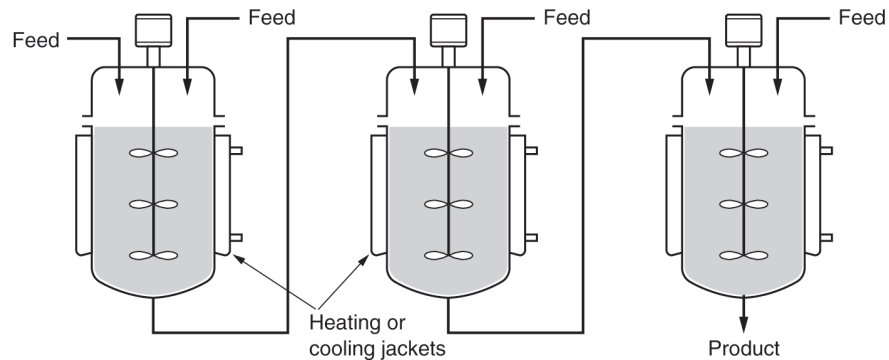


Figure 1-16 Battery of stirred tanks. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]



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 Aaron Equipment Company (www.aaronequipment.com) or Loeb Equipment Supply (www.loebequipment.com/).

What are the advantages and disadvantages of a PFR?

CSTR: liquids
PFR: gases

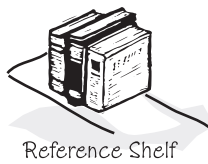
[2] Gas-Phase Reactions. The tubular reactor (i.e., plug-flow reactor [PFR]) is relatively easy to maintain (no moving parts), and it usually produces the highest conversion per reactor volume of any of the flow reactors. The disadvantage of the tubular reactor is that it is difficult to control temperature 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 Figures 1-8(a) and (b). Most homogeneous liquid-phase flow reactors are CSTRs, whereas most homogeneous gas-phase flow reactors are tubular.

The costs of PFRs and PBRs (without catalyst) are similar to the costs of heat exchangers and can be found in *Plant Design and Economics for Chemical Engineers*, 5th ed., by M. S. Peters and K. D. Timmerhaus (New York: McGraw-Hill, 2002). From Figure 15-12 of the Peters and Timmerhaus 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 most often used to catalyze gas reactions. This reactor has the same difficulties with temperature control as other tubular reactors; 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 1-15[b]) reactor, which 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 can only be approximately modeled as a CSTR (Example 10.3); for higher precision it requires a model of its own (Section PRS12.3). 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. A thorough discussion of a gas-phase industrial reactor and process can be found on the Professional Reference Shelf of the CD-ROM for Chapter 1. The process is the manufacture of paraffins from synthesis gas (CO and H₂) in a straight-through transport reactor (see Chapter 10).



Reference Shelf



Solved Problems

In this chapter, and on the CD-ROM, we've introduced each of the major types of industrial reactors: batch, semibatch, stirred tank, 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.³

The CD-ROM describes industrial reactors, along with typical feed and operating conditions. In addition, two solved example problems for Chapter 1 can be found on the CD.

Closure. The goal of this text is to weave the fundamentals of chemical reaction engineering into a structure or algorithm that is easy to use and apply to a variety of problems. We have just finished the first building block of this algorithm: mole balances. This algorithm and its corresponding building blocks will be developed and discussed in the following chapters:

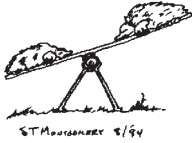
- Mole Balance, Chapter 1
- Rate Law, Chapter 3
- Stoichiometry, Chapter 3
- Combine, Chapter 4
- Evaluate, Chapter 4
- Energy Balance, Chapter 8

With this algorithm, one can approach and solve chemical reaction engineering problems through logic rather than memorization.

³ S. M. Walas, *Reaction Kinetics for Chemical Engineers* (New York: McGraw-Hill, 1959), Chapter 11.

SUMMARY

Each chapter summary gives the key points of the chapter that need to be remembered and carried into succeeding chapters.



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

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt} \tag{S1-1}$$

If, and only if, the contents of the reactor are well mixed, then a mole balance (Equation S1-1) on species A gives

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt} \tag{S1-2}$$


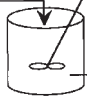

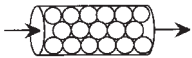
2. The kinetic rate law for r_j is:

- Solely a function of properties of reacting materials and reaction conditions (e.g., concentration [activities], temperature, pressure, catalyst or solvent [if any])
- The rate of formation of species j per unit volume (e.g., mol/s·dm³)
- An intensive quantity (i.e., it does not depend on the total amount)
- An algebraic equation, not a differential equation (e.g., $-r_A = kC_A$, $-r_A = kC_A^2$)

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 species A in four common reactors are as follows:

TABLE S-1 SUMMARY OF REACTOR MOLE BALANCES

Reactor	Comment	Mole Balance Differential Form	Algebraic Form	Integral Form
	No spatial variations	$\frac{dN_A}{dt} = r_A V$		$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$
	No spatial variations, steady state	—	$V = \frac{F_{A0} - F_A}{-r_A}$	—
	Steady state	$\frac{dF_A}{dV} = r_A$		$V_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$
	Steady state	$\frac{dF_A}{dW} = r'_A$		$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$

CD-ROM MATERIAL



Summary Notes

• Learning Resources

1. Summary Notes
2. Web Material
 - A. Problem-Solving Algorithm
 - B. Getting Unstuck on a Problem
This site on the web and CD-ROM gives tips on how to overcome mental barriers in problem solving.
 - C. Smog in L.A. basin

B. Getting Unstuck



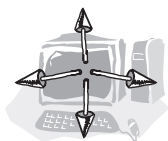
C. Smog in L.A.



Fotografiert von ©2002 Hank Good.

3. Interactive Computer Modules

A. Quiz Show I



Kinetics Challenge I

Mole Balance	Reactions	Rate Laws	Reactor Types
100		100	100
200	200	200	200
300	300	300	300
400	400	400	400
500	500	500	500

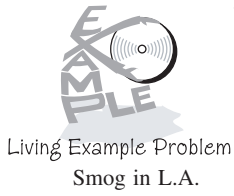
Score: 100
Lavoisier

Score: 0
Arrhenius

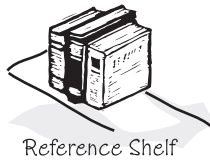
Score: 0
Nigel

Worth 3 module points

Total Module Points (75 needed for mastery): 3

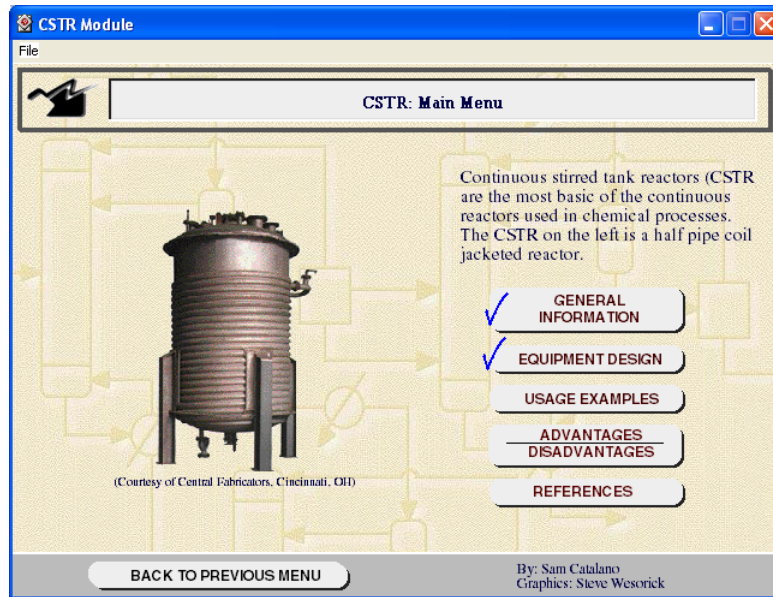


4. *Solved Problems*
 - A. CDP1-A_B Batch Reactor Calculations: A Hint of Things to Come
 - B. P1-14_B Modeling Smog in the L.A. Basin
 - **FAQ [Frequently Asked Questions]**—In Updates/FAQ icon section
 - **Professional Reference Shelf**
 1. **Photos of Real Reactors**



2. **Reactor Section of the *Visual Encyclopedia of Equipment***

This section of the CD-ROM shows industrial equipment and discusses its operation. The reactor portion of this encyclopedia is included on the CD-ROM accompanying this book.





Examples of industrial reactions and reactors

3. **The production of nitrobenzene example problem.** Here the process flow-sheet is given, along with operating conditions.

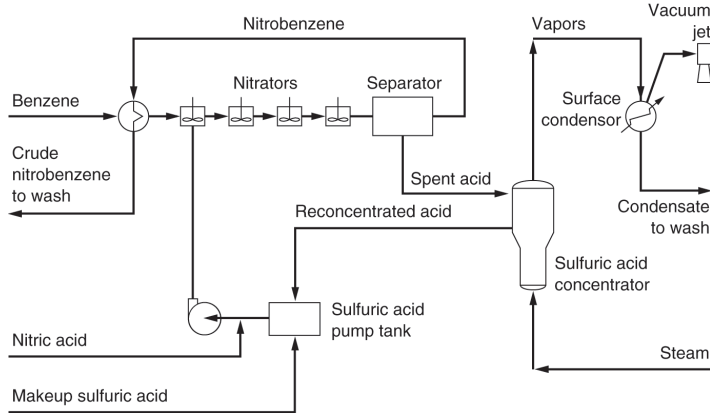
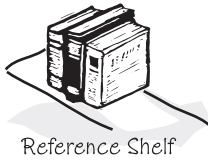


Figure PRS.A-1 Flowsheet for the manufacture of nitrobenzene.



4. **Fischer-Tropsch Reaction and Reactor Example.** A Fischer-Tropsch reaction carried out in a typical straight-through transport reactor (Riser).

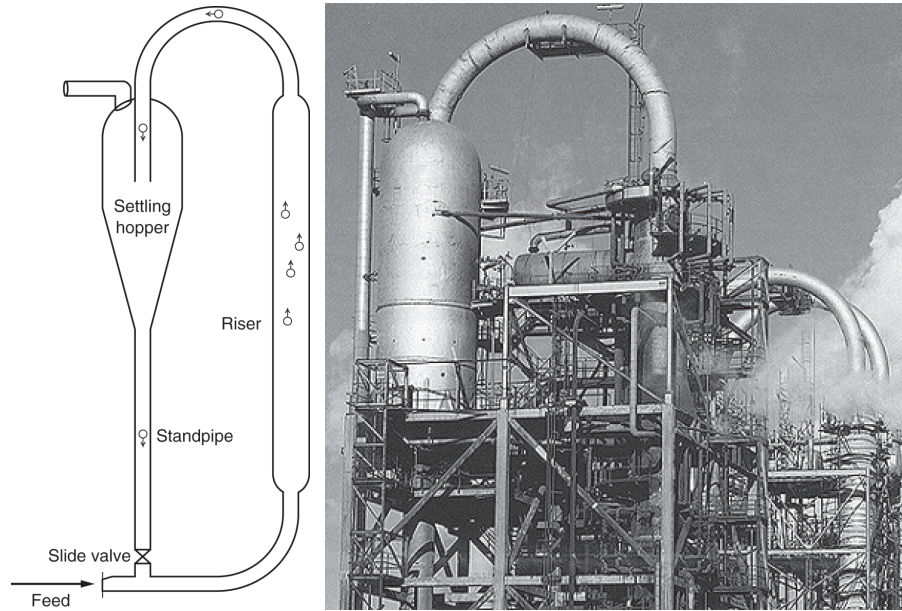
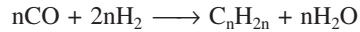


Figure PRS.B-1 The reactor is 3.5 m in diameter and 38 m tall. [Schematic and photo courtesy of Sasol/Sastech PT Limited.]

Here photographs and schematics of the equipment along with the feed rates, reactor sizes, and principal reactions



are also discussed in the PRS.



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*, 4th Ed. (New York: Macmillan, 2000) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace*, 6th Ed. (Glenview, Ill.: Scott, Foresman, 1999) to enhance the quality of your sentences.




 = Hint on the web.

Before solving the problems, state or sketch qualitatively the expected results or trends.



- P1-1_A** (a) Read through the Preface. Write a paragraph describing both the content goals and the intellectual goals of the course and text. Also describe what's on the CD and how the CD can be used with the text and course.
 (b) List the areas in Figure 1-1 you are most looking forward to studying.
 (c) Take a quick look at the web modules and list the ones that you feel are the most novel applications of **CRE**.
 (d) Visit the problem-solving web site, www.engin.umich.edu/~cre/probsolv/closed/cep.htm, to find ways to "Get Unstuck" on a problem and to review the "Problem-Solving Algorithm." List four ways that might help you in your solutions to the home problems.
- P1-2_A** (a) After reading each page or two ask yourself a question. Make a list of the four best questions for this chapter.
 (b) Make a list of the five most important things you learned from this chapter.
- P1-3_A** Visit the web site on Critical and Creative Thinking, www.engin.umich.edu/~cre/probsolv/strategy/crit-n-creat.htm.
 (a) Write a paragraph describing what "critical thinking" is and how you can develop your critical thinking skills.
 (b) Write a paragraph describing what "creative thinking" is and then list four things you will do during the next month that will increase your creative thinking skills.

P1-4_A

- (c) Write a question based on the material in this chapter that involves critical thinking and explain why it involves critical thinking.
- (d) Repeat (c) for creative thinking.
- (e) Brainstorm a list of ways you could work problems P-XX (to be specified by your instructor—e.g., Example E-1, or P1-15_B) incorrectly.
- Surf the CD-ROM and the web (www.engin.umich.edu/~cre). Go on a scavenger hunt using the summary notes for Chapter 1 on the CD-ROM.
- (a) What Frequently Asked Question (FAQ) is not really frequently asked?
- (b) What  hot button leads to a picture of a cobra?
- (c) What  hot button leads to a picture of a rabbit?
- (d) What  hot button leads to a picture of a hippo?
- (e) Review the objectives for Chapter 1 in the Summary Notes on the CD-ROM. Write a paragraph in which you describe how well you feel you met these objectives. Discuss any difficulties you encountered and three ways (e.g., meet with professor, classmates) you plan to address removing these difficulties.
- (f) Look at the Chemical Reactor section of the *Visual Encyclopedia of Equipment* on the CD-ROM. Write a paragraph describing what you learned.
- (g) 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 (e.g., www.loebequipment.com), on the CD-ROM, and in the text? How do the used reactor prices compare with those in Table 1-1?

ICM Quiz Show

Mole Balance	Reactions	Rate Laws
100	100	100
200	200	200
300	300	300

P1-5_A

Load the Interactive Computer Module (ICM) from the CD-ROM. Run the module and then record your performance number for the module which indicates your mastery of the material.

ICM Kinetics Challenge 1 Performance # _____

P1-6_B

Example 1-1 Calculate the volume of a CSTR for the conditions used to figure the plug-flow reactor volume in Example 1-1. Which volume is larger, the PFR or the CSTR? Explain why. Suggest two ways to work this problem incorrectly.

P1-7_A

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 1-1.

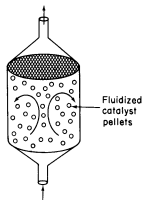
P1-8_A

What assumptions were made in the derivation of the design equation for:

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

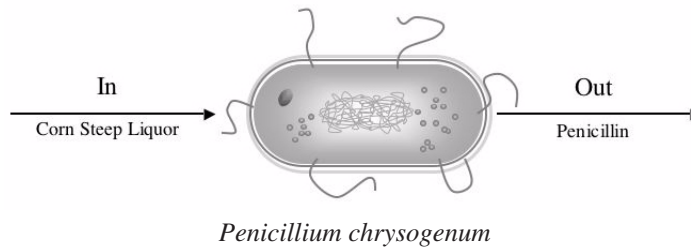
P1-9_A

Use the mole balance to derive an equation analogous to Equation (1-7) for a fluidized CSTR containing catalyst particles in terms of the catalyst weight, W , and other appropriate terms. *Hint:* See margin figure.



P1-10_A 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?

P1-11_B We are going to consider the cell as a reactor. The nutrient corn steep liquor enters the cell of the microorganism *Penicillium chrysogenum* and is decomposed to form such products as amino acids, RNA, and DNA. Write an unsteady mass balance on (a) the corn steep liquor, (b) RNA, and (c) penicillin. Assume the cell is well mixed and that RNA remains inside the cell.



P1-12_A The United States produced 32.5% of the world's chemical products in 2002 according to "Global Top 50," *Chemical and Engineering News*, July 28, 2003. Table P1-12.1 lists the 10 most produced chemicals in 2002.

TABLE P1-12.1. CHEMICAL PRODUCTION

2002 Chemical	Thousands of Metric Tons	1995 Rank	2002 Chemical	Thousands of Metric Tons	1995 Rank
1. H ₂ SO ₄	36,567	1	6. H ₂	13,989	—
2. N ₂	26,448	2	7. NH ₃	13,171	6
3. C ₂ H ₄	23,644	4	8. Cl ₂	11,362	10
4. O ₂	16,735	3	9. P ₂ O ₅	10,789	—
5. C ₃ H ₆	14,425	9	10. C ₂ H ₂ Cl ₂	9,328	—

Reference: *Chemical and Engineering News*, July 7, 2003, <http://pubs.acs.org/cen/>



- What were the 10 most produced chemicals for the year that just ended? Were there any significant changes from the 1995 statistics? (See Chapter 1 of 3rd edition of *Elements of CRE*.) The same issue of *C&E News* ranks chemical companies as given in Table P1-12.2.
- What 10 companies were tops in sales for the year just ended? Did any significant changes occur compared to the 2002 statistics?
- Why do you think H₂SO₄ is the most produced chemical? What are some of its uses?
- What is the current annual production rate (lb/yr) of ethylene, ethylene oxide, and benzene?
- Why do you suspect there are so few organic chemicals in the top 10?

TABLE P1-12.2. TOP COMPANIES IN SALES

Rank 2002	Rank 2001	Rank 2000	Rank 1999	Rank 1995	Company	Chemical Sales [\$ millions]
1	1	2	2	1	Dow Chemical	27,609
2	2	1	1	2	Dupont	26,728
3	3	3	3	3	ExxonMobil	16,408
4	5	5	6	6	General Electric	7,651
5	4	4	4	—	Huntsman Corp.	7,200
6	8	10	9	—	PPG Industries	5,996
7	9	8	10	—	Equistar Chemicals	5,537
8	7	7	—	—	Chevron Phillips	5,473
9	—	—	—	—	Eastman Chemical	5,320
10	—	—	—	—	Praxair	5,128

References:

Rank 2002: *Chemical and Engineering News*, May 12, 2003.
 Rank 2001: *Chemical and Engineering News*, May 13, 2002.
 Rank 2000: *Chemical and Engineering News*, May 7, 2001.
 Rank 1999: *Chemical and Engineering News*, May 1, 2000.
<http://pubs.acs-org/cen/>

P1-13_A Referring to the text material and the additional references on commercial reactors given at the end of this chapter, fill in Table P1-13.

TABLE P1.13 COMPARISON OF REACTOR TYPES

Type of Reactor	Characteristics	Kinds of Phases Present	Use	Advantages	Disadvantages
Batch	_____	_____	_____	_____	_____
CSTR	_____	_____	_____	_____	_____
PFR	_____	_____	_____	_____	_____
PBR	_____	_____	_____	_____	_____



P1-14_B Schematic diagrams of the Los Angeles basin are shown in Figure P1-14. 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.

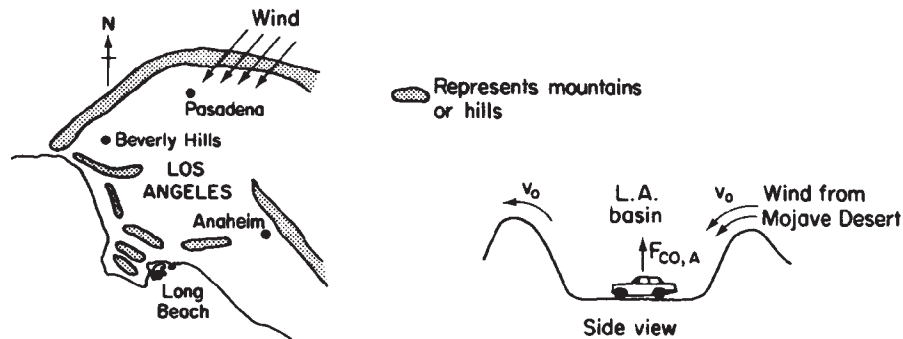


Figure P1-14 Schematic diagrams of the Los Angeles basin.



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. Load the **Smog in Los Angeles Basin Web Module**. Use the data in the module to work part 1–14 (a) through (h) given in the module. Load the **living example polymath code** and explore the problem. For part (i), vary the parameters v_0 , a , and b , and write a paragraph describing what you find.

There is heavier traffic in the L.A. basin in the mornings and in the evenings as workers go to and from work in downtown L.A. Consequently, the flow of CO into the L.A. basin might be better represented by the sine function over a 24-hour period.

P1-15_B 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 dm³/h. (Note: $F_A = C_A v$. For a constant volumetric flow rate $v = v_0$, then $F_A = C_A v_0$. Also, $C_{A0} = F_{A0}/v_0 = [5 \text{ mol/h}]/[10 \text{ dm}^3/\text{h}] = 0.5 \text{ mol/dm}^3$.)

(d) Repeat (a), (b), and (c) to calculate the time necessary to consume 99.9% of species A in a 1000 dm³ constant volume batch reactor with $C_{A0} = 0.5 \text{ mol/dm}^3$.

P1-16_B 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. What did you learn from this article? Why is the article important?



- P1-17_B** (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:

$$\frac{dx}{dt} = k_1 x - k_2 x \cdot y$$

$$\frac{dy}{dt} = k_3 x \cdot y - k_4 y$$

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.

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.

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

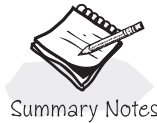
$$x^3 y - 4y^2 + 3x = 1$$

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

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

Screen shots on how to run Polymath are shown at the end of Summary Notes for Chapter 1 on the CD-ROM and on the web.

Polymath Tutorial



Summary Notes

- P1-18_C** **What if:**

- the benzene feed stream in Example R1.3-1 in the PRS were not pre-heated 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 1-1 were specified at 0.1% of the entering concentration?
- only one operator showed up to run the nitrobenzene plant. What would be some of your first concerns?

- P1-19_A** **Enrico Fermi (1901–1954) Problems (EEP).** Enrico Fermi was an Italian physicist who received the Nobel Prize for his work on nuclear processes. Fermi was famous for his “Back of the Envelope Order of Magnitude Calculation” to obtain an estimate of the answer through *logic* and making reasonable assumptions. He used a process to set bounds on the answer by saying it is probably larger than one number and smaller than another and arrived at an answer that was within a factor of 10.

<http://mathforum.org/workshops/sum96/interdisc/sheila2.html>

Enrico Fermi Problem (EFP) #1

How many piano tuners are there in the city of Chicago? Show the steps in your reasoning.

- Population of Chicago _____
- Number of people per household _____



Web Hint

Chap. 1 Supplementary Reading

3. Number of households _____
4. Households with pianos _____
5. Average number of tunes per year _____
6. Etc. _____

An answer is given on the web under Summary Notes for Chapter 1.

P1-20_A EFP #2. How many square meters of pizza were eaten by an undergraduate student body population of 20,000 during the Fall term 2004?

P1-21_B This problem will be used in each of the following chapters to help develop critical-thinking skills.

- (a) Write a question about this problem that involve critical thinking.
- (b) What generalizations can you make about the results of this problem?
- (c) Write a question that will expand this problem.

P1-22 New material for the 2nd printing the following changes/additions have been made to the 2nd printing.

NOTE TO INSTRUCTORS: Additional problems (cf. those from the preceding editions) can be found in the solutions manual and on the CD-ROM. These problems could be photocopied and used to help reinforce the fundamental principles discussed in this chapter.



Solved Problems

- CDP1-A_A** 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_A** Derive the differential mole balance equation for a foam reactor. [2nd Ed. P1-10_B]

SUPPLEMENTARY READING

1. For further elaboration of the development of the general balance equation, see not only the web site www.engin.umich.edu/~cre but also

FELDER, R. M., and R. W. ROUSSEAU, *Elementary Principles of Chemical Processes*, 3rd ed. New York: Wiley, 2000, Chapter 4.

HIMMELBLAU, D. M., and J. D. Riggs, *Basic Principles and Calculations in Chemical Engineering*, 7th ed. Upper Saddle River, N.J.: Prentice Hall, 2004, Chapters 2 and 6.

SANDERS, R. J., *The Anatomy of Skiing*. Denver, CO: Golden Bell Press, 1976.

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.

4. A discussion of some of the most important industrial processes is presented by

MEYERS, R.A., *Handbook of Chemicals 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

AUSTIN, G. T., *Shreve's Chemical Process Industries*, 5th ed. New York: McGraw-Hill, 1984.

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* and on the ACS web site <http://pubs.acs.org/cen>.

