

# CHAPTER 1

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## REACTOR BASICS

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In this chapter we first review some of the basics of chemical equilibrium and reaction kinetics. We need to understand clearly the fundamentals about chemical reaction rates and chemical equilibrium, particularly the effects of temperature on rate and equilibrium for different types of reactions. Reactions are generally categorized as exothermic (releasing energy) or endothermic (requiring energy), as reversible (balance of reactants and products) or irreversible (proceeding completely to products), and as homogeneous (single-phase) or heterogeneous (multiphase).

One major emphasis in this book is the focus of reactor design on the control of temperature, simply because temperature plays such a dominant role in reactor operation. However, in many reactors the control of other variables is the ultimate objective or determines the economic viability of the process. Some examples of these other properties include reactant or product compositions, particle size, viscosity, and molecular weight distribution. These issues are discussed and studied in subsequent chapters.

Many polymer reactions, for example, are highly exothermic, so the temperature control concepts outlined in this book must be applied. At the same time, controlling just the temperature in a polymer reactor may not adequately satisfy the economic objectives of the plant, since many of the desired polymer product properties (molecular weight, composition, etc.) are created within the polymerization reactor. These key properties must be controlled using other process parameters (i.e. vessel pressure in a polycondensation reactor or chain transfer agent composition in a free-radical polymerization reactor).

Many agricultural chemicals (pesticides, fungicides, etc.), for another example, are generated in a series of often complex batch or semibatch reaction and separation steps. The efficacy of the chemical often depends on its ultimate purity. Operation and control of the reactor to minimize the formation of undesirable and hard-to-separate byproducts

then become of urgent priority. Trajectories of reactor and feed process conditions must be developed and followed to ensure the economic success of the enterprise.

Returning now to the issue of reactor temperature control, we can generally state that reactors with either substantially reversible or endothermic reactions seldom present temperature control problems. Endothermic reactions require that heat be supplied to generate products. Hence, they do not undergo the dangerous phenomenon of “runaway” because they are self-regulating, that is, an increase in temperature increases the reaction rate, which removes more heat and tends to decrease the temperature.

Reversible reactions, even if they are exothermic, are also self-regulating because an increase in temperature decreases the chemical equilibrium constant. This reduces the net reaction rate between the forward and reverse reactions and limits how much product can ultimately be generated.

We also can generally state that major temperature control problems can and often do occur when the reactions are both exothermic and irreversible. These systems are not inherently self-regulatory because an increase in temperature increases the reaction rate, which increases temperature even further. The potential for reactor runaways is particularly high if the reactor is operating at a low level of conversion. The large inventory of reactant provides plenty of “fuel” for reaction runaway. These concepts will be quantitatively studied in later chapters.

Probably the most important aspect of reactor design and control for a substantial number of industrial processes involves heat transfer, that is, maintaining stable and safe temperature control. Temperature is the “dominant variable” in many chemical reactors. By *dominant variable*, we mean it plays a significant role in determining the economics, quality, safety, and operability of the reactor. The various heat transfer methods for chemical reactors are discussed in a qualitative way in this chapter, while subsequent chapters deal with these issues in detail with several illustrative quantitative examples.

The key element in temperature control of chemical reactors is to provide sufficient heat transfer surface area or some other heat removal mechanism so that dynamic disturbances can be safely handled without reactor runaways.

In this chapter the design and operation of the three types of classical reactors are discussed. Their advantages and disadvantages, limitations, and typical application areas are also enumerated.

The final subject discussed in this chapter is the issue of reactor scaleup. Moving from a laboratory test tube in a constant temperature bath to a 20-L pilot plant reactor to a 200,000-L commercial plant reactor involves critical design and control decisions. One major problem is the reduction of the heat transfer area relative to the reactor volume (and heat transfer duty) as we move to larger reactors. This has an important effect on temperature control and reactor stability.

Another major problem with scaleup involves mixing within the reactor. The larger the reactor, the more difficult it potentially becomes to ensure that the entire contents are well mixed and at uniform conditions (if that is the reactor type) or that the contents remain distributed and not mixed (if that is the reactor type). Mixing is typically achieved using internal agitators. Gas sparging is also used to achieve mixing in systems that involve a gaseous feedstream. Mixing also affects the heat transfer film coefficient

between the vessel wall and the process liquid. Therefore it impacts the ability to measure and control temperature effectively. For a given total reactor volume, the physical dimensions of the reactor vessel (the ratio of diameter to height) affect both the heat transfer area and the level of mixing. All these issues are discussed in several examples in subsequent chapters.

## 1.1 FUNDAMENTALS OF KINETICS AND REACTION EQUILIBRIUM

The rate at which a chemical reaction occurs in homogeneous systems (single-phase) depends primarily on temperature and the concentrations of reactants and products. Other variables, such as catalyst concentration, initiator concentration, inhibitor concentration, or pH, also can affect reaction rates. In heterogeneous systems (multiple phases), chemical reaction rates can become more complex because they may not be governed solely by chemical kinetics but also by the rate of mass and/or heat transfer, which often play significant roles.

### 1.1.1 Power-Law Kinetics

If we consider the *irreversible* reaction with two reactants forming a product



the overall rate of reaction  $\mathfrak{R}$  can be viewed as the moles of component A being consumed per unit time per unit volume. Sometimes reaction rates are based per mass of catalyst present. Of course, by stoichiometry in this system, the moles of component B consumed have to equal the moles of A, along with the moles of component C produced. If component B had a stoichiometric coefficient of 2, then the rate of consumption of B would be twice that for A.

The overall reaction rate has a temperature dependence governed by the specific reaction rate  $k_{(T)}$  and a concentration dependence that is expressed in terms of several concentration-based properties depending on the suitability for the particular reaction type: mole or mass concentration, component vapor partial pressure, component activity, and mole or mass fraction. For example, if the dependence is expressed in terms of molar concentrations for components A( $C_A$ ) and B( $C_B$ ), the overall reaction rate can be written as

$$\mathfrak{R} = k_{(T)} C_A^\alpha C_B^\beta \quad (1.2)$$

where the exponents  $\alpha$  and  $\beta$  are the “order” of the reaction for the respective two reactants. The actual reaction mechanism determines the form of the kinetic expression. More than one mechanism can give the same rate expression. Only in elementary reaction steps is the reaction order equal to the stoichiometry. The concept of a single rate-controlling step is often used in the development of kinetic expressions.

The temperature-dependent specific reaction rate  $k_{(T)}$  is represented by the Arrhenius equation

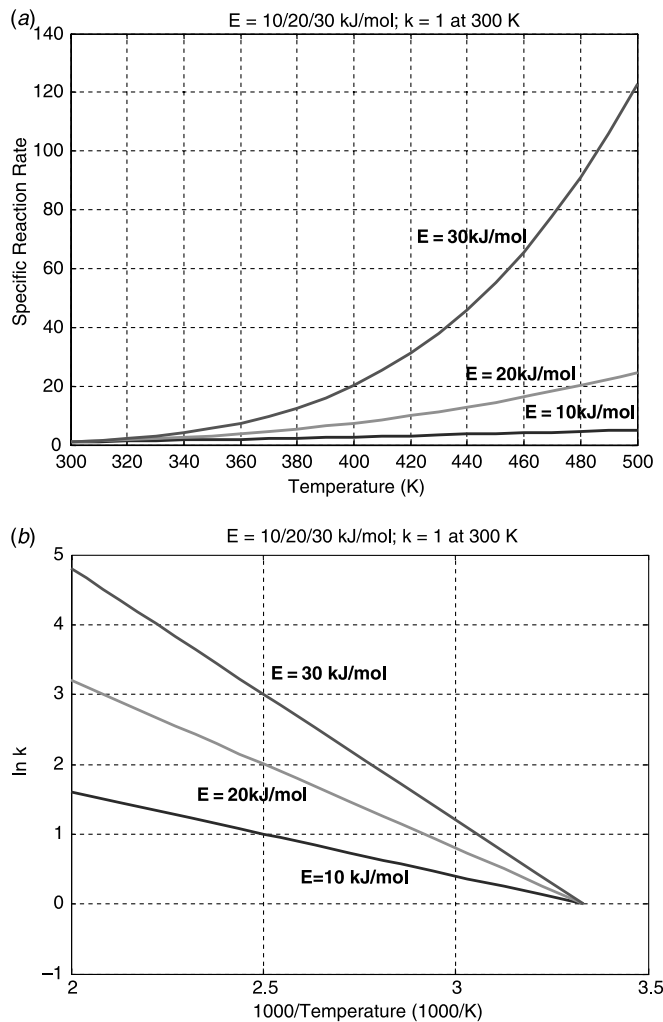
$$k_{(T)} = k_0 e^{-E/RT} \quad (1.3)$$

where  $k_0$  is a constant called the *preexponential factor*,  $E$  is the activation energy (typical units are kcal/mol, kJ/kmol, or Btu/lb · mol),  $R$  is the ideal-gas constant (in suitable units

that depend on the units of  $E$  and  $T$ ), and  $T$  is the absolute temperature [in K (degrees Kelvin) or  $^{\circ}\text{R}$  (degrees Rankine)].

The  $k_0$  preexponential factor is a large positive number (much greater than one) and has units that depend on the concentration units and the order of the reaction with respect to each component. The exponential term in Eq. (1.3) is a small positive number. Its minimum value is zero (when  $E/RT$  is infinite at very low absolute temperatures because of the negative sign in the exponential). Its maximum value is unity (when  $E/RT$  is zero at very high temperatures). Therefore at low temperature the  $E/RT$  term becomes large, which makes the exponential small and produces a low specific reaction rate. Conversely, at high temperature the  $E/RT$  term becomes small, which makes the exponential approach unity (in the limit as temperature goes to infinity, the exponential term goes to one). Thus the specific reaction rate *increases* with increasing temperature.

Clearly the rate of change of  $k(T)$  with temperature depends on the value of the activation energy. Figure 1.1 compares the relative rates of reaction as a function of activation



**Figure 1.1** Effect of activation energy on temperature dependence of reaction rate.

energy and temperature. The activation energies are 10, 20, and 30 kJ/mol, and the reaction rates are calculated relative to a rate of unity at 300 K. Reactions with low activation energies are relatively insensitive to temperature, whereas reactions with high activation energies are quite sensitive to temperature. This can be seen by comparing the slopes of the lines for the relative reaction rates versus  $1/T$ . With an activation energy of 10 kJ/mol, the change in reaction rate from 300 to 500 K is much less than the change at an activation energy of 30 kJ/mol. Also, we see that the sensitivity of reaction rate to temperature is relatively greater at lower than at higher temperatures. Both of these observations play a role in the control of temperature in a chemical reactor.

The main point of the discussion above is

Specific reaction rates always increase as temperature increases and the higher the activation energy, the more sensitive the reaction rate is to temperature.

Now we consider the reversible reaction where we do not achieve complete conversion of the reactants:



We can express the forward reaction rate in terms of molar concentrations of reactants  $C_A$  and  $C_B$  that are dependent on the reaction orders  $\alpha$  and  $\beta$

$$\mathfrak{R}_F = k_{F(T)} C_A^\alpha C_B^\beta \quad (1.5)$$

with the specific rate

$$k_{F(T)} = k_{0F} e^{-E_F/RT} \quad (1.6)$$

The reverse reaction rate can also be written in terms of the molar concentration of product  $C_C$  dependent on the reaction order  $\gamma$

$$\mathfrak{R}_R = k_{R(T)} C_C^\gamma \quad (1.7)$$

with the specific rate

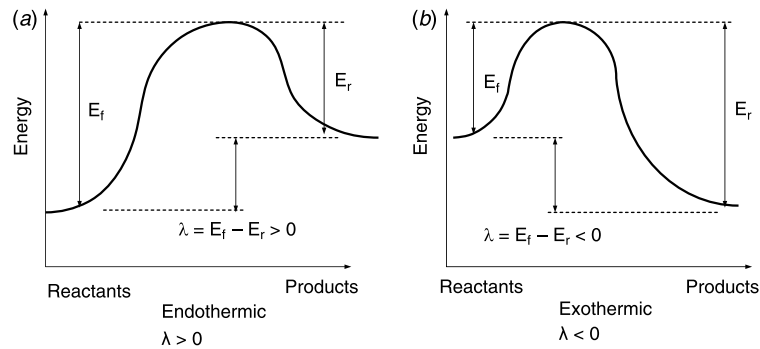
$$k_{R(T)} = k_{0R} e^{-E_R/RT} \quad (1.8)$$

The net overall reaction rate is the difference between the forward and the reverse

$$\mathfrak{R} = \mathfrak{R}_F - \mathfrak{R}_R = k_{F(T)} C_A^\alpha C_B^\beta - k_{R(T)} C_C^\gamma \quad (1.9)$$

Under conditions of chemical equilibrium, the net overall reaction rate is zero, which leads to the relationship between the forward and reverse specific reaction rates and the chemical equilibrium constant ( $K_{EQ}$ ) for the reaction:

$$K_{EQ} = \frac{C_A^\alpha C_B^\beta}{C_C^\gamma} = \frac{k_{F(T)}}{k_{R(T)}} \quad (1.10)$$



**Figure 1.2** Energy change from reactants to products.

$$K_{\text{EQ}} = \frac{k_{F(T)}}{k_{R(T)}} = \frac{k_{0F}e^{-E_F/RT}}{k_{0R}e^{-E_R/RT}} = \frac{k_{0F}}{k_{0R}} e^{(E_R - E_F)/RT} \quad (1.11)$$

Just as the specific reaction rates  $k_F$  and  $k_R$  depend only on temperature, the same is true for the chemical equilibrium constant  $K_{\text{EQ}}$ . This temperature dependence is governed by the difference between the activation energies of the reverse and forward reactions. We can visualize the relative change in energy from reactants to products as shown in Figure 1.2. If the activation energies of forward and reverse reactions are equal, the equilibrium constant is independent of temperature. If the activation energy of the reverse reaction  $E_R$  is greater than the activation energy of the forward reaction  $E_F$ , then we release energy going from reactants to products. For this case, the numerator in the exponential term in Eq. (1.11) is positive; therefore as temperature *increases* the exponential term becomes smaller, and the equilibrium constant *decreases*. If the difference between the activation energies is the opposite (with  $E_F$  larger than  $E_R$ ), then we require energy going from reactants to products. For this case, the numerator is negative, which means that the exponential term becomes larger as temperature increases, and the equilibrium constant *increases*.

The van't Hoff equation in thermodynamics gives the temperature dependence of the chemical equilibrium constant

$$\frac{d(\ln K_{\text{EQ}})}{dT} = \left( \frac{\lambda}{RT^2} \right) \quad (1.12)$$

where  $\lambda$  is the heat of reaction. This equation shows that the sign of the heat of reaction determines whether the equilibrium constant increases or decreases with increasing temperature. Exothermic reactions have negative heats of reaction, so the equilibrium constant *decreases* with increasing temperature:

The chemical equilibrium constant of a reversible exothermic reaction decreases as temperature increases.

Endothermic reactions have positive heats of reaction, so the equilibrium constant of a reversible endothermic reaction increases with increasing temperature.

Differentiating Eq. (1.11) with respect to temperature and combining with Eq. (1.12) give the relationship between the activation energies and the heat of reaction  $\lambda$ :

$$E_F - E_R = \lambda \quad (1.13)$$

From the previous discussion about the temperature sensitivity of reaction rate as a function of activation energy, we can understand why the chemical equilibrium constant of an exothermic reversible reaction decreases with increasing temperature. An exothermic reaction has a negative heat of reaction, since the activation energy of the reverse reaction exceeds that of the forward reaction. As temperature increases, the reverse reaction increases relatively more rapidly than the forward reaction, which means that at chemical equilibrium we have relatively more reactants than products and a lower equilibrium constant.

We note that particular catalysts or initiators used in chemical reactors change only the effective specific reaction rate and *do not* change the value of the chemical equilibrium constant.

### 1.1.2 Heterogeneous Reaction Kinetics

Power-law kinetic rate expressions can frequently be used to quantify homogeneous reactions. However, many reactions occur among species in different phases (gas, liquid, and solid). Reaction rate equations in such heterogeneous systems often become more complicated to account for the movement of material from one phase to another. An additional complication arises from the different ways in which the phases can be contacted with each other. Many important industrial reactors involve heterogeneous systems. One of the more common heterogeneous systems involves gas-phase reactions promoted with porous solid catalyst particles.

One approach to describe the kinetics of such systems involves the use of various resistances to reaction. If we consider an irreversible gas-phase reaction  $A \rightarrow B$  that occurs in the presence of a solid catalyst pellet, we can postulate seven different steps required to accomplish the chemical transformation. First, we have to move the reactant A from the bulk gas to the surface of the catalyst particle. Solid catalyst particles are often manufactured out of aluminas or other similar materials that have large internal surface areas where the active metal sites (gold, platinum, palladium, etc.) are located. The porosity of the catalyst typically means that the interior of a pellet contains much more surface area for reaction than what is found only on the exterior of the pellet itself. Hence, the gaseous reactant A must diffuse from the surface through the pores of the catalyst pellet. At some point, the gaseous reactant reaches an active site, where it must be adsorbed onto the surface. The chemical transformation of reactant into product occurs on this active site. The product B must desorb from the active site back to the gas phase. The product B must diffuse from inside the catalyst pore back to the surface. Finally, the product molecule must be moved from the surface to the bulk gas fluid.

To look at the kinetics in heterogeneous systems, we consider the step of adsorbing a gaseous molecule A onto an active site s to form an adsorbed species As. The adsorption rate constant is  $k_a$ . The process is reversible, with a desorption rate constant  $k_d$ :



Since we are dealing with gaseous molecules, we usually write the rate of adsorption in terms of the partial pressure of A ( $P_A$ ) rather than molar concentration. The net rate of adsorption and desorption is

$$r = k'_a P_A C_S - k'_d C_{AS} \quad (1.15)$$

where  $C_S$  is the concentration of open active sites and  $C_{AS}$  is the concentration of sites occupied by an adsorbed molecule of A. The total number of sites ( $C_T$ ) is fixed and is the sum of the open and occupied sites:

$$C_T = C_S + C_{AS} \quad (1.16)$$

If we define  $\theta$  as the fraction of total sites covered by the adsorbed molecules, then

$$\theta = \frac{C_{AS}}{C_T} \quad (1.17)$$

We can rewrite these equations and combine constant parameters into the following rate expression:

$$r = k_a P_A (1 - \theta) - k_d \theta \quad (1.18)$$

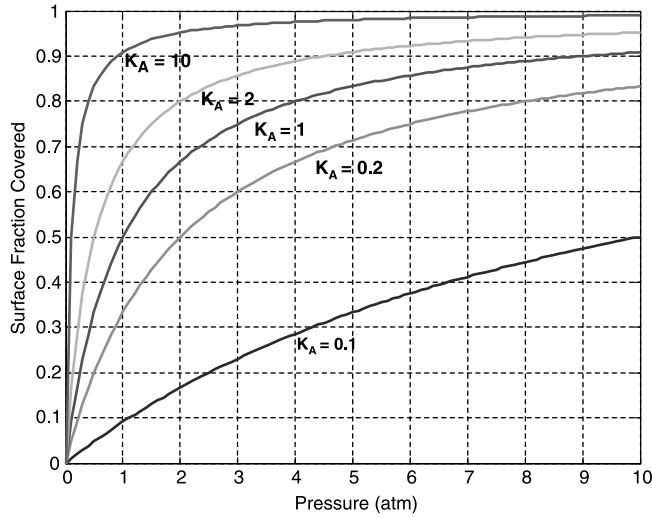
At equilibrium the net rate is zero, and we can define an adsorption equilibrium constant ( $K_A$ ) to produce the following expressions that define what is typically called *Langmuir isotherm behavior*:

$$K_A = \frac{k_a}{k_d} \quad (1.19)$$

$$\theta = \frac{K_A P_A}{1 + K_A P_A}$$

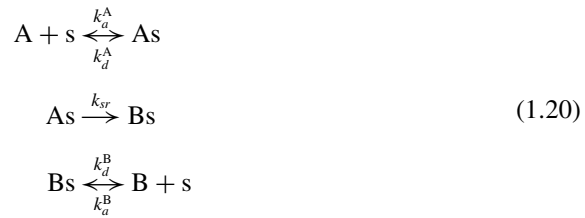
Figure 1.3 shows a plot of  $\theta$  versus partial pressure for various values of the adsorption equilibrium constant. These show that as the equilibrium constant increases for a given pressure, we increase the surface fraction covered, up to a value of 1. As the pressure increases, we increase the fraction of the surface covered with A. But we have only a finite amount of catalyst surface area, which means that we will eventually reach a point where increasing the partial pressure of A will have little effect on the amount that can be adsorbed and hence on the rate of any reaction taking place. This is a kind of behavior fundamentally different from that of simple power-law kinetics, where increasing the reactant concentration always leads to an increase in reaction rate proportional to the order in the kinetic expression.

We now consider the irreversible reaction  $A \rightarrow B$ , where both components are gaseous and the reaction occurs on a solid catalyst. We can consider three steps to the mechanism: the adsorption of reactant A onto the surface (assumed to be reversible), the transformation of A into B on the catalyst surface (assumed to be irreversible), and finally the desorption



**Figure 1.3** Langmuir isotherms for heterogeneous systems.

of product B from the surface (assumed to be reversible):



The assumption of which step is slowest governs the form of the final kinetic expression. For the purposes of this simple example, we assume that the second step is the slowest and is first-order with respect to the adsorbed A species. Therefore the rate  $r$  is determined by a rate constant and the concentration of A adsorbed on the surface ( $C_{AS}$ ) according to standard power-law kinetics:

$$r = k_{sr} C_{AS} \tag{1.21}$$

We can write the absorption equilibrium coefficients for A and B in terms of their partial pressures ( $P_A$  and  $P_B$ ) and the concentration of open sites ( $C_S$ ):

$$\begin{aligned}
 K_A &= \frac{C_{AS}}{P_A C_s} = \frac{k_a^A}{k_d^A} \\
 K_B &= \frac{C_{BS}}{P_B C_s} = \frac{k_a^B}{k_d^B}
 \end{aligned} \tag{1.22}$$

The total concentration of sites is a constant ( $C_T$ ) and is the sum of open and occupied sites. We can express this in terms of the equilibrium constants under the assumption

that the transformation step is the slowest:

$$C_T = C_s + C_{AS} + C_{BS} = C_s(1 + K_A P_A + K_B P_B) \quad (1.23)$$

We can write the overall reaction rate as

$$r = \frac{k_{(T)} P_A}{1 + K_A P_A + K_B P_B} \quad (1.24)$$

where  $k_{(T)}$  is a kinetic rate constant that is a function of temperature.

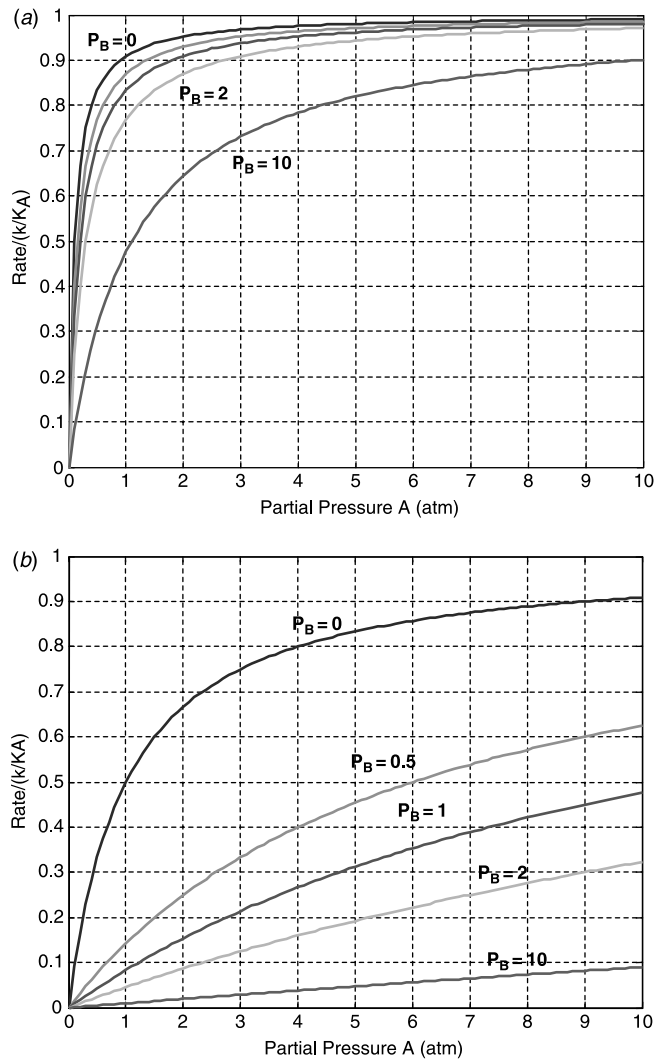
For this assumed mechanism of what is an irreversible overall reaction, we observe that the reaction rate is a function not only of the partial pressure of reactant A but also the partial pressure of product B. The reaction rate decreases as we increase the amount of B because it occupies active sites on the catalyst and inhibits the reaction. At a given partial pressure of A, the reaction rate is largest when the partial pressure of B goes to zero. As the concentration of B increases, the reaction rate decreases. When the partial pressure of A is small and the term  $K_A P_A + K_B P_B$  is much less than one, the reaction rate turns into first-order power-law kinetics that depends on  $P_A$ . In the limit of large partial pressures of A, the rate no longer depends on the concentration of A and becomes only a constant value equal to  $k/K_A$ . Figure 1.4 shows the reaction rate normalized by  $(k/K_A)$  for various values of  $P_B$  as a function of  $P_A$ . When the value of  $K_A$  is large compared with  $K_B$  (as shown in Fig. 1.4a), the reaction rates are relatively large and do not depend as much on  $P_B$ . This is because more of reactant A is adsorbed onto active sites of the catalyst. Since the transformation of adsorbed A to adsorbed B is the slowest step, the higher concentration of adsorbed A increases the reaction rate. On the other hand, when the value of  $K_A$  is small compared with  $K_B$  (Fig. 1.4b), the reaction rates are much slower and depend more on  $P_B$ . This is caused by the large concentration of adsorbed B on the active catalyst sites inhibiting the reaction.

The general forms of rate expressions in heterogeneous systems can have concentration or partial pressure dependences in both numerator and denominator along with various exponents. In heterogeneous reactors, it is not unusual to derive kinetic expressions that are more complicated than just a power-law expression. This, of course, has implications on how the reactor is controlled and the potential for runaway in exothermic systems. In some cases, where kinetics are very fast relative to mass transfer rates, the reactor behavior is governed by mass transfer and the variables that affect it.

### 1.1.3 Biochemical Reaction Kinetics

One special type of heterogeneous reactor involves biological systems with enzymes or microorganisms that convert some organic starting material into chemicals, pharmaceuticals, foodstuffs, and other substances. The conversion of sugar into alcohol via fermentation represents historically one of the oldest types of chemical reactors for the production of beer and wine. In fermentation, a reactant such as glucose (typically called the *substrate* S) is converted into a product P by the action of a microorganism or by the catalytic effect of an enzyme produced by a microorganism.

We can view an enzyme as a biological catalyst, and as such it leads to kinetic rate expressions that are of similar form to those derived in heterogeneous reaction



**Figure 1.4** Normalized reaction rate as a function of  $P_A$  and  $P_B$ ,  $k = 1$ ; (a)  $K_A = 10$ ,  $K_B = 1$ ; (b)  $K_A = 1$ ,  $K_B = 2$ .

systems. The Michaelis–Menten kinetic expression is one standard formulation used in enzyme-catalyzed fermentation. It assumes that the substrate and enzyme (E) form a complex (ES) via a reversible reaction. The enzyme–substrate complex is assumed to be very reactive and goes on to form the product in an irreversible reaction:



The reaction rate for the formation of product ( $r_p$ ) can then be derived from certain assumptions to take the following form that represents observed experimental

behavior reasonably well:

$$r_P = \frac{kC_{E0}C_S}{C_S + K_M} \quad (1.26)$$

Here  $k$  is the rate constant for the irreversible reaction,  $C_{E0}$  is the total enzyme concentration,  $C_S$  is the substrate concentration, and  $K_M$  is the Michaelis–Menton constant. Both  $k$  and  $K_M$  may be functions of pH, temperature, and other properties of the fermentation medium. From this kinetic expression, we see that at high substrate concentrations the rate of product formation is independent of  $C_S$  and is approximately equal to  $kC_{E0}$ . This is due to the presence of a limited amount of enzyme, which is required for the reaction to proceed, and adding more substrate under these conditions will not cause the reaction rate to increase further. At low substrate concentrations, the rate of product formation becomes first-order with respect to  $C_S$ . Under these conditions the substrate concentration becomes the determinant for product formation, and increasing  $C_S$  produces a proportional increase in rate. The rate is also proportional to the total enzyme concentration under all conditions of substrate concentration.

Substrate can also be converted into product in fermenters by cells or microbes or “bugs,” which not only act as the reaction catalyst but also reproduce themselves to promote further reaction. The substrate fed to the cell biomass supplies carbon, hydrogen, and oxygen to the organisms. The substrate is also the energy source for the cells and goes into maintaining their existence and into growing new cells. Sometimes, such as in wastewater treatment, we want the cells to break down the substrate and generate carbon dioxide and water. In other cases, such as yeast production, we are after the cells themselves. Further, such as in chemical or pharmaceutical production, we often want the cells to take the substrate and produce a desired “product” that is one part of the organism’s biochemical pathway.

Fermentations may be aerobic when the cells must be in the presence of an  $O_2$  environment or anaerobic when they cannot. Water is the standard fermentation medium and is also one of the products, as is carbon dioxide, which is removed from the liquid and leaves in a vapor product stream since it may have a negative effect on the cells. Other nutrients or media (sources of nitrogen, phosphorus, minerals, vitamins, etc.) typically must be supplied to keep the organisms happy and healthy.

Since many biochemical reactions and their stoichiometry are not well understood, we often find a more empirical approach to the quantitative assessment of the kinetics. Mass concentration units (e.g., g/L) are often used along with yield coefficients to calculate the distribution of products formed and the amount of substrate consumed. In the absence of any inhibition effects and in the presence of an infinite supply of substrate, the rate of cell growth  $r_X$  is autocatalytic, that is, it depends only on the concentration of cells ( $C_X$ ), and the more cells we have, the higher the growth rate. The cell biomass is typically represented by X:

$$r_X = \mu_{\max} C_X \quad (1.27)$$

Here  $\mu_{\max}$  is the nomenclature for the maximum cell growth rate [typically in  $h^{-1}$  (reciprocal hours)] and  $C_X$  is the mass concentration of cells (g/L). Hence the cell growth rate initially is exponential with time (called the *exponential* growth phase).

The value of  $\mu_{\max}$  depends on temperature and pH. Different organisms operate in different optimal temperature and pH ranges. Once we go beyond the boundaries of these ranges (either too low or too high), the organism behavior changes significantly and cannot be represented by the same kinetics.

Unfortunately, the cell growth rate is limited or inhibited by a number of factors. First is the limitation created by the substrate S or some other nutrient. The Monod kinetic model is typically used to represent the behavior of such biochemical systems according to the following equation:

$$\mu = \mu_{\max} \frac{C_S}{K_S + C_S} \quad (1.28)$$

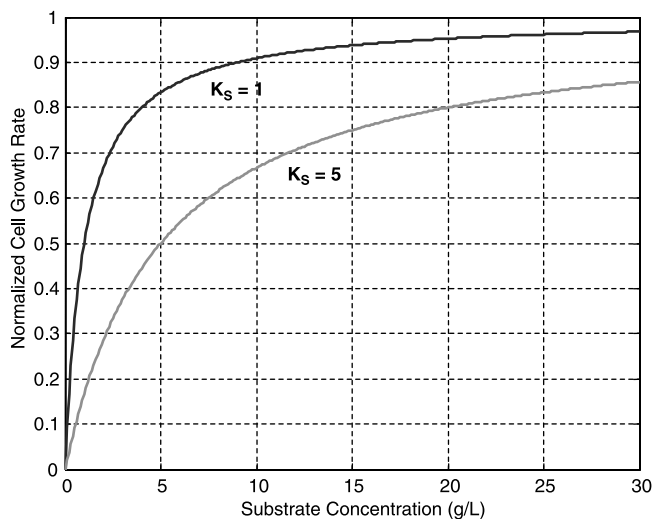
Here  $\mu$  is the specific cell growth rate ( $\text{h}^{-1}$ ),  $C_S$  is the substrate concentration, and  $K_S$  is a constant that is equal to the value of substrate concentration at half the maximum cell growth rate. This model produces the relationship shown in Figure 1.5. At low substrate concentrations, the growth rate is first-order with respect to  $C_S$ . At high substrate concentrations, the specific growth rate is independent of concentration. The value of  $K_S$  determines how quickly we reach the maximum specific growth rate.

The reaction rate for cell growth then becomes

$$r_X = \mu C_X = \mu_{\max} \frac{C_S C_X}{K_S + C_S} \quad (1.29)$$

In addition to the depletion of substrate (or a lack of oxygen in aerobic systems), the cell growth rate can also be slowed by inhibition caused by products generated by the cells themselves (the desired product or byproducts such as carbon dioxide). This is incorporated into the kinetic rate expression by the effect of an inhibition term:

$$r_X = \mu_{\max} \frac{C_S C_X}{K_S + C_S} \left[ 1 - \frac{C_P}{C_{P, \max}} \right]^{n_p} \quad (1.30)$$



**Figure 1.5** Normalized cell growth rate as a function of substrate concentration.

Here  $C_p$  is the product concentration,  $C_{p,max}$  is the maximum product concentration when cell growth stops, and  $n_p$  is the order of inhibition. At low values of  $C_p$ , the inhibition term plays no significant role. However, as the product concentration increases, the cell growth rate begins to decrease until the biomass concentration eventually reaches a plateau (what is called the “stationary” phase). From there, the fermentation broth is typically harvested before the cells start to die and the biomass concentration starts to decrease.

Empirically determined yield factors are typically used to relate the mass of cells produced per unit mass of substrate consumed ( $Y_{XS}$ ) and the mass of product generated per unit mass of biomass produced ( $Y_{PX}$ ).

Fermentation reactors generally produce heat, so temperature control is an important issue for such reactors. This becomes more aggravated at larger scales when the surface area of a cooling jacket may not be large enough in relation to the volume. Because sterility is a key requirement for successful fermentations, there is a strong reluctance to insert anything, such as cooling coils, into the fermenter itself. The biological nature of the cells, however, has direct consequences on their sensitivity to a temperature runaway. The temperature in the fermenter can increase only so much before it begins to place physiological stress on the cells, which then slows their growth rate and the heat generation rate. If the temperature rises too much, it may be fatal for the organisms. So, temperature control is one key part of effective fermenter control, but the control of other variables, such as pH, vessel backpressure, agitation rate, substrate concentration, and dissolved oxygen concentration (for aerobic systems), is also essential.

#### 1.1.4 Literature

This section has presented a brief review of some of the important kinetic concepts encountered in reactor analysis, modeling, and control. These concepts must be understood within the context of how they affect reactor temperature control and other aspects of reactor control. We recognize that many excellent reference books on chemical reaction engineering are available. These books cover the topic of kinetics and a host of other reactor design concepts in extensive depth. Our intention is not to attempt to provide anything like the scope of that material, so we assume some familiarity with it. A short list of excellent reference books includes

- K. G. Denbigh, *Chemical Reactor Theory*, Cambridge University Press, 1965.
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- K. R. Westerterp, W. P. M. van Swaaij, and A. A. C. M. Beenackers, *Chemical Reactor Design and Operation*, Wiley, 1984.

## 1.2 MULTIPLE REACTIONS

It is most unusual for only a single desired reaction to occur in a chemical reactor. Nature is typically not that generous and exacts a penalty that takes the form of side reactions generating undesired impurity components. The side reactions can involve other transformations of the reactant species (in *parallel* with the desired reaction) or further

transformations of the desired product species (in *series* with the desired reaction). Typically we encounter some combination of both types. We discuss each of these schemes in some detail here because they often play a critical role in understanding the behavior of the reactor, how it has to be operated, and also how it can be controlled.

They also have a major impact on the design of the entire process. To suppress undesirable side reactions, it is often necessary to operate the reactor with a low concentration of one of the reactants and an excess of other reactants. These must be recovered in a separation section and recycled back to the reaction section.

### 1.2.1 Parallel Reactions

The first reaction type is when the reactants form, not just the desired products, but also other undesired products in parallel with the main reaction. We want to show here the implications of parallel reactions, so we consider a simple *batch isothermal* reactor at constant volume:



Assuming first-order kinetics, we can express the change with time in the concentrations of reactant A ( $C_A$ ) and products B ( $C_B$ ) and C ( $C_C$ ):

$$\frac{dC_A}{dt} = -(k_B + k_C) C_A \quad (1.32)$$

$$\frac{dC_B}{dt} = k_B C_A \quad (1.33)$$

$$\frac{dC_C}{dt} = k_C C_A \quad (1.34)$$

The kinetic rate constants are  $k_B$  and  $k_C$ . We can analytically solve these differential equations, assuming that we start at time zero with only reactant A ( $C_{A0}$ ):

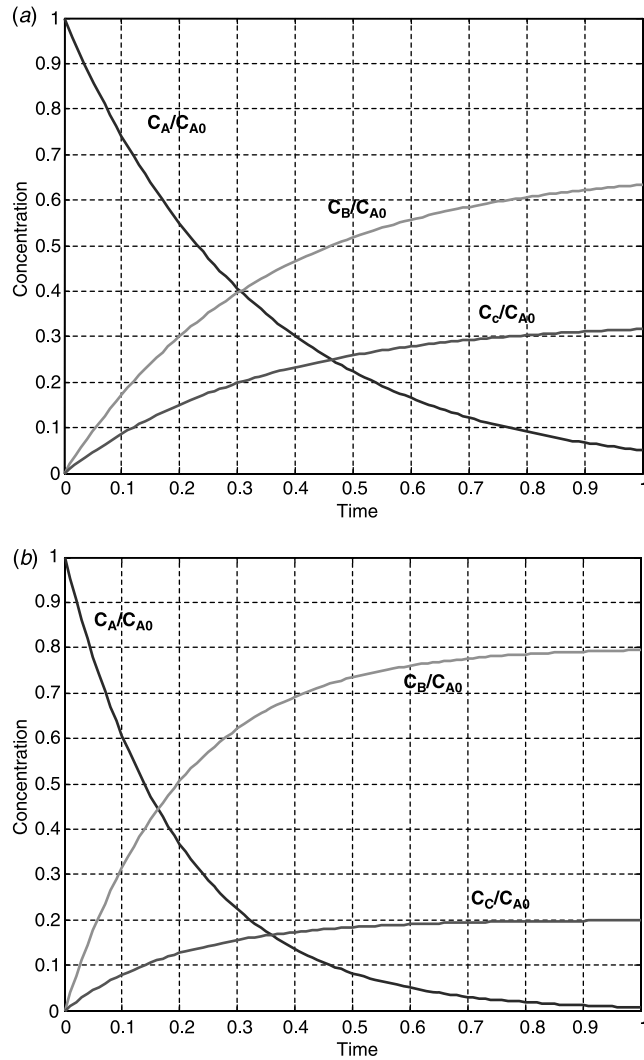
$$\frac{C_{A(t)}}{C_{A0}} = e^{-(k_B+k_C)t} \quad (1.35)$$

$$\frac{C_{B(t)}}{C_{A0}} = \frac{k_B}{k_B + k_C} [1 - e^{-(k_B+k_C)t}] \quad (1.36)$$

$$\frac{C_{C(t)}}{C_{A0}} = \frac{k_C}{k_B + k_C} [1 - e^{-(k_B+k_C)t}] \quad (1.37)$$

Figure 1.6 shows the normalized concentrations as functions of time during the batch for different values of the two rate constants  $k_B$  and  $k_C$ . The higher the value of  $k_B$  compared with  $k_C$ , the more of product B is generated. This is expressed in terms of the selectivity ( $S$ ) to the desired product, which we preferentially want to be as large as possible:

$$S = \frac{C_B}{C_C} \quad (1.38)$$



**Figure 1.6** Concentrations for parallel reactions: (a)  $k_B = 2$ ,  $k_C = 1$ ; (b)  $k_B = 4$ ,  $k_C = 1$ .

One aspect of optimizing the operation of a batch reactor is establishing the temperature such that the selectivity is as high as possible. If the activation energies of the two reactions are different, changing temperature shifts the ratio of the rates.

If the chemistry involves two reactants, selectivity is affected by the concentrations of the reactants. For example, supposed that there are two parallel reactions in which C is the desired product and D is the undesired product:



Keeping the concentration of A low in the reactor and the concentration of B high in the reactor will help improve the yield of the desired product. An important industrial example of this type of system is the production of isooctane from the reaction of isobutene and isobutane. The isobutene can react with itself to form polymer, so a large excess of isobutane is used and the concentration of isobutene is kept small by distributing the fresh feed among a number of reactors.

### 1.2.2 Series Reactions

The second reaction type involves reactants forming products, but then the products undergo further reaction in series with the main reaction. We want to show here the implications of series reactions, so we consider a simple batch isothermal reactor at constant volume:



Assuming first-order kinetics, we can write the change with time in the concentrations of reactant A ( $C_A$ ) and products B ( $C_B$ ) and C ( $C_C$ ):

$$\frac{dC_A}{dt} = -k_B C_A \quad (1.41)$$

$$\frac{dC_B}{dt} = k_B C_A - k_C C_B \quad (1.42)$$

$$\frac{dC_C}{dt} = k_C C_B \quad (1.43)$$

The kinetic rate constants are  $k_B$  and  $k_C$ . We can solve these differential equations analytically, assuming that we start at time zero with only reactant A ( $C_{A0}$ ).

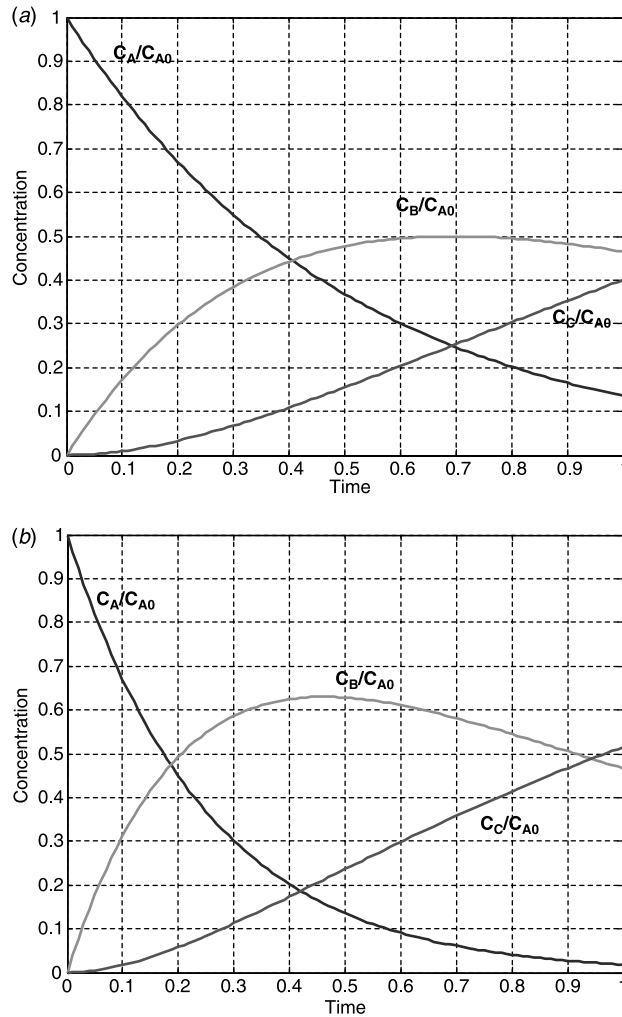
$$\frac{C_{A(t)}}{C_{A0}} = e^{-k_B t} \quad (1.44)$$

$$\frac{C_{B(t)}}{C_{A0}} = \frac{k_B}{k_C - k_B} [e^{-k_B t} - e^{-k_C t}] \quad (1.45)$$

$$\frac{C_{C(t)}}{C_{A0}} = 1 - \frac{C_{A(t)}}{C_{A0}} - \frac{C_{B(t)}}{C_{A0}} \quad (1.46)$$

Figure 1.7 shows typical composition profiles. Notice that there is a peak in the  $C_B$  at some point in time. The higher the value of  $k_B$  relative to  $k_C$ , the higher the peak in  $C_B$  and the earlier in the batch the peak occurs. The batch should be stopped when the peak occurs if we wish to maximize selectivity. Thus batch time is an important operating parameter for series reactions. This is not the case for parallel reactions. Reactor temperature should be adjusted to favor  $k_B$ .

If series reactions are conducted in a CSTR, the concentrations in the reactor can be adjusted to influence selectivity and conversion. Because the production of the undesirable product C depends on the concentration of the desired product B, this concentration should be kept small. The reactor can be operated with low conversion (small concentration of B).



**Figure 1.7** Concentrations for series reactions: (a)  $k_B = 2$ ,  $k_C = 1$ ; (b)  $k_B = 4$ ,  $k_C = 1$ .

Of course, this means that the concentration of A is large, so recovery and recycle of unreacted A is required to make the process economical.

In the case where there are two reactants, one of which is involved in an undesirable series reaction ( $A + B \rightarrow C$  and  $C + B \rightarrow D$ ), the concentration of B in the reactor can be kept small to improve selectivity. An important industrial example of this type of series reactions is in the production of ethylbenzene. The desired reaction is the formation of ethylbenzene from ethylene and benzene. The undesirable reaction is the formation of diethylbenzene from ethylene and ethylbenzene. To suppress this second series reaction, the concentration of ethylene is kept low and an excess of benzene is employed, which must be recovered and recycled.

This classical tradeoff between selectivity and recycle is considered in several examples in subsequent chapters.

### 1.3 DETERMINING KINETIC PARAMETERS

The many preexponential factors, activation energies and reaction order parameters required to describe the kinetics of chemical reactors must be determined, usually from laboratory, pilot plant, or plant experimental data. Ideally, the chemist or biologist has made extensive experiments in the laboratory at different temperatures, residence times and reactant concentrations. From these data, parameters can be estimated using a variety of mathematical methods. Some of these methods are quite simple. Others involve elegant statistical methods to attack this nonlinear optimization problem. A discussion of these methods is beyond the scope of this book. The reader is referred to the textbooks previously mentioned.

In many practical applications, the engineer often has only plant performance data to use to backcalculate kinetic parameters. Data of this type are seldom extensive enough to permit precise calculation of all parameters since the plant normally operates in a fairly narrow window of operating conditions. However, useful simplified kinetics and parameters can often be determined that describe the major kinetics inside this region. Extrapolation outside the region from which the data has been obtained is very risky.

### 1.4 TYPES AND FUNDAMENTAL PROPERTIES OF REACTORS

In this section we discuss in a qualitative way the *classical* types of reactors: batch, continuous stirred-tank reactor (CSTR), and plug flow reactor (PFR). Our purpose is to point out the features of each that impact the ease or difficulty of their temperature control.

These classical reactors are idealizations of real industrial reactors. Perfect mixing is assumed in classical batch and CSTR reactors, but mixing is never perfect in an agitated vessel, no matter how intense the mixing. No axial mixing and no radial gradients (plug flow) are assumed in the classical PFR tubular reactor, but the flow patterns in a real tubular reactor are never without some axial mixing and differences in flow velocities and properties at different radial positions. However, the classical idealizations are usually close enough to reality so that they can be used for studying both steady-state design and the dynamic control of chemical reactors.

#### 1.4.1 Continuous Stirred-Tank Reactor

Figure 1.8 shows a vessel with an agitator for mixing, a jacket that surrounds the vessel for heating or cooling, feedlines entering the vessel and a liquid product stream exiting from the bottom. The liquid in the reactor is assumed to be perfectly mixed, that is, with no radial, axial, or angular gradients in properties (temperature and composition). The product stream has a composition and a temperature that are exactly the same as the contents of the liquid throughout the vessel. This is always true, both under steady-state conditions and dynamically at any point in time.

This characteristic of a CSTR immediately generates an inherent weakness of the CSTR type of reactor, that is, the concentration of reactant in the vessel is the same as the concentration of reactant in the product. The concentration of reactant is inversely related to conversion.

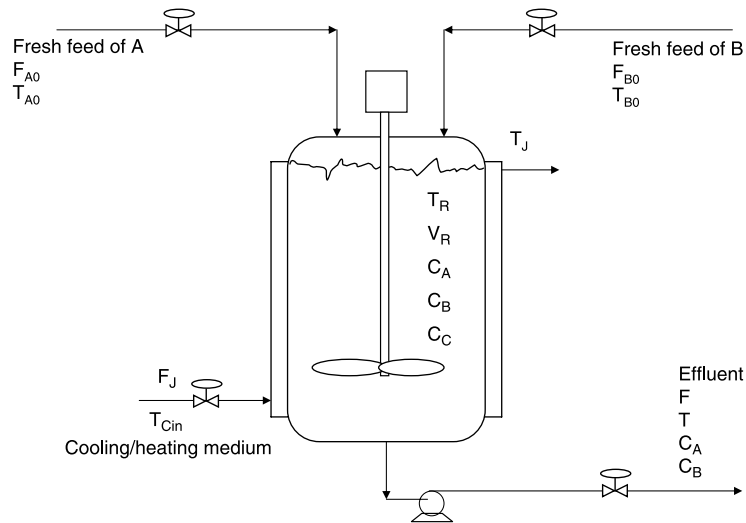


Figure 1.8 CSTR with jacket.

Fractional conversion  $\chi$  defined as

$$\chi = \frac{C_{A0} - C_A}{C_{A0}} \quad (1.47)$$

If a high conversion is desired, the reactant concentration must be small. But the reaction rate depends directly on the reactant concentration. It also depends on the reactor volume. So, if a high conversion desired, the reactor must be large to compensate for the small reactant concentration. Thus a single CSTR is seldom used if high conversion is desired. Of course, using several CSTRs in series is one way to reduce the total reactor volume because only the last vessel will have the small reactant concentration.

We will develop detailed steady-state and dynamic mathematical models of CSTRs in Chapters 2 and 3 with several types of reactions and quantitatively explore the effect of kinetic and design parameters on controllability. For the moment, let us just make some qualitative observations. There are several features of a CSTR that impact controllability:

1. A variety of methods and configurations can be used for heat transfer. These are described in Section 1.5. Since heat transfer is one of the key issues in reactor control, the CSTR is usually more easily controlled than a tubular reactor. It is physically difficult to adjust the heat removal down the length of a tubular reactor.
2. The temperature of the feed has some effect on controllability, but it is much less important in a CSTR than in a tubular reactor, as discussed in Section 1.4.3. If heat is being removed from the reactor, a feed that is at a lower temperature than the temperature in the reactor will reduce the heat transfer requirements.
3. Conversion is the fraction of a reactant that is fed to the reactor that reacts in the reactor. The level of conversion in a CSTR has a very significant impact on its stability and controllability. This is discussed in detail in Chapter 2. A high conversion means a small reactant concentration in the reactor vessel, so there is little “fuel”

available to permit a reactor runaway. On the other hand, a low conversion means that there is plenty of reactant available to react. If the reaction is exothermic and irreversible, a reactor temperature runaway can more easily occur in a CSTR operating with low reactant conversion than in one operating with high reactant conversion. In addition to affecting reactant concentration, the design conversion affects reactor size. Low conversion means a smaller reactor. This small reactor has less heat transfer area if an external jacket or an internal coil is used, which has a negative impact on controllability.

### 1.4.2 Batch Reactor

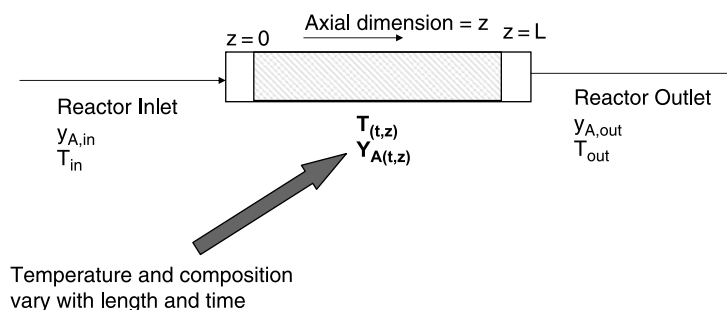
The classical batch reactor is a perfectly mixed vessel in which reactants are converted to products during the course of a batch cycle. All variables change dynamically with time. The reactants are charged into the vessel. Heat and/or catalyst is added to initiate reaction. Reactant concentrations decrease and product concentrations increase with time. Temperature or pressure is controlled according to some desired time trajectory. Batch time is also a design and operating variable, which has a strong impact on productivity.

Temperature profiles are established so that conversion and yield objectives are achieved while not exceeding heat transfer capacity limitations. These optimum temperature profiles depend on the chemistry. For example, if the reaction is reversible and exothermic, the temperature profile may ramp up to a high temperature to get the reactions going and then drop off with time to avoid the decrease in the chemical equilibrium constant at high temperature. If the reaction is reversible and endothermic, the temperature profile would rise to the highest possible temperature as quickly as possible because the chemical equilibrium constant increases with temperature.

If all the reactants are charged to the reactor, the reactant concentrations are initially large, which means that the reaction rate is high and the heat transfer load is high at the beginning of the batch cycle unless the temperature is kept low. The initial high reactant concentration problem can be avoided by using a “fed-batch reactor.” Some material is initially charged to the reactor, but most of the reactant is fed during the course of the batch cycle. This causes the volume of the liquid in the reactor to increase with time, so volume as well as compositions and temperatures are all time-varying.

Several special features of a batch reactor impact control:

1. The process is inherently time-varying. There is no steady state. This causes process parameters to change with time, which means that controller parameters may have to change with time. Control strategies such as “gain scheduling” (changing controller gain and integral time) are frequently required in batch reactor control.
2. Rigorous nonlinear models must be used in analyzing batch reactors because of the changing process parameters. Continuous reactors operate around some steady-state level, so linear models are sometime adequate for establishing controller tuning constants.
3. Selecting the best time–temperature trajectory is a challenging dynamic optimization problem with constraints. There are rigorous nonlinear programming approaches to this problem, but there are also some more simple and practical methods that can be employed, as discussed in Chapter 4.
4. All the heat transfer configurations used on CSTRs can be applied to batch reactors.



**Figure 1.9** Adiabatic tubular reactor.

Mathematical models of batch reactors and control strategies are developed in Chapter 4. Both classical batch and fed-batch reactors are discussed using numerical examples.

### 1.4.3 Tubular Plug Flow Reactor

Figure 1.9 gives a sketch of a typical adiabatic tubular reactor. The major distinguishing characteristic of tubular reactors is their distributed-parameter nature, that is, variables change with physical dimensions as well as with time. The classical plug flow reactor assumes that the reactor vessel is cylindrical, that fluid flows down the length of the reactor with a flat velocity profile, that no axial mixing occurs, and that no radial gradients exist in temperature or compositions.

The tubular reactor can be an empty vessel if no catalyst is used. If a solid catalyst is required, the vessel is packed with catalyst, either in a bed or inside tubes. The dynamic behavior of the reactor is significantly affected by the presence of catalyst in the reactor because the thermal capacitance of the catalyst is usually greater than that of the process fluid, particularly if the system is gas-phase. The temperatures of both the process fluid and the catalyst change with time. Of course, under steady-state conditions, the two temperatures are equal at any axial position.

There are several modes of operation of tubular reactors:

1. *Adiabatic.* There is no heat transfer to or from the reactor. Temperature and compositions change with length. Since there is no heat transfer, there are no radial gradients in temperature. The adiabatic temperature change depends on the per-pass conversion in the reactor and the amount of material fed to the reactor and its heat capacity. The adiabatic temperature change is small if conversion is low. If the feed contains materials (inerts or product components) that do not react, this material can serve as a “heat sink” to reduce the adiabatic temperature change. The sensible heat of this material can soak up some of the heat of reaction. Of course, this nonreacting material usually has to be recovered and recycled, so this mode of operation increases the capital and energy costs of the separation section of the plant.

2. *With Heat Transfer.* The tubular reactor is constructed in a similar way as a tube-in-shell heat exchanger or a fired furnace. Process fluid flows inside the tubes and is cooled or heated by the heat transfer medium within the shell. Radial temperature gradients are inherent in tubular reactors with heat transfer, so the plug flow assumption

is less accurate. These radial gradients depend strongly on tube diameter and fluid properties and fluid velocities. The larger the tubes, the larger the radial temperature gradients. One standard reactor design and development procedure is to study the system and/or catalyst in a single tube in the laboratory or pilot plant and then use multiple tubes of the same diameter in parallel in the plant reactor. The furnace or reactor used in steam–methane reforming to produce synthesis gas (a mixture of hydrogen, carbon monoxide, and carbon dioxide) is an important example. The furnace has multiple parallel tubes that are heated by burning fuel to provide the required heat to drive the endothermic reactions at a high temperature level. The problem of flow maldistribution among a large number of parallel tubes presents further potential complications.

3. *Adiabatic with Intermediate Heat Transfer.* Many tubular reactor systems use a series of adiabatic reactors with heating or cooling between the reactor vessels. For example, naphtha reforming has endothermic reactions of removing hydrogen from saturated cyclical naphthene hydrocarbons to form aromatics. The process has multiple adiabatic reactors with fired furnaces between the reactors to heat the material back up to the required reactor inlet temperature.

4. *Adiabatic with “Cold-Shot Cooling.”* Some exothermic reactions are conducted in vessels with multiple beds of catalyst, which operate adiabatically (temperature increases through the bed). At the exit of each bed, a cold stream is mixed with the hot stream leaving the bed to bring the temperature back down to the desired inlet temperature for the downstream bed. This cold stream is typically some of the feedstream that has been bypassed around the reactor feed preheating system.

All of these alternatives are discussed in Chapter 5.

The control of tubular reactors is probably the most difficult of all reactor systems. The reasons for this difficulty and the special features of tubular reactors are summarized below:

1. The distributed nature of the process leads to complex dynamic responses in which axial changes in variables can sometimes result in counter-intuitive dynamic behavior. One example of this is the “wrongway” response that occurs in some adiabatic packed-bed tubular reactors. A decrease in the reactor inlet temperature will eventually result in a lower reactor exit temperature. But there may be a transient *increase* in the exit temperature. This is caused by the colder feed decreasing the temperature in the front end of the reactor. The lower reaction rate consumes less reactant, so the reactant concentration increases at locations further down the reactor. The solid catalyst packing is still hotter at this location because of its thermal capacitance. So the combination of higher reactant concentration and higher temperature causes a rapid reaction rate at locations further down the length of the reactor, which raises the temperature above the normal steady-state value that will eventually be established.

2. Temperature and composition transients move in waves down the length of the reactor, and this can lead to limit cycles when the reactor is part of a complete plant with feed preheating and recycle streams.

3. Tubular reactors often have high-temperature limitations because of the occurrence of undesirable reactions, catalyst degradation, or materials of construction. This means that the maximum temperature anywhere in the reactor cannot exceed this limit. An exothermic reaction in an adiabatic reactor produces a maximum temperature at the exit under steady-state conditions. An exothermic reaction in a cooled reactor can

have the maximum temperature at some intermediate axial position or at the end. Both the magnitude and the location of the “peak” temperature vary with the design of the system and the age of the catalyst. They also vary with the operation of the system as disturbances occur. Controlling this peak temperature requires that multiple temperature measurements must be used down the length of the reactor for its detection.

4. Feed temperature is a very important design parameter in tubular reactors. A low feed temperature results in low reaction rates. So a long reactor is required to achieve the desired level of conversion. A high feed temperature results in a high exit temperature. If the reaction is exothermic and if there is a maximum temperature limitation, the per-pass conversion may have to be reduced or more “heat sink” material may have to be fed to lower the temperature rise. This usually means higher recycle flowrates with the associated higher capital and energy costs of the downstream separation system.

5. In cooled or heated tubular reactors the heat transfer options are limited. It is mechanically very difficult to change the temperature of the cooling or heating medium with axial position. The usual configuration is an essentially constant temperature of the heat transfer medium down the length of the reactor. In systems requiring cooling at fairly high temperatures, steam is generated on the shell side of the reactor to remove heat. The steam temperature is the same at any axial position. In systems requiring heating, burning fuel or condensing high-pressure steam is used at an essentially constant temperature at any axial position. If a heat transfer medium is used that does change in temperature down the length of the reactor, the available design parameters are the direction of flow (co-current or countercurrent flow of the cooling medium with respect to the direction of the process flow), the inlet temperature of the heat transfer medium and its flowrate. All of these must be balanced so that the desired temperatures and conversions are achieved. In systems requiring cooling at very high temperatures, molten salt is sometimes used as the heat removal medium.

The need to reduce energy consumption and reuse the exothermic heat of reaction so that we achieve a certain inlet temperature in a tubular reactor often leads to the use of a feed-effluent heat exchanger (FEHE). This can create some challenging control problems. Consider an exothermic reaction occurring in an adiabatic tubular reactor that has an inlet temperature of 450 K and an exit temperature of 500 K. One inefficient way to achieve the inlet temperature is to use a hot utility (steam or combustion of fuel) to heat up the cold feed. Energy can be saved by using the hotter reactor effluent stream in a FEHE. We study the dynamic problems that occur in reactor–FEHE systems like this in Chapter 4 and show that the positive feedback of energy can produce an openloop unstable process. The system can be made closedloop-stable by the use of an inlet temperature controller that bypasses cold material around the heat exchanger and mixes it with the heated stream to achieve the desired inlet reactor temperature. Chapter 7 contains a quantitative discussion of the interesting steady-state and dynamic tradeoff between energy and controllability in this type of system.

## 1.5 HEAT TRANSFER IN REACTORS

Batch and CSTR reactors can be cooled or heated in a variety of ways, which accounts in part for their superior controllability compared to tubular reactors. Figure 1.10a–1.10f show several of these alternatives.

The use of a jacket surrounding the reactor vessel is probably the most common method for providing heat transfer because it is relatively inexpensive in terms of equipment capital cost (see Fig. 1.10a). If heating is required, steam is condensed in the jacket or a hot heat transfer fluid stream is fed to the jacket. If cooling is required, a cooling medium is fed to the jacket. For moderate reactor temperatures (between 50 and 80°C), cooling water at 30°C is typically used. For lower temperature reactors, a cold refrigeration stream (brine) is used.

For reactor temperatures between 80 and 130°C, a tempered water or oil cooling medium is used. Plain cooling water should not be used because the large temperature difference between the reactor and the cooling medium leads to dynamic control problems. This is illustrated quantitatively in Chapter 2. It occurs because the temperature difference can be changed by only a small amount, which means that the heat removal rate cannot be changed much. Therefore the magnitude of the dynamic upsets that can be handled is quite limited.

For reactor temperatures above 130°C, steam can be generated in the jacket at a suitable pressure (to provide a 30–50°C temperature differential between the steam and the reactor; see Fig. 1.10b). Reactors operating at very high temperatures usually employ a molten salt for heat removal.

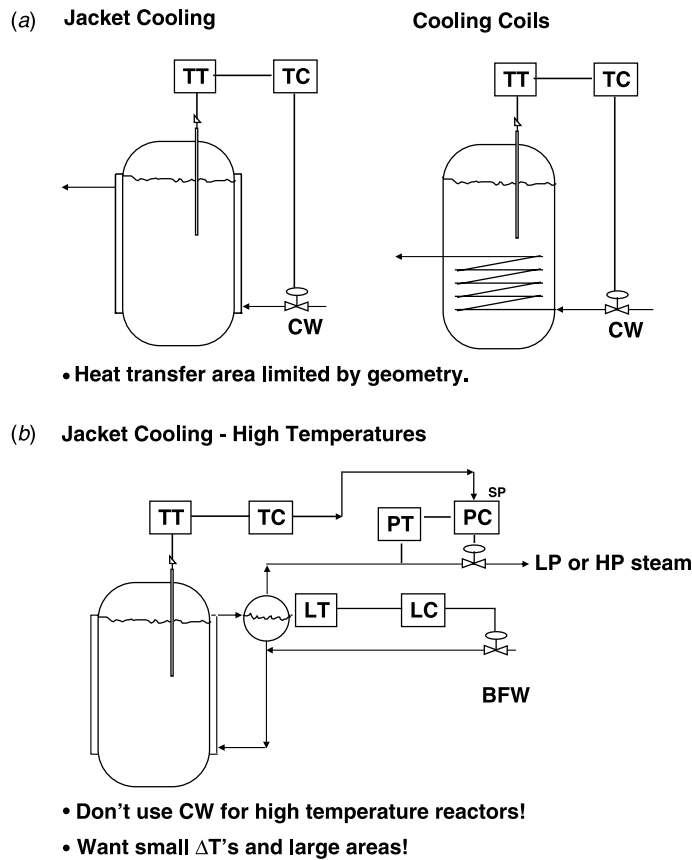
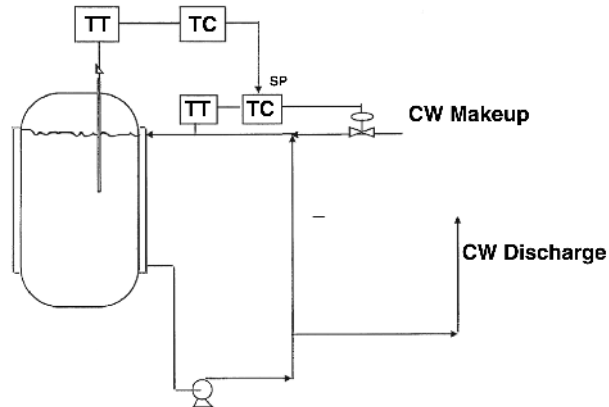


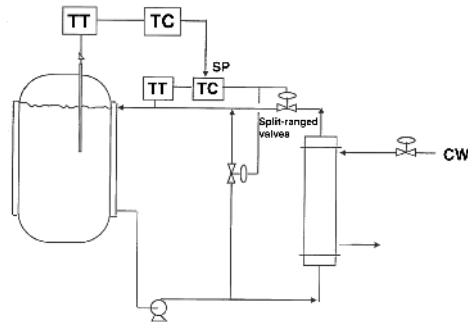
Figure 1.10 Reactor heat transfer methods.

(c) Jacket Cooling; Circulating Water System; Direct Addition of CW



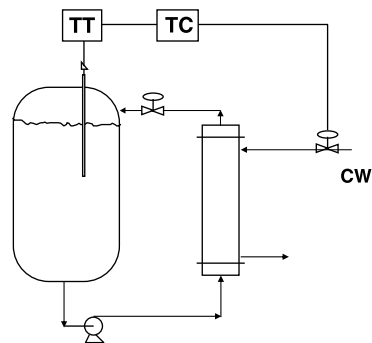
- Gives better temperature control, but requires more area.

Jacket Cooling; Circulating Water System; Heat Exchanger and Bypass



- Can use tempered water or oil for high temperature reactor
- Bypassing and blending avoids dynamics of heat exchanger

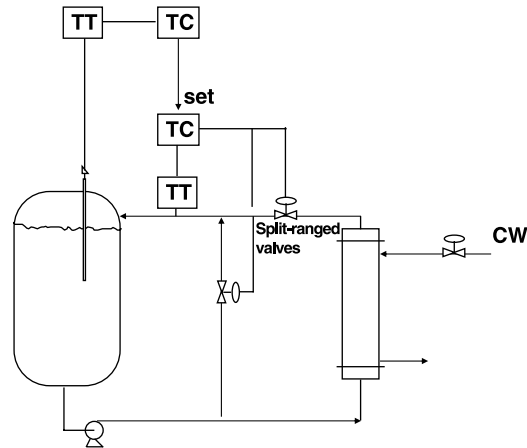
(d) External Heat Exchanger



- Area independent of reactor size.
- Must be able to pump reaction mass.

Figure 1.10 Continued.

## (e) External Heat Exchanger with Blending and Cascade Control



## (f) Autorefrigeration

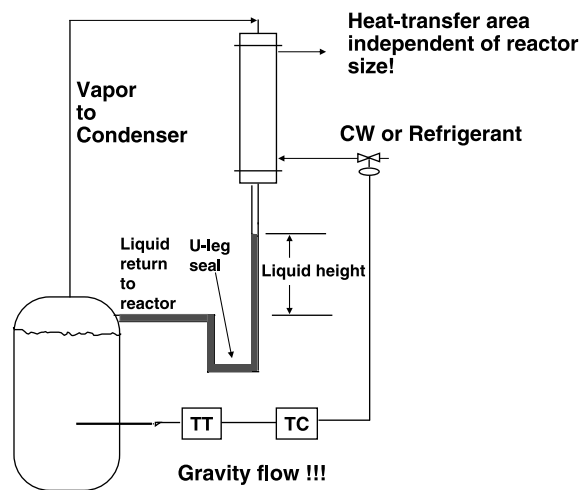


Figure 1.10 Continued.

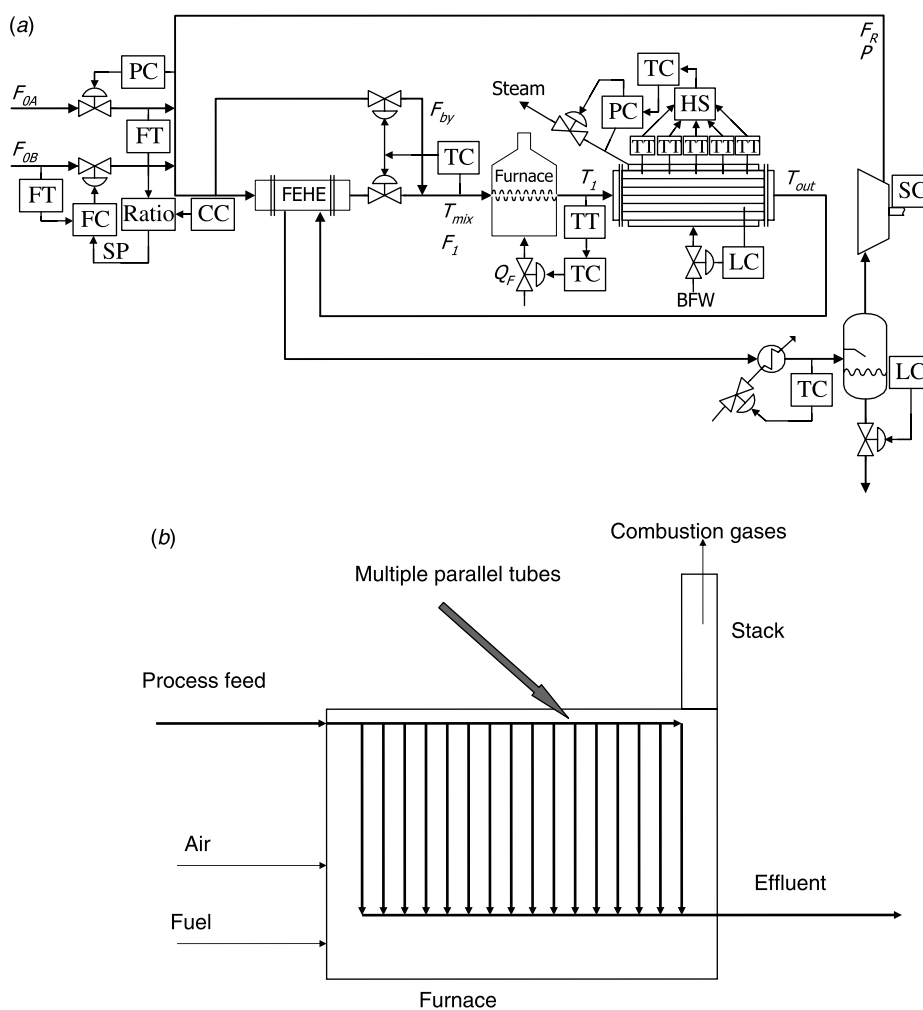
Instead of using a once-through system of coolant through the jacket or coil, circulating cooling water systems are frequently used, as shown in Figure 1.10c. The circulation rate is large, so all the coolant in the jacket is essentially at the same temperature. The flowrate is fixed, so the heat-transfer coefficient does not change with the flowrate of make-up water, as is the case with a once-through system. This results in tighter reactor temperature control. Circulating water systems will be used in many of the examples in this book.

These circulating coolant systems come in two flavors. As shown in the top flowsheet in Figure 1.10c, the cold make-up water can be added directly into the circulating loop as needed to control the temperature of the circulating water. The hot water is removed to keep the inventory in the circulating loop constant. As shown in the bottom flowsheet in Figure 1.10c, an external heat exchanger that is cooled by some cooling medium can be

used in the circulating loop to provide cooling. The material in the circulating loop can be tempered water or oil if reactor temperature is too high for cooling water. The bypassing and blending of hot and cold streams give very tight temperature control of the circulating fluid.

Another effective alternative is to circulate the reaction liquid through an external heat exchanger as shown in Figure 1.10e and 1.10d. This system has the advantage of being able to provide whatever heat transfer area is desired. With jacket and coil systems, the heat transfer area is limited by the physical dimension of the reactor vessel. With the external heat exchanger, the heat transfer area can be easily set at any desired level. As discussed in Section 1.6, this feature avoids some of the problems of reactor scaleup. Of course, the scheme requires pumping the liquid in the reactor, which can be undesirable in some processes with toxic materials (that can leak in pump seals), or with materials that are sensitive to shearing (some biological systems) or can foul the small tubes in the external heat exchanger.

The final heat removal scheme discussed here is called *autorefrigeration* or *evaporative cooling* (Fig. 1.10f). The pressure in the reactor is adjusted so that the liquid can boil if



**Figure 1.11** (a) Cooled tubular reactor; (b) heated tubular reactor.

temperature increases. The latent heat of vaporization of this phase change removes heat from the reactor. The vapor flows up to a condenser, and the condensed liquid is returned back to the reactor. The system has several desirable features. The boiling facilitates mixing of the liquid and prevents hotspots. The heat transfer area can be as large as desired, so scaleup problems are reduced.

However, this method also has several undesirable features. In the usual configuration, gravity with a U-leg seal is used to get the liquid to flow from the condenser back into the reactor, which is at a higher pressure (provides the driving force for the vapor to flow from the reactor to the condenser). The hydraulics of these gravity flow systems can lead to severe control problems. For example, if the vapor rate increases by 50%, the pressure drop in the vapor line increases by 225% (1.5 squared is 2.25). This means that the height of liquid in the U-leg must more than double. A large upset can back liquid up into the condenser and cover heat transfer area, which limits heat removal and can lead to a temperature runaway. Autorefrigerated systems must be designed for very small vapor pressure drop and enough elevation difference between the reactor and the condenser to provide a height of liquid that will handle the worst-case situation.

The other disadvantage of this type of system is that the temperature in the condenser is lower than in the reactor because of both the lower pressure and the more volatile components that are in the vapor phase. This means that a lower-temperature coolant must be used in the condenser compared to what could be used in a jacket- or coil-cooled system.

Many tubular reactors are operated adiabatically because of the problems in providing heat transfer. Figure 1.11a shows a complete gas-phase reaction process with a high-temperature tubular reactor that is cooled by generating steam. Figure 1.11b shows a fuel-fired furnace being used as a tubular reactor.

## 1.6 REACTOR SCALEUP

One of the most challenging aspects of chemical engineering is the problem of scaling up a process unit from a small laboratory or pilot plant to a large commercial size. Reactors are perhaps one of the more difficult to deal with. In this section we show quantitatively what the heat transfer scaleup problem is for a CSTR.

Suppose that a pilot plant reactor has a volume of  $0.019 \text{ m}^3$  [5 gal (gallons)] and is fed  $3.506 \text{ g/s}$  of feed with a density of  $801 \text{ kg/m}^3$  and a temperature of  $294 \text{ K}$ . The reaction is  $A \rightarrow B$ , which takes place in the liquid phase at a reactor temperature of  $333 \text{ K}$ . The concentration of reactant in the feed is  $8.01 \text{ kmol/m}^3$  and the specific reaction at  $333 \text{ K}$  is  $2.409 \times 10^{-4} \text{ s}^{-1}$ . With the given feedflow, reactor volume, and temperature, the reactant concentration of the product stream is  $3.926 \text{ kmol/m}^3$  (conversion is 51%).

The reactor is cooled by a circulating cooling water system. The heat of reaction is  $69.71 \times 10^6 \text{ J/kmol}$ . The heat that must be transferred to the jacket is  $817 \text{ W}$ . If an aspect ratio (height to diameter) of 2 is assumed, the diameter and jacket area can be calculated:

$$\text{Volume} = 0.019 \text{ m}^3 = \left(\frac{\pi D^2}{4}\right)(L) = \left(\frac{\pi D^2}{4}\right)(2D) = \frac{\pi D^3}{2} \Rightarrow D = 0.229 \text{ m}$$

$$\text{Jacket area} = \pi DL = \pi D(2D) = 2\pi D^2 = 0.3295 \text{ m}^2$$

Assuming an overall heat transfer coefficient of  $851 \text{ W K}^{-1} \text{ m}^{-2}$ , the required temperature differential between the reactor and the jacket is only 2.9 K, giving a jacket temperature of 330 K. If the supply cooling water temperature is 294 K, the cooling water makeup flowrate is 5.43 g/s.

If the flowrate of the makeup cooling water were made very large, the jacket temperature could be reduced to almost 294 K, which would give a differential temperature of  $333 - 294 = 39 \text{ K}$ . But we are using only 2.9 K of the potential driving force. Thus there is plenty of cooling “muscle” available to achieve very tight temperature control.

Now suppose that we design a plant-scale reactor that is 1000 times larger in volume ( $19 \text{ m}^3$ ). The feed flowrate is 1000 times larger (3.506 kg/s), and the required heat transfer is 1000 times larger (817 kW).

Assuming the same aspect ratio ( $L/D = 2$ ), the diameter is 10 times larger (2.29 m), which gives a heat transfer area that is only 100 times larger ( $32.95 \text{ m}^2$ ). If the overall heat transfer coefficient is the same as in the pilot plant (we will come back to this issue in Chapter 2), the required temperature differential between the reactor and jacket increases by a factor of 10 (jacket temperature is 304 K instead of 330 K). The flowrate of makeup cooling water (19.54 kg/s) increases by a factor of 4000.

In this large reactor the temperature differential driving force under design conditions is  $333 - 304 = 29 \text{ K}$ . The largest it can ever be is  $333 - 294 = 39 \text{ K}$ . Since we are using a large fraction of this maximum differential temperature, there is less “muscle” available. We demonstrate quantitatively in Chapter 3 the deterioration in temperature control as a larger fraction of the maximum differential is used.

One issue that should be mentioned here is the selection of the aspect ratio. We have used  $L/D = 2$  in the example above, and this is commonly used for reactors. But why not use a larger aspect ratio? The larger the aspect ratio, the larger the heat transfer area for a given volume, which would improve temperature control. For example, the  $19 \text{ m}^3$  reactor would have a diameter of 1.822 m and a heat transfer area of  $41.71 \text{ m}^2$  if an aspect ratio of 4 were used. Using an aspect ratio of 10 gives a diameter of 1.446 m and a heat transfer area of  $52.55 \text{ m}^2$ . These areas should be compared with the smaller  $32.95 \text{ m}^2$  in the  $L/D = 2$  design.

There are two factors that explain why aspect ratios between 1 and 2 are frequently used for reactors. The first is the capital cost. The weight of metal required to build a reactor of a fixed volume is minimized using an aspect ratio of  $\sim 1$ . The second consideration is mixing. It becomes more difficult to achieve good mixing as the aspect ratio increases. More details are provided in Chapter 2.

## 1.7 CONCLUSION

Several fundamental concepts have been reviewed in the chapter, and some of the important characteristics of the different types of reactors have been discussed. Most of the treatment in this chapter has been qualitative in nature so as to convey basic ideas.

The next two chapters delve into the dynamics and control of CSTR systems in a much more detailed and quantitative way. The effects on controllability of a variety of parameter values (specific reaction rates, throughput, heats of reaction, and heat transfer coefficients), heat removal schemes, and design conversion levels are studied.