CHEMICAL REACTOR DESIGN AND CONTROL

WILLIAM L. LUYBEN
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PREFACE

Chemical reactors are unquestionably the most vital parts of many chemical, biochemical, polymer, and petroleum processes because they transform raw materials into valuable chemicals. A vast variety of useful and essential products are generated via reactions that convert reactants into products. Much of modern society is based on the safe, economic, and consistent operation of chemical reactors.

In the petroleum industry, for example, a significant fraction of our transportation fuel (gasoline, diesel, and jet fuel) is produced within process units of a petroleum refinery that involve reactions. Reforming reactions are used to convert cyclical saturated naphthenes into aromatics, which have higher octane numbers. Light C4 hydrocarbons are alkylated to form high-octane C8 material for blending into gasoline. Heavy (longer-chain) hydrocarbons are converted by catalytic or thermal cracking into lighter (shorter-chain) components that can be used to produce all kinds of products. The unsaturated olefins that are used in many polymerization processes (ethylene and propylene) are generated in these reactors. The polluting sulfur components in many petroleum products are removed by reacting them with hydrogen.

The chemical and materials industries use reactors in almost all plants to convert basic raw materials into products. Many of the materials that are used for clothing, housing, automobiles, appliances, construction, electronics, and healthcare come from processes that utilize reactors. Reactors are important even in the food and beverage industries, where farm products are processed. The production of ammonia fertilizer to grow our food uses chemical reactors that consume hydrogen and nitrogen. The pesticides and herbicides we use on crop fields and orchards aid in the advances of modern agriculture. Some of the drugs that form the basis of modern medicine are produced by fermentation reactors. It should be clear in any reasonable analysis that our modern society, for better or worse, makes extensive use of chemical reactors.

Many types of reactions exist. This results in chemical reactors with a wide variety of configurations, operating conditions, and sizes. We encounter reactions that occur in solely the liquid or the vapor phase. Many reactions require catalysts (homogeneous if the catalyst is the same phase as the reactants or heterogeneous if the catalyst has a different phase). Catalysts and the thermodynamic properties of reactants and products can lead to multiphase reactors (some of which can involve vapor, multiple liquids, and solid phases). Reactions can be exothermic (producing heat) or endothermic (absorbing heat). An example of the first is the nitration of toluene to form TNT. A very important example of the second is steam–methane reforming to produce synthesis gas.

Reactors can operate at low temperature (e.g., C4 sulfuric acid alkylation reactors run at 10°C) and at high temperatures (hydrodealkylation of toluene reactors run at 600°C). Some reactors operate in a batch or fed-batch mode, others in a continuous mode, and still others in a periodic mode. Beer fermentation is conducted in batch reactors. Ammonia is produced in a continuous vapor-phase reactor with a solid "promoted" iron catalyst.

The three classical generic chemical reactors are the batch reactor, the continuous stirred-tank reactor (CSTR), and the plug flow tubular reactor (PFR). Each of these reactor types has its own unique characteristics, advantages, and disadvantages. As the name implies, the *batch reactor* is a vessel in which the reactants are initially charged and the reactions proceed with time. During parts of the batch cycle, the reactor contents can be heated or cooled to achieve some desired temperature–time trajectory. If some of the reactant is fed into the vessel during the batch cycle, it is called a "fed-batch reactor." Emulsion polymerization is an important example. The reactions conducted in batch reactors are almost always liquid-phase and typically involve slow reactions that would require large residence times (large vessels) if operated continuously. Batch reactors are also used for small-volume products in which there is little economic incentive to go to continuous operation. In some systems batch reactors can provide final product properties that cannot be achieved in continuous reactors, such as molecular weight distribution or viscosity. Higher conversion can be achieved by increasing batch time. Perfect mixing of the liquid in the reactor is usually assumed, so the modeling of a batch reactor involves ordinary differential equations. The control of a batch reactor is a "servo" problem, in which the temperature and/or concentration profiles follow some desired trajectory with time.

The CSTR reactor is usually used for liquid-phase or multiphase reactions that have fairly high reaction rates. Reactant streams are continuously fed into the vessel, and product streams are withdrawn. Cooling or heating is achieved by a number of different mechanisms. The two most common involve the use of a jacket surrounding the vessel or an internal coil. If high conversion is required, a single CSTR must be quite large unless reaction rates are very fast. Therefore, several CSTRs in series are sometimes used to reduce total reactor volume for a given conversion. Perfect mixing of the liquid in the reactor is usually assumed, so the modeling of a CSTR involves ordinary differential equations. The control of a CSTR or a series of CSTRs is often a "regulator" problem, in which the temperature(s) and/or concentration(s) are held at the desired values in the face of disturbances. Of course, some continuous processes produce different grades of products at different times, so the transition from one mode of operation to another is a servo problem.

The PFR tubular reactor is used for both liquid and gas phases. The reactor is a long vessel with feed entering at one end and product leaving at the other end. In some applications the vessel is packed with a solid catalyst. Some tubular reactors run adiabatically (i.e., with no heat transferred externally down the length of the vessel). The heat generated or consumed by the reaction increases or decreases the temperature of the process material as it flows down the reactor. If the reaction is exothermic, the adiabatic temperature rise may produce an exit temperature that exceeds some safety limitation. It may also yield a low reaction equilibrium constant that limits conversion. If the reaction is endothermic, the adiabatic temperature change may produce reactor temperatures so low that the resulting small chemical reaction rate limits conversion.

In these cases, some type of heat transfer to or from the reactor vessel may be required. The reactor vessel can be constructed like a tube-in-shell heat exchanger. The process fluid flows inside the tubes, which may contain catalyst, and the heating/cooling medium is on the shell side. Variables in a PFR change with both axial position and time, so the modeling of a tubular reactor involves partial differential equations. The control of a PFR can be quite challenging because of the distributed nature of the process (i.e., changes in temperature and composition variables with length and sometime radial position). Tubular reactor control is usually a regulator problem, but grade transitions can lead to servo problems in some processes.

The area of reactor design has been widely studied, and there are many excellent textbooks that cover this subject. Most of the emphasis in these books is on steady-state operation. Dynamics are also considered, but mostly from the mathematical standpoint (openloop instability, multiple steady states, and bifurcation analysis). The subject of developing effective stable closedloop control systems for chemical reactors is treated only very lightly in these textbooks. The important practical issues involved in providing reactor control systems that achieve safe, economic, and consistent operation of these complex units are seldom understood by both students and practicing chemical engineers.

The safety issue is an overriding concern in reactor design and control. The US Chemical Safety Board (CSB) published a report in 2002 in which they listed 167 serious incidents involving uncontrolled chemical reactivity between 1980 and 2001. There were 108 fatalities as a result of 48 of these incidents. The CSB has a number of reports on these and more recent incidents that should be required reading for anyone involved in reactor design and control. In 2003 the American Institute of Chemical Engineers published *Essential Practices for Managing Chemical Reactivity Hazard*, which is well worth reading.

There are hundreds of papers dealing with the control of a wide variety of chemical reactors. However, there is no textbook that pulls the scattered material together in a cohesive way. One major reason for this is the very wide variety in types of chemistry and products, which results in a vast number of different chemical reactor configurations. It would be impossible to discuss the control of the myriad of reactor types found in the entire spectrum of industry. This book attempts to discuss the design and control of some of the more important generic chemical reactors.

The development of stable and practical reactors and effective control systems for the three types of classical reactors are covered. Notice that “reactors” are included, not just control schemes. Underlying the material and approaches in this book is my basic philosophy (theology) that the design of the process and the process equipment has a much greater effect on the successful control of a reactor than do the controllers that are hung on the process or the algorithms that are used in these controllers. This does not imply that the use of models is unimportant in reactor control, since in a number of important cases they are essential for achieving the desired product properties.

The basic message is that the essential problem in reactor control is temperature control. Temperature is a dominant variable and must be effectively controlled to achieve the desired compositions, conversions, and yields in the safe, economic, and consistent operation of chemical reactors. In many types of reactors, this is achieved by providing plenty of heat transfer area and cooling or heating medium so that dynamic disturbances can be handled. Once temperature control has been achieved, providing base-level stable operation, additional objectives for the control system can be specified. These can be physical property specifications (density, viscosity, molecular weight distribution, etc.) or economic objectives (conversion, yield, selectivity, etc.).

The scope of this book, like that of all books, is limited by the experience of the author. It would be impossible to discuss all possible types of chemical reactors and presumptuous to include material on reactors with which I have little or no familiarity. Despite its limitations, I hope the readers find this book interesting and useful in providing some guidance for handling the challenging and very vital problems of chemical reactor control.

The many helpful comments and suggestions of Michael L. Luyben are gratefully acknowledged.

WILLIAM L. LUYBEN

CHAPTER 1

REACTOR BASICS

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 catagorized 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

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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

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \tag{1.1}$$

the overall rate of reaction $\Re$ 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 $\mathrm{A}(C_\mathrm{A})$ and $\mathrm{B}(C_\mathrm{B})$, the overall reaction rate can be written as

$$\Re = k_{(T)} C_\mathrm{A}^{\alpha} C_\mathrm{B}^{\beta} \tag{1.2}$$

where the exponents α and β 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

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

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 °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

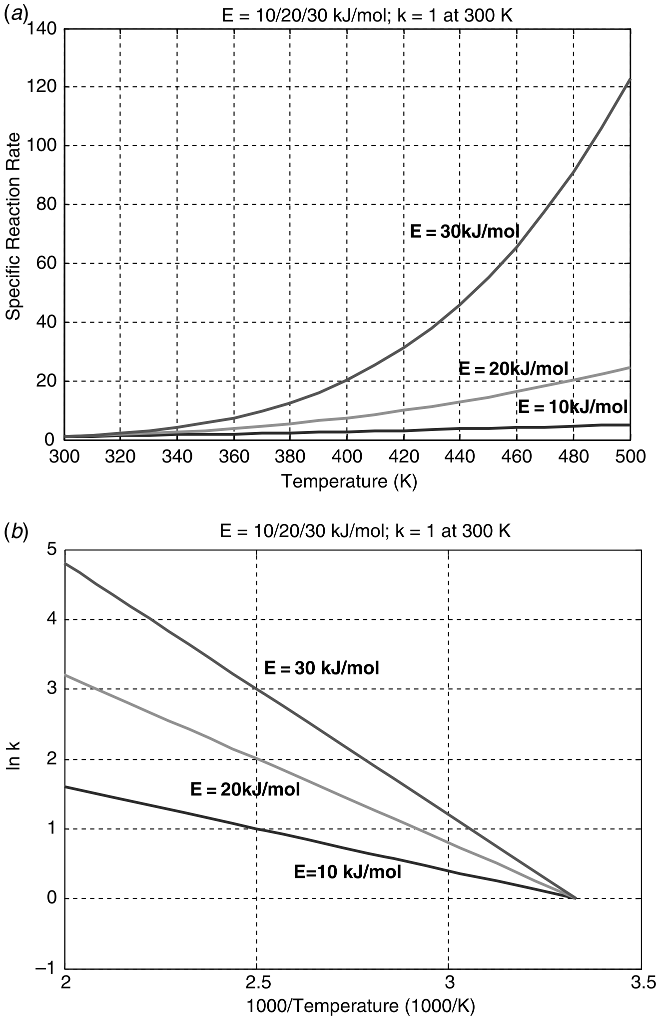

Figure 1.1 Effect of activation energy on temperature dependence of reaction rate.

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:

$$\mathrm{A} + \mathrm{B} \Leftrightarrow \mathrm{C} \tag{1.4}$$

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 α and β

$$\Re_F = k_{F(T)} C_\mathrm{A}^{\alpha} C_\mathrm{B}^{\beta} \tag{1.5}$$

with the specific rate

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

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

$$\Re_R = k_{R(T)} C_\mathrm{C}^{\gamma} \tag{1.7}$$

with the specific rate

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

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

$$\Re = \Re_F - \Re_R = k_{F(T)} C_\mathrm{A}^{\alpha} C_\mathrm{B}^{\beta} - k_{R(T)} C_\mathrm{C}^{\gamma} \tag{1.9}$$

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:

$$K_\mathrm{EQ} = \frac{C_\mathrm{A}^{\alpha} C_\mathrm{B}^{\beta}}{C_\mathrm{C}^{\gamma}} = \frac{k_{F(T)}}{k_{R(T)}} \tag{1.10}$$

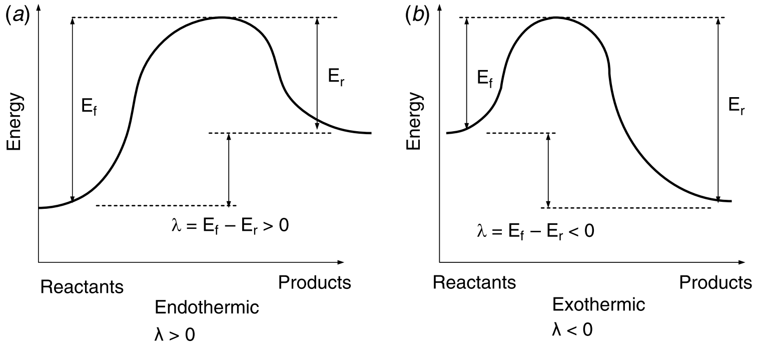

Figure 1.2 Energy change from reactants to products.

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

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_{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

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

where λ 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 λ:

$$E_F - E_R = \lambda \tag{1.13}$$

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 → 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:

$$\mathrm{A} + \mathrm{s} \underset{k_d}{\overset{k_a}{\longleftrightarrow}} \mathrm{As} \tag{1.14}$$

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

$$r = k_a' P_A C_S - k_d' C_{AS} \tag{1.15}$$

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:

$$C_T = C_S + C_{AS} \tag{1.16}$$

If we define θ as the fraction of total sites covered by the adsorbed molecules, then

$$\theta = \frac{C_{AS}}{C_T} \tag{1.17}$$

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

$$r = k_a P_A (1 - \theta) - k_d \theta \tag{1.18}$$

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*:

$$\begin{aligned} K_A &= \frac{k_a}{k_d} \\ \theta &= \frac{K_A P_A}{1 + K_A P_A} \end{aligned} \tag{1.19}$$

Figure 1.3 shows a plot of θ 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 → 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

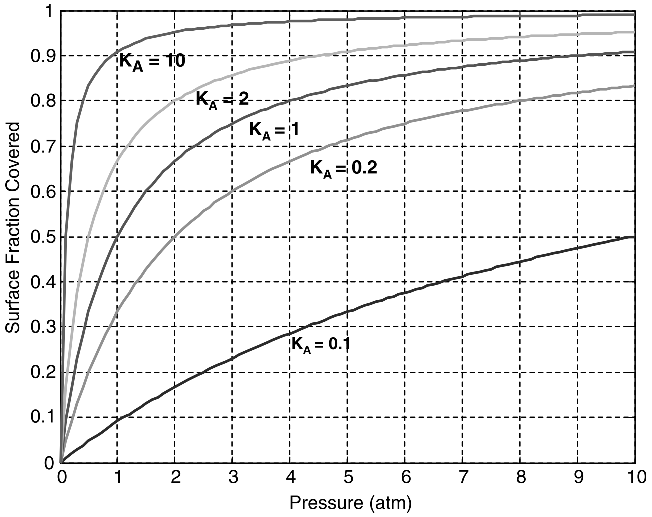

Figure 1.3 Langmuir isotherms for heterogeneous systems.

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

$$\begin{gathered}
\mathrm{A} + \mathrm{s} \underset{k_d^{\mathrm{A}}}{\overset{k_a^{\mathrm{A}}}{\longleftrightarrow}} \mathrm{As} \\
\mathrm{As} \xrightarrow{k_{sr}} \mathrm{Bs} \\
\mathrm{Bs} \underset{k_a^{\mathrm{B}}}{\overset{k_d^{\mathrm{B}}}{\longleftrightarrow}} \mathrm{B} + \mathrm{s}
\end{gathered} \tag{1.20}$$

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 absorbed on the surface (C_{AS}) according to standard power-law kinetics:

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

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}):

$$\begin{aligned}
K_{\mathrm{A}} &= \frac{C_{\mathrm{AS}}}{P_{\mathrm{A}} C_{\mathrm{s}}} = \frac{k_a^{\mathrm{A}}}{k_d^{\mathrm{A}}} \\
K_{\mathrm{B}} &= \frac{C_{\mathrm{BS}}}{P_{\mathrm{B}} C_{\mathrm{s}}} = \frac{k_a^{\mathrm{B}}}{k_d^{\mathrm{B}}}
\end{aligned} \tag{1.22}$$

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:

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

We can write the overall reaction rate as

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

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. 1.4*a*), 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. 1.4*b*), 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

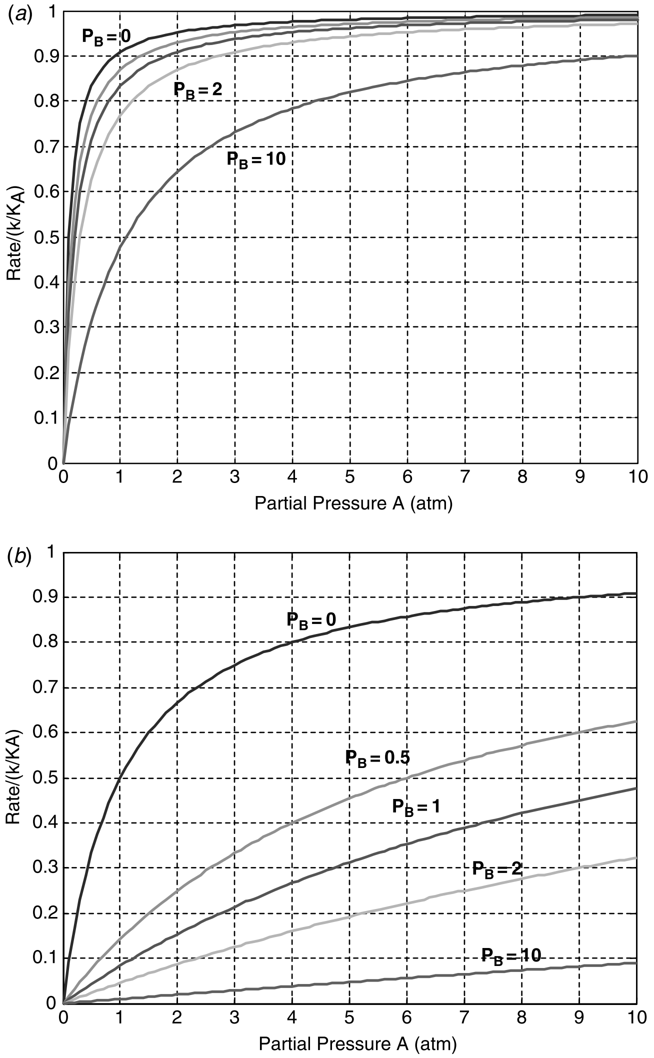

Figure 1.4 Normalized reaction rate as a function of P_A and P_B, $k = 1$; (*a*) $K_A = 10$, $K_B = 1$; (*b*) $K_A = 1$, $K_B = 2$.

systems. The Michaelis–Menton 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:

$$\begin{aligned} S + E &\longleftrightarrow ES \\ ES &\longrightarrow P \end{aligned} \tag{1.25}$$

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:

$$r_P = \frac{kC_{E0}C_S}{C_S + K_M} \tag{1.26}$$

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:

$$r_X = \mu_{\max} C_X \tag{1.27}$$

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).