

Chapter 1

Elementary Reactions in Ideal Reactors

Material and energy balances are the heart of chemical engineering. Combine them with chemical kinetics, and they are the heart of chemical reaction engineering. Add transport phenomena and you have the intellectual basis for chemical reactor design. This chapter begins the study of chemical reactor design by combining material balances with kinetic expressions for elementary chemical reactions. The resulting equations are then solved for several simple but important types of chemical reactors. More complicated reactions and more complicated reactors are treated in subsequent chapters, but the real core of chemical reactor design is here in Chapter 1. Master it, and the rest will be easy.

1.1 MATERIAL BALANCES

Consider any region of space having a finite volume and prescribed boundaries that unambiguously separate the region from the rest of the universe. Such a region is called a *control volume*, and the laws of conservation of mass and energy may be applied to it. We ignore nuclear processes so that there are separate conservation laws for mass and energy. For mass,

$$\begin{aligned} & \text{Rate at which mass enters the volume} \\ & = \text{rate at which mass leaves the volume} \\ & + \text{rate at which mass accumulates within the volume} \end{aligned} \quad (1.1)$$

where “entering” and “leaving” apply to the flow of material across the boundaries. See Figure 1.1. Equation 1.1 is an *overall mass balance* that applies to the total mass within the control volume, as measured in kilograms or pounds. It can be written as

$$(Q_{\text{mass}})_{\text{in}} = (Q_{\text{mass}})_{\text{out}} + \frac{dI}{dt} \quad (1.2)$$

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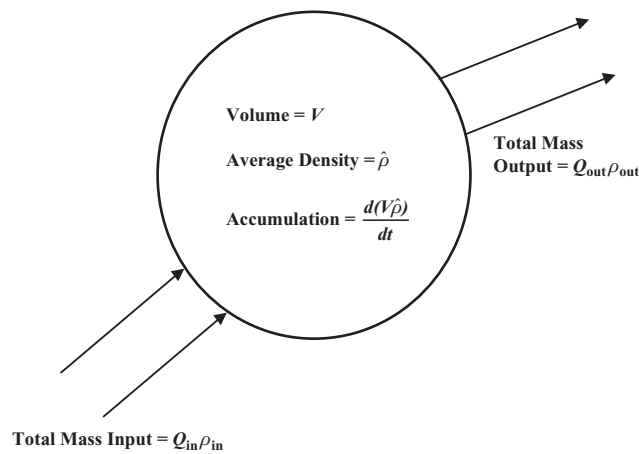


Figure 1.1 Control volume for total mass balance.

where Q_{mass} is the mass flow rate and I is the mass inventory in the system. We often write this equation using volumetric flow rates and volumes rather than mass flow rates and mass inventories.

$$Q_{\text{in}}\rho_{\text{in}} = Q_{\text{out}}\rho_{\text{out}} + \frac{d(\hat{\rho}V)}{dt} \quad (1.3)$$

where Q is the volumetric flow rate (volume per time) and ρ is the mass density (mass per volume). Note that $\hat{\rho}$ is the average mass density in the control volume so that $\hat{\rho}V = I$.

Equations 1.1–1.3 are different ways of expressing the overall mass balance for a flow system with variable inventory. In steady-state flow, the derivatives vanish, the total mass in the system is constant, and the overall mass balance simply states that input equals output. In batch systems, the flow terms are zero, the time derivative is zero, and the total mass in the system remains constant. We will return to the general form of Equation 1.3 when unsteady reactors are treated in Chapter 14. Until then, the overall mass balance merely serves as a consistency check on more detailed **component balances** that apply to individual substances.

In reactor design, we are interested in chemical reactions that transform one kind of mass into another. A material balance can be written for each component; but since chemical reactions are possible, the rate of formation of the component within the control volume must now be considered. The **component balance** for some substance A is

$$\begin{aligned} &\text{Rate at which component A enters the volume} \\ &\quad + \text{net rate at which component A is formed by reaction} \\ &= \text{rate at which component A leaves the volume} \\ &\quad + \text{rate at which component A accumulates within the volume} \end{aligned} \quad (1.4)$$

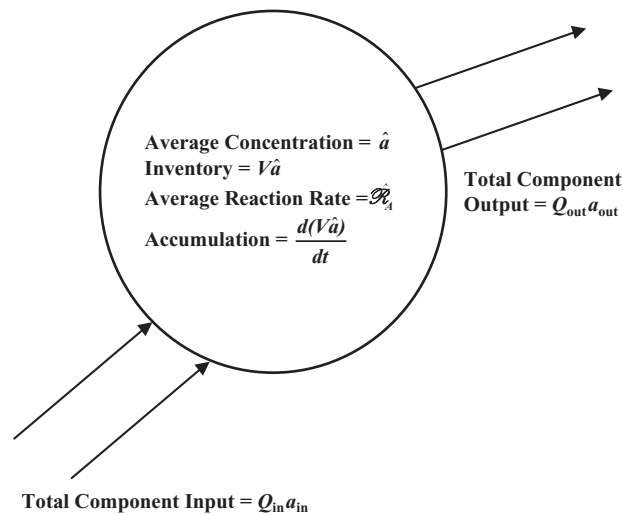


Figure 1.2 Control volumes for component balance.

More briefly,

$$\text{Input} + \text{formation} = \text{output} + \text{accumulation} \quad (1.5)$$

See Figure 1.2. A component balance can be expressed in mass units, and this is done for materials such as polymers that have an ill-defined molecular weight. Usually, however, component A will be a distinct molecular species, and it is more convenient to use molar units:

$$Q_{in}a_{in} + \hat{\mathcal{R}}_A V = Q_{out}a_{out} + \frac{d(V\hat{a})}{dt} \quad (1.6)$$

where a is the concentration or molar density of component A in moles per volume and $\hat{\mathcal{R}}_A$ is the volume-average rate of formation of component A in moles per volume per time.

There may be several chemical reactions occurring simultaneously, some of which generate A while others consume it. The net rate $\hat{\mathcal{R}}_A$ will be positive if there is net production of component A and negative if there is net consumption. Unless the system is very well mixed, concentrations and reaction rates will vary from point to point within the control volume. The component balance applies to the entire control volume so that \hat{a} and $\hat{\mathcal{R}}_A$ denote spatial averages.

A version of Equation 1.4 can be written for each component, A, B, C, If these equations are written in terms of mass and then summed over all components, the sum must equal Equation 1.1 since the net rate of mass formation must be zero. When written in molar units as in Equation 1.6, the sum need not be zero since chemical reactions can cause a net increase or decrease in the number of moles.

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1.1.1 Measures of Composition

This book uses the term *concentration* to mean the molar density of a component, for example, moles of A per unit volume of the reacting mixture. In the International System of Units (SI) concentration is in moles per cubic meters where the moles are gram moles. *Molarity* is classically defined as moles per liter of solution and is a similar concentration measurement. *Molality* is classically defined as moles per kilogram of solvent (not of solution) and is thus not a standard measure of concentration. For gases at low pressure and moderate temperatures, partial pressures are sometimes used instead of concentrations since partial pressures are proportional to concentration for ideal gases.

Other measures of composition such as mole fraction and mass fraction are less commonly used to express chemical reaction rates. Weight measurements are frequently used to prepare solutions or fill reactors. The resulting composition will have a known ratio of moles and masses of the various components, but the numerical value for concentration requires that the density be known. Good practice is to prepare solutions in mass units and then convert to standard concentration units based on the known or observed density of the solution under reaction conditions. To avoid ambiguity, modern analytical chemists frequently define both molarity and molality in weight units as moles per kilogram of solution or moles per kilogram of solvent.

EXAMPLE 1.1

Sucrose, 342.3 g, is dissolved in one liter of water at “room temperature.” Calculate the composition by various measures.

SOLUTION: The molecular weight of sucrose is 342.3 so the molality of the solution is approximately 1.0. It would be exactly 1.0 if molality were defined per liter of solvent rather than per kilogram of solvent. Room temperature in the scientific literature means 20–25°C, with 25°C being usual in the United States. The density of water at 25°C is 0.997 g cm⁻³ so that the solution used 0.997 kg of water, giving a molality of 1.003. The weight percent of sucrose is 25.56. The mole fraction of sucrose is 0.0177. The concentration of sucrose cannot be determined without knowing the density of the solution. It is about 1.10 g cm⁻³ at the experimental conditions. Thus the concentration of sucrose is $1/(997 + 342.3)/1.10 = 8.21 \times 10^{-4} \text{ mol cm}^{-3} = 821 \text{ mol m}^{-3}$. The molarity is 0.821 mol L⁻¹.

A word of caution involves the definition of mole. As indicated above, SI moles are gram moles, the mass in grams of 6.02×10^{23} molecules. There is an inconsistency in the SI system of units that may cause problems when converting molar densities and molar flow rates to mass densities and mass flow rates. A point in the system with molar concentrations (i.e., molar densities) of a and b has a mass density of $\rho = aM_A + bM_B$, where M_A and M_B are the molecular weights of the two components.

The resulting units on ρ are grams per cubic meter and must be divided by 1000 to obtain conventional SI units of kilograms per cubic meter.

1.1.2 Measures of Reaction Rate

The SI units for reaction rate are moles per cubic meter per second, but other time units are frequently used and other volume units are sometimes used. It is obviously necessary to specify to what compound the reaction rate refers. This book makes the specification essentially automatic by defining a rate, \mathcal{R} , for the reaction as a whole. The reaction rate for component A is denoted \mathcal{R}_A and is found from

$$\mathcal{R}_A = \nu_A \mathcal{R} \quad (1.7)$$

where ν_A is the stoichiometric coefficient for component A in the (single) reaction. The next section discusses this more fully, and Chapter 2 extends the treatment to multiple reactions. However, reaction rate expressions and data taken from other sources may not follow the convention and need careful scrutiny, particularly if the reaction is something like $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$.

To design a chemical reactor, the spatial-average concentrations \hat{a} , \hat{b} , \hat{c} , . . . must be found for a batch reactor and the outlet concentrations are needed for a flow reactor. Finding these concentrations is relatively easy for the single, elementary reactions and ideal reactors that are considered here in Chapter 1. We begin by discussing elementary reactions, of which there are just a few basic types.

1.2 ELEMENTARY REACTIONS

Consider the reaction of two chemical species according to the stoichiometric equation



This reaction is said to be *homogeneous* if it occurs within a single phase. For the time being we are concerned only with reactions that take place in the gas phase or in a single liquid phase. These reactions are said to be *elementary* if they result from a single interaction (i.e., a collision) between the molecules appearing on the left-hand side of Equation 1.8. The rate at which collisions occur between A and B molecules should be proportional to their concentrations, a and b . Not all collisions cause a reaction, but at constant environmental conditions (e.g., temperature), some definite fraction should react. Thus we expect

$$\mathcal{R} = k[\text{A}][\text{B}] = kab \quad (1.9)$$

where k is a constant of proportionality known as the *rate constant*.

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1.2.1 Kinetic Theory of Gases

The kinetic theory of gases can be used to rationalize the functional form of Equation 1.9. Suppose that a collision between an A and B molecule is necessary but not sufficient for reaction to occur. Thus we expect

$$\mathcal{R} = \frac{C_{AB} f_R}{\mathbf{A}v} \quad (1.10)$$

where C_{AB} is the collision rate (collisions per volume per time) and f_R is the reaction efficiency. Avogadro's number, $\mathbf{A}v$, has been included in Equation 1.10 so that \mathcal{R} will have normal units, moles per cubic meter per second, rather than units of molecules per cubic meter per second. By hypothesis $0 < f_R < 1$.

Ideal gas theory treats the molecules as rigid spheres having radii r_A and r_B . They collide if they approach each other within a distance $r_A + r_B$. A result from kinetic theory is

$$C_{AB} = \left[\frac{8\pi R_g T (m_A + m_B)}{\mathbf{A}v m_A m_B} \right]^{1/2} (r_A + r_B)^2 \mathbf{A}v^2 ab \quad (1.11)$$

where R_g is the gas constant, T is the absolute temperature, and m_A and m_B are the molecular masses in kilograms per molecule. The collision rate is proportional to the product of the concentrations as postulated in Equation 1.9. The reaction rate constant is

$$k = \left[\frac{8\pi R_g T (m_A + m_B)}{\mathbf{A}v m_A m_B} \right]^{1/2} (r_A + r_B)^2 \mathbf{A}v f_R \quad (1.12)$$

Collision theory is mute about the value of f_R . Typically $f_R \ll 1$ so that the number of molecules colliding is much greater than the number reacting. See Problem 1.2. Not all collisions have enough energy to produce a reaction. Steric effects may also be important. As will be discussed in Chapter 5, f_R is strongly dependent on temperature. This dependence usually overwhelms the $T^{1/2}$ dependence predicted for the collision rate.

1.2.2 Rate of Formation

Note that the rate constant k is positive so that \mathcal{R} is positive. Here, \mathcal{R} is defined as the *rate of the reaction*, not the rate at which a particular component reacts or is formed. Components A and B are consumed by the reaction of Equation 1.8 and thus are "formed" at a negative rate:

$$\mathcal{R}_A = \mathcal{R}_B = -kab$$

while P is formed at a positive rate:

$$\mathcal{R}_P = +kab$$

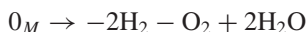
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The sign convention we have adopted is that the rate of a reaction is always positive. The *rate of formation of a component* is positive when the component is formed by the reaction and is negative when the component is consumed.

A general expression for any single reaction is



As an example, the reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ can be written as



This form is obtained by setting all participating species, whether products or reactants, on the right-hand side of the stoichiometric equation. The remaining term on the left is the *zero molecule*, which is denoted by 0_M to avoid confusion with atomic oxygen. The ν_A, ν_B, \dots are the *stoichiometric coefficients* for the reaction. They are positive for products and negative for reactants. The general relationship between the rate of the reaction and the rate of formation of component A is

$$\mathcal{R}_A = \nu_A \mathcal{R} \quad (1.14)$$

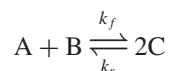
Stoichiometric coefficients can be fractions. However, for elementary reactions, they must be small integers, of magnitude 2, 1, or 0. If the reaction of Equation 1.13 were reversible and elementary, its rate would be

$$\mathcal{R} = k_f [A]^{-\nu_A} [B]^{-\nu_B} \cdots - k_r [R]^{\nu_R} [S]^{\nu_S} \quad (1.15)$$

where A, B, ... are reactants; R, S, ... are products; k_f is the rate constant for the forward reaction; and k_r is the rate constant for the reverse reaction.

The functional form of the reaction rate in Equation 1.15 is dictated by the reaction stoichiometry, Equation 1.13. Only the constants k_f and k_r can be adjusted to fit the specific reaction. This is the hallmark of an elementary reaction; its rate is consistent with the reaction stoichiometry and is given by Equation 1.15. However, reactions can have the form of Equation 1.15 without being elementary.

As a shorthand notation for indicating that a reaction is elementary, we shall include the rate constants in the stoichiometric equation by showing the rate constant above the arrow and, if reversible, below the arrow. Thus the reaction



is elementary and reversible and has the following rate expression:

$$\mathcal{R} = k_f ab - k_r c^2$$

The relative magnitudes of k_f and k_r are constrained by an equilibrium constant. For this example, $\nu_A = \nu_B = -1$, $\nu_C = +2$, and the equilibrium constant is

$$K_{\text{kinetic}} = \frac{k_f}{k_r} = [A]^{-1} [B]^{-1} [C]^2 = \frac{[C]^2}{[A][B]} = \frac{c^2}{ab} \quad (1.16)$$

Reversible reactions and equilibrium constants are discussed at length in Section 7.2.

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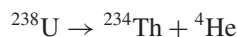
Chemical engineers deal with many reactions that are not elementary. Most industrially important reactions go through a complex kinetic mechanism before the final products are reached. The mechanism may give a rate expression far different than Equation 1.15 even though it involves only short-lived intermediates that never appear in conventional chemical analyses. Elementary reactions are generally limited to the following types: first order, second order unimolecular, and second order with two reactants. Third-order reactions exist but are rare.

1.2.3 First-Order Reactions

An irreversible first-order reaction involves only one reactant:



Since \mathcal{R} has units of moles per volume per time and a has units of moles per volume, the rate constant for a first-order reaction has units of reciprocal time, for example, reciprocal seconds. The best example of a truly first-order reaction is radioactive decay, for example,



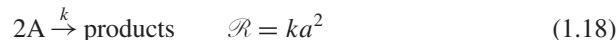
since it occurs spontaneously as a single-body event. Among strictly chemical reactions, thermal decompositions such as



follow first-order kinetics at normal gas densities. The student of chemistry will recognize that the complete decomposition of dimethyl ether into methane, carbon monoxide, and hydrogen will not occur in a single step. Short-lived intermediates will exist, but since the reaction is irreversible, they will not affect the rate of the decomposition reaction since it is first order and has the form of Equation 1.17. The decomposition does require energy, and collisions between the reactant and other molecules are the usual mechanism for acquiring this energy. Thus a second-order dependence may be observed for the pure gas at very low densities since reactant molecules must collide with themselves to acquire energy.

1.2.4 Second-Order Reactions with One Reactant

The simplest example of a second-order reaction has one type of molecule reacting with itself:

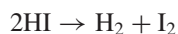


where k has units of cubic meters per mole per second. It is important to note that $\mathcal{R}_A = -2ka^2$ according to the convention of Equation 1.14. Pesky factors of 2 are common in chemical kinetics. In using literature data, be sure to check the source to

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see if the author defined the reaction rate as $\mathcal{R} = ka^2$ so that $\mathcal{R}_A = -2ka^2$. Another common possibility is to have $\mathcal{R}_A = -k_2a^2$ where $k_2 = 2k$.

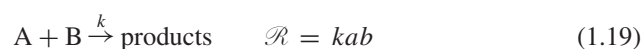
A gas phase reaction believed to be elementary and second order is



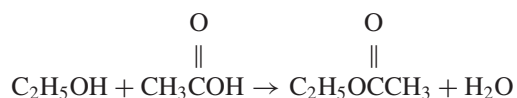
Here, collisions between two HI molecules supply energy and also supply the reactants needed to satisfy the observed stoichiometry.

1.2.5 Second-Order Reactions with Two Reactants

Second-order reactions with two reactants are common:



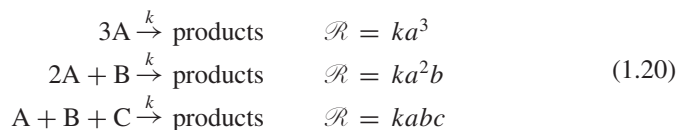
Liquid phase esterifications such as



typically follow second-order kinetics.

1.2.6 Third-Order Reactions

Elementary third-order reactions are vanishingly rare because they require a statistically improbable three-way collision. In principle there are three types of third-order reactions:



A homogeneous gas phase reaction that follows a third-order kinetic scheme is



although the mechanism is believed to involve two steps (Tsukahara et al., 1999) and thus is not elementary. Reactions may approximate third-order and even higher order kinetics without being elementary.

1.3 REACTION ORDER AND MECHANISM

As suggested by these examples, the *order* of a reaction is the sum of the exponents m, n, \dots in

$$\mathcal{R} = ka^m b^n \dots \quad \text{Reaction order} = m + n + \dots \quad (1.21)$$

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This definition for reaction order is directly meaningful only for irreversible or forward reactions that have rate expressions in the form of Equation 1.21. If the reaction is reversible, the reverse reaction can have a different order. Thus

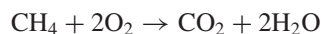


is second order for the forward reaction and first order for the reverse reaction.

Components A, B, . . . are consumed by the reaction and have negative stoichiometry coefficients so that $m = -\nu_A$, $n = -\nu_B$, . . . are positive (or zero). For elementary reactions, m and n must be integers of 2 or less and, practically speaking, must sum to 2 or less so that the only real possibilities for elementary reactions are first and second order.

Equation 1.21 is frequently used to correlate data from complex reactions. Complex reactions can give rise to rate expressions that have the form of Equation 1.21 but with fractional or even negative exponents. Complex reactions with observed orders of $\frac{1}{2}$ or $\frac{3}{2}$ can be explained theoretically based on mechanisms discussed in Chapter 2. Negative orders arise when a compound retards a reaction, say by competing for active sites in a heterogeneously catalyzed reaction or when the reaction is reversible. Observed reaction orders above 3 are occasionally reported. An example is the reaction of styrene with nitric acid where an overall order of 4 has been observed (Lewis and Moodie, 1997). The likely explanation is that the acid serves both as a catalyst and as a reactant. The reaction is far from elementary.

Complex reactions can be broken down into a number of series and parallel elementary steps, possibly involving short-lived intermediates such as free radicals. These individual reactions collectively constitute the *mechanism* of the complex reaction. The individual reactions are usually second order, and the number of reactions needed to explain an observed, complex reaction can be surprisingly large. For example, a good model burning methane such as

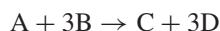


will involve 20 or more elementary reactions even assuming that the indicated products are the only ones formed in significant quantities. A detailed model for the oxidation of toluene involves 141 chemical species in 743 elementary reactions (Lindstedt and Maurice, 1996). A model for the creation of carbon nanotubes by the high-pressure carbon monoxide process (Dateo et al., 2002) involves 917 species and 1948 chemical reactions, although the experimental data are well explained by a simple model containing a mere 14 species and 22 reactions.

As a simpler example of a complex reaction, consider the nitration of toluene to give TNT, 2,4,6-trinitrotoluene (kindly do this abstractly, not experimentally like the evil professor in Problem 1.13). The reaction is



or, in shorthand,



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This reaction cannot be elementary. We can hardly expect three nitric acid molecules to react at all three toluene sites (these are primarily the ortho and para sites; meta substitution is not favored) in a glorious, four-body collision. Thus the fourth-order rate expression $\mathcal{R} = kab^3$ is implausible. Instead, the mechanism of the TNT reaction involves at least seven steps (two reactions leading to *ortho*- or *para*-nitrotoluene, three reactions leading to 2,4- or 2,6-dinitrotoluene, and two reactions leading to 2,4,6-trinitrotoluene). Each step would require only a two-body collision, could be elementary, and could be governed by a second-order rate equation. Chapter 2 shows how the component balance equations can be solved for multiple reactions so that an assumed mechanism can be tested experimentally. For the toluene nitration, even the set of seven series and parallel reactions may not constitute an adequate mechanism since an experimental study (Chen et al., 1996) found the reaction to be 1.3 order in toluene and 1.2 order in nitric acid for an overall order of 2.5 rather than the expected value of 2. Furthermore, the reaction is not even homogeneous as it is normally conducted (Milligan, 1986).

An irreversible, elementary reaction must have Equation 1.21 as its rate expression. A complex reaction may have an empirical rate equation with the form of Equation 1.21 and with integral values for n and m without being elementary. The classic example of this statement is a second-order reaction where one of the reactants is present in great excess. Consider the slow hydrolysis of an organic compound in water. A rate expression of the form

$$\mathcal{R} = k[\text{water}][\text{organic}]$$

is plausible, at least for the first step of a possibly complex mechanism. Suppose $[\text{organic}] \ll [\text{water}]$ so that the concentration of water does not change appreciably during the course of the reaction. Then the water concentration can be combined with k to give a composite rate constant. The rate expression appears to be first order in $[\text{organic}]$:

$$\mathcal{R} = k[\text{water}][\text{organic}] = k'[\text{organic}] = k'a$$

where $k' = k[\text{water}]$ is a ***pseudo-first-order rate constant***. From an experimental viewpoint, the reaction cannot be distinguished from first order even though the actual mechanism is second order. Gas phase reactions can appear first order when one reactant is dilute. Kinetic theory still predicts the collision rates of Equation 1.11, but the concentration of one species, call it B, remains approximately constant. The observed rate constant is

$$k' = \left[\frac{8\pi R_g T (m_A + m_B)}{Av m_A m_B} \right]^{1/2} (r_A + r_B)^2 \mathbf{A}v f_R b$$

The only reactions which are strictly first order are radioactive decay. Among chemical reactions, thermal decompositions may seem first order, but an external energy source is generally required to excite the reaction. As noted earlier, this energy is usually acquired by intermolecular collisions. Thus the reaction rate could be written as

$$\mathcal{R} = k[\text{reactant molecules}] [\text{all molecules}]$$

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The concentration of all molecules is normally much higher than the concentration of reactant molecules so that it remains essentially constant during the course of the reaction. Thus, what is truly a second-order reaction appears first order.

1.4 IDEAL, ISOTHERMAL REACTORS

Section 1.2 developed rate expressions for elementary reactions. These expressions are now combined with the material balances of Section 1.1 to develop reactor design equations, that is, equations to predict final concentrations in a batch reactor or outlet concentrations in a flow reactor. Since reaction rate expressions have units of concentration per time, it may seem that \mathcal{R}_A is identical to da/dt . This is true only for an ideal batch reactor. In flow reactors, the concentration changes can be caused by any of convection, diffusion, and reaction.

There are four kinds of ideal reactors:

1. The batch reactor
2. The piston flow reactor (PFR)
3. The perfectly mixed continuous flow stirred tank reactor (CSTR)
4. The completely segregated continuous flow stirred tank.

This chapter discusses the first three types. These are overwhelmingly the most important. The fourth type is interesting theoretically but has limited practical importance. It is discussed in Chapter 15.

The batch reactor is an unsteady-state system. Reactants are charged to a vessel and the reaction proceeds in time. Piston flow and stirred tank reactors are normally designed to operate at a steady state where reactants are continuously charged and products continuously removed. Until Chapter 5, the reactors are assumed to be isothermal. This means that the operating temperature is known, is uniform throughout the reactor, and does not change with time in a batch reactor. Here in Chapter 1, we also assume that fluid properties and especially density are constant, independent of the extent of reaction. Finally, we assume that the system is homogeneous and that there is a single reaction that either is elementary or else has a rate expression identical to one of the elementary reactions. These various assumptions are realistic for some industrial reactors and grossly unrealistic for others. The simplified results in this chapter provide a starting point.

1.4.1 Ideal Batch Reactors

This is the classic reactor used by organic chemists. The typical volume in glassware is a few hundred milliliters. Reactants are charged to the system, rapidly mixed, and rapidly brought up to temperature so that operating conditions are well defined. Heating is done with an oil bath or an electric heating mantel. Mixing is done with a magnetic stirrer or a small mechanical agitator. Temperature is controlled by regulating the bath temperature or by allowing a solvent to reflux.

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Batch reactors are the most common type of industrial reactor and may have volumes well in excess of 100,000 L. They tend to be used for small-volume, specialty products (e.g., an organic dye) rather than large-volume, commodity chemicals (e.g., ethylene oxide) that are normally reacted in continuous flow equipment. Industrial-scale batch reactors can be heated or cooled by external coils or a jacket, by internal coils, or by an external heat exchanger in a pump-around loop. Reactants are often preheated by passing them through heat exchangers as they are charged to the vessel. Heat generation due to the reaction can be significant in large vessels. Refluxing is one means for controlling the exotherm. Mixing in large batch vessels is usually done with a mechanical agitator, but is occasionally done with an external pump-around loop where the momentum of the returning fluid causes the mixing.

Heat and mass transfer limitations are rarely important in the laboratory but may emerge upon scaleup. Batch reactors with internal variations in temperature or composition are difficult to analyze and remain a challenge to the chemical reaction engineer. Tests for such problems are considered in Section 1.5. For now assume an *ideal batch reactor* with the following characteristics:

1. Reactants are quickly charged, mixed, and brought to temperature at the beginning of the reaction cycle.
2. The reaction mass constitutes a single, fluid phase.
3. Mixing and heat transfer are sufficient to assure that the batch remains completely uniform in temperature and composition throughout the reaction cycle.
4. The operating temperature is held constant.

A batch reactor has no input or output of mass after the initial charging. The amounts of individual components may change due to reaction but not due to flow into or out of the system. The component balance for component A, Equation 1.6, reduces to

$$\frac{d(Va)}{dt} = \mathcal{R}_A V \quad (1.22)$$

Together with similar equations for the other reactive components, Equation 1.22 constitutes the *reactor design equation* for an ideal batch reactor. Note that \hat{a} and $\hat{\mathcal{R}}_A$ have been replaced with a and \mathcal{R}_A due to the assumption of good mixing throughout the vessel. An ideal batch reactor has no temperature or concentration gradients within the system volume. The concentration will change with time due to the reaction, but at any time it is everywhere uniform. The temperature may also change with time, but this complication will be deferred until Chapter 5. The reaction rate will vary with time but is always uniform throughout the vessel. Here in Chapter 1, we make the additional assumption that the volume is constant. In a liquid phase reaction, this corresponds to assuming constant fluid density, an assumption that is usually reasonable for preliminary calculations. Industrial gas phase reactions are normally conducted in flow systems rather than batch systems. When batch reactors are used for a gas phase reaction, they are normally constant-volume devices so that the system pressure can vary during the batch cycle. Constant-pressure devices were used in early

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kinetic studies and are occasionally found in industry. The constant pressure at which they operate is usually atmospheric pressure.

If the volume is constant, Equation 1.22 simplifies to

$$\frac{da}{dt} = \mathcal{R}_A \quad (1.23)$$

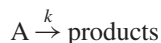
Equation 1.23 is an ordinary differential equation (ODE). Its solution requires an initial condition:

$$a = a_0 \quad \text{at } t = 0 \quad (1.24)$$

When \mathcal{R}_A depends on a alone, the ODE is variable separable and can usually be solved analytically. If \mathcal{R}_A depends on the concentration of several components (e.g., a second-order reaction of the two-reactant variety, $\mathcal{R}_A = -kab$), versions of Equations 1.23 and 1.24 can be written for each component and the resulting equations solved simultaneously. Alternatively, stoichiometric relations can be used to couple the concentrations, but this approach becomes awkward in multicomponent systems and is avoided by the methodology introduced in Chapter 2.

First-Order Batch Reactions

The reaction is



The rate constant over the reaction arrow indicates that the reaction is assumed to be elementary. Thus the rate equation is

$$\mathcal{R} = ka$$

and

$$\mathcal{R}_A = v_A \mathcal{R} = -ka$$

Substituting into Equation 1.23 gives

$$\frac{da}{dt} + ka = 0$$

Solving this ODE and applying the initial condition of Equation 1.24 give

$$a = a_0 e^{-kt} \quad (1.25)$$

Equation 1.25 is arguably the most important result in chemical reaction engineering. It shows that the concentration of a reactant being consumed by a first-order batch reaction decreases exponentially. Dividing through by a_0 gives the ***fraction unreacted***,

$$Y_A = \frac{a}{a_0} = e^{-kt} \quad (1.26)$$

and

$$X_A = 1 - \frac{a}{a_0} = 1 - e^{-kt} \quad (1.27)$$

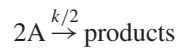
gives the *conversion*. The *half-life* of the reaction is defined as the time necessary for a to fall to half its initial value:

$$t_{1/2} = 0.693/k \quad (1.28)$$

The half-life of a first-order reaction is independent of the initial concentration. Thus the time required for the reactant concentration to decrease from a_0 to $a_0/2$ is the same as the time required to decrease from $a_0/2$ to $a_0/4$. This is not true for reactions of order other than first.

Second-Order Batch Reactions with One Reactant

We now choose to write the stoichiometric equation as



Compare this to Equation 1.18 and note the difference in rate constants. For the current formulation,

$$\mathcal{R} = \left(\frac{1}{2}k\right) a^2 \quad \mathcal{R}_A = \nu_A \mathcal{R} = -2\mathcal{R} = -ka^2$$

Substituting into Equation 1.22 gives

$$\frac{da}{dt} + ka^2 = 0$$

Solution gives

$$-a^{-1} + C = -kt$$

where C is a constant. Applying the initial condition gives $C = (a_0)^{-1}$ and

$$Y_A = \frac{a}{a_0} = \frac{1}{1 + a_0kt} \quad (1.29)$$

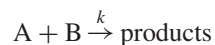
The initial half-life of a second-order reaction corresponds to a decrease from a_0 to $a_0/2$ and is given by

$$t_{1/2} = \frac{1}{a_0k} \quad (1.30)$$

The second half-life, corresponding to a decrease from $a_0/2$ to $a_0/4$, is twice the initial half-life.

Second-Order Batch Reactions with Two Reactants

The batch reaction is now



$$\mathcal{R} = kab \quad \mathcal{R}_A = \nu_A \mathcal{R} = -\mathcal{R} = -kab$$

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Substituting into Equation 1.23 gives

$$\frac{da}{dt} + kab = 0$$

A similar equation can be written for component B:

$$\frac{db}{dt} + kab = 0$$

The pair can be solved simultaneously. A simple way to proceed is to note that

$$\frac{da}{dt} = \frac{db}{dt}$$

which is solved to give

$$a = b + C$$

where C is a constant of integration that can be determined from the initial conditions for a and b . The result is

$$a - a_0 = b - b_0 \quad (1.31)$$

which states that A and B are consumed in equal molar amounts as required by the reaction stoichiometry. Applying this result to the ODE for component A gives

$$\frac{da}{dt} + ka(a - a_0 + b_0) = 0$$

The equation is variable separable. Integrating and applying the initial condition give

$$\frac{a}{a_0} = \frac{b_0 - a_0}{b_0 \exp[(b_0 - a_0)kt] - a_0} \quad (1.32)$$

This is the general result for a second-order batch reaction. The mathematical form of the equation presents a problem when the initial stoichiometry is perfect, $a_0 = b_0$. Such problems are common with analytical solutions to ODEs. Special formulas are needed for special cases.

One way of treating a special case is to do a separate derivation. For the current problem, perfect initial stoichiometry means $b = a$ throughout the reaction. Substituting this into the ODE for component A gives

$$\frac{da}{dt} + ka^2 = 0$$

which is the same as that for the one-reactant case of a second-order reaction and the solution is Equation 1.29.

An alternative way to find a special formula for a special case is to apply L'Hospital's rule to the general case. When $b_0 \rightarrow a_0$, Equation 1.32 has an indeterminate form of the $0/0$ type. Differentiating the numerator and denominator with

respect to b_0 and then taking the limit give

$$\frac{a}{a_0} = \lim_{b_0 \rightarrow a_0} \left[\frac{1}{\exp[(b_0 - a_0)kt] + b_0kt \exp[(b_0 - a_0)kt]} \right] = \frac{1}{1 + a_0kt}$$

which is again identical to Equation 1.29.

Any Single Reaction in an Ideal Batch Reactor

The above results are directly useful when the batch reaction time t is known and $a(t)$ is sought. An alternative form is sometimes used when $a(t)$ is specified and the batch reaction time is sought. For this case, a general solution to Equation 1.23 is

$$t = \int_{a_0}^{a(t)} \frac{da_1}{\mathcal{R}_A(a_1)} \quad (1.33)$$

Here, a_1 is a dummy variable of integration that will be replaced by the upper and lower limits after the integral is evaluated. The results are equivalent to those obtained earlier, for example, Equations 1.26 and 1.29 depending on the reaction order, and all the restrictive assumptions still apply: a single reaction in a constant-volume, isothermal, perfectly mixed batch reactor. Note that Equation 1.33 becomes useless for the multiple reactions treated in Chapter 2.

1.4.2 Reactor Performance Measures

There are four common measures of reactor performance: fraction unreacted, conversion, yield, and selectivity. The fraction unreacted is the simplest and is usually found directly when solving the component balance equations. It is $a(t)/a_0$ for a batch reaction and $a_{\text{out}}/a_{\text{in}}$ for a flow reactor. The conversion is just 1 minus the fraction unreacted. The terms conversion and fraction unreacted refer to a specific reactant, usually the stoichiometrically limiting reactant. See Equations 1.26 and 1.27 for the first-order case.

For most reactions, a batch reactor give the lowest possible fraction unreacted, the highest possible conversion, the best yield, and the highest selectivity. Fraction unreacted and conversion refer to the reactants. Yield and selectivity refer to the desired products. The **molar yield** is the number of moles of a specified product that are made per mole of reactant charged. There is also a **mass yield**. Either of these yields can be larger than 1 since one reactant may form more than 1 mol of product or there may be several reactants that contribute to the mass of a product. Thus $A \rightarrow 2B$ can have a molar yield of 2 if the reaction goes to completion. The yield of a reaction like $A + B \rightarrow C$ can be based on either A or B. The mass yield of this reaction depends on the extent of reaction and on the relative molecular weights of A and B. The **theoretical yield** is the amount of product that would be formed if all the reactant was converted to the desired product. This too can be expressed on either a molar or a mass basis and can be larger than 1. **Selectivity** is defined as the fractional amount of the converted portion of a reactant that is converted to the desired product. The selectivity will always be 100% when there is only one reaction even though the conversion may

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be less than 100%. Selectivity is a trivial concept when there is only one reaction but becomes an important consideration when there are competing reactions. The following example illustrates a reaction with high conversion but low selectivity.

EXAMPLE 1.2

Suppose it is desired to make 1,4-dimethyl-2,3-dichlorobenzene by the direct chlorination of *para*-xylene. The desired reaction is



But, there are many other reactions that can occur and it is implausible that the desired reaction will occur as a single, elementary step. A feed stream containing 40 mol % *p*-xylene and 60 mol % chlorine was fed to the reactor. The results of one experiment in a batch reactor gave the following results on a molar basis:

Component	Moles Output per Mole of Mixed Feed
<i>p</i> -Xylene	0.001
Chlorine	0.210
Monochloroxylene	0.032
1,4-Dimethyl-2,3-dichlorobenzene	0.131
Other dichloroxylenes	0.227
Trichloroxylene	0.009
Tetrachloroxylenes	0.001
Total	0.611

Compute various measures of reactor performance.

SOLUTION: Write the reaction as $A + B \rightarrow D + 2E$ where D is the desired dichlorobenzene. Some measures of performance based on xylene as the limiting component are

$$\text{Fraction unreacted} = \frac{a_{\text{out}}}{a_{\text{in}}} = \frac{0.001}{0.4} = 0.0025$$

$$\text{Conversion} = 1 - \frac{a_{\text{out}}}{a_{\text{in}}} = 1 - 0.0025 = 0.9975$$

$$\text{Yield} = \frac{d_{\text{out}}}{a_{\text{in}}} = \frac{0.131}{0.40} = 0.3275 \text{ moles of product per mole xylene charged}$$

$$\text{percent theoretical yield} = \frac{0.131}{0.4} (100) = 32.75\%$$

$$\text{Selectivity} = \frac{0.131}{(0.9975)(0.4)} (100) = 32.83\%$$

This example expresses all the performance measures on a molar basis. The mass yield of 1,4-dimethyl-2,3-dichlorobenzene sounds a bit better. It is 0.541 lb of the desired product per pound of xylene charged.

Note that the performance measures and definitions given here are the typical ones, but other terms and other definitions are sometimes used. Be sure to ask for the definition if there is any ambiguity.

1.4.3 Piston Flow Reactors

Continuous flow reactors are usually preferred for long production runs of high-volume chemicals. They tend to be easier to scale up; they are easier to control; the product is more uniform; material-handling problems are lessened; and the capital cost for the same annual capacity is lower.

There are two important types of ideal continuous flow reactors: the PFR and the CSTR. They behave very differently with respect to conversion and selectivity. The PFR behaves exactly like a batch reactor. It is usually visualized as a long tube, as illustrated in Figure 1.3. Consider a small clump of material that enters the reactor at time $t = 0$ and flows from the inlet to the outlet. We suppose there is no mixing between this particular clump and other clumps that enter at different times. The clump stays together, ages, and reacts as it flows down the tube. After it has been in the PFR for t seconds, the clump will have the same composition as if it had been in a batch reactor for t seconds. The composition of a batch reactor varies with time. The composition of a small clump flowing through a PFR varies with time in the same way. It also varies with position down the tube. The relationship between time and position is

$$t = \frac{z}{\bar{u}} \quad (1.34)$$

where z denotes distance measured from the inlet of the tube and \bar{u} is the velocity of the fluid. Chapter 1 assumes steady-state operation so that the composition at point z is always the same. It also assumes constant fluid density and constant reactor cross section so that \bar{u} is constant. The age of material at point z is t and the composition at this point is given by the constant-volume version of the component balance for a batch reaction, Equation 1.23. All that has to be done is to substitute $t = z/\bar{u}$. The result is

$$\bar{u} \frac{da}{dz} = \mathcal{R}_A \quad (1.35)$$

The initial condition is that

$$a = a_{\text{in}} \quad \text{at } z = 0 \quad (1.36)$$

Only the notation is different from the initial condition used for batch reactors. The subscripts “in” and “out” are used for flow reactors compared to a_0 and $a(t)$ for a batch reactor. The outlet concentration is found by setting $z = L$.

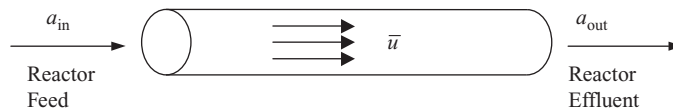


Figure 1.3 Piston flow reactor.

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EXAMPLE 1.3

Find the outlet concentration of component A from a PFR assuming A is consumed by a first-order reaction.

SOLUTION: Equation 1.35 becomes

$$\bar{u} \frac{da}{dz} = -ka.$$

Integrating, applying the initial condition of Equation 1.36, and evaluating the result at $z = L$ give

$$a_{\text{out}} = a_{\text{in}} \exp\left(-\frac{kL}{\bar{u}}\right) \quad (1.37)$$

The quantity L/\bar{u} has units of time and is the mean residence time \bar{t} . Thus, we can write Equation 1.37 as

$$a_{\text{out}} = a_{\text{in}} \exp(-k\bar{t}) \quad (1.38)$$

where

$$\bar{t} = \frac{L}{\bar{u}} \quad (1.39)$$

Equation 1.39 is a special case of a far more general result. The **mean residence time** \bar{t} is the average amount of time that a material spends in a reactor. The concept of mean residence time is most useful for flow systems. In a steady-state flow system \bar{t} is equal to the mass inventory of fluid in the system divided by the mass flow rate through the system:

$$\bar{t} = \frac{\text{mass inventory}}{\text{mass throughput}} = \frac{\hat{\rho}V}{\rho Q} \quad (1.40)$$

where $\rho Q = \rho_{\text{out}} Q_{\text{out}} = \rho_{\text{in}} Q_{\text{in}}$ is a consequence of steady-state operation. For the special case of a constant-density fluid,

$$\bar{t} = \frac{V}{Q} \quad (1.41)$$

where $Q = Q_{\text{in}} = Q_{\text{out}}$ when the system is at steady state and the mass density is constant. This reduces to

$$\bar{t} = \frac{L}{\bar{u}} \quad (1.42)$$

for a tubular reactor with constant fluid density and constant cross-sectional area. Piston flow is a still more special case where all molecules have the same velocity and the same residence time. We could write $\bar{t} = L/u$ for piston flow since the velocity is uniform across the tube but prefer to use Equation 1.42 for this case as well.

We now formalize the definition of piston flow. Denote position in the reactor using a cylindrical coordinate system (r, θ, z) so that the concentration at a point is denoted as $a(r, \theta, z)$. For the reactor to be a **piston flow reactor** (also called plug flow, slug flow, or ideal tubular reactor), three conditions must be satisfied:

- (i) The axial velocity is independent of r and θ but may be a function of z , $V_z(r, \theta, z) = \bar{u}(z)$.
- (ii) There is complete mixing across the reactor so that concentration is a function of z alone, that is, $a(r, \theta, z) = a(z)$.
- (iii) There is no mixing in the axial direction.

Here in Chapter 1 we make the additional assumptions that the fluid has constant density, that the cross-sectional area of the tube is constant, and that the walls of the tube are impenetrable (i.e., no transpiration through the walls), but these assumptions are not required in the general definition of piston flow. In the general case, it is possible for \bar{u} , temperature, and pressure to vary as a function of z . The axis of the tube need not be straight. Helically coiled tubes usually approximate piston flow more closely than straight tubes because the coiling promotes cross-channel mixing. Reactors with square or triangular cross sections are occasionally used. However, in most of this book, we will assume that PFRs are circular tubes of length L and constant radius R .

Application of the general component balance, Equation 1.6, to a steady-state flow system gives

$$Q_{\text{in}}a_{\text{in}} + \hat{\mathcal{R}}_A V = Q_{\text{out}}a_{\text{out}}$$

While true, this result is not helpful. The derivation of Equation 1.6 used the entire reactor as the control volume and produced a result containing the average reaction rate $\hat{\mathcal{R}}_A$. In piston flow, a varies with z so that the local reaction rate also varies with z , and there is no simple way of calculating $\hat{\mathcal{R}}_A$. Equation 1.6 is an overall balance applicable to the entire system. It is also called an **integral balance**. It just states that, if more of a component leaves the reactor than enters, then the difference had to be formed inside the reactor.

A **differential balance** is written for a vanishingly small control volume within which \mathcal{R}_A is approximately constant. Such a differential balance is needed to derive the design equation for a PFR. The differential volume element has volume ΔV , cross-sectional area A_c , and length Δz . See Figure 1.4. The general component balance applied to this differential volume gives

$$\text{Moles in} + \text{moles formed} = \text{moles out}$$

or

$$Qa(z) + \mathcal{R}_A \Delta V = Qa(z + \Delta z)$$

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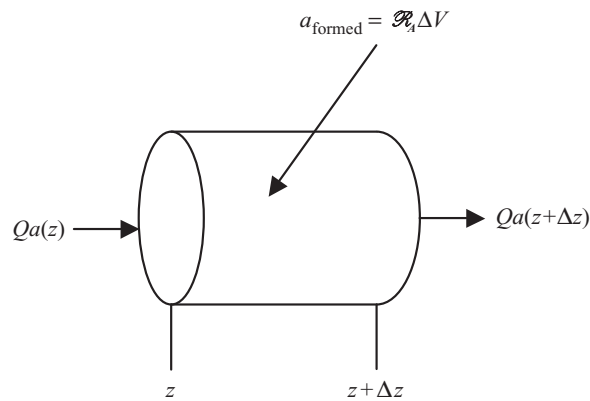


Figure 1.4 Differential element in a PFR.

Note that $Q = \bar{u}A_c$ and $\Delta V = A_c \Delta z$. Then

$$Q \frac{a(z + \Delta z) - a(z)}{\Delta V} = \bar{u} \frac{a(z + \Delta z) - a(z)}{\Delta z} = \mathcal{R}_A$$

Recall the definition of a derivative and take the limit as $\Delta z \rightarrow 0$:

$$\lim_{\Delta z \rightarrow 0} \left[\bar{u} \frac{a(z + \Delta z) - a(z)}{\Delta z} \right] = \bar{u} \frac{da}{dz} = \mathcal{R}_A \quad (1.43)$$

which agrees with Equation 1.35. Equation 1.35 was derived by applying a variable transformation to an unsteady batch reactor. Equation 1.43 was derived by applying a steady-state component balance to a differential flow reactor. Both methods work for this problem, but differential balances are the more general approach and can be extended to multiple dimensions where concentration can vary with radial and even tangential position. However, the strong correspondence between time in a batch reactor and position in a PFR is very important. The composition at time t in an ideal batch reactor is identical to the composition at position $z = \bar{u}t$ in an ideal PFR. This correspondence, which extends beyond the isothermal, constant-density case, is detailed in Table 1.1.

EXAMPLE 1.4

Determine the reactor design equations for the various elementary reactions in a PFR. Assume constant temperature, constant density, and constant reactor cross section. (Whether or not all these assumptions are needed will be explored in subsequent chapters.)

SOLUTION: Substitute the various rate equations into Equation 1.35 and integrate and apply the initial condition of Equation 1.36. Two versions of these equations can be used for a second-order reaction with two reactants. Another solution technique is to use the results obtained previously for a batch reactor and to replace t with z/\bar{u} and a_0 with a_{in} . The result is $a(z)$ for the various reaction types.

For a first-order reaction,

$$\frac{a(z)}{a_{in}} = \exp\left(\frac{-kz}{\bar{u}}\right) \tag{1.44}$$

For second order with one reactant,

$$\frac{a(z)}{a_{in}} = \frac{1}{1 + a_{in}kz/\bar{u}} \tag{1.45}$$

For second order with two reactants,

$$\frac{a(z)}{a_{in}} = \frac{b_{in} - a_{in}}{b_{in} \exp[(b_{in} - a_{in})kz/\bar{u}] - a_{in}} \tag{1.46}$$

The outlet concentration is found by setting $z = L$. At the reactor outlet, $z/\bar{u} = L/\bar{u} = \bar{t}$.

Piston flow reactors and most other flow reactors have spatial variations in concentration such as $a = a(z)$. Such systems are called *distributed*. Their behavior is governed by an ODE when there is only one spatial variable and by a partial differential equation (PDE) when there are two or three spatial variables or when the system has a spatial variation and also varies with time. We turn now to a special type of flow reactor where the entire reactor volume is well mixed and has the same concentration, temperature, pressure, and so forth. There are no spatial variations in

Table 1.1 Relationships between batch and piston flow reactors

Batch Reactors	Piston Flow Reactors
Concentrations vary with time; composition is uniform at any time t	Concentrations vary with axial position; composition is uniform at any position z
Governing equation, 1.23	Governing equation, 1.43
Initial condition, a_0	Initial condition, a_{in}
Final condition, $a(t)$	Final condition, $a(L) = a_{out}$
Time equivalent to position in PFR, $t = z/\bar{u}$	Position equivalent to time in batch reactor, $z = \bar{u}t$
Variable density, $\rho(t)$	Variable density, $\rho(z)$
Variable temperature, $T(t)$	Variable temperature, $T(z)$
Heat transfer to wall, $dq = hA_{wall}(T - T_{wall}) dt$	Heat transfer to wall, $dq = h(2\pi R)(T - T_{wall}) dz$
Variable wall temperature, $T_{wall}(t)$	Variable wall temperature, $T_{wall}(z)$
Variable pressure, $P(t)$	Pressure drop, $P(z)$
Variable volume (e.g., constant-pressure reactor), $V(t)$	Variable cross section, $A_c(z)$
Fed-batch reactors, $Q_{in} \neq 0$	Transpired-wall reactors
Nonideal batch reactors may have spatial variations in concentration	Nonideal tubular reactors may have concentrations that vary in r and θ directions

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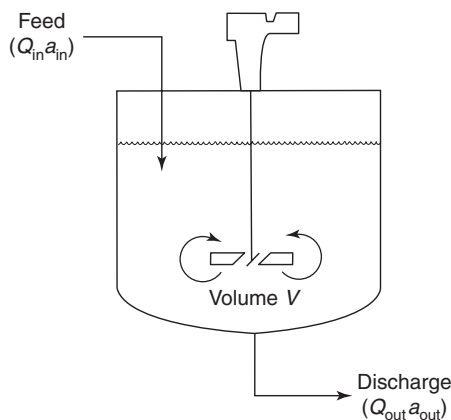


Figure 1.5 Classic CSTR: continuous flow stirred tank reactor with mechanical agitation.

these parameters. Such systems are called *lumped* and their behavior is governed by an algebraic equation when the system is at steady state and by an ODE when the system varies with time. The CSTR is the chemical engineer's favorite example of a lumped system. It has one lump, the entire reactor volume.

1.4.4 Continuous Flow Stirred Tanks

Figure 1.5 illustrates a flow reactor in which the contents are mechanically agitated. If mixing caused by the agitator is sufficiently fast, the entering feed will be quickly dispersed throughout the vessel and the composition at any point will approximate the average composition. Thus the reaction rate at any point will be approximately the same. Also, the outlet concentration will be identical to the internal composition, $a_{\text{out}} = \hat{a}$.

There are only two possible values for concentration in a CSTR. The inlet stream has concentration a_{in} and everywhere else has concentration a_{out} . The reaction rate will be the same throughout the vessel and is evaluated at the outlet concentration, $\hat{\mathcal{R}}_A = \mathcal{R}_A(a_{\text{out}}, b_{\text{out}}, \dots)$. For the single reactions considered in this chapter, \mathcal{R}_A continues to be related to \mathcal{R} by the stoichiometric coefficient and Equation 1.14. With \mathcal{R}_A known, the integral component balance, Equation 1.6, now gives useful information. For component A,

$$Q a_{\text{in}} + \mathcal{R}_A(a_{\text{out}}, b_{\text{out}}, \dots) V = Q a_{\text{out}} \quad (1.47)$$

Note that we have assumed steady-state operation and set $Q = Q_{\text{in}} = Q_{\text{out}}$, which assumes constant density. Dividing through by Q and setting $\bar{t} = V/Q$ gives

$$a_{\text{in}} + \mathcal{R}_A(a_{\text{out}}, b_{\text{out}}, \dots) \bar{t} = a_{\text{out}} \quad (1.48)$$

In the usual case, \bar{t} and a_{in} will be known. Equation 1.48 is an algebraic equation that can be solved for a_{out} . If the reaction rate depends on the concentration of more than one component, versions of Equation 1.48 are written for each component and the resulting set of equations is solved simultaneously for the various outlet concentrations.

Even concentrations of components that do not affect the reaction rate can be found by writing versions of Equation 1.48 for them as well. As in the case of batch and piston flow reactors, the stoichiometric coefficient is used to relate the rate of formation of a component, say \mathcal{R}_C , to the rate of the reaction \mathcal{R} using the stoichiometric coefficient for component C, ν_C , and Equation 1.14. After this, the stoichiometry takes care of itself.

A reactor with performance governed by Equation 1.48 is a steady-state, constant-density, perfectly mixed, continuous flow reactor. This mouthful is usually shortened in the chemical engineering literature to **CSTR** (for continuous flow stirred tank reactor). In subsequent chapters, we will relax the assumptions of steady state and constant density but will still call it a CSTR. It is also called an ideal mixer, a continuous flow perfect mixer, or a mixed flow reactor. This terminology is ambiguous in light of micromixing theory, discussed in Chapter 13, but is well entrenched. Unless otherwise qualified, we accept the term CSTR to mean that the reactor is perfectly mixed. Such a reactor is sometimes called a *perfect mixer*. The term denotes instantaneous and complete mixing on the molecular scale. Obviously, no real reactor can achieve this ideal state just as no tubular reactor can achieve true piston flow. However, it is often possible to design reactors that very closely approach these limits.

EXAMPLE 1.5

Determine the reactor design equations for elementary reactions in a CSTR.

SOLUTION: The various rate equations for the elementary reactions are substituted into Equation 1.48, which is then solved for a_{out} .

For a first-order reaction, $\mathcal{R}_A = -ka$. Set $a = a_{\text{out}}$, substitute \mathcal{R}_A into Equation 1.48, and solve for a_{out} to obtain

$$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{1}{1 + k\bar{t}} \quad (1.49)$$

For a second-order reaction with one reactant, $\mathcal{R}_A = -ka^2$, and Equation 1.48 becomes a quadratic in a_{out} . The solution is

$$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{-1 + \sqrt{1 + 4a_{\text{in}}k\bar{t}}}{2a_{\text{in}}k\bar{t}} \quad (1.50)$$

The negative root was rejected since $a_{\text{out}} \geq 0$.

For a second-order reaction with two reactants, $\mathcal{R}_A = \mathcal{R}_B = -kab$. Write two versions of Equation 1.48, one for a_{out} and one for b_{out} . Solve them simultaneously to give

$$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{-1 - (b_{\text{in}} - a_{\text{in}})k\bar{t} + \sqrt{[1 + (b_{\text{in}} - a_{\text{in}})k\bar{t}]^2 + 4a_{\text{in}}k\bar{t}}}{2a_{\text{in}}k\bar{t}} \quad (1.51)$$

Again, a negative root was rejected. The simultaneous solution also produces the stoichiometric relationship

$$b_{\text{in}} - b_{\text{out}} = a_{\text{in}} - a_{\text{out}} \quad (1.52)$$

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Any Single Reaction in a CSTR

The above examples have assumed that a_{in} and \bar{t} are known. The solution then gives a_{out} . The case where a_{in} is known and a desired value for a_{out} is specified can be easier to solve. The solution for \bar{t} is

$$\bar{t} = \frac{a_{\text{out}} - a_{\text{in}}}{\mathcal{R}_A(a_{\text{out}}, b_{\text{out}}, \dots)} \quad (1.53)$$

This result assumes constant density and is useful when the reaction rate depends on a single concentration or on multiple concentrations that are linked by a stoichiometric relationship such as Equation 1.52. It is not useful for the general case of multiple reactions.

EXAMPLE 1.6

Apply Equation 1.53 to calculate the mean residence time needed to achieve 90% conversion in a CSTR for (a) a first-order reaction and (b) a second-order reaction of the type $A + B \rightarrow \text{products}$. The rate constant for a first-order reaction has units of reciprocal time. For the current example, assume $k = 0.1 \text{ s}^{-1}$. The rate constant for a second-order reaction has units of reciprocal time and reciprocal concentration. It is common practice to multiply a second-order rate constant by the initial or inlet concentration of the stoichiometrically limiting coefficient. This gives a rate constant with units of reciprocal time. For the second-order reaction suppose $a_{\text{in}}k = 0.1 \text{ s}^{-1}$.

SOLUTION: For the first-order reaction, $\mathcal{R}_A = -ka_{\text{out}} = -k(0.1 a_{\text{in}})$. Equation 1.53 gives

$$\bar{t} = \frac{a_{\text{out}} - a_{\text{in}}}{-ka_{\text{out}}} = \frac{0.1a_{\text{in}} - a_{\text{in}}}{-k(0.1a_{\text{in}})} = \frac{9}{k} = 90 \text{ s}$$

For the second-order case, $\mathcal{R}_A = -ka_{\text{out}}b_{\text{out}}$. To use Equation 1.53, stoichiometry is needed to find the value for b_{out} that corresponds to a_{out} . Suppose, for example, that B is in 50% excess so that $b_{\text{in}} = 1.5a_{\text{in}}$. Then $b_{\text{out}} = 0.6a_{\text{in}}$ if $a_{\text{out}} = 0.1a_{\text{in}}$. Equation 1.53 gives

$$\bar{t} = \frac{a_{\text{out}} - a_{\text{in}}}{-ka_{\text{out}}b_{\text{out}}} = \frac{0.1a_{\text{in}} - a_{\text{in}}}{-k(0.1a_{\text{in}})(0.6a_{\text{in}})} = \frac{15}{ka_{\text{in}}} = 150 \text{ s}$$

Equation 1.53 is a beautifully simple way of designing a reactor for the few cases to which it applies. More commonly, the numerical methods introduced in Chapter 2 are needed.

1.5 MIXING TIMES AND SCALEUP

Suppose a homogeneous reaction is conducted in a pilot plant reactor that is equipped with a variable-speed agitator. Does changing the agitator speed (say by $\pm 20\%$) change the outcome of the reaction? Does varying the addition rate of reactants change the selectivity? If so, there is a potential scaleup problem. The reaction is sensitive

1.5 Mixing Times and Scaleup 27

to mixing. If the reaction is multiphase, the agitator speed can affect interphase mass transfer. See Chapter 11. If the reaction is single phase, the reaction is sensitive to the **mixing time** t_{mix} .

The mixing time in a batch stirred tank is easily measured. Add unmixed ingredients and determine how long it takes for the contents of the vessel to become uniform. For example, fill a vessel with plain water and start the agitator. At time $t = 0$, add a small quantity of a salt solution. Measure the concentration of salt at various points inside the vessel until it is constant within measurement error or by some other standard of near equality. Record the result as t_{mix} . A popular alternative is to start with a weak-acid solution that contains an indicator so that the solution is initially colored. An excess of concentrated base is added quickly at one point in the system. The mixing time t_{mix} corresponds to the disappearance of the last bit of color. The acid–base titration is very fast so that the color will disappear just as soon as the base is distributed throughout the vessel. This is an example where the reaction in the vessel is limited strictly by mixing. There is no kinetic limitation. For very fast reactions such as combustion or acid–base neutralization, no vessel will be perfectly mixed. The components must be transported from point to point in the vessel by fluid flow and diffusion, and these transport processes will be slower than the reaction. Whether a reactor can be considered to be perfectly mixed depends on the speed of the reaction. What is effectively perfect mixing is easy to achieve when the reaction is an esterification with a half-life of several hours. It is impossible to achieve in acid–base neutralizations that have half-lives of nanoseconds. One requirement for “perfect mixing” is that

$$t_{\text{mix}} \ll t_{1/2} \quad (1.54)$$

This requirement applies to batch reactors and to CSTRs. (For PFRs, we assume that the components are perfectly mixed when they enter the reactor.) When Equation 1.54 is satisfied, the conversion in the reactor will be limited by the reaction kinetics, not by the mixing rate. The assumption of perfect mixing is probably reasonable when $t_{1/2}$ is 8 times larger than t_{mix} .

What happens to t_{mix} upon scaleup? Mixing times in mechanically agitated vessels typically range from a few seconds in laboratory glassware to a few minutes in large industrial reactors. As the size of the vessel increases, t_{mix} will increase, and the increase will eventually limit the size at which the reactor is operable. No process is infinitely scaleable. Sooner or later, additional scaleup becomes impossible, and further increases in production cannot be achieved in **single-train** plants but must use units in parallel. Fortunately for the economics of the chemical industry, this size limit is often very large.

Plant sizes are usually characterized by their production capacity or throughput. Define the **throughput scaleup factor** as

$$S_{\text{throughput}} = \frac{\text{mass flow through full-scale unit}}{\text{mass flow through pilot unit}} = \frac{(\rho Q)_{\text{full scale}}}{(\rho Q)_{\text{pilot scale}}} \quad (1.55)$$

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Assume that the pilot-scale and full-scale vessels operate with the same inlet density. Then ρ cancels in Equation 1.55 and

$$S_{\text{throughput}} = \frac{Q_{\text{full scale}}}{Q_{\text{pilot scale}}} \quad (\text{constant density})$$

There is also an inventory scaleup factor defined as

$$S_{\text{inventory}} = \frac{\text{mass inventory in full-scale unit}}{\text{mass inventory in pilot unit}} = \frac{(\hat{\rho}V)_{\text{full scale}}}{(\hat{\rho}V)_{\text{pilot scale}}} \quad (1.56)$$

For successful scaleup we expect the volume-average density $\hat{\rho}$ to be the same in the large and small reactors. Thus, normally,

$$S_{\text{inventory}} = S_{\text{volume}} = \frac{V_{\text{full scale}}}{V_{\text{pilot scale}}} \quad (1.57)$$

This book deals with the scaleup of chemical reactors. The product from the scaled-up reactor should be the same as the product from the pilot reactor. The extent of reaction should be the same in the two reactors and thus the mean residence time \bar{t} should be held constant upon scaleup. According to Equation 1.40, inventory and throughput are increased by the same factor when \bar{t} is held constant. Unless explicitly stated otherwise, it is understood that inventory, volume, and throughput all increase proportionately:

$$S_{\text{throughput}} = S_{\text{inventory}} = S_{\text{volume}} = S \quad (1.58)$$

Use of S without subscripts indicates that Equation 1.58 is satisfied. This is true for the great majority of reactor scaleups for both liquids and gases.

It is common practice to use *geometric similarity* in the scaleup of stirred tanks (but not tubular reactors). Geometric similarity means that the production-scale reactor will have the same shape as the pilot-scale reactor. All linear dimensions such as reactor diameter, impeller diameter, and liquid height will change by the same factor, $S^{1/3}$. Surface areas will scale as $S^{2/3}$. Now, what happens to t_{mix} upon scaleup? A classic correlation by Norwood and Metzner (1960) for turbine impellers in baffled vessels can be used to estimate t_{mix} . The full correlation shows t_{mix} to be a complex function of the Reynolds number, the Froude number, the ratio of tank to impeller diameter, and the ratio of tank diameter to liquid level. However, to a reasonable first approximation for geometrically similar vessels operating at high Reynolds numbers,

$$(N_I t_{\text{mix}})_{\text{large}} = \text{const} = (N_I t_{\text{mix}})_{\text{small}} \quad (1.59)$$

where N_I is the rotational velocity of the impeller. This means that scaleup with constant agitator speed will, to a reasonable approximation, give constant t_{mix} . The rub is that the power requirements for the agitator will increase sharply in the larger vessel. To a reasonable first approximation for geometrically similar vessels operating at high Reynolds numbers,

$$\left(\frac{P_I}{\rho N_I^3 D_I^5} \right)_{\text{large}} = \left(\frac{P_I}{\rho N_I^3 D_I^5} \right)_{\text{small}} = \mathbf{Po} \quad (1.60)$$

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where P_I is the impeller power, D_I is the impeller diameter, and \mathbf{Po} is a dimensionless group known as the **power number**. If N_I is held constant, the impeller power will increase as D_I^5 and as $S^{5/3}$ since D_I scales as $S^{1/3}$ using geometric similarity. A factor of 10 increase in the linear dimensions gives $S = 1000$ and allows a factor of 1000 increase in throughput. Unfortunately, it requires a factor of 100,000 increase in agitator power! The horsepower per unit volume must increase by a factor of 100 to maintain a constant t_{mix} . Let us hope that there is some latitude before the constraint of Equation 1.54 is seriously violated. Most scaleups are done with approximately constant power per unit volume, which causes N_I to decrease and t_{mix} to increase upon scaleup.

EXAMPLE 1.7

A factor of 10 scaleup in the linear dimensions of a CSTR, $S^{1/3} = 10$, requires a factor of 100,000 increase in total power and a factor of 100 increase in power per unit volume if t_{mix} is held constant. Such a scaleup would be absurd. A more reasonable scaleup rule is to maintain constant power per unit volume so that a 1000-fold increase in reactor volume requires a 1000-fold increase in power. What happens to t_{mix} in this case?

SOLUTION: Rearrange Equation 1.60 to give

$$\frac{(\text{Power})_{\text{large}}}{(\text{Power})_{\text{small}}} = \frac{(\rho N_I^3 D_I^5)_{\text{large}}}{(\rho N_I^3 D_I^5)_{\text{small}}}$$

Divide both sides by D_{tank}^3 to obtain power per unit volume:

$$\frac{(\text{Power per unit volume})_{\text{large}}}{(\text{Power per unit volume})_{\text{small}}} = \frac{(\rho N_I^3 D_I^5 / D_{\text{tank}}^3)_{\text{large}}}{(\rho N_I^3 D_I^5 / D_{\text{tank}}^3)_{\text{small}}}$$

Cancel out density, set the ratio of powers to 1, and note that D_I and D_{tank} scale by the same factor, $S^{1/3}$, for a geometrically similar scaleup. The result is

$$1 = \frac{(N_I^3 D_I^2)_{\text{large}}}{(N_I^3 D_I^2)_{\text{small}}} = \frac{(N_I^3)_{\text{large}}}{(N_I^3)_{\text{small}}} S^{2/3}$$

or

$$\frac{(N_I)_{\text{large}}}{(N_I)_{\text{small}}} = S^{-2/9}$$

For constant power per unit volume with a factor of 10 scaleup in linear dimensions, the agitator speed in the large reactor must be $10^{-2/9} = 0.6$ times that in the small reactor. If the small reactor operated at 100 revolutions per minute (RPM), the large reactor should operate at 60 RPM. What does this do to t_{mix} ? Rearrange Equation 1.59 to obtain

$$\frac{(t_{\text{mix}})_{\text{large}}}{(t_{\text{mix}})_{\text{small}}} = \frac{(N_I)_{\text{small}}}{(N_I)_{\text{large}}}$$

For the case at hand, the mixing time increases by a factor of 1.67. Is Equation 1.54 still satisfied? Decreasing the speed of the pilot agitator to 60% of its initial value can experimentally test this.

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Is the product still good? If so, scaleup should be possible from the viewpoint of mixing time. If not, a departure from geometric similarity, say by using multiple injection points for added ingredients, may solve the problem. The use of multiple injection points can be tested on the pilot scale. The logic assumes that the pilot reactor with a single injection point gave a good product. Determine t_{mix} for this original configuration. Then add injection points to the pilot reactor. Presumably, this will cause little change in product quality. Measure t_{mix} in the new configuration. Given simultaneous injection through all the ports, t_{mix} should be lower than the original value. Estimate what it will become upon scaleup, again using Equation 1.59. If the scaled value of t_{mix} remains smaller than the original t_{mix} (before adding injection points), then scaleup of the multiple-point design should be satisfactory. The reader will appreciate that scaleup is sometimes more engineering art than rigorous science.

Several caveats should be mentioned at this point. When there are multiple reactions, the half-life in Equation 1.54 is the shortest half-life that affects yield and selectivity. In complex reaction schemes, there may be some important fast reactions that are mixing dependent even though the overall reaction is slow. An example is a catalyst that may react with itself if not rapidly diluted. Equations 1.59 and 1.60 are approximations that are reasonable for turbine agitators in stirred tanks at high Reynolds numbers. Many detailed correlations are available in the literature and should be used if the reaction is at all sensitive to mixing effects. This can be tested at the pilot scale by varying agitator speed. Mixing experts may recommend scaleups other than constant power per unit volume. Scaleup limitations other than mixing time are common. Heat transfer is a common limitation and is discussed in Chapter 5. The reader interested in agitator design should look at Problem 1.17 and then go to the cited literature.

In a batch vessel, the question of good mixing will arise at the start of the batch and whenever an ingredient is added to the batch. The component balance, Equation 1.22, assumes that uniform mixing is achieved before any appreciable reaction occurs. This will be true if Equation 1.54 is satisfied. Consider the same vessel being used as a CSTR. Now, the mixing time must be short compared to the mean residence time, else newly charged material could flow out of the reactor before being thoroughly mixed with the contents. A new condition to be satisfied is

$$t_{\text{mix}} \ll \bar{t} \quad (1.61)$$

In practice, Equation 1.61 will be satisfied if Equation 1.54 is satisfied since a CSTR will normally operate with $t_{1/2} \ll \bar{t}$.

The net flow through the reactor will be small compared to the circulating flow caused by the agitator. The existence of the throughput has little influence on the mixing time so that mixing time correlations for batch vessels can be used for CSTRs as well.

In summary, we have considered three characteristic times associated with a CSTR: t_{mix} , $t_{1/2}$, and \bar{t} . Treating the CSTR as a perfect mixer is reasonable provided t_{mix} is substantially shorter than the other characteristic times.

1.6 DIMENSIONLESS VARIABLES AND NUMBERS

Equation 1.35 governs the performance of an ideal PFR:

$$\bar{u} \frac{da}{dz} = \mathcal{R}_A \quad a = a_{\text{in}} \quad \text{at } z = 0 \quad (1.62)$$

where for a circular tube $\bar{u} = Q/(\pi R^2)$ and for a first-order reaction $\mathcal{R}_A = -ka$. Reactor performance depends on many dimensioned parameters that can be manipulated by the designer or the experimentalist to change the response of the system, $a_{\text{out}} = a(L)$. The tube radius R and reactor length L would normally be considered *design variables* while the volumetric flow rate Q , rate constant k (which can be changed using temperature or catalyst concentration), and inlet concentration a_{in} (which can be changed with diluents) would be considered *operating variables*. The distinction between design and operating variable is not absolute. The operator of an industrial reactor may have no freedom to change the flow rate, but the operator of a pilot reactor may be able to quickly change the reactor length.

The response of the system, a_{out} , depends on at least five potentially manipulatable parameters ($Q, R, L, k, a_{\text{in}}$), and a plot showing the dependence of a_{out} would need an impossible six dimensions. However, the solution to Equation 1.62 can be written as

$$\frac{a_{\text{out}}}{a_{\text{in}}} = \exp(-k\bar{t}) \quad (1.63)$$

There are only two variables, $a_{\text{in}}/a_{\text{out}}$ and $k\bar{t}$, so an ordinary two-dimensional graph can be used.

A dramatic reduction in dimensionality is often possible by converting a design equation from dimensioned to dimensionless form. Equation 1.62 contains the dependent variable a and the independent variable z . The process begins by selecting characteristic values for these variables. By “characteristic value” we mean some known parameter that has the same dimensions as the variable and that characterizes the system. For a PFR, the variables are concentration and length. A characteristic value for concentration is a_{in} and a characteristic value for length is L . These are used to define the dimensionless variables $a^* = a/a_{\text{in}}$ and $\mathcal{Z} = z/L$. The governing equation for a first-order reaction in an ideal PFR becomes

$$\frac{da^*}{d\mathcal{Z}} = \frac{L}{\bar{u}} \mathcal{R}_A = \frac{-Lka}{\bar{u}a_{\text{in}}} = -k\bar{t}a^* = -k^*a^* \quad (1.64)$$

which is subject to the initial condition that $a^* = 1$ at $\mathcal{Z} = 0$. The outlet concentration is found from the solution of Equation 1.64 evaluated at $\mathcal{Z} = 1$. The result is identical to Equation 1.63. The product $k^* = k\bar{t}$ is the *dimensionless first-order rate constant*. Here, $k^* = k\bar{t}$ can be changed by changing any of Q, R, L , or k , but it is only their composite value in the form of k^* that determines reactor performance as measured by the *dimensionless outlet concentration*, $a_{\text{out}}/a_{\text{in}}$.

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EXAMPLE 1.8

Find the equivalent to Equation 1.63 for second-order reactions.

SOLUTION: Begin with the case of one reactant, $2A \rightarrow kC$. The same variable transformations are used for a and z to give

$$\frac{da^*}{dz} = \frac{L}{\bar{u}} \mathcal{R}_A = \frac{-2k\bar{t}a^*}{a_{in}} = -2a_{in}k\bar{t}(a^*)^2 \quad a' = 1 \quad \text{at } z = 0$$

The solution is

$$\frac{a_{out}}{a_{in}} = \frac{1}{1 + 2a_{in}k\bar{t}} = \frac{1}{1 + 2k^*}$$

where $k^* = a_{in}k\bar{t}$ is the dimensionless rate constant for a second-order reaction.

For the two-reactant case, $A + B \rightarrow kC$, with perfect stoichiometry, the result is

$$\frac{a_{out}}{a_{in}} = \frac{1}{1 + a_{in}k\bar{t}} = \frac{1}{1 + k^*}$$

Note that the factor of 2 could have been included in the definition of k^* for the single-reactant case, but the results as given remind us that 2 moles of A are consumed to form each mole of C in the single-reactant case.

The other results for ideal flow reactors can be put into dimensionless form almost by inspection. For example, the results for a CSTR, Equations 1.49 and 1.50, are already in dimensionless form.

The conversion of the design equation for a batch reactor to dimensionless form is somewhat artificial since there is no natural time constant analogous to \bar{t} that characterizes the reactor. A batch reaction can be continued indefinitely simply by running the reaction longer. A PFR has a natural time constant $\bar{t} = L/\bar{u}$, but there is nothing that prevents increasing the reactor length, thereby continuing the reaction. For a batch reactor, pick some arbitrary value for t_{batch} as a characteristic time. Then the treatment of batch reactors becomes identical to that for PFRs when kt_{batch} replaces $k\bar{t}$.

Consider now the more general rate equation

$$\mathcal{R} = ka^m b^n$$

The two concentration variables, a and b , are made dimensionless using the same characteristic value, a_{in} , so that $a^* = a/a_{in}$ and $b^* = b/a_{in}$. Choose A so that it is the stoichiometrically limiting reactant. If the reaction is $A + B \rightarrow \text{products}$, then $a^* = 1$ and $b^* \geq 1$ at $t = 0$ or $z = 0$. The result of converting to dimensionless form is

$$\frac{\bar{t}\mathcal{R}}{a_{in}} = k\bar{t}a_{in}^{m+n-1}(a^*)^m(b^*)^n = k^*(a^*)^m(b^*)^n$$

where $k^* = k\bar{t}a_{in}^{m+n-1}$ is the dimensionless rate constant for this $(m + n)$ -order reaction. The restriction that m and n be integers is removed in Chapter 2.

Table 1.2 summarizes the design equations for elementary reactions in ideal reactors. Note that component A is the only component or else is the stoichiometrically limiting component. Thus $a^* = a/a_0$ for batch reactions and $a^* = a/a_{in}$ for flow reactors and $Y_A = a^*$ in both cases. For the case of a second-order reaction with two reactants, the stoichiometric ratio is also needed:

$$S_{AB} = \frac{a_0}{b_0} \leq 1 \quad \text{or} \quad S_{AB} = \frac{a_{in}}{b_{in}} \leq 1 \quad (1.65)$$

1.7 BATCH VERSUS FLOW AND TANK VERSUS TUBE

Some questions that arise early in a design are: Should the reactor be batch or continuous? If continuous, is the goal to approach piston flow or perfect mixing?

For producing high-volume chemicals, flow reactors are usually preferred. The ideal PFR exactly duplicates the kinetic behavior of the ideal batch reactor, and the reasons for preferring one over the other involve secondary considerations such as heat and mass transfer, ease of scaleup, and the logistics of materials handling. For small-volume chemicals, the economics usually favor batch reactors. This is particularly true when general-purpose equipment can be shared between several products. Batch reactors are used for the greater number of products and produce products of higher economic value. Note that most pharmaceutical products are made in batch processes. Flow reactors are typically used for the commodity products of the petrochemical industry. They produce the overwhelmingly larger volume as measured in tons, but these tons have a lower economic value than the myriad specialty chemicals and pharmaceuticals made in batch processes.

Flow reactors are operated continuously, that is, at steady state with reactants continuously entering the vessel and with products continuously leaving. Batch reactors are operated discontinuously. A batch reaction cycle has periods for charging, reaction, and discharging. The continuous nature of a flow reactor lends itself to larger productivities and greater economies of scale than the cyclic operation of a batch reactor. The volume productivity (moles of product per unit volume of reactor) for batch systems is identical to that of PFRs and is higher than most real flow reactors. However, this volume productivity is achieved only when the reaction is actually occurring and not when the reactor is being charged or discharged, being cleaned, and so on. Within the class of flow reactors, piston flow is usually desired for reasons of productivity and selectivity. However, there are instances where a close approach to piston flow is infeasible or where a superior product results from the special reaction environment possible in stirred tanks.

Although they are both flow reactors, there are large differences in the behavior of PFRs and CSTRs. Reaction rates decrease as the reactants are consumed (autocatalytic reactions are an exception). In piston flow, the reactant concentration gradually declines with increasing axial position. The local rate is higher at the reactor inlet

Table 1.2 Design equations for elementary reactions in ideal reactors

Elementary Reaction	Dimensionless Rate Constant	Design Equation for Piston Flow or Batch Reactors	Design Equation for CSTR
First order: $A \xrightarrow{k} P$ $\mathcal{R}_A = -ka$	$k^* = k\bar{t}$ or $k^* = kt_{\text{batch}}$	$\frac{a_{\text{out}}}{a_{\text{in}}} = \exp(-k^*)$	$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{1}{1+k^*}$
Second order, one reactant: $2A \xrightarrow{k/2} P$ $\mathcal{R}_A = -ka^2$	$k^* = a_{\text{in}}k\bar{t}$ or $k^* = a_0k_{\text{batch}}$	$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{1}{1+k^*}$	$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{-1 + \sqrt{1+4k^*}}{2k^*}$
Second order, two reactants: $A + B \xrightarrow{k} P$ $\mathcal{R}_A = -kab$	Same as second-order, one-reactant case but supplemented by stoichiometric ratio S_{AB}	$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{1 - S_{AB}}{\exp[(1 - S_{AB})k^*/S_{AB}] - S_{AB}}$ where $S_{AB} = \frac{a_{\text{in}}}{b_{\text{in}}}$ or $S_{AB} = \frac{a_0}{b_0}$	$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{-1 - (1 - S_{AB})k^*/S_{AB} + \sqrt{[1 + (1 - S_{AB})k^*/S_{AB}]^2 + 4k^*}}{2k^*}$
Third order, one reactant: $3A \xrightarrow{k/3} P$ $\mathcal{R}_A = -ka^3$	$k^* = a_{\text{in}}^2k\bar{t}$ or $k^* = a_0^2k_{\text{batch}}$	$\frac{a_{\text{out}}}{a_{\text{in}}} = \frac{1}{\sqrt{1+2K}}$	There is an analytical solution to the cubic equation $k^*(a^*)^3 + a^* - 1 = 0$, but numerical solutions are easier to evaluate; See Chapter 2

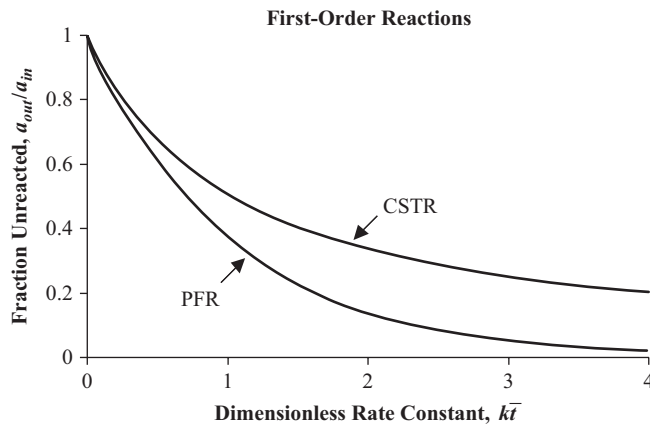


Figure 1.6 Relative performance of piston flow and continuous stirred tank reactors for first-order reactions.

than at the outlet, and the average rate for the entire reactor will correspond to some average composition that is between a_{in} and a_{out} . In contrast, the entire volume of a CSTR is at concentration a_{out} , and the reaction rate throughout the reactor is lower than that at any point in a PFR going to the same conversion.

Figures 1.6 and 1.7 display the conversion behavior for first- and second-order reactions in a CSTR and contrast the behavior to that of a PFR. It is apparent that a PFR is substantially better than the CSTR for obtaining high conversions. The comparison is even more dramatic when made in terms of the volume needed to achieve a given conversion (Fig. 1.8). The generalization that

Conversion in PFR > conversion in CSTR

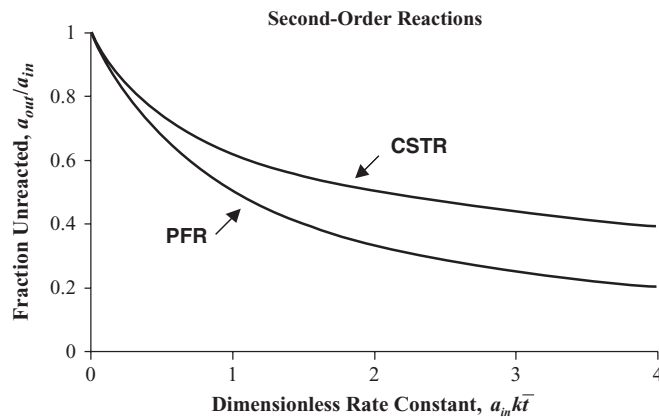


Figure 1.7 Relative performance of piston flow and continuous stirred tank reactors for second-order reactions.

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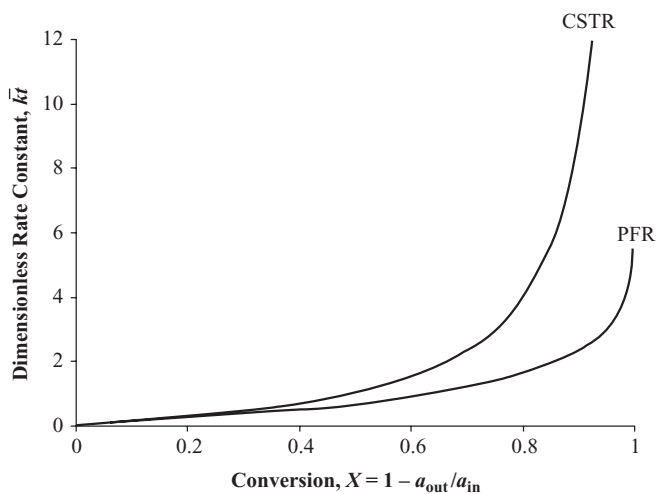


Figure 1.8 Comparison of reactor volume required for given conversion for a first-order reaction in PFR and CSTR.

is true for most kinetic schemes. The important exceptions to this rule, autocatalytic reactions, are discussed in Chapter 2. A second generalization is

$$\text{Selectivity in PFR} > \text{selectivity in CSTR}$$

which also has a few exceptions.

SUGGESTED FURTHER READINGS

There are many books on chemical engineering kinetics, and the reader may wish to browse through several of them to see how they introduce the subject. Most of them are intended for the introductory, undergraduate course. Here are two examples primarily aimed at the U.S. market:

O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed., Wiley, New York, 1998.

L. D. Schmidt, *The Engineering of Chemical Reactions*, 2nd ed., Oxford University Press, New York, 2004.

Here is an example primarily aimed at the U.K. market:

M. B. King and M. B. Winterbottom, *Reactor Design for Chemical Engineers*, Chapman & Hall, London, 1998.

A relatively advanced book primarily used for graduate courses is:

F. Froment and K. B. Bischoff, *Chemical Reactor Analysis and Design*, 2nd ed., Wiley, New York, 1990.

An extended treatment of material balance equations with substantial emphasis on component balances in reacting systems is given in:

G. V. Reklaitis and D. R. Schneider, *Introduction to Material and Energy Balances*, Wiley, New York, 1983.

See also:

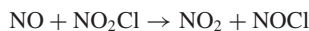
R. M. Felder and R. W. Rousseau, *Elementary Principles of Chemical Processes*, 3rd ed., Wiley, New York, 2000.

A general reference on mixing, especially in stirred tank reactors is:

E. L. Paul et al., *Handbook of Industrial Mixing*, Wiley, New York, 2003.

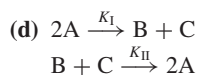
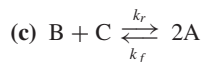
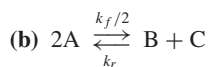
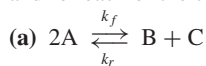
PROBLEMS

- 1.1** (a) Write the overall and component mass balances for an unsteady, perfectly mixed, continuous flow reactor.
- (b) Simplify for the case of constant reactor volume and for constant-density, time-independent flow streams.
- (c) Suppose there is no reaction but that the input concentration of some key component varies with time according to $C_{in} = C_0$, $t < 0$; $C_{in} = 0$, $t > 0$. Find $C_{out}(t)$.
- (d) Repeat (c) for the case where the key component is consumed by a first-order reaction with rate constant k .
- 1.2** The homogeneous gas phase reaction



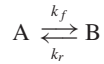
is believed to be elementary with rate $\mathcal{R} = k[\text{NO}][\text{NO}_2\text{Cl}]$. Use the kinetic theory of gases to estimate f_R at 300 K. Assume $r_A + r_B = 3.5 \times 10^{-10}$ m. The experimentally observed rate constant at 300 K is $k = 8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

- 1.3** Determine the initial half-life for an elementary, second-order reaction for which $a_0 < b_0$. Note that the half-life should be based on the stoichiometrically limiting component, A.
- 1.4** The data in Example 1.2 are in moles of the given component per mole of mixed feed. These are obviously calculated values. Check their consistency by using them to calculate the feed composition given that the feed contained only *para*-xylene and chlorine. Is your result consistent with the stated molar composition of 40% xylene and 60% chlorine?
- 1.5** Suppose that the following reactions are elementary. Write rate equations for the reaction and for each of the components:



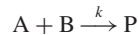
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1.6 Determine $a(t)$ for a first-order, reversible reaction



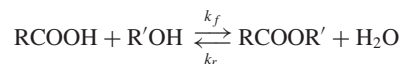
in a batch reactor.

- 1.7** Compare $a(z)$ for a first- and second-order reaction in a PFR. Plot the profiles on the same graph and arrange the rate constants so that the initial and final concentrations are the same for the two reactions.
- 1.8** Equation 1.44 gives the spatial distribution of concentration, $a(z)$, in a PFR for a component that is consumed by a first-order reaction. The local concentration can be used to determine the local reaction rate $\mathcal{R}_A(z)$.
- Integrate the local reaction rate over the length of the reactor to determine $\hat{\mathcal{R}}_A$.
 - Show that this $\hat{\mathcal{R}}_A$ is consistent with the general component balance, Equation 1.6.
 - To what value of a does rate $\hat{\mathcal{R}}_A$ correspond?
 - At what axial position does this average value occur?
 - Now integrate a down the length of the tube. Is this spatial average the same as the average found in part (c)?
- 1.9** One type of (supposedly) third-order reaction is $2A + B \xrightarrow{k/2} C$. Determine the fraction unreacted of component A in an ideal batch reactor.
- 1.10** Consider the reaction



with $k = 1 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Suppose $b_{\text{in}} = 10 \text{ mol m}^{-3}$. It is desired to achieve $b_{\text{out}} = 0.01 \text{ mol m}^{-3}$.

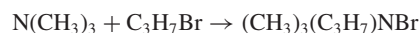
- Find the mean residence time needed to achieve this assuming piston flow and $a_{\text{in}} = b_{\text{in}}$.
 - Repeat (a) assuming that the reaction occurs in a CSTR.
 - Repeat (a) and (b) assuming $a_{\text{in}} = 10 b_{\text{in}}$.
- 1.11** The esterification reaction



can be driven to completion by removing the water of condensation. This might be done continuously in a stirred tank reactor or in a horizontally compartmented, progressive flow reactor. This type of reactor gives a reasonable approximation to piston flow in the liquid phase while providing a vapor space for the removal of the byproduct water. Suppose it is desired to obtain an ester product containing not more than 1% (by mole) residual alcohol and 0.01% residual acid.

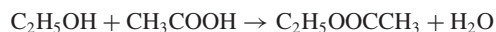
- What are the limits on initial stoichiometry if the product specifications are to be achieved?
 - What value of $a_{\text{out}}k\bar{t}$ is needed in a CSTR?
 - What value of $a_{\text{out}}k\bar{t}$ is needed in the progressive reactor?
 - Discuss the suitability of a batch reactor for this situation.
- 1.12** Can an irreversible elementary reaction go to completion in a batch reactor in finite time?

- 1.13** An evil young professor was worried about getting tenure. He thought his chances would be better if he eliminated the competition, an untenured colleague who happened to be a beautiful princess who had a lab next to his and was arguably better at both research and teaching than the evil professor. The evil professor has heard about TNT and decided to make some and use it in diabolical ways. He began by writing a simplified but plausible reaction mechanism, including appropriate rate expressions, for the toluene nitration. He then charged toluene, nitric acid, and sulfuric acid (as a catalyst) to a small reactor and carefully monitored the results. He was surprised to observe that the rates of even the first nitration steps increased with increasing agitator speed. The mixing times in the vessel were very short compared to the reaction time even at the slowest agitator speed, and the reactor temperature was closely controlled. What is a plausible reaction mechanism and what is a reason for the evil professor's unexpected results? He asked his colleague, and she suggested he read at least the title of Chapter 11.
- 1.14** The reaction of trimethylamine with *n*-propyl bromide gives a quaternary ammonium salt:



Suppose laboratory results at 110°C using toluene as a solvent show the reaction to be second order with rate constant $k = 5.6 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Suppose $[\text{N}(\text{CH}_3)_3]_0 = [\text{C}_3\text{H}_7\text{Br}]_0 = 80 \text{ mol m}^{-3}$.

- (a) Estimate the time required to achieve 99% conversion in a batch reactor.
- (b) Estimate the volume required in a CSTR to achieve 99% conversion if a production rate of 100 kg h^{-1} of the salt is desired.
- (c) Suggest means for increasing the productivity, that is, reducing the batch reaction time or the volume of the CSTR.
- 1.15** Ethyl acetate can be formed from dilute solutions of ethanol and acetic acid according to the reversible reaction



Ethyl acetate is somewhat easier to separate from water than either ethanol or acetic acid. For example, the relatively large acetate molecule has much lower permeability through a membrane ultrafilter. Thus esterification is sometimes proposed as an economical approach for recovering dilute fermentation products. Suppose fermentation effluents are available as separate streams containing 3% by weight acetic acid and 5% by weight ethanol. Devise a reaction scheme for generating ethyl acetate using the reactants in stoichiometric ratio. After reaction, the ethyl acetate concentration is increased first to 25% by weight using ultrafiltration and then to 99% by weight using distillation. The reactants must ultimately be heated for the distillation step. Thus we can suppose both the esterification and membrane separation to be conducted at 100°C. At this temperature,

$$k_f = 8.0 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad k_r = 2.7 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Determine \bar{t} and a_{out} for a CSTR that approaches equilibrium within 5%, that is,

$$\frac{a_{\text{out}} - a_{\text{equil}}}{a_{\text{in}} - a_{\text{equil}}} = 0.05.$$

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- 1.16** Rate expressions for gas phase reactions are sometimes based on partial pressures. Smith (1956, p. 131) gives $k = 1.1 \times 10^{-3} \text{ mol cm}^{-3} \text{ atm}^{-2} \text{ h}^{-1}$ for the reaction of gaseous sulfur with methane at 873 K:



where $\mathcal{R} = k P_{\text{CH}_4} P_{\text{S}_2}$, $\text{mol cm}^{-3} \text{ h}^{-1}$. Determine k when the rate is based on concentrations: $\mathcal{R} = k[\text{CH}_4][\text{S}_2]$. Give k in SI units.

- 1.17** You have a flat-bottomed reactor with 1 m internal diameter that operates with a 1-m liquid level. It is agitated by a six-bladed, pitched turbine that is located 0.5 m above the reactor bottom. Paul et al. (2003) give $\mathbf{Po} = 1.3$ provided the vessel Reynolds number $\mathbf{Re} = \rho D_t^2 N_t / \mu$ is larger than about 500. The mixing time under these conditions is given by $\mathbf{Po}^{1/3} N_t t_{\text{mix}} (D_t / D_{\text{tank}})^2 = 5.2$, where d_t is the tank diameter. You wish to achieve a mixing time of 30 s with a waterlike liquid. What RPM should you use and how much power will be needed?
- 1.18** A second-order reaction of the type $2A \rightarrow B$ reacts to 90% completion when the reactor in Problem 1.17 is operated with a batch reaction time of 1 h. It is proposed to operate it as a CSTR. What is the mean residence time needed to achieve 90% conversion in the continuous mode of operation?