8

Chemical Reactors

This chapter is concerned with chemical reactors. As with all the chapters in Part II, there are several sections: overview, several technical topics, illustrative open-ended problems open-ended problems. The purpose of the first section is to introduce the reader to the subject of chemical reactors. As one might suppose, a comprehensive treatment is not provided although several technical section are also included. The next section contains three open-ended problems; the authors' solution (there may be other solutions) are also provided. The last section contains 36 problems; *no* solutions are provided here.

8.1   Overview

This overview section is concerned—as can be noted from the chapter title—with chemical reactors. As one might suppose, it was not possible to address all topics directly or indirectly related to chemical reactors. However, additional details may be obtained from either the references

provided at the end of this Overview section and/or at the end of the chapter.

Note: Those readers already familiar with the details associated with this subject may choose to bypass this Overview.

Almost every chemical process is designed to produce a desired product economically from a variety of starting materials through a succession of treatment steps. The raw materials may first undergo a number of physical treatment steps to put them in the form in which they can be reacted chemically. They then pass through a reactor. The discharge, or products of the reaction then usually undergoes additional physical treatment processes; i.e., separations, purifications, etc., for the final desired product to be obtained. The physical treatment processes were discussed in the earlier chapters. This chapter, however, is concerned with the chemical treatment processes that involve chemical reactors.

A major objective of this chapter is to prepare the reader to solve real-world engineering and design problems that involved chemical reactors. There are several classes of reactors. The three that are most often encountered in practice are batch (B), continuous stirred tank (CSTR), and tubular flow (TF). As such they receive the bulk of the treatment to follow. Another reactor reviewed is the semi-batch unit. Other topics reviewed include catalytic reactors and thermal effects.

The remainder of the chapter addresses 6 topics that are either directly or indirectly concerned with chemical reactors. They include:

1. Chemical Kinetics
2. Batch Reactors (B)
3. Continuous Stirred Tank Reactors (CSTR)
4. Tubular Flow Reactors (TF)
5. Catalytic Reactors
6. Thermal Effects

The reader should note that the bulk of the material in this chapter has been from L. Theodore, "Chemical Reaction Kinetics," A Theodore Tutorial, Theodore Tutorials, East Williston, NY, originally published by the USEPA/APTI, RTP, NC, 1995 [1]. Also note that in an attempt to be consistent with the chemical reactor literatures, the volumetric flow rate is represented by Q (not q, as in most of the chapters in this text).

8.2   Chemical Kinetics

Chemical kinetics involves the study of reaction rates and the variables that effect these rates. It is a topic that is critical for the analysis of reacting systems and chemical reactors. The rate of a chemical reaction can be described in any of several different ways. The most commonly used definition involves the time rate of change in the amount of one of the components participating in the reaction; the rate is also based on some arbitrary factor related to the reacting system size or geometry, such as volume, mass, and interfacial area.

Based on experimental evidence, the rate of reaction is a function of:

1. the concentration of components existing in the reaction mixture (this includes reacting and inert species);
2. temperature;
3. pressure; and (if applicable)
4. catalyst variables.

This may be put in equation form as:

$$r_A = r_A(C, P, T, catalyst\ variables) \tag{8.1}$$

or simply

$$r_A = \pm k_A f(C) \tag{8.2}$$

where k_A incorporates all the variables other than concentration. The $\pm$ notation is included to account for the reaction or formation of A. One may think of k_A as a constant of proportionality. It is defined as the *specific reaction rate* or more commonly the *reaction velocity constant*. It is a "constant" which is *independent* of concentration but *dependent* on the other variables. This approach has, in a sense, isolated one of the variables. The reaction velocity constant, k, like the rate of reaction, *must* refer to one of the species in the reacting system. However, k almost always is based on the same species as the rate of reaction.

Consider, for example, the reaction

$$aA + bB \rightarrow cC + dD \tag{8.3}$$

The notation $\rightarrow$ represents an irreversible reaction; i.e., if stoichiometric amounts of A and B are initially present, the reaction will proceed to the right until all the A and B have reacted (disappeared) and C and D have been formed. If the reaction is *elementary*, the rate of the above reaction is given by

$$r_A = -k_A C_A^a C_B^b \qquad (8.4)$$

where the negative sign is introduced to account for the disappearance of A, and the product concentrations do not affect the rate. For elementary reactions, the reaction mechanism for r_A is simply obtained by multiplying the molar concentrations of the reactants raised to powers of their respective stoichiometric coefficients (power law kinetics). For *non-elementary* reactions, the mechanism can take any form.

The order of the above reaction with respect to a particular species is given by the exponent of that concentration term appearing in the rate of expression. The above reaction is, therefore of order a with respect to A and of order b with respect to B. The *overall order* n, usually referred to as "the order", is the sum of the individual orders; i.e.,

$$n = a + b \qquad (8.5)$$

All real and naturally occurring reactions are *reversible*. A reversible reaction is one in which products react to form reactants back. Unlike irreversible reactions, which proceed to the right until completion, reversible reactions achieve an equilibrium state, in which rates of forward and reverse reactions are nearly the same for an infinite period of time. Reactants and products are still present in the system. At this (equilibrium) state, the reaction rate is zero. For example, consider the following reversible reaction:

$$aA + bB \rightleftharpoons cC + dD \qquad (8.6)$$

where the notation $\rightleftharpoons$ is a reminder that the reaction is reversible $\rightarrow$ represents the forward reaction contribution to the total net rate, while $\leftarrow$ represents the contribution of the reverse reaction. The notation = is employed if the reaction system is at equilibrium. The rate of the reaction (see Equation 8.6) is then given by

$$r_A = \underbrace{-k_A C_A^a C_B^b}_{\substack{forward \\ reaction}} + \underbrace{k_A' C_C^c C_D^d}_{\substack{reverse \\ reaction}} \qquad (8.7)$$

and

$$K_A = \frac{k_A}{k_A'} \tag{8.8}$$

With regard to chemical reactions, there are two important questions that are of concern to the chemical engineer: (1) how far will the reaction go, and (2) how fast will the reaction go? Chemical thermodynamics (reaction equilibrium principles provides the answer to the first question; however, it provides no information regarding the latter question, which is concerned with kinetics. Reaction rates fall within the domain of chemical kinetics.

The two most common conversion variables employed by practitioners are denoted by α and X. The term α is employed to represent the change in the number of moles of a particular species due to chemical reaction. However, the most commonly used conversion variable is X; it is used to represent the change in the number of moles of a particular species (say A) relative to the number of moles of A *initially present* or *initially introduced* (to a flow reactor). Thus,

$$X_A = \frac{moles\ of\ A\ reacted}{initial\ moles\ of\ A} = \frac{N_A}{N_{A_0}} \tag{8.9}$$

Other conversion (related) variables include: N_A, the number of moles of species A at some later time (or position); C_A, the concentration of A at some later time (or position); and x_A, the moles of A reacted/ total moles initially present. Also note that all of the above conversion variables can be based on mass, but this is rarely employed in practice. The conversion variable of choice is almost always X. In addition, the *yield* of a reaction is a measure of how much of the desired product is produced relative to how much would have been produced if only the desired reactions occurred, and if that reaction went to completion. Alternatively, *selectivity* is a measure of how a desired reaction performs relative to one of the side reactions.

Equations to describe the rate of reaction at the macroscopic level have been developed in terms of meaningful and measurable quantities. As noted earlier the reaction rate is affected not only by the concentration of species in a reacting system but also by the temperature. An increase in temperature will almost always result in an increase in the rate of reaction; in fact, the literature states that, as a general rule, a 10°C increase in reaction temperature will double the reaction velocity constant. However, this is generally no longer regarded as a truism, particularly at elevated temperatures.

The Arrhenius equation relates the reaction velocity constant with temperature, T. It is given by

$$A \exp\left(\frac{-E_a}{RT}\right) \tag{8.10}$$

where A = frequency factor constant and is usually assumed to be independent of temperature

R = universal gas constant

E_a = activation energy and is usually assumed independent of temperature.

8.3   Batch Reactors

Batch reactors are commonly used in experimental studies. Their industrial applications are somewhat limited. They are used for gas phase, e.g. combustion reactions since small quantities (mass) of product are produced with even a very large-sized reactor. It is used for liquid phase reactions when small quantities of reactants are to be processed. It finds its major application in the pharmaceutical industry. As a rule, batch reactors are less expensive to purchase but more expensive to operate than either continuous stirred tank or tubular flow reactors.

The extent of a chemical reaction and/or the amount of product produced can be affected by the relative quantities of reactants introduced to the reactor. For two reactants, each is normally introduced through separate feed lines normally located at or near the top of the reactor. Both are usually fed simultaneously over a short period of time. Mixing is accomplished with the aid of a turning/spinning impeller. (See also Figure 8.1). The reaction is assumed to begin after both reactants are in the reactor. No spatial variations in concentration, temperature, etc., are generally assumed.

In most liquid-phase batch systems, the reactor volume is considered to be constant. However, in many systems, these parameters may vary, depending on the phase and reaction stoichiometry. Such variance must be included in the analysis of gas phase reaction systems [1–4].

As noted above, a batch reactor is normally used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operation. The batch reactor has the advantage of high conversions that can be obtained by leaving the reactants in the reactor
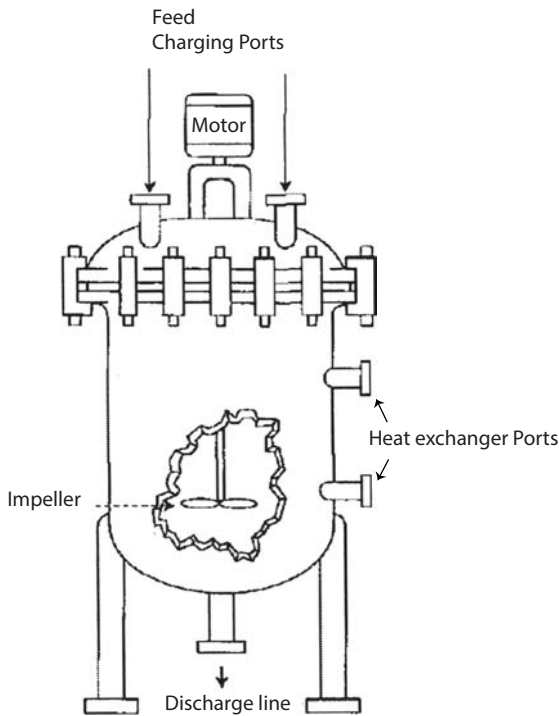
Figure 8.1 Batch reactor schematic.

for long periods of time, but it also has the disadvantage of high labor costs per unit production, and large-scale production, which is usually difficult.

A batch reactor is a solid vessel or container (see Figure 8.1). It may be open or closed. As noted, reactants are usually added to the reactor simultaneously. The contents are then mixed (if necessary) to ensure no spatial variations in the concentration of the species present. The reaction then proceeds. There is no transfer of mass into or out of the reactor during this period. The concentration of reactants and products changes with time; thus, this is a *transient* or *unsteady state* operation. The reaction is terminated when the desired chemical change has been achieved. The contents are then discharged and sent elsewhere, usually for further processing.

The describing equation for chemical reaction mass transfer is obtained by applying the conservation law for either mass or moles on a time-rate basis to the contents of a batch reactor. It is best to work with moles rather than mass since the rate of reaction is most conveniently described in terms of molar concentrations. The describing equation for species A in a batch reactor takes the form

$$\frac{dN_A}{dt} = -r_A V \tag{8.11}$$

where N_A = moles A at time t

r_A = rate of reaction of A; change in moles A/timevolume

V = reactor volume *contents*.

The above equation may also be written in terms of the conversion variable X since

$$N_A = N_{A_0} - N_{A_0} X \tag{8.12}$$

where N_{A_0} = initial moles of A.

Thus (setting X = X_A),

$$N_{A_0}\left(\frac{dX}{dt}\right) = -r_A V \tag{8.13}$$

The integral form of this equation is

$$t = N_{A_0}\int_0^X \left(\frac{-1}{r_A V}\right) dX \tag{8.14}$$

If V is constant (as with most liquid phase reactions)

$$t = \frac{N_{A_0}}{V}\int_0^X \left(\frac{-1}{r_A}\right) dX$$

$$= C_{A_0}\int_0^X \left(\frac{-1}{r_A}\right) dX \tag{8.15}$$

8.4   Continuous Stirred Tank Reactors (CSTRs)

Another reactor where mixing is important is the tank flow or continuously stirred tank reactor (CSTR). This type of reactor, like the batch reactor, also consists of a tank or kettle equipped with an agitator. It may be operated under steady or transient conditions. Reactant(s) are fed continuously, and the product(s) are withdrawn continuously (see Figure 8.2). The
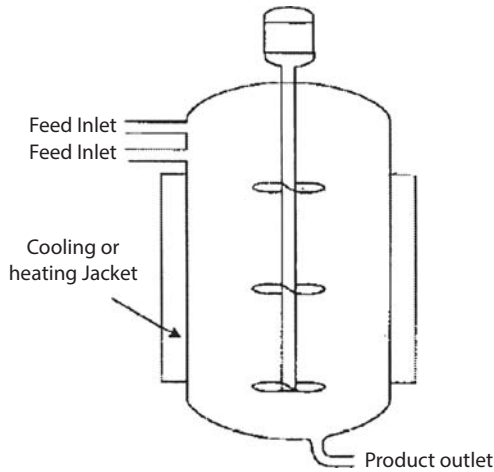
Figure 8.2 Continuously stirred tank reactor schematic. (CSTR)

reactant(s) and product(s) may be liquid, gas, or solid, or a combination of these. If the contents are perfectly mixed, the reactor design problem is greatly simplified for steady conditions because the mixing results in uniform concentrations, temperature, etc., throughout the reactor. This means that the rate of reaction is constant and the describing equations are not differential, and therefore, do not require integration. In addition, since the reactor contents are perfectly mixed, the concentration and/or conversion in a CSTR in exactly equal to the concentration and/or conversion *leaving* the reactor. The describing equation for the CSTR can then be shown to be:

$$V = \frac{F_{A_0} X_A}{(-r_A)} \qquad (8.16)$$

where V = volume of reacting mixture
F_{A_0} = inlet molar feed rate of A
X_A = conversion of A
$-r_A$ = rate of reaction of A.

If the volumetric flow rate Q entering and leaving the CSTR are constant (this is equivalent to a constant density system), the above equation becomes

$$\frac{V}{Q} = \frac{C_{A_1} - C_{A_0}}{(r_A)}$$

$$= \frac{C_{A_0} - C_{A_1}}{(-r_A)} \qquad (8.17)$$

where Q = total volumetric flow rate through the CSTR
C_{A_0} = inlet molar concentration of A
C_{A_1} = exit molar concentration of A.

In general, CSTRs are used for liquid phase reactions. High reactant concentrations can be maintained with low flow rates so that conversion approaching 100% can often be achieved. However, the overall economics of the system is reduced because of the low throughput.

CSTRs (as well as the tubular flow reactors described next) are often connected in series in such a manner that the exit stream of one reactor is the feed stream for another reactor. Under these conditions, it is convenient to define the conversion at any point downstream in the battery of CSTR reactors in terms of *inlet* conditions, rather than with respect to any one of the reactors in the series. The conversion X is then the total moles of A that have reacted up to that point per mole of A fed to the *first* reactor. However, this definition should only be employed if there are no side stream withdrawals and the only feed stream enters the first reactor in the series. The conversion from reactors 1, 2, 3,… in the series are usually defined as X_1, X_2, X_3,…, respectively, and effectively represent the overall conversion for that reactor relative to the feed stream to the *first* reactor.

As indicated earlier, for liquid phase reactions the design equation can be written as

$$\theta = \frac{V}{Q} = \frac{C_{A_1} - C_{A_0}}{r_A} \tag{8.18}$$

The term on the left-hand side (LHS) of the above equation has the units of time and represents the average holdup (residence) time in the reactor. It is usually denoted by the symbol θ. The reciprocal of θ is defined as the space velocity (SV) and finds wide application with tubular flow reactors. However, there is a distribution [5] around this average, it is often important enough that this distribution effect be included in the analysis of certain type systems.

8.5   Tubular Flow Reactors

The last "traditional" reactor to be examined is the tubular flow reactor. The most common type is the single-pass cylindrical tube. Another type is one that consists of a number of tubes in parallel. The reactor(s) may

be vertical or horizontal. The feed is charged continuously at the inlet of the tube, and the products are continuously removed at the outlet. If heat exchange with surroundings is required, the reactor setup includes a jacketed tube (see Figure 8.3). If the reactor is empty, a homogenous reaction – one phase is present – usually occurs. If the reactor contains catalyst particles, the reaction is said to be heterogeneous; this type will be considered in the next section.

Tubular flow reactors are usually operated under steady conditions so that physical and chemical properties do not vary with time. Unlike the batch and tank flow reactors, there is no mechanical mixing. Thus, the state of the reacting fluid will vary spatially from point to point in the system, and this variation may be in both the radial and axial directions in tubular reactors. The describing equations are then differential, with position as the independent variable.

The reacting system for the describing equations presented below is assumed to move through the reactor in plug flow (no velocity variation through the cross-section of the reactor). It is further assumed that there is no mixing in the axial direction so that the concentration, temperature, etc., do not vary through the cross-section of the tube. Thus, the reacting fluid flows through the reactor in an undisturbed *plug* of mass. For these conditions, the describing equation for a tubular flow reactor is

$$\theta = \frac{V}{Q} = \frac{C_{A_1} - C_{A_0}}{r_A} \tag{8.19}$$

Since $F_{A_0} = C_{A_0} Q_0$

$$\frac{V}{Q_0} = C_{A_0} \int \left(\frac{-1}{r_A} \right) dX_A \tag{8.20}$$
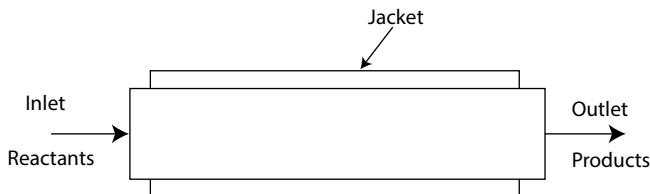

Figure 8.3 Tubular flow reactor; single pass.

The RHS (right hand side) of the above represents the residence time in the reactor based on inlet conditions. If Q does not vary through the reactor, then

$$\theta = \frac{V}{Q_0} \qquad (8.21)$$

where θ is once again the residence time in the reactor.

In actual practice, tubular flow reactors deviate from a plug flow model because of velocity variations in the radial direction. For this condition, the residence time for annular elements of fluid within the reactor will vary from some minimal value at a point where the velocity approaches zero. Thus, the concentration and temperature profiles, as well as the velocity profile, are not constant across the reactor and the describing equations based on the plug flow assumption are then not applicable. This situation can be further complicated if the reaction occurs in the gas phase. Volume effect changes that impact on the concentration term(s) in the rate equation need to be taken into account [1,2,4].

From a qualitative point of view, as the length of the reactor approached infinity, the concentration of a (single) reactant approaches zero for irreversible reactions (except zero order) and the equilibrium concentrations for reversible reactions. Since infinite time is required to achieve equilibrium conversion, this value is approached as the reactor length approaches infinity. For reactors of finite length, where the reaction is reversible, some fraction of the equilibrium conversion is achieved.

Note that the time for a hypothetical plug of material to flow through a tubular flow reactor is the same as the contact or reaction time in a batch reactor. Under these conditions, the same form of the describing equations for batch reactors will also apply to tubular flow reactors.

Another design variable is pressure drop. This effect is usually small for most liquid and gas phase reactions conducted in short or small reactors. This effect is usually estimated using Fanning's Equation (see also Chapter 5) [6].

$$\Delta P = \frac{4fLV^2}{2g_cD} \qquad (8.22)$$

where ΔP = pressure drop
$\quad\quad f$ = Fanning friction factor
$\quad\quad L$ = reactor length

V = average flow velocity
g_c = gravity conversion constant
D = reactor diameter

8.6   Catalytic Reactors

Metals in the platinum family are recognized for their ability to promote reactions at low temperatures. Other catalysts include various oxides of copper, chromium, vanadium, nickel, and cobalt. These catalysts are subject to poisoning, particularly from halogens, sulfur compounds, zinc, arsenic, lead, mercury, and particulates. High temperatures can reduce catalyst activity. It is therefore important that catalyst surfaces are clean and active to insure optimum performance. For example, catalysts can be regenerated with superheated steam.

Catalyst may be porous pellets, usually cylindrical or spherical in shape, ranging from 1/16 to ½ inch in diameter. Small sizes are recommended, but the pressure drop through the reactor increases. Other shapes include honeycombs, ribbons, wire mesh, etc. Since catalysis is a surface phenomena, an important physical property of these particles is that the total internal pore surface be many magnitudes greater than the outside surface. The reader is referred to the literature for more information on catalyst preparation, properties, comparisons, costs, and impurities [1,3]

Some of the advantages of catalytic reactors are:

1. low fuel requirements;
2. lower operating temperatures;
3. little or no insulation requirements;
4. reduced fire hazards; and
5. reduced flashback problems.

The disadvantages include:

1. high initial cost;
2. catalyst poisoning;
3. large particles must first be removed;
4. some liquid droplets must first be removed; and
5. catalyst regeneration problems.

Catalytic or heterogeneous reactors are an alternative to homogenous reactors. If a solid catalyst is added to the reactor, the reaction is said to be

heterogeneous. For simple reactions, the effect of the presence of a catalyst is item to: increase the rate of reaction, permit the reaction to occur at a lower temperature, permit the reaction (usually) to occur at a more favorable pressure, reduce the reactor volume, and increase the yield of a reactant(s). The basic problem in the design of a heterogeneous reactor is to determine the quantity of catalyst and/or reactor size required for a given conversion and flow rate. In order to obtain this, information on the rate equation(s) and their parameter(s) must be made available. A rigorous approach to the evaluation of reaction velocity constants, etc., for many industrial applications has yet to be accomplished for catalytic reactions. At this time, industry still relies on simple procedures set forth in the literature. (1, 3)

In many catalytic reactions, the rate equation is extremely complex and cannot be obtained either analytically or experimentally. A number of rate equations may result and some simplification is warranted. As mentioned earlier, it is safe in many cases to assume that the rate expression may be satisfactorily expressed by the rate of equation of a single step.

It is common practice to write the describing equations for mass and energy transfer for homogeneous and heterogeneous flow reactors in the same way. However, the (units of the) rate of reaction may be expressed as either

$$\left(\frac{moles\ reacted}{time}\right)(volume\ of\ reactor) \tag{8.23}$$

or

$$\left(\frac{moles\ reacted}{time}\right)(mass\ of\ catalyst) \tag{8.24}$$

The latter is normally the preferred method employed in industry since it is the mass of catalyst present in the reactor that significantly impacts the reactor design. As noted, the rate expression is often more complex for a catalytic reaction than for a non-catalytic (homogeneous) one, and this can make the design equation of the reactor difficult to solve analytically. Numerical solution of the reactor design equation is usually required when designing tubular flow reactors for catalytic reactions.

As indicated above, the principal difference between reactor design calculations involving homogeneous reactions and those involving catalytic (fluid-solid) heterogeneous reactions is that the reaction rate for the latter is based on the mass of solid catalyst, W, rather than on the reactor volume

V. The reaction of a substance A for a fluid-solid heterogeneous system is then defined as

$$-r_A' = \left(\frac{mols\ A\ reacted}{mass\ catalyst} \right)(time)$$

(8.25)

A brief discussion of the two major classes of catalytic reactors follows.

8.6.1   Fluidized Bed Reactors

One type of catalytic reactor in common use is the fluidized-bed. The fluidized-bed reactor is analogous to the CSTR in that its contents, though heterogeneous, are well mixed, resulting in a uniform concentration and temperature distribution through the bed. The fluidized-bed reactor can therefore be modeled, as a first approximation, as a CSTR. For the ideal CSTR, the reactor design equation based on volume is

$$V = \frac{F_{A_0} X_A}{(-r_A)}$$

(8.26)

The companion equation for catalytic or fluid-solid reactor, with the rate based on the mass of solid, is

$$W = \frac{F_{A_0} X_A}{(-r_A')}$$

(8.27)

The reactor volume is simply the catalyst weight, W, divided by the fluidized bed density, ρ_{fb}, of the catalyst in the reactor.

$$V = \frac{W}{\left(\rho_{fb} \right)}$$

(8.28)

The fluid bed catalyst density is normally expressed as some fraction of the catalyst bulk density ρ_B.

8.6.2   Fixed Bed Reactors

A fixed-bed (packed-bed) reactor is essentially a tubular flow reactor that is packed with solid catalyst particles. This type of heterogeneous

reaction system is most frequently used to catalyze gaseous reactions. The design equation for tubular flow reactor was previously shown to be

$$V = F_{A_0} \int_0^X \left(\frac{-1}{r_A} \right) dX; \ X = X_A$$

(8.29)

The companion equation based on the mass of catalyst for a fixed-bed reactor is

$$W = F_{A_0} \int_0^X \left(\frac{-1}{r_A{'}} \right) dX$$

(8.30)

The volume of the reactor, V, is then

$$V = \frac{W}{(\rho_B)}$$

(8.31)

where ρ_B = bulk density of the catalyst.

The aforementioned Ergun equation [7] is normally employed to estimate the pressure drop for fixed bed units.

8.7   Thermal Effects

It was shown in the Chemical Kinetics section that the rate of reaction, r_A, is a function of temperature and concentration. The application of r_A to the reactor equations is simplest for isothermal conditions since r_A is generally solely a function of concentration. If non-isothermal conditions exist, another equations must be written to describe temperature variations with time or position within the reactor. Details of this effect for batch, continuous stirred tank and tubular flow reactors follows.

8.7.1   Batch Reactors

The equation describing temperature variations in batch reactors is obtained by applying the conservation law for energy on a time-rate basis to the reactor contents. Since batch reactors are stationary (fixed in space),

kinetic and potential effects can be neglected. The equation describing the temperature variation in reactors due to energy transfer, subject to the assumptions in its development, is [2]

$$mC_p \left(\frac{dT}{dt} \right) = -UA_e \left(T - T_a \right) + V \left(-\Delta H_A \right) \left| -r_A \right|$$ (8.32)

where m = mass of the reactor contents
C_p = heat capacity
V = reactor volume
$-\Delta H_A$ = enthalpy of reaction of species A
$\left| -r_A \right|$ = absolute value of the rate of reaction of A
T = reactor temperature.

In addition (8-10) (see Chapter 6)

$$\dot{Q} = UA \left(T - T_a \right)$$ (8.33)

where Q = heat transfer rate across the walls of the reactor
U = overall heat transfer coefficient
A = area available for heat transfer
T_a = temperature surrounding the reactor walls

For non-isothermal reactors, one of the reactor design equations—the energy transfer equation (see above), and an expression for the rate in terms of concentration and temperature—must be solved simultaneously to give the conversion as a function of time. Note that the equations may be interdependent; i.e., each can contain terms that depend on the other equation(s). These equations, except for simple systems, are usually too complex for analytical treatment.

8.7.2 CSTR

If the conservation law for energy is applied to a CSTR, information on temperature changes and variations within the reactor can be obtained. For constant heat capacity, C_p, and enthalpy of reaction, ΔH_A, the describing equation becomes

$$FC_p \left(T_o - T_1 \right) + \left(-r_A \right) V \left(-\Delta H_A \right) = 0$$ (8.34)

where F = flow rate through the reactor, units consistent with C_p
T_o = inlet temperature
T_1 = outlet temperature

For adiabatic conditions, and noting that

$$\left(-r_A\right)V = F_{A_0} X_A; \ F_{A_0} = feed\ rate\ of\ A \tag{8.35}$$

the above equation becomes (with $T_1 = T$)

$$FC_p\left(T_o - T\right) = F_{A_0} X_A (-\Delta H_A) = 0 \tag{8.36}$$

The equation may be rearranged to give

$$T = T_o + \left[\frac{F_{A_0}\left(-\Delta H_A\right)}{FC_p}\right] X_A \tag{8.37}$$

Thus, the need for simultaneous solution of the mass and energy transfer equations is removed. Fogler [4] has also accounted for enthalpy of reaction variation with temperature in a slightly different form.

8.7.3   Tubular Flow Reactions

The temperature in a tubular flow reactor can vary with position (volume) due to enthalpy of reaction effects or transfer of energy in the form of heat across the walls of the reactor. The reactor design equation must then include temperature variations before being solved. In order to obtain information on the temperature at every point in the reactor, the conservation law for energy is applied to a system. For adiabatic operation, heat transfer with the surroundings is zero. The energy equation reduces to [2]

$$FC_p dT = \left|-r_A\right|(-\Delta H_A)dV \tag{8.38}$$

Since

$$\left|-r_A\right|dV = F_{A_0} dX_A \tag{8.39}$$

for a tubular flow reaction, the above equation becomes

$$FC_p dT = F_{A_0}\left(-\Delta H_A\right) dX_A \tag{8.40}$$

which may be integrated to give the previously developed equation for CSTRs:

$$T = T_o + \left[\frac{F_{A_0}\left(-\Delta H_A\right)}{FC_p}\right] X_A \tag{8.41}$$

The term in brackets is a constant if the enthalpy of reaction and the average heat capacity are assumed independent of temperature. The temperature is then a linear function of conversion [1]. Fogler [4], also provides an equation describing temperature variation within a tubular flow reactor. The equation also takes the same form as that provided for CSTRs.

A detailed and expanded treatment of chemical reactors is available in the following three references

1. L. Theodore, *Chemical Reactor Analysis and Applications for the Practicing Engineer*, John Wiley & Sons, Hoboken, NJ, 2012 [21].
2. D. Green and R. Perry editors, *Perry's Chemical Engineers' Handbook,* 8th edition, McGraw-Hill, New York City, NY, 2008 [9].
3. L. Theodore, *Chemical Engineering: The Essential Reference*, McGraw-Hill, New York City, NY, 2014 [10].

8.8   Illustrative Open-Ended Problems

This and the last section provides open-ended problems. However, solutions *are* provided for the three problems in this section in order for the reader to hopefully obtain a better understanding of these problems, which differ from the traditional problems/illustrative examples. The first problem is relatively straightforward while the third (and last problem) is somewhat more difficult and/or complex. Note that solutions are not provided for the 36 open-ended problems in the next section.

Problem 1: Discuss rate versus equilibrium considerations as they apply to chemical reactors.

Solution: With regard to chemical reactions, there are two important questions that are of concern to the chemical engineer:

1. How *far* will the reaction go?
2. How *fast* will the reaction go?

Chemical thermodynamics provides the answer to the first question; however, it provides nothing about the second [9]. What follows the development presented in chapter 4.

To illustrate the difference and importance of both of the above questions in an engineering analysis of a chemical reaction, consider the following process [1–4]. Substance A, which costs 1 cent/ton, can be converted to B, which costs $1 million/lb, by the reaction A→B. Chemical thermodynamics will provide information on the maximum amount of B that can be formed. If 99.99% of A can be converted into B, the reaction would then appear to be economically feasible, from a *thermodynamics* point of view. However, a *kinetic* analysis might indicate that the reaction is so slow that, for all practical purposes, its rate is vanishingly small. For example, it might take 10^9 years to obtain a 10^{-9}% conversion of A. The reaction is then economically unfeasible. Thus, it can be seen that both equilibrium and kinetic effects must often be considered in an overall engineering analysis of a chemical reaction.

Equilibrium and rate are therefore both important factors to be considered in the design and prediction of the performance of equipment employed for chemical reactions. The rate at which a reaction proceeds will depend on the displacement from equilibrium, with the rate at which equilibrium is established essentially dependent on a host of factors discussed in the previous section. As noted, this rate process ceases upon the attainment of equilibrium.

Problem 2: [1,2] The following *gas* phase reaction is carried out *isothermally* in a constant volume batch reactor:
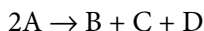
$$2A \rightarrow B + C + D$$

TABLE 8.1 Time – Pressure Data for Problem 2

Time (min)	0	1.20	1.95	2.90	4.14	5.70	8.10	∞
Total pressure (atm)	1	1.10	1.15	1.20	1.25	1.30	1.35	1.51

Pure A is initially in the reactor at STP (32°F, 1 atm). The following pressures in Table 8.1 were recorded at subsequent times during the reaction.

1. Calculate δ and ε.
2. Develop an expression for the conversion in terms of the total pressure.
3. Is the reaction reversible? Provide your explanation.
4. Verify that the order of the reaction is approximately 1.4, and then calculate the specific reaction rate constant using any convenient method of your choice.
5. Comment on the results.

Solution:

1. Rewrite the gas phase reaction

$$2A \rightarrow B + C + D$$

    as

$$A \rightarrow (1/2)B + (1/2)C + (1/2)D$$
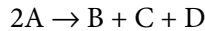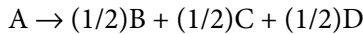
    Preliminary calculations:

$$y_{A_0} = 1.0$$

$$\delta = (3/2) - 1 = \tfrac{1}{2}$$

$$\varepsilon = (1.0)(1/2) = \tfrac{1}{2} = 0.5$$

$$V = V_0(1 + \varepsilon X)(T_0/T)(P/P_0); \quad T_0/T = 1.0$$

$$= V_0(1 + \varepsilon X)(P/P_0)$$

2. Since the volume is constant, $V = V_0$, so that

$$X = \frac{P - P_0}{\varepsilon P_0}; \quad P_0 = 1.0$$

$$= 2P - 2$$

(8.42)

For a batch reactor,

$$r_A = \frac{1}{V}\frac{dN_A}{dt} = \frac{dC_A}{dt}; \text{ constant volume} \tag{8.43}$$

Assume the mechanism to be of the form

$$r_A = kC_A^n \tag{8.44}$$

Since

$$C_A = C_{A_0}(1-X)$$
$$-C_{A_0}\frac{dX}{dt} = kC_A^n \tag{8.45}$$

and

$$C_A = C_{A_0}\left[1 - \left(\frac{P - P_0}{\varepsilon P_0}\right)\right] = \frac{C_{A_0}}{\varepsilon P_0}\left[(1+\varepsilon)P_0 - P\right] \tag{8.46}$$

Therefore

$$-r_A = k\left(\frac{C_{A_0}}{\varepsilon P_0}\right)^n\left[(1+\varepsilon)P_0 - P\right]^n = kC_A^n \tag{8.47}$$

And

$$X = \frac{P - P_0}{\varepsilon P_0} \tag{8.48}$$

3. The reaction equation indicates that 2 moles are converted to 3 moles, an increase of 50%. The pressure data indicates that the pressure increases from 1.0 atm to 1.5 atm (a 50% increase when the reaction goes to completion). Therefore the reaction is *irreversible*.

4. The derivative of the above Equation is

$$\frac{dX}{dt} = \frac{1}{\varepsilon P_0}\frac{dP}{dt} \tag{8.49}$$

Combining this equation with the rate equation yields

$$\frac{dP}{dt} = k\left(\frac{C_{A_0}}{\varepsilon P_0}\right)^{n-1} \left[(1+\varepsilon)P_0 - P\right]^n \qquad (8.51)$$

One may use any approach to generate dP/dt information. One approach requires a log – log plot of rate in terms of dP/dt vs. $[(1 + \varepsilon)P_0 - P]$; i.e., $[1.5 - P]$. The slope is then n. The plot yields $n = 1.4$.
5. Two concerns arise in integrating the results:
    a. The assumed mechanism
    b. Ideal gas law behavior.

Problem 3: A vertical fixed bed catalytic reactor pictured in Figure 8.4 is designed to operate at a specified conversion. Once the unit is installed and running, the unit operates with a lower conversion. What options would you recommend to bring the unit into compliance with the specified design conversion? [2]

Solution: Some possible solutions are provided below:

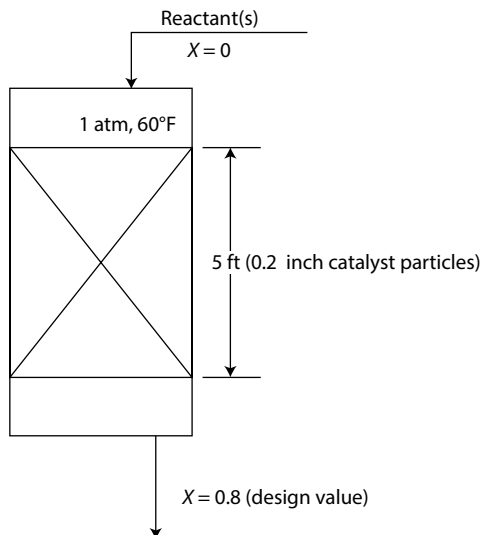1. Use a smaller catalyst size. A different size may produce a higher conversion.

Figure 8.4 Vertical fixed-bed reactor.

2. Use a different type of catalyst. A different type may produce a higher conversion.
3. Use a different physical shaped catalyst.
4. Make sure there is no channeling inside the reactor. The catalyst should be randomly distributed and there should be no open spots.
5. Consider increasing or decreasing the flow rate entering the reactor.
6. Check to see if the pressure drop is excessive.
7. Lower the initial concentration of the reactant (if possible).
8. Increase the height of the reactor bed.
9. Increase the temperature.
10. Modify the process that may be producing the reactant(s); since the details of this process are not included in the problem statement, no specific recommendations can be made.
11. Finally, before considering changes to the system, one should undertake a thorough inspection of the reactor and surrounding components.

The reader should note that some of the recommendations above could lead to higher pressure drops and potential problems with the flow. An example of this problem would be the implementation of suggestion (1). The reader is left the exercise of determining what other steps could lead to flow/pressure drop problems. *Hint*: There are at least six suggestions that fall into this category, including a consideration to fire the (chemical?) engineer who designed the reactor [12].

8.9   Open-Ended Problems

This last section of the chapter contains open-ended problems as they relate to chemical reactors. No detailed and/or specific solution is provided; that task is left to the reader, noting that each problem has either a unique solution or a number of solutions or (in some cases) no solution at all. These are characteristics of open-ended problems described earlier.

There are comments associated with some, but not all, of the problems. The comments are included to assist the reader while attempting to solve the problems. However, it is recommended that the solution to each problem should initially be attempted *without* the assistance of the comments.

There are 36 open-ended problems in this section. As stated above, if difficulty is encountered in solving any particular problem, the reader should next refer to the comment, if any is provided with the problem. The reader should also note that the more difficult problems are generally located at or near the end of the section.

1. Describe the early history associated with chemical reactors.
2. Discuss the recent advances in chemical reactor technology.
3. Select a referred, published article on chemical reactors from the literature and provide a review.
4. Develop an original problem that would be suitable as an illustrative example in a book on chemical reactors.
5. Prepare a list of the various books which have been written on chemical reactors. Select the three best (hopefully the a choice will include the text written by one of the authors) and justify your answer. Also select the three weakest books and, once again, justify your answer.
6. Describe what, if any, advantages are derived from writing chemical reactions on a mole basis.
7. Generate a time-concentration (or conversion) solution to a reaction that is described by a complex rate equation of your choice.
8. Describe the relationships and differences between conversion, yield, and selectivity.
9. Describe in general terms how to increase conversion in a
   • batch reactor,
   • CSTR, and
   • tubular flow reactor.
10. Reactions are often described by rate equations that are of a complex nature. Discuss the impact that these complex equations can have on designing and predicting the performance of:
    • batch reactors,
    • CSTRs, and
    • tubular flow reactors.
11. List and discuss the advantages and disadvantages of batch, CSTR, and tubular flow reactors.
12. List and describe all the classes of reactors that have been employed in the past.
13. Develop and/or design a *new* reactor.

14. A batch reactor is no longer delivering the degree of conversion required for a process. Rather than replace the unit, you have been asked to recommend what other possible steps can be taken to the existing reactor to get it back "on line".
    Comment: Refer to Problem 3 in the previous section.

15. A CSTR is designed to operate at a specified conversion. Once the unit is installed and running, the unit operates at a lower conversion. What options would you recommend to bring the unit into compliance with the specified design conversion?
    Comment: Refer to Problem 3 in the previous Section.

16. Over time, the heat required to keep a catcracker in refinery at its operating temperature has increased. You are asked to recommend possible ways to correct the problem.
    Comment: Refer to Problem 3 in the previous Section.

17. Discuss the options that are available to increase/decrease the temperature to a satisfactory value in a
    - batch reactor
    - CSTR
    - tubular flow reactor
    - fixed bed reactor
    - fluid bed reactor.

18. Design and/or develop a new catalyst.

19. Design and/or develop a new support plate for catalysts in a reactor.

20. Develop a general equation to describe temperature variation and its effect on conversion for a
    - batch reactor
    - CSTR
    - tubular flow reactor.

21. Describe the advantages and disadvantages of both the integration and differentiation method of analysis of experimental rate data.
    Comment: Refer to the literature [2].

22. There are numerous approaches that have been employed to describe the mechanism associated with catalytic reactors. Compare the various approaches.
    Comment: Refer to the literature [4]

23. Develop a simple model to describe the mechanism associated with a catalytic reactor.
    Comment: Refer to the literature [4].

24. Develop a method to design and/or predict the performance of fluid bed reactors.
25. Develop a method to design and/or predict the performance of fixed bed reactors.
26. Discuss the problems that can arise if ideal flow patterns are assumed in designing and/or predicting the performance of the various classes of flow reactors.
27. Discuss the calculational problems that can develop for reactions with phase change(s).
28. Discuss the various experimental approaches that can be employed to determine the mechanism of a chemical reactor.
29. Would incorrect chemical reaction kinetic data result in the under or over design of a reactor? Explain.
30. Describe the problems associated with scaleup of the various classes of chemical reactors.
31. You have been assigned the task of developing an operation, maintenance, and inspection (OM&I) program for the reactors at your site. Also discuss the differences that would exist for the different class of reactors.
32. Describe the process of a catalytic reaction in technical terms.
33. Describe the process of a catalytic reaction in layman terms.
34. Consider the following two chemical reactions

$$C_2H_4 + 2H_2O \rightarrow C_2H_6 + O_2 + H_2$$

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$$
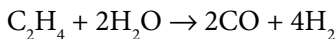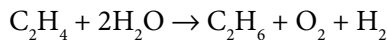
Although both equations balance stoichiometrically, explain in layman terms why the equations are different. (See also Chapter 3).
35. An auditorium room has a volume of 100,000 ft³. The CO_2 concentration in the air before a meeting is 0.04 per cent. The CO_2 concentration is 0.14 per cent one hour after the beginning of the session. The room is ventilated by 50,000 ft³/min of fresh air (0.04 per cent CO_2). Describe how to calculate the CO_2 concentration 6 hr after the session has ended if the CO_2 is disappearing/reacting via

- a zero order reaction
- a first order reaction, and
- an nth order reaction.

36. One option available to a plant manager when a tube within a tubular flow reactor fails is to simply plug the inlet of the tube. Develop an equation to describe the impact on the performance of the reactor as a function of the number of tubes with in the reactor and the number of plugged tubes for a first-order reaction. Repeat the calculation for different reaction mechanisms.

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