

AN INTRODUCTION TO  
Chemical  
Engineering  
Kinetics &  
Reactor  
Design

CHARLES G. HILL, Jr.

# **AN INTRODUCTION TO CHEMICAL ENGINEERING KINETICS & REACTOR DESIGN**

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To my family:  
Parents, Wife, and Daughters

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# 8 Basic Concepts in Reactor Design and Ideal Reactor Models

## 8.0 INTRODUCTION

The chemical reactor must be regarded as the very heart of a chemical process. It is the piece of equipment in which conversion of feedstock to desired product takes place and is thus the single irreplaceable component of the process. Several different factors must be considered in selecting the physical configuration and mode of operation to be used to accomplish a specified task. This chapter discusses the fundamental principles that the chemical engineer engaged in the practice of reactor design utilizes in making these selections.

### 8.0.1 The Nature of the Reactor Design Problem

The chemical engineer is required to choose the reactor configuration and mode of operation that yields the greatest profit consistent with market constraints for the raw material and product costs, capital and operating costs, safety considerations, pollution control requirements, and esthetic constraints that may be imposed by management, society, or labor unions. Usually there are many combinations of operating conditions and reactor size and/or type that will meet the requirements imposed by nature in terms of the reaction rate expression involved and those imposed by management in terms of the required production capacity. The engineer is thus faced with the task of maintaining a careful balance between analytical reasoning expressed in quantitative terms and sound engineering judgment. In an attempt to maintain this balance, some or all of the following questions must be answered.

1. What is the composition of the feedstock and under what conditions is it available? Are any purification procedures necessary?
2. What is the scale of the process? What capacity is required?

3. Is a catalyst necessary or desirable? If a catalyst is employed, what are the ramifications with respect to product distribution, operating conditions, most desirable type of reactor, process economics, and other pertinent questions raised below?
4. What operating conditions (temperature, pressure, degree of agitation, etc.) are required for most economic operation?
5. Is it necessary or desirable to add inerts or other materials to the feedstock to enhance yields of desired products, to moderate thermal effects, or to prolong the useful life of any catalysts that may be employed?
6. Should the process be continuous or intermittent? Would batch or semibatch operation be advantageous?
7. What type of reactor best meets the process requirements? Are there advantages associated with the use of a combination of reactor types, or with multiple reactors in parallel or series?
8. What size and shape reactor(s) should be used?
9. How are the energy transfer requirements for the process best accomplished? Should one operate isothermally, adiabatically, or in accord with an alternative temperature protocol?
10. Is single pass operation best, or is recycle needed to achieve the desired degree of conversion of the raw feedstock?
11. What facilities are required for catalyst supply, activation, and regeneration?
12. What are the reactor effluent composition and conditions? Are any chemical separation steps or physical operations required in order to bring the effluent to a point where it is satisfactory for the desired end use?
13. Are there any special materials requirements imposed by the process conditions? Are the

process fluids corrosive? Are extremely high temperatures or pressures required?

The remainder of this text attempts to establish a rational framework within which many of these questions can be attacked. We will see that there is often considerable freedom of choice available in terms of the type of reactor and reaction conditions that will accomplish a given task. The development of an optimum processing scheme or even of an optimum reactor configuration and mode of operation requires a number of complex calculations that often involve iterative numerical calculations. Consequently machine computation is used extensively in industrial situations to simplify the optimization task. Nonetheless, we have deliberately chosen to present the concepts used in reactor design calculations in a framework that insofar as possible permits analytical solutions in order to divorce the basic concepts from the mass of detail associated with machine computation.

The first stage of a logical design procedure involves the determination of a reaction rate expression that is appropriate for the range of conditions to be investigated in the design analysis. One requires a knowledge of the dependence of the rate on composition, temperature, fluid velocity, the characteristic dimensions of any heterogeneous phases present, and any other process variables that may be significant. There are several potential sources of the experimental data that are essential for proper reactor design.

1. *Bench scale experiments.* The reactors used in these experiments are usually designed to operate at constant temperature, under conditions that minimize heat and mass transfer limitations on reaction rates. This facilitates an accurate evaluation of the intrinsic chemical effects.
2. *Pilot plant studies.* The reactors used in these studies are significantly larger than those in bench scale laboratory experiments. One

uses essentially the reverse of the design procedures developed later in this chapter to determine the effective reaction rate from the pilot plant data. It may be difficult to separate the intrinsic chemical effects from any heat and mass transfer effects in the analysis of data of this type.

3. *Operating data from commercial scale reactors.* If one's company has access to actual operating data on another commercial installation of the same type as that contemplated, it provides the closest approximation to the conditions likely to be encountered in industrial practice. Such access may result from licensing arrangements or from previous experience within the company. Unfortunately, such data are often incomplete or inaccurate, and the problems of backing the intrinsic chemical kinetics out of the mass of data may be insurmountable. In such systems physical limitations on rates of heat and mass transfer may disguise the true kinetics to a significant degree.

In the design of an industrial scale reactor for a new process, or an old one that employs a new catalyst, it is common practice to carry out both bench and pilot plant studies before finalizing the design of the commercial scale reactor. The bench scale studies yield the best information about the intrinsic chemical kinetics and the associated rate expression. However, when taken alone, they force the chemical engineer to rely on standard empirical correlations and prediction methods in order to determine the possible influence of heat and mass transfer processes on the rates that will be observed in industrial scale equipment. The pilot scale studies can provide a test of the applicability of the correlations and an indication of potential limitations that physical processes may place on conversion rates. These pilot plant studies can provide extremely useful information on the temperature distribution in the reactor and on contacting patterns when



Figure 8.1  
Types of ta

more than a single phase reactant-catalyst system is employed.

### 8.0.2 Reactor Types

In terms of the physical configurations encountered, there are basically only two types of reactors: the tank and the tube.

The *ideal tank reactor* is one in which stirring is so efficient that the contents are always uniform in composition and temperature throughout. The simple tank reactor may be operated in a variety of modes: batch, semibatch, and continuous flow. These modes are illustrated schematically in Figure 8.1. In the simple *batch reactor* the fluid elements will all have the same composition, but the composition will be time dependent. The stirred tank reactor may also be

operated in *semibatch* fashion. In this mode the tank is partially filled with reactant(s), and additional reactants are added progressively until the desired end composition is achieved. Alternatively, one may charge the reactants all at once and continuously remove products as they are formed. In the continuous flow mode of operation the stirred tank reactor is continuously supplied with feed; at the same time an equal volume of reactor contents is discharged in order to maintain a constant level in the tank. The composition of the effluent stream is identical with that of the fluid remaining in the tank.

The *ideal tubular reactor* is one in which elements of the homogeneous fluid reactant move through a tube as plugs moving parallel to the tube axis. This flow pattern is referred to as

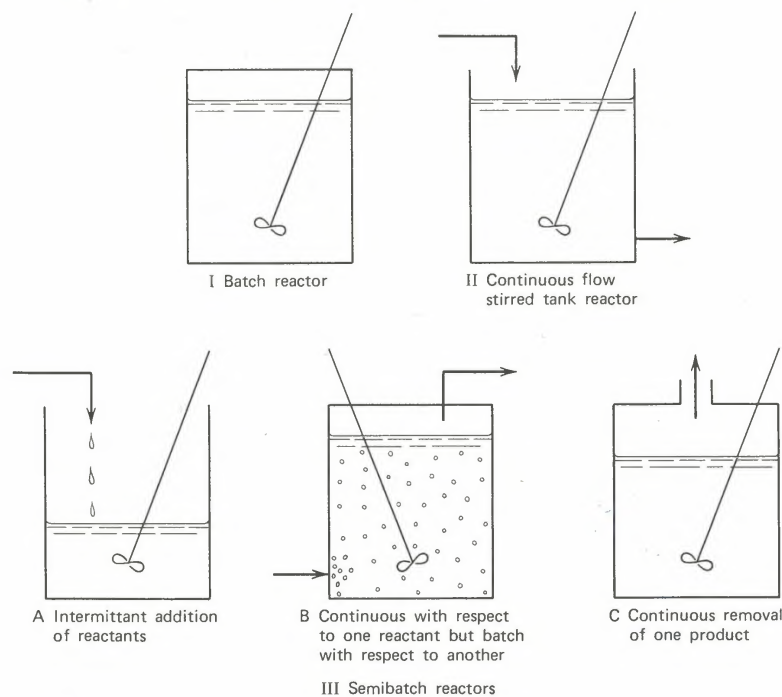


Figure 8.1  
Types of tank reactors.

*plug flow* or *piston flow*. The velocity profile at a given cross section is flat and it is assumed that there is no axial diffusion or back-mixing of fluid elements.

Batch reactors are often used for liquid phase reactions, particularly when the required production is small. They are seldom employed on a commercial scale for gas-phase reactions because the quantity of product that can be produced in reasonably sized reactors is small. Batch reactors are well suited for producing small quantities of material or for producing several different products from one piece of equipment. Consequently they find extensive use in the pharmaceutical and dyestuff industries and in the production of certain specialty chemicals where such flexibility is desired. When rapid fouling is encountered or contamination of fermentation cultures is to be avoided, batch operation is preferable to continuous processing because it facilitates the necessary cleaning and sanitation procedures.

When the specified production capacities are low, processes based on batch reactors will usually have lower capital investment requirements than processes calling for continuous operation, so batch reactors are often preferred for new and untried processes during the initial stages of development. As production requirements increase in response to market demands, it may become more economic to shift to continuous processing but, even in these cases, there are many industrial situations where batch operation is preferable. This is particularly true when the operating expenses associated with the reactor are a minor fraction of total product cost. At low production capacities, construction and instrumentation requirements for batch reactors are usually cheaper than for continuous process equipment. Moreover, it is generally easier to start up, shut down, and control a batch reactor than a comparable capacity continuous flow reactor.

The disadvantages associated with the use of a batch reactor include the high labor and

materials handling costs involved in filling, emptying, and cleaning of these reactors. While batch reactors are being filled, emptied, or cleaned, and while the reactor contents are being heated to the reaction temperature or cooled to a point suitable for discharge, batch reactors are not producing reaction products. The sum of the nonproductive periods may often be comparable in length to the time necessary to carry out the reaction. In determining long-term production capacities for batch reactors, these dead times must be taken into account.

Continuous flow reactors are almost invariably preferred to batch reactors when the processing capacity required is large. Although the capital investment requirements will be higher, the operating costs per unit of product will be lower for continuous operation than for batch reaction. The advantages of continuous operation are that it:

1. Facilitates good quality control for the product through the provision of greater constancy in reaction conditions.
2. Facilitates automatic process control.
3. Minimizes the labor costs per unit of product.

Often the decision to select a batch or continuous processing mode involves a determination of the relative contributions of capital and operating expenses to total process costs for the proposed level of capacity. As Denbigh (1) points out, what is best for a highly industrialized country with high labor costs is not necessarily best for a lesser developed country. In many cases selectivity considerations determine the processing mode, particularly when the reaction under study is accompanied by undesirable side reactions. The yield of the desired product may differ considerably between batch and continuous operation and between the two primary types of continuous processes. When the yield is lower for a continuous process, this factor may be so important in the



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overall process economics as to require the use of a batch reactor.

At this point we wish to turn to a brief discussion of the types of batch and flow reactors used in industrial practice for carrying out homogeneous fluid phase reactions. Treatment of heterogeneous catalytic reactors is deferred to Chapter 12.

**8.0.2.1 Batch Reactors (Stirred Tanks).** Batch reactors are usually cylindrical tanks and the orientation of such tanks is usually vertical. Cylindrical vessels are employed because they are easier to fabricate and clean than other geometries and because the construction costs for high-pressure units are considerably less than for alternative configurations. For simple stirred vertical batch reactors, the depth of liquid is usually comparable to the diameter of the reactor. For greater liquid height to diameter ratios more complex agitation equipment is necessary. Agitation can be supplied by stirrer blades of various shapes or by forced circulation with an external or built-in pump. Where more gas-liquid interfacial area is required for evaporation or gas absorption, or where it is necessary to minimize the hydrostatic head (e.g., to minimize the boiling point rise), horizontal reactors will be used. The latter orientation may also be preferable when the reactor contents are quite viscous or take the form of a slurry. Batch reactors may be fabricated from ordinary or stainless steel, but there are often advantages to using glass or polymer coatings on interior surfaces in order to minimize corrosion or sanitation problems.

Because of the large energy effects that often accompany chemical reaction, it is usually necessary to provide for heat transfer to or from the reactor contents. Heating or cooling may be accomplished using jacketed walls, internal coils, or internal tubes filled with a heat transfer fluid that is circulated through an external heat exchanger. Energy may also be supplied by electrical heating or direct firing. If the process

fluid is noncorrosive and readily and safely pumped, it may be preferable to employ an external heat exchanger and circulation pump. Good temperature control can be achieved using an external reflux condenser for cases where appreciable vapor is given off. The selection of either internal or external heat transfer equipment is governed by the required area, the susceptibility of the heat transfer surface to fouling, the temperature and pressure requirements imposed by the heat transfer medium, and the potential adverse effects that might occur if the process fluid and the heat transfer medium come in direct contact through leakage.

For high-pressure operation, safety considerations are extremely important and care must be taken to ensure proper mechanical design. Closures must be designed to withstand the same maximum pressure as the rest of the autoclave. Various authors have treated the problems involved in designing medium- and high-pressure batch reactors (2-4).

**8.0.2.2 Continuous Flow Reactors—Stirred Tanks.** The continuous flow stirred tank reactor is used extensively in chemical process industries. Both single tanks and batteries of tanks connected in series are used. In many respects the mechanical and heat transfer aspects of these reactors closely resemble the stirred tank batch reactors treated in the previous subsection. However, in the present case, one must also provide for continuous addition of reactants and continuous withdrawal of the product stream.

It is possible to employ either multiple individual tanks in series or units containing multiple stages within a single shell (see Figure 8.2). Multiple tanks are more expensive, but provide more flexibility in use, since they are more readily altered if process requirements change. In order to minimize pump requirements and maintenance, one often chooses to allow for gravity flow between stages. When the reactants are of limited miscibility, but differ

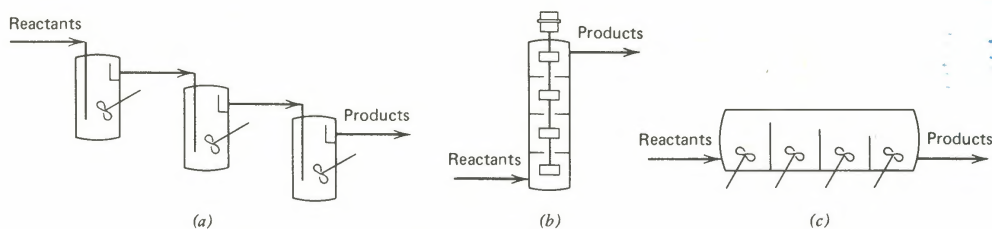


Figure 8.2

**Types of staged reactors. (a) Reactor battery. (b) Vertically staged. (c) Compartmented.** (Adapted from *Reaction Kinetics for Chemical Engineers* by S. M. Walas. Copyright © 1959. Used with permission of McGraw-Hill Book Company.)

in density, the vertical staged shell lends itself to countercurrent operation. This approach is useful when dealing with reversible reactions between immiscible fluids.

For purposes of calculation, each stage in a multiple-stage unit is treated as an individual reactor. The process stream flows from one reactor to the next, so that there is essentially a step change of composition between successive reactors. The step change is a direct consequence of efficient mixing. Unless the fluid phase is highly viscous, it is not difficult to approach perfect mixing in industrial scale equipment. All that is required is that the time necessary to distribute an entering element of fluid uniformly throughout the tank be very small compared to the average residence time in the tank.

Because of the dilution that results from the mixing of entering fluid elements with the reactor contents, the average reaction rate in a stirred tank reactor will usually be less than it would be in a tubular reactor of equal volume and temperature supplied with an identical feed stream. Consequently, in order to achieve the same production capacity and conversion level, a continuous flow stirred tank reactor or even a battery of several stirred tank reactors must be much larger than a tubular reactor. In many cases, however, the greater volume requirement is a relatively unimportant economic factor, particularly when one operates at ambient pres-

sure in tanks constructed of inexpensive materials such as mild steel.

In addition to lower construction costs, a continuous flow stirred tank reactor possesses other advantages relative to a tubular flow reactor, such as the facilitation of temperature control. Efficient stirring of the reactor contents insures uniform temperature and the elimination of local hot spots. The large heat capacity of the reactor contents also acts as a heat sink to moderate temperature excursions when changes occur in process conditions. The physical configuration of cylindrical tanks provides a large heat transfer area on the external surface of the tank and permits augmentation of this area through the use of submerged coils within the tank. However, the rate of heat transfer per unit volume of reaction mixture is generally lower in a conventional stirred tank reactor than in conventional tubular reactors because of the lower ratio of heat transfer surface area to volume in the tank reactor. Consequently, tubular reactors are preferred for fast reactions when energy transfer requirements are very large.

Ease of access to the interior surface of stirred tanks is an additional advantage of this type of reactor. This consideration is particularly significant in polymerization reactors, where one needs to worry about periodic cleaning of internal surfaces.

Selectivity considerations may also dictate the use of stirred tank reactors. They are preferred if undesirable side reactions predominate at high reactant concentrations, and they are also useful when one desires to "skip" certain concentration or temperature ranges where by-product formation may be excessive.

Stirred tank reactors are employed when it is necessary to handle gas bubbles, solids, or a second liquid suspended in a continuous liquid phase. One often finds that the rates of such reactions are strongly dependent on the degree of dispersion of the second phase, which in turn depends on the level of agitation.

Large stirred tank reactors are generally not suited for use at high pressures because of mechanical strength limitations. *They are used mainly for liquid phase reaction systems at low or medium pressures when appreciable residence times are required.*

**8.0.2.3 Continuous Flow Reactors—Tubular Reactors.** The tubular reactor is so named because the physical configuration of the reactor is normally such that the reaction takes place within a tube or length of pipe. The idealized model of this type of reactor assumes that an entering fluid element moves through the reactor as a plug of material that completely fills the reactor cross section. Thus the terms piston flow or *plug flow reactor (PFR)* are often employed to describe the idealized model. The contents of a given elemental plug are presumed to be uniform in temperature and composition. This model may be used to treat both the case where the tube is packed with a solid catalyst (see Section 12.1) and the case where the fluid phase alone is present.

The majority of tubular reactors may be classified in terms of three major categories:

1. Single-jacketed tubes.
2. Shell-and-tube heat exchangers.
3. Tube furnaces, in which the tubes are exposed to thermal radiation and heat transfer from combustion gases.

The single-jacketed tube reactor is the simplest type of tubular reactor to conceptualize and to fabricate. It may be used only when the heat transfer requirements are minimal because of the low surface area to volume ratio characteristic of these reactors.

When the shell-and-tube configuration is utilized, the reaction may take place on either the tube side or the shell side. The shell-and-tube tubular reactor has a much greater area for heat transfer per unit of effective reactor volume than the single-jacketed tube. Consequently, it may be used for reactions where the energy transfer requirements are large. On occasion the reaction zone may be packed with granular solids to promote increased turbulence or better contacting of heterogeneous fluid phases or to act as a thermal sink to facilitate control of the reactor. In many cases energy economies can be achieved using countercurrent flow of a hot product stream to preheat an incoming reactant stream to the temperature where the reaction occurs at an appreciable rate. Two commercial scale processes that employ this technique are the synthesis of ammonia from its elements and the oxidation of sulfur dioxide to sulfur trioxide.

Tubular furnaces are used only when it is necessary to carry out *endothermic* reactions at fairly high temperatures on very large quantities of feedstock. Thermal reforming reactions and other reactions used to increase the yield of gasoline from petroleum-based feedstocks are commercial scale processes that employ this type of reactor. A tubular furnace is basically a combustion chamber with reactor tubes mounted on its walls and ceiling. Tube dimensions are typically 3 to 6 in. in diameter with lengths ranging from 20 to 40 ft. As many as several hundred tubes may be used, with either series or parallel connections possible depending on the required residence time.

Because there is no back-mixing of fluid elements along the direction of flow in a tubular reactor, there is a *continuous* gradient in reactant concentration in this direction. One does not

encounter the step changes characteristic of multiple stirred tank reactors. Consequently, for the same feed composition and reaction temperature, the average reaction rate will generally be significantly higher in a plug flow reactor than it would be in a single stirred tank or a battery of stirred tanks with a total volume equal to that of the tubular reactor. The more efficient utilization of reactor volume is an advantage of the tubular reactor that permits one to use it in processes which demand very large capacity. Because variations in temperature and composition may occur in the axial direction in tubular reactors, these systems may be somewhat more difficult to control than continuous flow stirred tank reactors. However, the problems are usually not insurmountable, and one can normally obtain steady-state operating conditions which give rise to uniform product quality.

Other advantages of the tubular reactor relative to stirred tanks include suitability for use at higher pressures and temperatures, and the fact that severe energy transfer constraints may be readily surmounted using this configuration. The tubular reactor is usually employed for liquid phase reactions when relatively short residence times are needed to effect the desired chemical transformation. It is the reactor of choice for continuous gas phase operations.

**8.0.2.4 Semibatch or Semiflow Reactors.** Semibatch or semiflow operations usually take place in a single stirred tank using equipment extremely similar to that described for batch operations. Figure 8.1 indicates some of the many modes in which semibatch reactors may be operated.

One common mode of operation involves loading some of the reactants into a stirred tank as a single charge and then feeding in the remaining material gradually. This mode of operation is advantageous when large heat effects accompany the reaction. Exothermic reactions may be slowed down and temperature control maintained by regulating the rate at which one

of the reactants is fed. This point is demonstrated quite dramatically in Illustration 10.7. This mode of operation is also desirable when high reactant concentrations favor the formation of undesirable side products or when one of the reactants is a gas of limited solubility.

Another mode of semibatch operation involves the use of a purge stream to remove continuously one or more of the products of a reversible reaction. For example, water may be removed in esterification reactions by the use of a purge stream or by distillation of the reacting mixture. Continuous removal of product(s) increases the net reaction rate by slowing down the reverse reaction.

Semibatch or semiflow processes are among the most difficult to analyze from the viewpoint of reactor design because one must deal with an open system under nonsteady-state conditions. Hence the differential equations governing energy and mass conservation are more complex than they would be for the same reaction carried out batchwise or in a continuous flow reactor operating at steady state.

### 8.0.3 Fundamental Concepts Used in Chemical Reactor Design

The bread and butter tools of the practicing chemical engineer are the material balance and the energy balance. In many respects chemical reactor design can be regarded as a straightforward application of these fundamental principles. This section indicates in general terms how these principles are applied to the various types of idealized reactor models.

**8.0.3.1 Material and Energy Balances in the Design of Industrial Reactors.** The analysis of chemical reactors in terms of material and energy balances differs from the analysis of other process equipment in that one must take into account the rate at which molecular species are converted from one chemical form to another and the rate at which energy is transformed by the process. When combined with material and

energy balances on the reactor, the reaction rate expression provides a means of determining the production rate and the composition of the products as functions of time. Both steady-state and time varying situations may be analyzed using the same fundamental relations. Differences in the analyses result from the retention of different terms in the basic balance equations.

A material balance on a reactant species of interest for an element of volume  $\Delta V$  can be written as:

$$\left( \begin{array}{c} \text{Rate of flow} \\ \text{of reactant} \\ \text{into volume} \\ \text{element} \end{array} \right) = \left( \begin{array}{c} \text{Rate of flow} \\ \text{of reactant} \\ \text{out of volume} \\ \text{element} \end{array} \right) + \left( \begin{array}{c} \text{Rate of disappearance} \\ \text{of reactant by chemical} \\ \text{reactions within the} \\ \text{volume element} \end{array} \right) + \left( \begin{array}{c} \text{Rate of accumulation} \\ \text{of reactant within the} \\ \text{volume element} \end{array} \right) \quad (8.0.1)$$

or, in shorter form,

$$\text{Input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} \quad (8.0.2)$$

The flow terms represent the convective and diffusive transport of reactant into and out of the volume element. The third term is the product of the size of the volume element and the reaction rate per unit volume evaluated using the properties appropriate for this element. Note that the reaction rate per unit volume is equal to the intrinsic rate of the chemical reaction only if the volume element is uniform in temperature and concentration (i.e., there are no heat or mass transfer limitations on the rate of conversion of reactants to products). The final term represents the rate of change in inventory resulting from the effects of the other three terms.

In the analysis of batch reactors the two flow terms in equation 8.0.1 are omitted. For con-

tinuous flow reactors operating at steady state, the accumulation term is omitted. However, for the analysis of continuous flow reactors under transient conditions and for semibatch reactors it may be necessary to retain all four terms. For ideal well-stirred reactors the composition and temperature are uniform throughout the reactor and all volume elements are identical. Hence the material balance may be written over the entire reactor in these cases. For tubular flow reactors the composition is not independent of position

and the balance must be written on a differential element of reactor volume and then integrated over the entire reactor using appropriate flow conditions and concentration and temperature profiles. Where nonsteady-state conditions are involved, it will be necessary to integrate over time as well as over volume in order to determine the performance characteristics of the reactor.

Since the rate of a chemical reaction is normally strongly temperature dependent, it is essential to know the temperature at each point in the reactor in order to be able to utilize equation 8.0.1 properly. When there are temperature gradients within the reactor, it is necessary to utilize an energy balance in conjunction with the material balance in order to determine the temperature and composition prevailing at each point in the reactor at a particular time.

The general energy balance for an element of volume  $\Delta V$  over a time  $\Delta t$  can be written as:

$$\left( \begin{array}{c} \text{Accumulation of} \\ \text{energy within the} \\ \text{volume element} \end{array} \right) = \left( \begin{array}{c} \text{Energy transferred} \\ \text{from surroundings} \\ \text{to volume element} \\ \text{by heat and shaft} \\ \text{work interactions} \end{array} \right) + \left( \begin{array}{c} \text{Energy effects} \\ \text{associated with} \\ \text{the entry of} \\ \text{matter into the} \\ \text{volume element} \end{array} \right) - \left( \begin{array}{c} \text{Energy effects} \\ \text{associated with} \\ \text{the transfer of} \\ \text{matter out of the} \\ \text{volume element} \end{array} \right) \quad (8.0.3)$$

For completeness, the terms corresponding to the entry of material to the volume element and exit therefrom must contain, in addition to the ordinary enthalpy of the material, its kinetic and potential energy. However, for virtually all cases of interest in chemical reactor design, only the enthalpy term is significant. Since only changes in internal energy or enthalpy can be evaluated, the datum conditions for the first, third, and fourth terms must be identical in order to achieve an internally consistent equation. Although heat interactions in chemical reactors are significant, shaft work effects are usually negligible. The chemical reaction rate does not appear explicitly in equation 8.0.3, but its effects are implicit in all terms except the second. The first, third, and fourth terms reflect differences in temperature and/or in composition of the entering and leaving streams. The energy effects associated with composition changes are a direct reflection of the enthalpy change associated with the reaction.

There are a variety of limiting forms of equation 8.0.3 that are appropriate for use with different types of reactors and different modes of operation. For stirred tanks the reactor contents are uniform in temperature and composition throughout, and it is possible to write the energy balance over the entire reactor. In the case of a batch reactor, only the first two terms need be retained. For continuous flow systems operating at steady state, the accumulation term disappears. For adiabatic operation in the absence of shaft work effects the energy transfer term is omitted. For the case of semibatch operation it may be necessary to retain all four terms. For tubular flow reactors neither the composition nor the temperature need be independent of position, and the energy balance must be written on a differential element of reactor volume. The resultant differential equation must then be solved in conjunction with the differential equation describing the material balance on the differential element.

**8.0.3.2 Vocabulary of Terms Used in Reactor Design.** There are several terms that will be used extensively throughout the remainder of this text that deserve definition or comment. The concepts involved include steady-state and transient operation, heterogeneous and homogeneous reaction systems, adiabatic and isothermal operation, mean residence time, contacting and holding time, and space time and space velocity. Each of these concepts will be discussed in turn.

Large-scale industrial reactions are almost invariably carried out on a continuous basis with reactants entering at one end of the reactor network and products leaving at the other. Usually such systems are designed for *steady-state* operation but, even during the design of such systems, adequate care must be made to provide for the *transient* condition that will invariably be incurred during start-up and shut-down periods. By the term steady-state operation we imply that conditions at any point in the reactor are time-invariant. Changes in composition occur in the spatial dimension instead of in a time dimension. It should be emphasized that operation at steady state does not imply *equilibrium*. The last term is restricted to isolated systems that undergo no net change with time. Insofar as the analysis of continuous flow reactors is concerned, the major thrust of this and succeeding chapters involves steady-state operation. The basic principles described in the previous subsection remain valid for the analysis of transient systems. However, in most transient cases it is necessary to resort to numerical solutions in order to predict the response of a continuous flow reactor network to changes in operating conditions. Batch reactors are inherently unsteady-state systems, even when the reactor contents are uniform throughout.

Both homogeneous and heterogeneous reaction systems are frequently encountered in commercial practice. The term *homogeneous* reaction system is restricted in this text to fluid systems in

which the system properties *vary continuously* from point to point within the reactor. The term embraces both catalytic and noncatalytic reactions, but it requires that any catalysts be uniformly dispersed throughout the fluid phase. The term *heterogeneous* reaction system refers to systems in which there are two or more phases involved in the reaction process, either as reactants or as catalysts.

*Adiabatic* operation implies that there is no heat interaction between the reactor contents and their surroundings. *Isothermal* operation implies that the feed stream, the reactor contents, and the effluent stream are equal in temperature and have a uniform temperature throughout. The present chapter is devoted to the analysis of such systems. Adiabatic and other forms of non-isothermal systems are treated in Chapter 10.

The terms *holding time*, *contact time*, and *residence time* are often used in discussions of the performance of chemical reactors. As employed by reactor designers, these terms are essentially interchangeable. They refer to the length of time that an element of process fluid spends in the reactor in question. For a batch reactor it is usually assumed that no reaction occurs while the reaction vessel is being filled or emptied or while its contents are brought up to an ignition temperature. The holding time is thus the time necessary to "cook" the contents to the point where the desired degree of conversion is achieved. The terms "contact time" and "mean residence time" are used primarily in discussions of continuous flow processes. They represent the average length of time that it takes a fluid element to travel from the reactor inlet to the reactor outlet. For plug flow reactors, all fluid elements will have the same residence time. However, for stirred tank reactors or other reactors in which mixing effects are significant, there will be a spread of residence times for the different fluid elements. This has important implications for the conversions that will be achieved in such reactors.

Although the concept of "mean residence time" is easily visualized in terms of the average time necessary to cover the distance between reactor inlet and outlet, it is not the most fundamental characteristic time parameter for purposes of reactor design. A more useful concept is that of the reactor *space time*. For continuous flow reactors the space time ( $\tau$ ) is defined as the ratio of the reactor volume ( $V_R$ ) to a characteristic volumetric flow rate of fluid ( $\mathcal{V}$ ).

$$\tau = \frac{V_R}{\mathcal{V}} \quad (8.0.4)$$

The reactor volume is taken as the volume of the reactor *physically occupied by the reacting fluids*. It does not include the volume occupied by agitation devices, heat exchange equipment, or headroom above liquids. One may arbitrarily select the temperature, pressure, and even the state of aggregation (gas or liquid) at which the volumetric flow rate to the reactor will be measured. For design calculations it is usually convenient to choose the reference conditions as those that prevail at the inlet to the reactor. However, it is easy to convert to any other basis if the pressure-volume-temperature behavior of the system is known. Since the reference volumetric flow rate is arbitrary, care must be taken to specify precisely the reference conditions in order to allow for proper interpretation of the resultant space time. Unless an explicit statement is made to the contrary, *we will choose our reference state as that prevailing at the reactor inlet and emphasize this choice by the use of the subscript zero*. Henceforth,

$$\tau = \frac{V_R}{\mathcal{V}_0} \quad (8.0.5)$$

where  $\mathcal{V}_0$  is the volumetric flow rate at the inlet temperature and pressure and a fraction conversion of zero.

Using this convention, a space time of 30 min means that every 30 min one reactor volume of

feed (measured at inlet conditions) is processed by the reactor. One reactor volume enters and one reactor volume leaves, but this statement does *not* imply that we have simply displaced the original charge from the reactor. Some or all of the original contents may leave, and some of the fresh charge may leave as well. In the latter circumstance the reactor contents become a mixture of the original contents and new material.

The space time is not necessarily equal to the average residence time of an element of fluid in the reactor. Variations in the number of moles on reaction as well as variations in temperature and pressure can cause the volumetric flow rate at arbitrary points in the reactor to differ appreciably from that corresponding to inlet conditions. Consequently, even though the reference conditions may be taken as those prevailing at the reactor inlet, the space time need not be equal to the mean residence time of the fluid. The two quantities are equal only if *all* of the following conditions are met.

1. Pressure and temperature are constant throughout the reactor.
2. The density of the reaction mixture is independent of the extent of reaction. For gas phase reactions this requirement implies that there can be no change in the number of moles on reaction. In terms of equation 3.1.45, we require that  $\delta = 0$ .
3. The reference volumetric flow rate is evaluated at reactor inlet conditions.

When the space time and the mean residence time differ, it is the space time that should be regarded as the independent process variable that is directly related to the constraints imposed on the system. We will see in Sections 8.2 and 8.3 that it is convenient to express the fundamental design relations for continuous flow reactors in terms of this parameter. We will also see that for these reactors the mean residence time cannot be considered as an independent variable, but that it is a parameter that can be determined only

after the nature of the changes occurring within the reactor is known.

The reciprocal of the space time is known as the *space velocity* ( $S$ ).

$$S = \frac{1}{\tau} = \frac{V}{V_R} \quad (8.0.6)$$

Like the definition of the space time, the definition of the space velocity involves the volumetric flow rate of the reactant stream measured at some reference condition. A space velocity of  $10 \text{ hr}^{-1}$  implies that every hour, 10 reactor volumes of feed can be processed.

When dealing with reactions where a liquid feed must be vaporized prior to being fed to the reactor proper, one must state very clearly whether the space velocity is based on the volumetric flow rate of the feed as a liquid or as a gas. Unless an explicit statement to the contrary is made, the term space velocity in this text will refer to the ratio of the volumetric flow rate *evaluated at reactor inlet conditions* to the reactor volume.

The term *space velocity* has somewhat different connotations when dealing with heterogeneous catalytic reactors. In this case it denotes the ratio of the mass flow rate of feed to the mass of catalyst used ( $W$ ).

$$\text{WHSV} = \frac{\rho V}{W} \quad (8.0.7)$$

where  $\rho$  is the mass density of the feed and WHSV is termed the *weight hourly space velocity*. Sometimes the term *volumetric hourly space velocity* (VHSV) is used to denote the ratio of the volumetric flow rate of a gaseous feed to the weight of the catalyst bed.

$$\text{VHSV} = \frac{V}{W} \quad (8.08)$$

On other occasions the volume of catalyst instead of the mass of catalyst may be used in the denominator. The units associated with a parti-

cular space velocity indicate the definition employed.

### 8.1 DESIGN ANALYSIS FOR THE BATCH REACTOR

Batch reactors are widely used in the chemical industry for producing materials that are needed in limited quantity, particularly in those cases where the processing cost represents only a small fraction of the total value of the product. Since modern industry stresses the use of continuous processes because they lend themselves most readily to mass production, chemical engineers may, in some instances, tend to overlook the economic superiority of batch operations. One should not become so fascinated with the continuous process, or the more complex and interesting design analysis associated therewith, as to lose sight of the economic penalty exacted by this degree of technical sophistication.

The starting point for the development of the basic design equation for a well-stirred batch reactor is a material balance involving one of the species participating in the chemical reaction. For convenience we will denote this species as  $A$  and we will let  $(-r_A)$  represent the *rate of disappearance* of this species by reaction. For a well-stirred reactor the reaction mixture will be uniform throughout the effective reactor volume, and the material balance may thus be written over the entire contents of the reactor. For a batch reactor equation 8.0.1 becomes

$$\left( \begin{array}{c} \text{Rate of accumulation} \\ \text{of reactant } A \text{ within} \\ \text{the reactor} \end{array} \right) = - \left( \begin{array}{c} \text{Rate of disappearance of} \\ \text{reactant } A \text{ within the reactor} \\ \text{by chemical reaction} \end{array} \right) \quad (8.1.1)$$

The accumulation term is just the time derivative of the number of moles of reactant  $A$  contained within the reactor ( $dN_A/dt$ ). This term also may be written in terms of either the extent of reaction ( $\xi$ ) or the fraction conversion of the limiting reagent ( $f_A$ ). ( $A$  is presumed to be the

limiting reagent.) Thus,

$$\begin{aligned} \text{Rate of accumulation} &= \frac{dN_A}{dt} = v_A \frac{d\xi}{dt} \\ &= -N_{A0} \frac{df_A}{dt} \end{aligned} \quad (8.1.2)$$

where  $N_{A0}$  is number of moles of species  $A$  present when the fraction conversion is zero.

The total rate of disappearance of reactant  $A$  is given by

$$\text{Rate of disappearance} = (-r_A)V_R \quad (8.1.3)$$

We again emphasize that  $V_R$  is the volume physically occupied by the reacting fluid. Combining equations 8.1.1 to 8.1.3 gives

$$N_{A0} \frac{df_A}{dt} = (-r_A)V_R \quad (8.1.4)$$

Rearrangement and integration gives

$$t_2 - t_1 = N_{A0} \int_{f_{A1}}^{f_{A2}} \frac{df_A}{(-r_A)V_R} \quad (8.1.5)$$

where  $f_{A2}$  and  $f_{A1}$  represent the fraction conversion at times  $t_2$  and  $t_1$ , respectively. This equation is the most general form of the basic design relationship for a batch reactor. It is valid for both isothermal and nonisothermal operation as well as for both constant volume and constant pressure operation. Both the reaction rate and the reactor volume should be retained inside the integral sign, since either or both may change as the reaction proceeds.

There are a number of limiting forms of equation 8.1.5 that should be mentioned briefly. If  $t_1 = 0$  and  $f_{A1} = 0$ ,

$$t = N_{A0} \int_0^{f_A} \frac{df_A}{(-r_A)V_R} \quad (8.1.6)$$