

# X

## Kinetics and Reaction Engineering

---

**John L. Falconer**

*University of Colorado*

75 **Reaction Kinetics** *K. H. Lin*

Fundamentals • Analysis of Kinetic Data

76 **Chemical Reaction Engineering** *H. S. Fogler*

The Algorithm • Pressure Drop in Reactors • Multiple Reactions • Heat Effects • Summary

77 **The Scaleup of Chemical Reaction Systems from Laboratory to Plant** *J. B. Cropley*

General Considerations in the Rational Design of Chemical Reactors • Protocol for the Rational Design of Chemical Reactors

CHEMICAL REACTORS ARE THE MOST IMPORTANT PART of a chemical plant. In most cases, multiple reactions take place, multiple reactors are required, and catalysts are used to obtain sufficient rates and desired selectivities. Improvements in reaction rates and selectivities to desired products can have significant influences on other parts of the chemical plant such as the separations processes. Thus, design of the chemical reactor can control the economics of a plant even though the reactor is not the most expensive part. The chemical reactor also determines the amounts of waste products that form and thus the plant's effect on the environment. Because highly exothermic reactions are often carried out in chemical reactors on a large scale, the reactor is also the biggest safety hazard in the plant.

The first chapter of Section X is concerned with chemical kinetics and the analysis of kinetic data. The most important aspect of chemical kinetics is the rate at which a chemical reaction takes place and the selectivity to reaction products. Also of interest is how the rate and selectivity depend on concentrations, temperature, and other reaction conditions. Reaction rates and the products that form for a given set of reactants and reaction conditions cannot be predicted; such kinetic information must be measured. These measurements are particularly sensitive to temperature because most chemical reactions exhibit an exponential dependence on temperature. They also must be made in the absence of transport effects such as diffusion and mass transfer. Moreover, many large-scale chemical processes use catalysts, and the composition and preparation of the catalyst can have a large influence on both the rate of reaction and the product distribution. The basic methods for analyzing laboratory kinetic data to determine rate expressions are presented in this section, and the mechanisms by which reactions occur on a molecular scale are also discussed.

The second chapter discusses the design and analysis of chemical reactors. Reaction engineering involves determining how the type of reactor, its size, and its operating conditions affect production rates and distribution of products. Industrial processes almost always involve multiple reactions taking place simultaneously, and the desired product is often not the more favored

thermodynamically. Batch, semibatch, continuous stirred tank (CSTR), and plug flow reactors are discussed. These ideal reactor types are often used in combination and are used to model real reactors, which may deviate significantly from ideal behavior. Once kinetic data have been obtained in the laboratory, the kinetic rate expression, thermodynamic equilibrium, and reaction stoichiometry can be used in material balances (conservation of mass) and energy balances (first law of thermodynamics) to obtain equations that predict how a large-scale reactor will behave. Large-scale reactors must take account of pressure drop, nonideal flow patterns, and transport limitations.

The last chapter describes scale-up of a reaction system from the laboratory to a large-scale plant using laboratory data and correlations, and presents a protocol for rational design. This could be called scale-down since it starts from a potential type of commercial reactor, and then a laboratory system is designed to generate the necessary kinetic data. A statistically valid kinetic model is then developed from the data, and this is used with the material and energy balances to develop a model that simulates the reactor. This model of a reactor can then be used to develop an optimal design, which is then validated in a pilot plant. This chapter also discusses industrial reactor types, reactor mass balances, and design of laboratory reactors. In addition to the basic ideal reactors, fluidized beds, shell-and-tube packed beds, multiphase packed beds, and slurry reactors are discussed.

## 75.1 Fundamentals

Basic Terms and Equations • Rate Constant and Elementary Reactions • Complex (or Multiple) Reactions • Uncatalyzed Heterogeneous Reactions • Homogeneous and Heterogeneous Catalytic Reactions

## 75.2 Analysis of Kinetic Data

Data Acquisition • Evaluation of Reaction Mechanism • Development of Rate Equation • Determination of Rate Constant and Arrhenius Parameters

### **K. H. Lin**

*Oak Ridge National Laboratory*

This chapter presents a brief overview of reaction kinetics primarily for engineers who are not directly involved in the investigation of reaction kinetics or in the design of chemical reactors. For a comprehensive treatise on reaction kinetics, the reader should consult the references at the end of the chapter.

In contrast to the static and equilibrium concept of thermodynamics, reaction kinetics is concerned with dynamics of chemical changes. Thus, reaction kinetics is the science that investigates the rate of such chemical changes as influenced by various process parameters and attempts to understand the mechanism of the chemical changes. For any reaction system to change from an initial state to a final state, it must overcome an energy barrier. The presence of such an energy barrier is commonly manifested in the observed relationship between the reaction rate and temperature, which will be discussed in some detail in the section to follow.

## 75.1 Fundamentals

---

### **Basic Terms and Equations**

One of the key terms in reaction kinetics is the **rate of reaction**,  $r_A$ , the general definition of which is given by

$$r_A = \frac{1}{y} \frac{dN_A}{dt} \quad (75.1)$$

which expresses the rate  $r_A$  as the amount of a chemical component of interest being converted or produced per unit time per unit quantity of a reference variable  $y$  [e.g., volume of reacting mixture ( $V$ ) or of reactor ( $V_R$ ), mass ( $W$ ), surface area ( $S$ ), etc.]. It delineates the time

dependence of chemical changes involving component  $A$  as a derivative. In homogeneous fluid reactions,  $y$  is normally represented by  $V$  or  $V_R$ , whereas the mass ( $W$ ) or the surface area ( $S$ ) of the solid reactant may be taken as  $y$  in heterogeneous solid-fluid reactions. Here,  $N_A$  refers to the amount of component  $A$ , and  $t$  is time. By convention,  $r_A$  is negative when  $A$  is a reactant and positive when  $A$  is a product. Molal units are commonly used as the amount of  $N_A$ , but other units such as mass, radioactivity, pressure, and optical property are also used. When  $V$  remains constant (as in a liquid-phase batch reactor), Eq. (75.1) is simplified to

$$r_A = dC_A/dt \quad (75.2)$$

where  $C_A$  represents the concentration of component  $A$ .

## Rate Constant and Elementary Reactions

In general, the rate of reaction in terms of component  $i$  is a function of the concentration of all components participating in the reaction,  $C$ ; the temperature,  $T$ ; the pressure,  $P$ ; and other parameters,  $m$ :

$$r_i = \text{function}(C, T, P, m) \quad (75.3)$$

Thus, the rate expression for a simple irreversible reaction in terms of the reacting components may assume the following form:

$$-r_A = k(C_A)^{n_1}(C_B)^{n_2} \dots (C_i)^{n_i} \quad (75.4)$$

The proportionality constant,  $k$ , is the **rate constant** that is markedly influenced by the temperature and may be subject to the influence of pressure, pH, kinetic isotopes, and so on, and the presence of catalysts. The exponents  $n_1, n_2, \dots, n_i$  are *orders of reaction* with respect to individual reacting components  $A, B, \dots, i$ . The *overall order of reaction* refers to the sum of  $n_1, n_2, \dots, n_i$ , which does not have to be an integer and may be determined empirically.

The units and value of rate constant  $k$  vary with the units of  $C$ , the specific component that  $k$  refers to, and the reaction order. The effect of temperature on  $k$  was first described by Arrhenius through the following equation:

$$k = Ae^{-\frac{E}{RT}} \quad (75.5)$$

where  $A$ , termed the *frequency factor*, has the same units as  $k$ ,  $E$  is **activation energy**, and  $R$  is the gas law constant.  $E$  was considered by Arrhenius as the amount of energy that a reacting system must have in excess of the average initial energy level of reactants to enable the reaction to proceed.

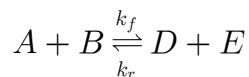
A *simple* or *elementary* reaction is one in which the order of reaction is identical to the *molecularity* (the number of molecules actually participating in the reaction). Under these circumstances, the chemical stoichiometric equation represents the true reaction mechanism, and

the rate equation may therefore be derived directly from the stoichiometric equation. Thus, for an elementary reaction  $n_1A + n_2B = n_3D$ , the rate equation in terms of disappearance of A would be  $-r_A = k(C_A)^{n_1}(C_B)^{n_2}$ . The values of  $n_1$  and  $n_2$  in this equation are positive integers.

## Complex (or Multiple) Reactions

A reaction that proceeds by a mechanism involving more than a single reaction path or step is termed a *complex reaction*. Unlike elementary reactions, the mechanisms of complex reactions differ considerably from their stoichiometric equations. Most industrially important reactions are complex reactions, the mechanisms of which can often be determined by assuming that the overall reaction consists of several elementary reaction steps. The resulting overall rate expression is then compared with the experimental data, and the procedure is repeated until a desired degree of agreement is obtained. Each of the elementary reaction steps may proceed *reversibly*, *concurrently*, or *consecutively*.

A *reversible reaction* is one in which conversion of reactants to products is incomplete at equilibrium because of an increasing influence of the reverse reaction as the forward reaction approaches equilibrium. For a reversible reaction of the type

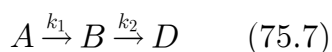


the net forward rate of reaction in terms of disappearance of A is

$$-r_A = k_f C_A C_B - k_r C_D C_E \quad (75.6)$$

which assumes both forward and reverse reactions to be elementary.

A simple example of *consecutive reaction* is illustrated by



Again, assuming an elementary reaction for each reaction step, the following rate equations result:

$$-r_A = k_1 C_A \quad (75.8)$$

$$r_D = k_2 C_B \quad (75.9)$$

$$r_B = k_1 C_A - k_2 C_B \quad (75.10)$$

*Parallel or simultaneous reactions* are those involving one or more reactants undergoing reactions of more than one scheme, as in



The rate equations may assume the following forms:

$$-r_A = k_1(C_A)^a + k_2(C_A)^b \quad (75.11)$$

$$r_B = k_1(C_A)^a \quad (75.12)$$

$$r_D = k_2(C_A)^b \quad (75.13)$$

Under a constant-volume condition,  $r_B = dC_B/dt$  and  $r_D = dC_D/dt$ . Therefore, the relative rate of formation of  $B$  and  $D$  is derived from Eqs. (75.12) and (75.13) as

$$dC_B/dC_D = (k_1/k_2)(C_A)^{a-b} \quad (75.14)$$

The ratio  $dC_B/dC_D$  is termed the *point selectivity*, which is the ratio of the *rate* of formation of product  $B$  to the *rate* for product  $D$ . The *overall* (or *integrated*) *selectivity* is obtained by integration of this ratio, and it represents the ratio of the overall *amount* of product  $B$  to that of product  $D$ . Equation (75.14) implies that the relative rate of formation of  $B$  is proportional to  $C_A$  when  $a > b$ , whereas it is inversely proportional to  $C_A$  when  $a < b$ .

In a chemical process involving complex reactions that consist of several reaction steps, one or more steps may represent major factors in governing the overall rate of reaction. Such reaction steps are termed the **rate-controlling steps**. The rate-controlling reaction steps are observed in homogeneous complex reactions and heterogeneous reactions.

## Uncatalyzed Heterogeneous Reactions

Heterogeneous reactions involve more than one phase (e.g., gas-liquid, gas-solid, liquid-solid, and gas-liquid-solid) and are generally more complicated than homogeneous reactions due to interaction between physical and chemical processes; that is, reactants in one phase have to be transported (physical process) to the other phase, containing other reactants where the reactions take place.

In a gas-solid reaction, for example, the reaction may proceed in several steps, as follows:

1. Reactants in the gas phase diffuse to the gas-solid interface.
2. When there is a layer of solid product and/or inert material at the interface (e.g., ash), the reactants from the gas phase would have to diffuse through this layer before they can reach the unreacted solid core containing other reactants.
3. The chemical reaction takes place between the reactants from the gas phase and those in the unreacted solid core.
4. The reaction products diffuse within the solid phase and/or diffuse out of the solid phase into the bulk of gas phase.

The step that controls the overall reaction rate will be determined by the nature of the phases and specific reactions involved and by process conditions. Thus, the overall reaction rate is subject to the influence of parameters that affect both the physical and chemical processes, including (a)

patterns of phase contact, (b) the reactor geometry, (c) fluid dynamic factors (e.g., velocity and degree of turbulence), (d) interfacial surface area, (e) mass transfer factors, (f) chemical kinetics of reactions involved, and (g) process parameters (e.g., temperature and pressure). Some of these parameters may interact with one another. For example, in a reaction involving two distinct fluid phases (e.g., gas-liquid or liquid-liquid), parameters (d) and (e) would be affected by parameter (c).

The overall reaction rate expression of a heterogeneous reaction is fairly complex, since it considers all of these parameters. Further, the form of rate equation varies with the type of heterogeneous reaction system and with the nature of the controlling step. Some examples of the industrially significant uncatalyzed heterogeneous reactions are given in [Table 75.1](#).

**Table 75.1** Examples of Uncatalyzed Heterogeneous Reactions

<p><i>Gas-liquid reactions</i></p> <ul style="list-style-type: none"> <li>• Production of ammonium nitrate by reaction between ammonia gas and nitric acid</li> <li>• Hydrogenation of vegetable oil with hydrogen gas</li> <li>• Production of nitric acid by absorption of nitric oxide in water</li> </ul> <p><i>Gas-solid reactions</i></p> <ul style="list-style-type: none"> <li>• Gasification of coal</li> <li>• Production of hydrogen gas by reaction of steam with iron</li> <li>• Production of volatile uranium chloride by reaction of uranium oxide with chlorine gas</li> </ul> <p><i>Liquid-liquid reactions</i></p> <ul style="list-style-type: none"> <li>• Aqueous sulfuric acid treatment of petroleum liquid</li> <li>• Nitration of organic solvents with aqueous nitric acid</li> <li>• Production of soaps by reaction of aqueous alkalies and fatty acids</li> </ul>	<p><i>Liquid-solid reactions</i></p> <ul style="list-style-type: none"> <li>• Reaction of aqueous sulfuric acid with phosphate rock</li> <li>• Ion exchange process</li> <li>• Recovery of uranium by leaching of uranium ores with sulfuric acid</li> </ul> <p><i>Solid-solid reactions</i></p> <ul style="list-style-type: none"> <li>• Production of calcium carbide by reaction of carbon with lime</li> <li>• Production of Portland cement by reaction of limestone with clay</li> <li>• Production of glass by melting a mixture of calcium carbonate, sodium carbonate, and silica</li> </ul> <p><i>Gas-liquid-solid reaction</i></p> <ul style="list-style-type: none"> <li>• Liquefaction of coal by reaction of hydrogen with coal-oil slurry</li> </ul>
--	---

## Homogeneous and Heterogeneous Catalytic Reactions

A catalytic reaction is a chemical reaction the rate of which is modified in the presence of a catalyst. A **catalyst** is a substance that may or may not change chemically during the reaction and is regenerated at the end of the reaction. The catalytic reaction proceeds appreciably faster than does an uncatalyzed reaction, presumably because an intermediate compound, formed between the catalyst and some reactants, reacts with other reactants by a mechanism that requires a lower activation energy to form desired products. In *homogeneous catalysis* the catalyst forms a homogeneous phase with the reaction mixture. In *heterogeneous catalysis*, however, the catalyst is present in a phase different from that of the reaction mixture.

## Homogeneous Catalysis

Most homogeneous catalysis takes place in the liquid phase. Perhaps the most widely studied type of liquid-phase catalysis is the acid-base catalysis that exerts influence on the rates of many important organic reactions, including (a) esterification of alcohols, (b) hydrolysis of esters, and (c) inversion of sugars. One of the industrially important gas-phase catalytic reactions is the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the production of sulfuric acid, catalyzed by nitric oxide in the lead chamber.

## Solid-Catalyzed Reaction

This reaction, the most common type of heterogeneous catalysis, finds extensive applications in many important industrial processes that produce inorganic and organic chemicals. Well-known examples of such chemicals include  $\text{HNO}_3$ ,  $\text{HCl}$ , ammonia, aniline, butadiene, ethanol, formaldehyde, methanol, organic polymers, and petrochemicals. The generally accepted, simplified mechanism of solid-catalyzed fluid (gas or liquid) phase reactions is outlined as follows:

1. Reactants diffuse from the main body of the fluid phase to the exterior surface of catalyst pellets, and subsequently into catalyst pores.
2. Reactants are adsorbed onto both the catalyst exterior and pore surfaces.
3. Products are formed from interaction of the reactants on the surfaces (catalyst exterior and pore).
4. Products thus formed are desorbed (or released) from the surfaces; those formed on the pore surface are released to the fluid phase within the pores and then diffuse out of pores to the exterior surface of the catalyst pellet.
5. Products then diffuse from the exterior surfaces into the bulk of the fluid phase.

The relative importance of these steps in influencing the overall reaction rate depends upon a variety of factors, among which are thermal factors, fluid dynamic factors, properties of the catalyst, and diffusion characteristics of the reactants and products. Besides the process steps described earlier, there are various deactivation processes that cause loss of catalytic efficiency, such as fouling and poisoning.

## 75.2 Analysis of Kinetic Data

---

### Data Acquisition

Because chemical reactions involved in most industrial processes are complex, development of the database for the design of the chemical reactor facility can be quite time consuming. Accordingly, selection of experimental methods and equipment for acquisition of kinetic data is crucial in determining the development cost as well as the accuracy and reliability of the data obtained. In essence, the selection process is concerned with both the methods and the equipment to conduct the reactions and to monitor the progress of the reactions. The type of equipment to be used is generally determined by the experimental method for data acquisition. Acquisition of the kinetic

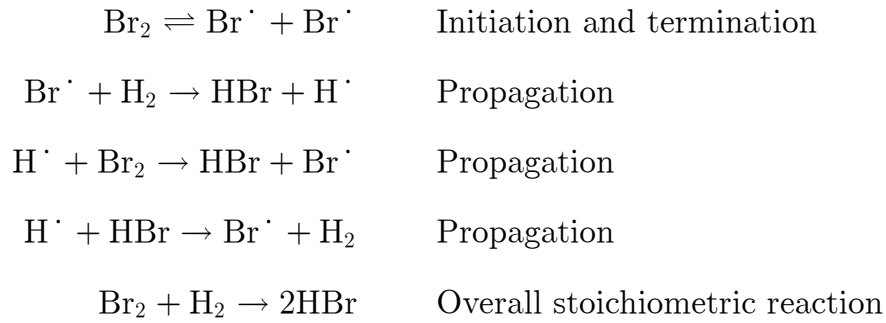
data for homogeneous reactions is frequently carried out using a batch reactor because of its relatively simple design and versatility. In heterogeneous reactions a flow reactor is often utilized for the data acquisition. For detailed discussion on various methods and equipment for obtaining the experimental kinetic data, the reader is referred to the references at the end of the chapter.

## Evaluation of Reaction Mechanism

Understanding of the reaction mechanism is important in the selection and design of an industrial reactor for a specific reaction. Full elucidation of the mechanism, however, is not always possible, in which case derivation of the rate equation may have to resort to the empirical method (see the following subsection). No simple standardized method is available for evaluation of the reaction mechanism. Nevertheless, a trial-and-error method is often used based on the experimental kinetic data acquired—including analysis of the reaction mixture to determine the distribution of the residual reactants, intermediates, and final products—following these steps:

1. Assume a simple elementary reaction mechanism and a corresponding stoichiometry and derive a rate equation from the assumed mechanism.
2. Evaluate the experimental data based on the proposed reaction mechanism and the corresponding rate equation using the integral method (described in the section to follow) first since it is relatively easy to use.
3. If the experimental data do not agree with the proposed mechanism, possibly suggesting a nonelementary reaction, propose a new mechanism that consists of several elementary reaction steps with formation of intermediate compounds.
4. Develop rate equations for individual elementary reaction steps and combine the individual rate equations to represent the overall rate expression.
5. If the experimental kinetic data do not fit into the rate equation developed above, assume an alternate mechanism, and repeat step 4. Continue this process until a desired degree of agreement is reached between the experimental data and the rate expression.
6. Evaluation of the reaction mechanism may also be accomplished using the differential method (see the next subsection), especially for complicated reactions. The method of approach is similar to that using the integral method, but it requires more accurate and extensive experimental data.

An example of a nonelementary complex reaction consisting of several elementary reaction steps is the formation of hydrogen bromide from hydrogen and bromine:



Based on the above reaction mechanism, the following rate equation has been derived:

$$r_{\text{HBr}} = \frac{k_1 C_{\text{H}_2} C_{\text{Br}_2}^{0.5}}{1 + k_2 (C_{\text{HBr}} / C_{\text{Br}_2})} \quad (75.15)$$

## Development of Rate Equation

For reactions with simple mechanism under isothermal conditions, either the integral method or the differential method (discussed in a later section) may be used in the derivation of rate equations. It is assumed that the data representing the extent of an isothermal reaction are available in terms of the time variation of a selected component  $A$ .

### Integral Method

An elementary reaction mechanism is first assumed; for example, a second-order isothermal homogeneous reaction under *constant-volume* conditions,  $A + B \rightarrow C + D$ , results in the rate equation of the form

$$-r_A = \frac{dC_A}{dt} = k C_A C_B \quad (75.16)$$

and the integrated rate equation becomes

$$kt = \frac{1}{C_{B_0} - C_{A_0}} \ln \frac{C_{A_0} (C_A + C_{B_0} - C_{A_0})}{C_A C_{B_0}} \quad (75.17)$$

where  $C_{A_0}$  and  $C_{B_0}$  represent the initial concentrations of reactants  $A$  and  $B$ , respectively. One way to confirm the proposed reaction mechanism is to compute values of  $k$  at various values of  $C_A$  and  $t$ . If the values of  $k$  remain nearly constant, the proposed mechanism is accepted. Otherwise, another mechanism is assumed and the process is repeated until a desired degree of agreement is reached.

When the volume of the reaction mixture varies with the extent of reaction, the rate equation becomes more complicated. In this case, if it is assumed that the volume varies linearly with the

extent of reaction, derivation of the rate equation could be simplified. Using the fractional conversion  $x_A$  to replace  $C_A$  as the variable, the volume  $V$  is expressed as

$$V = V_0(1 + f_A x_A) \quad (75.18)$$

Here,  $V_0$  represents the initial volume of the reaction mixture and  $f_A$  is the fractional change in  $V$  between no conversion and complete conversion with respect to reactant  $A$ , as defined by

$$f_A = (V_{x_A=1} - V_{x_A=0})/V_{x_A=0} \quad (75.19)$$

Thus, for a *variable-volume* reaction, the reaction rate defined by Eq. (75.1) assumes the following form,

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = -\frac{1}{V_0(1 + f_A x_A)} \frac{d}{dt} N_{A_0}(1 - x_A) \quad (75.20)$$

which simplifies to

$$-r_A = \frac{C_{A_0}}{1 + f_A x_A} \frac{dx_A}{dt} \quad (75.21)$$

and the integrated rate equation is

$$t = C_{A_0} \int_0^{x_A} \frac{dx_A}{(1 + f_A x_A)(-r_A)} \quad (75.22)$$

where  $-r_A$  stands for the rate expression for the assumed reaction mechanism to be evaluated. For example, for a first-order homogeneous reaction,

$$-r_A = kC_A = kC_{A_0} \frac{1 - x_A}{1 + f_A x_A} \quad (75.23)$$

Introducing this expression for  $-r_A$  into Eq. (75.22),

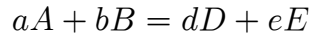
$$kt = -\ln(1 - x_A) \quad (75.24)$$

The steps to be taken to evaluate the assumed reaction mechanism for the variable-volume case are identical to the constant-volume case.

### Differential Method

This approach is based on the direct application of the differential rate equation in the analysis of the experimental kinetic data to determine the reaction mechanism. The method requires more accurate and extensive experimental data than the integral method. The basic principle of the method is illustrated by an example of assumed  $n$  th-order reaction under the isothermal and

constant-volume condition:



With initially equimolal concentrations of  $A$  and  $B$  (i.e.,  $C_A = C_B$ ), the rate equation may take the following form,

$$-r_A = kC_A^a C_B^b = kC_A^{a+b} = kC_A^n \quad (75.25)$$

which is rearranged into

$$\log(-r_A) = \log(-dC_A/dt) = \log k + n \log C_A \quad (75.26)$$

The assumption of the  $n$  th-order reaction mechanism is confirmed if a log-log plot of  $(dC_A/dt)$  versus  $C_A$  results in a straight line.

The next step is to evaluate the values of the rate constant  $k$  and the overall order of reaction  $n$  from the plot. With the known values of  $k$  and  $n$ , the reaction orders with respect to  $A$  and  $B$  can be determined by the method that follows. Rearranging Eq. (75.25),

$$-r_A = kC_A^a C_B^{n-a} = kC_B^n (C_A/C_B)^a \quad (75.27)$$

On further rearrangement,

$$\log\left(-\frac{r_A}{kC_B^n}\right) = a \log(C_A/C_B) \quad (75.28)$$

A log-log plot of Eq. (75.28) yields the reaction order  $a$  with respect to  $A$ , whereas the reaction order  $b$  is obtained as the difference between  $n$  and  $a$ .

### Empirical Method

This method, which finds uses when the reaction mechanism appears to be complex, is often based on a mathematical approach using the curve-fitting procedure. The method involves a trial-and-error technique to fit the experimental data to a relatively simple form of the empirical equation, including (a) linear form,  $y = a + bx$ , (b) semilogarithmic form,  $y = ae^{bx}$ , (c) logarithmic form,  $y = c + ax^n$ , and so forth. The initial step usually consists of plotting the experimental data on graph papers of different coordinates that may produce a straight line. Upon selection of a proper form of the empirical equation, the constants in the empirical equation are determined either by the graphic means or by the analytical technique using the method of averages or the method of least squares. Computer software is available for performing the curve-fitting procedure.

## Determination of Rate Constant and Arrhenius Parameters

The rate constant  $k$  can be obtained by using either a differential form [e.g., Eq. (75.16)] or an integrated form [e.g., Eq. (75.17)] of the rate equation. It is an average of values calculated at various experimental kinetic data points (i.e., reactant concentrations at various reaction times).

*Arrhenius parameters* consist of the activation energy  $E$  and the frequency factor  $A$ . The value of  $E$  may be calculated from the rate constants at two distinct but adjacent temperatures,  $T_1$  and  $T_2$ , as follows:

$$k_1 = Ae^{-E/RT_1}; \quad k_2 = Ae^{-E/RT_2}$$

Combining the above two equations,

$$E = R \frac{\ln(k_2/k_1)}{1/T_1 - 1/T_2} \quad (75.29)$$

The value of  $A$  is calculated from one of the Arrhenius equations shown above.

### Defining Terms

**Activation energy:** A parameter associated with the Arrhenius equation and considered by Arrhenius as the energy in excess of the average energy level of reactants required to enable the reaction to proceed.

**Catalyst:** A substance that accelerates the reaction, presumably by making available a reaction path that requires a lower activation energy. The catalyst may or may not change chemically during the reaction and is regenerated at the end of the reaction.

**Rate constant:** A proportionality constant in the rate equation. The rate constant is markedly influenced by temperature and, to lesser degree, by pressure and the presence of catalysts. The units and value of the rate constant depend on the specific chemical component to which it refers, the units for concentration (or other quantity) of the component, and the reaction order.

**Rate-controlling step:** The slow steps that tend to control the overall rate of reaction. In a complex reaction consisting of several chemical reaction steps (and physical process steps in heterogeneous reaction), the reaction rate (and physical process rate) of one or more steps may be much slower than other steps.

**Rate equation:** A functional expression describing the relationship between the rate of reaction and the amounts (e.g., concentrations) of selected chemical components participating in the reaction at any time under isothermal condition.

**Rate of reaction:** The amount of a chemical component of concern being converted or produced per unit time per unit quantity of a reference variable. Examples of the reference variable include the volume of reacting mixture, the reactor volume, the mass of solid (solid-fluid reaction), and the surface area of solid.

## References

- Carberry, J. J. 1976. *Chemical and Catalytic Reaction Engineering*. McGraw-Hill, New York.
- Connors, K. A. 1990. *Chemical Kinetics*  $\frac{3}{4}$  *The Study of Reaction Rates in Solution*. VCH, New York.
- Katakis, D. and Gordon, G. 1987. *Mechanisms of Inorganic Reactions*. John Wiley & Sons, New York.
- Lin, K. H. 1984. Reaction kinetics, reactor design (section 4). In *Perry's Chemical Engineers' Handbook* -4.52. McGraw-Hill, New York.
- Moore, J. W. and Pearson, R. G. 1981. *Kinetics and Mechanism*, 3rd ed. John Wiley & Sons, New York.

## Further Information

The following professional journals provide good sources for examples of basic and applied reaction kinetic studies on specific reactions of industrial importance:

*AIChE Journal*. Published monthly by the American Institute of Chemical Engineers, New York, NY.

*Chem. Eng. Sci.* Published semimonthly by Elsevier Science, Oxford, U.K.

*Ind. Eng. Chem. Res.* Published monthly by the American Chemical Society, Washington, D.C.

*J. Am. Chem. Soc.* Published biweekly by the American Chemical Society, Washington, D.C.

*J. Catal.* Published monthly by Academic Press, Orlando, FL.

*J. Chem. Soc.*  $\frac{3}{4}$  *Faraday Trans.* Published semimonthly by The Royal Society of Chemistry, Cambridge, U.K.

*Trans. Inst. Chem. Eng. (London)*  $\frac{3}{4}$  *Chem. Eng. and Design*. Published bimonthly by the Institute of Chemical Engineers, Basinstoke, U.K.

# Chemical Reaction Engineering

## 76.1 The Algorithm

Mole Balances • Rate Laws • Stoichiometry

## 76.2 Pressure Drop in Reactors

## 76.3 Multiple Reactions

## 76.4 Heat Effects

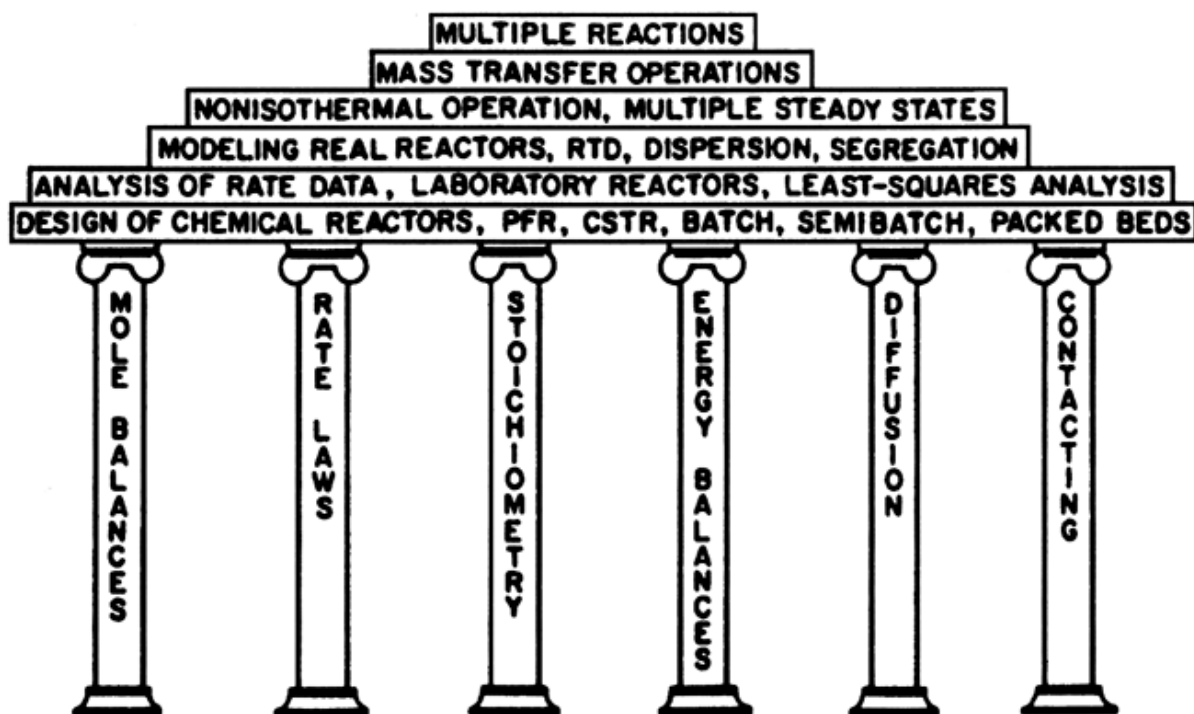
## 76.5 Summary

### H. Scott Fogler

University of Michigan

Chemical reaction engineering (CRE) sets chemical engineers apart from other engineers. Students and professionals can easily learn the elements of CRE because it has a very logical structure. The six basic pillars that hold up what you might call the "temple" of chemical reaction engineering are shown in Fig. 76.1 .

**Figure 76.1** Pillars of the temple of chemical reaction engineering. (Source: Fogler, H. S. 1992. *The Elements of Chemical Reaction Engineering*, 2nd ed. Prentice Hall, Englewood Cliffs, NJ.)



The pillar structure shown in Fig. 76.1 allows one to develop a few basic concepts and then to arrange the parameters (equations) associated with each concept in a variety of ways. Without such a structure, one is faced with the possibility of choosing or perhaps memorizing the correct equation from a multitude of equations that can arise for a variety of reactions, reactors, and sets of conditions. This chapter shall focus on five types of chemical reactors commonly used in industry: **batch**, **semibatch**, **CSTR**, **plug flow**, and **packed bed reactors**. Table 76.1 describes each of these reactors.

**Table 76.1** Comparison of Five Types of Chemical Reactors

Type of Reactor	Characteristics	Usage	Advantages	Disadvantages
Batch	<ul style="list-style-type: none"> <li>Reactor is charged (filled) via two holes in the top of the tank; while reaction is carried out, nothing else is put in or taken out until reaction is done; tank easily cooled or heated by jacket</li> </ul>	<ul style="list-style-type: none"> <li>Small-scale production</li> <li>Intermediate or one-shot productions</li> <li>Pharmaceuticals</li> <li>Fermentations</li> </ul>	<ul style="list-style-type: none"> <li>High conversion per unit volume for one pass</li> <li>Same reactor can be used to produce one product one time and a different product the next</li> </ul>	<ul style="list-style-type: none"> <li>High operating cost (labor)</li> <li>Product quality more variable than with continuous operation</li> </ul>
Semibatch	<ul style="list-style-type: none"> <li>Either one reactant is charged and the other is fed continuously (at small concentrations) or else one of the products can be removed continuously (to avoid side reactions)</li> </ul>	<ul style="list-style-type: none"> <li>Small-scale production</li> <li>Competing reactions</li> </ul>	<ul style="list-style-type: none"> <li>Good selectivity; feed can be controlled so as to minimize side runs.</li> </ul>	<ul style="list-style-type: none"> <li>High operating labor cost</li> <li>Product quality more variable than with continuous operation</li> </ul>
Continuously stirred tank reactor (CSTR)	<ul style="list-style-type: none"> <li>Run at steady state with continuous flow of reactants and products; the feed assumes a uniform composition throughout the reactor, exit stream has the same composition as in the tank</li> </ul>	<ul style="list-style-type: none"> <li>When agitation is required</li> <li>Series configuration for different concentration streams</li> </ul>	<ul style="list-style-type: none"> <li>Continuous operation</li> <li>Good temperature control</li> <li>Good control</li> <li>Simplicity of construction</li> <li>Low operating (labor) cost</li> </ul>	<ul style="list-style-type: none"> <li>Lowest conversion per unit volume</li> <li>Bypassing and channeling possible with poor agitation</li> </ul>
Plug flow reactor (PFR)	<ul style="list-style-type: none"> <li>Arranged as one long reactor or many short reactors in a tube bank; no radial variation in reaction rate (concentration); concentration changes with length down the reactor</li> </ul>	<ul style="list-style-type: none"> <li>Large-scale production</li> <li>Homogeneous reactions</li> <li>Heterogeneous reactions</li> <li>Continuous production</li> <li>High temperature</li> </ul>	<ul style="list-style-type: none"> <li>Highest conversion per unit volume</li> <li>Low operating labor cost</li> <li>Continuous operation</li> <li>Good heat transfer</li> </ul>	<ul style="list-style-type: none"> <li>Undesired thermal gradients may exist</li> <li>Poor temperature control</li> <li>Shutdown, cleaning may be expensive</li> </ul>
Tubular packed bed reactor (PBR)	<ul style="list-style-type: none"> <li>Tubular reactor that is packed with solid catalyst particles</li> </ul>	<ul style="list-style-type: none"> <li>Used primarily in heterogeneous gas phase reactions with a catalyst</li> </ul>	<ul style="list-style-type: none"> <li>Highest conversion per unit mass of catalyst</li> <li>Low operating cost</li> <li>Continuous operation</li> </ul>	<ul style="list-style-type: none"> <li>Undesired thermal gradients may exist</li> <li>Poor temperature control</li> <li>Channeling may occur</li> </ul>

By using an algorithm to formulate CRE problems, we can formulate and solve CRE problems in a very logical manner. Step 1 in the CRE algorithm is to begin by choosing the mole balance for one of the five types of reactors shown. In step 2 we choose the rate law and in step 3 we specify whether the reaction is gas or liquid phase. Finally, in step 4 we combine steps 1, 2, and 3 and obtain an analytical solution or solve the equations using an *ordinary differential equation (ODE) solver* [Sacham and Cutlip, 1988].

## 76.1 The Algorithm

We now address each of the individual steps in the algorithm to design isothermal reactors: (1) mole balances, (2) rate laws, (3) stoichiometry, and (4) combine.

### Mole Balances

The general mole balance equation (GBE) on species  $j$  in a system volume  $V$  is:

$$\left[ \begin{array}{c} \text{Molar flow} \\ \text{rate} \\ \text{IN} \end{array} \right] - \left[ \begin{array}{c} \text{Molar flow} \\ \text{rate} \\ \text{OUT} \end{array} \right] + \left[ \begin{array}{c} \text{Molar rate} \\ \text{of} \\ \text{GENERATION} \end{array} \right] = \left[ \begin{array}{c} \text{Molar rate} \\ \text{of} \\ \text{ACCUMULATION} \end{array} \right]$$

$$F_{j0} - F_j + \int_0^v r_j dV = \frac{dN_j}{dt} \quad (76.1)$$

We now make use of the definition of conversion,  $X$ , with respect to the limiting reactant, which we shall call species  $A$ ,

$$\begin{array}{cc} \text{Batch} & \text{Flow} \\ X = (N_{A0} - N_A)/N_{A0} & X = (F_{A0} - F_A)/F_{A0} \end{array}$$

and apply the GME to each of the following reactors: batch, continuous stirred tank reactors (CSTR), plug flow reactor (PFR), and packed bed reactor (PBR). The CSTR, PFR, and PBR are all operated at steady state (i.e.,  $dN_j/dt = 0$ ) and it is assumed that the PBR and PFR are in plug flow (no radial gradients or dispersion) and that the contents of the CSTR are well mixed. There is no in-flow or out-flow ( $F_{j0} = F_j = 0$ ) in the batch reactor. When these conditions and the definition of conversion are applied to the general mole balance, the design equations (76.2 to 76.8) in [Table 76.2](#) result.

**Table 76.2** Design Equations

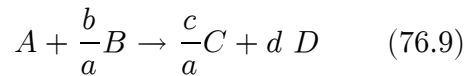
Reactor	Differential	Algebraic	Integral
Batch	$N_{A0} \frac{dX}{dt} = -r_A V \quad (76.2)$		$t = N_{A0} \int_0^x \frac{dX}{-r_A V} \quad (76.3)$
CSTR		$V = \frac{F_{A0} X}{-r_A} \quad (76.4)$	
PFR	$F_{A0} \frac{dX}{dV} = -r_A \quad (76.5)$		$V = F_{A0} \int_0^x \frac{dX}{-r_A} \quad (76.6)$
PBR	$F_{A0} \frac{dX}{dW} = -r'_A \quad (76.7)$		$W = F_{A0} \int_0^x \frac{dX}{-r'_A} \quad (76.8)$

In order to evaluate the design equations given in [Table 76.2](#) we must determine the form of the rate of formation,  $r_A$ . We do this with the aid of a rate law.

## Rate Laws

The power law model is one of the most commonly used forms for the rate law. It expresses the rate of reaction as a function of the concentrations of the species involved in the reaction.

For the irreversible reaction in which  $A$  is the limiting reactant,



the rate law is

$$-r_A = kC_A^\alpha C_B^\beta \quad (76.10)$$

We say the reaction is  $\alpha$  order in  $A$ ,  $\beta$  order in  $B$ , and overall order =  $\alpha + \beta$ . For example, if the reaction  $A + B \rightarrow C + D$  is said to be second order in  $A$  and first order in  $B$  and overall third order, then the rate law is

$$-r_A = kC_A^2 C_B \quad (76.11)$$

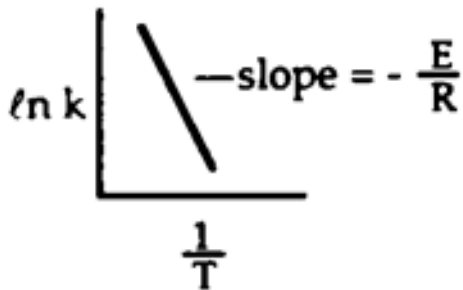
The temperature dependence of specific reaction rate,  $k$ , is given by the Arrhenius equation,

$$k = Ae^{-E/RT} \quad (76.12)$$

where  $A$  is the frequency factor and  $E$  the activation energy. Taking the natural log of both sides of Eq. (76.12),

$$\ln k = \ln A - \frac{E}{R} \left( \frac{1}{T} \right) \quad (76.13)$$

we see the slope of a plot of  $\ln k$  versus  $(1/T)$  will be a straight line equal to  $(-E/R)$ .



The specific reaction rate at temperature  $T$  is commonly written in terms of the specific reaction rate,  $k_1$ , at a reference temperature  $T_1$  and the activation energy  $E$ . That is,

$$k = k_1(T_1) \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (76.14)$$

**Example.** The following reaction is carried out in a constant volume batch reactor:

$A \rightarrow \text{Products}$

Determine the appropriate linearized concentration-time plots for zero-, first-, and second-order reactions.

**Solution.** Use the algorithm to determine the concentration of A as a function of time.

$$\text{Mole balance: } \frac{dN_A}{dt} = r_A V \quad (76.15)$$

$$\text{Rate law: } -r_A = kC_A^\alpha \quad (76.16)$$

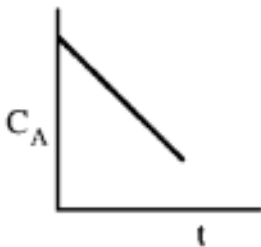
$$\text{Stoichiometry: } V = V_0 \quad C_A = N_A/V_0 \quad (76.17)$$

$$\text{Combine: } -\frac{dC_A}{dt} = kC_A^\alpha \quad (76.18)$$

Solving Eq. (76.18) for a first-, second-, and third-order rate law, we can arrive at the following linearized concentration-time plots.

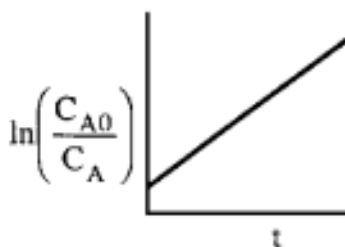
**Zero order,  $\alpha = 0$**

$$C_A = C_{A0} - kt$$



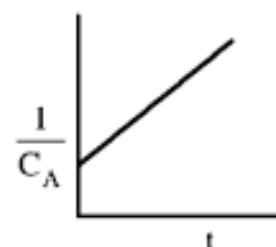
**First Order,  $\alpha = 1$**

$$\ln \frac{C_{A0}}{C_A} = kt$$



**Second Order,  $\alpha = 2$**

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$



For reversible reactions at equilibrium the rate law must reduce to a thermodynamically consistent equation for the equilibrium constant.

## Stoichiometry

Now that we have the rate law as a function of concentration (i.e.,  $-r_A = kC_A^\alpha C_B^\beta$ ), we need to express the concentrations of the reacting species as functions of conversion in order to evaluate any one of the reactor design equations.

### Concentration

We start by defining concentration for a flow system and a batch system. For a flow system,

$$C_i = \frac{F_i}{v} \quad (76.19)$$

where  $v$  is the volumetric flow rate. For a batch system,

$$C_i = \frac{N_i}{V} \quad (76.20)$$

The next step is to express  $N_i$  and  $F_i$  as a function of conversion using a stoichiometric table.

### The Stoichiometry Table

Using our definition of conversion we can construct the following stoichiometric table.

Stoichiometry	$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$			
Batch systems Species	Symbol	Initial	Change	Remaining
$A$	$A$	$N_{A0}$	$-N_{A0}X$	$N_A = N_{A0}(1 - X)$
$B$	$B$	$N_{A0}\Theta_B$	$-\frac{b}{a}N_{A0}X$	$N_B = N_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
$C$	$C$	$N_{A0}\Theta_C$	$+\frac{c}{a}N_{A0}X$	$N_C = N_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
$D$	$D$	$N_{A0}\Theta_D$	$+\frac{d}{a}N_{A0}X$	$N_D = N_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
Inert	$I$	$N_{A0}\Theta_I$	—	$N_I = N_{A0}\Theta_I$
		$N_{T0}$		$N_T = N_{T0} + \delta N_{A0}X$
where $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$ , $\varepsilon = y_{A0}\delta$ , and $\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{y_{i0}}{y_{A0}} = \frac{C_{i0}}{C_{A0}}$				

For flow systems the number of moles of species  $i$ ,  $N_i$  in this table are simply replaced by the molar flow rates of species  $i$ ,  $F_i$ .

### Expressing Concentration as a Function of Conversion in Batch System

Constant volume batch:  $V = V_0$ .

$$C_B = \frac{N_B}{V} = \frac{N_B}{V_0} = \frac{N_{A0}}{V_0} \left( \Theta_B - \frac{b}{a}X \right)$$

$$C_B = C_{A0} \left( \Theta_B - \frac{b}{a}X \right) \quad (76.21)$$

### Expressing Concentration as a Function of Conversion in Flow System

For flow systems, the stoichiometric table is the same, except replace  $N_i$  by  $F_i$ . Because there is hardly ever a volume change with reaction, the concentration of  $A$  in a *liquid* flow system is as follows. For liquid systems,

$$C_A = \frac{F_A}{v_0} = \frac{F_{A0}}{v_0}(1 - X) = C_{A0}(1 - X) \quad (76.22)$$

For gas systems,

$$C_A = \frac{F_A}{v} \quad (76.23)$$

In ideal gas systems the gas volumetric flow rate,  $v$ , can change with conversion, temperature, and pressure according to the following equation:

$$v = v_0 \left( \frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \frac{T}{T_0} \quad (76.24)$$

Taking the ratio of  $F_T/F_{T0}$  and then using the stoichiometric table, we arrive at the following equation for the volumetric flow rate at any point in the reactor.

$$v = v_0(1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0} \quad (76.25)$$

Substituting this result and Eq. (76.22) into Eq. (76.23) gives

$$C_A = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)} \frac{P}{P_0} \frac{T_0}{T} \quad (76.26)$$

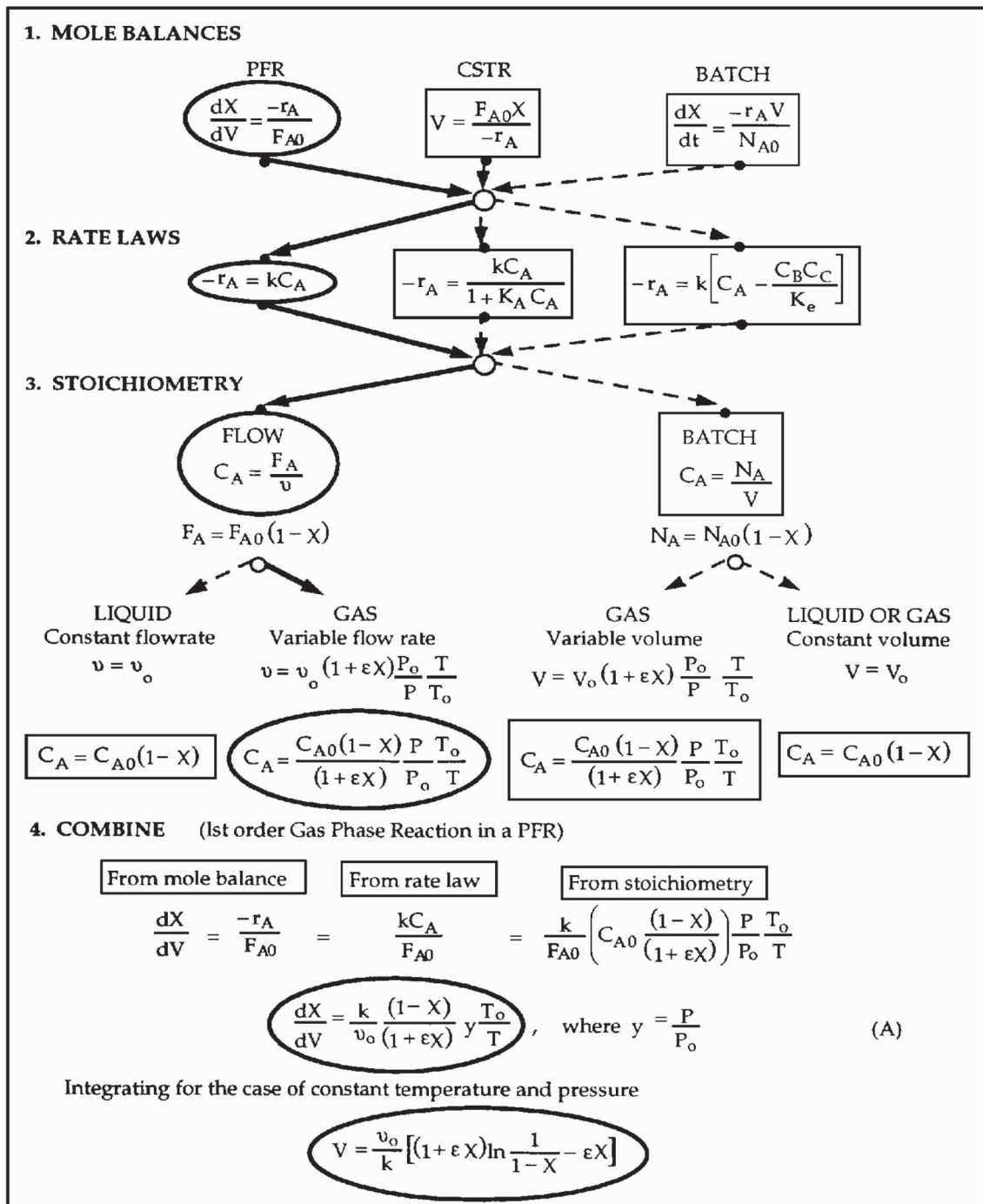
We now will apply the algorithm described earlier to a specific situation. Suppose we have, as shown in Fig. 76.2, mole balances for three reactors, three rate laws, and the equations for concentrations for both liquid and gas phases. In Fig. 76.3 the algorithm is used to formulate the equation to calculate the PFR reactor volume for a first-order gas-phase reaction. The pathway to arrive at this equation is shown by the ovals connected to the dark lines through the algorithm. The dashed lines and the boxes represent other pathways for other solutions. For the reactor and reaction specified, we follow these steps:

1. Choose the *mole balance* on species  $A$  for a PFR.
2. Choose the *rate law* for an irreversible first-order reaction.
3. Choose the equation for the concentration of  $A$  in the gas phase (*stoichiometry*).
4. Finally, *combine* to calculate the volume necessary to achieve a given conversion or calculate the conversion that can be achieved in a specified reaction volume.

For the case of isothermal operation with no pressure drop, we were able to obtain an analytical

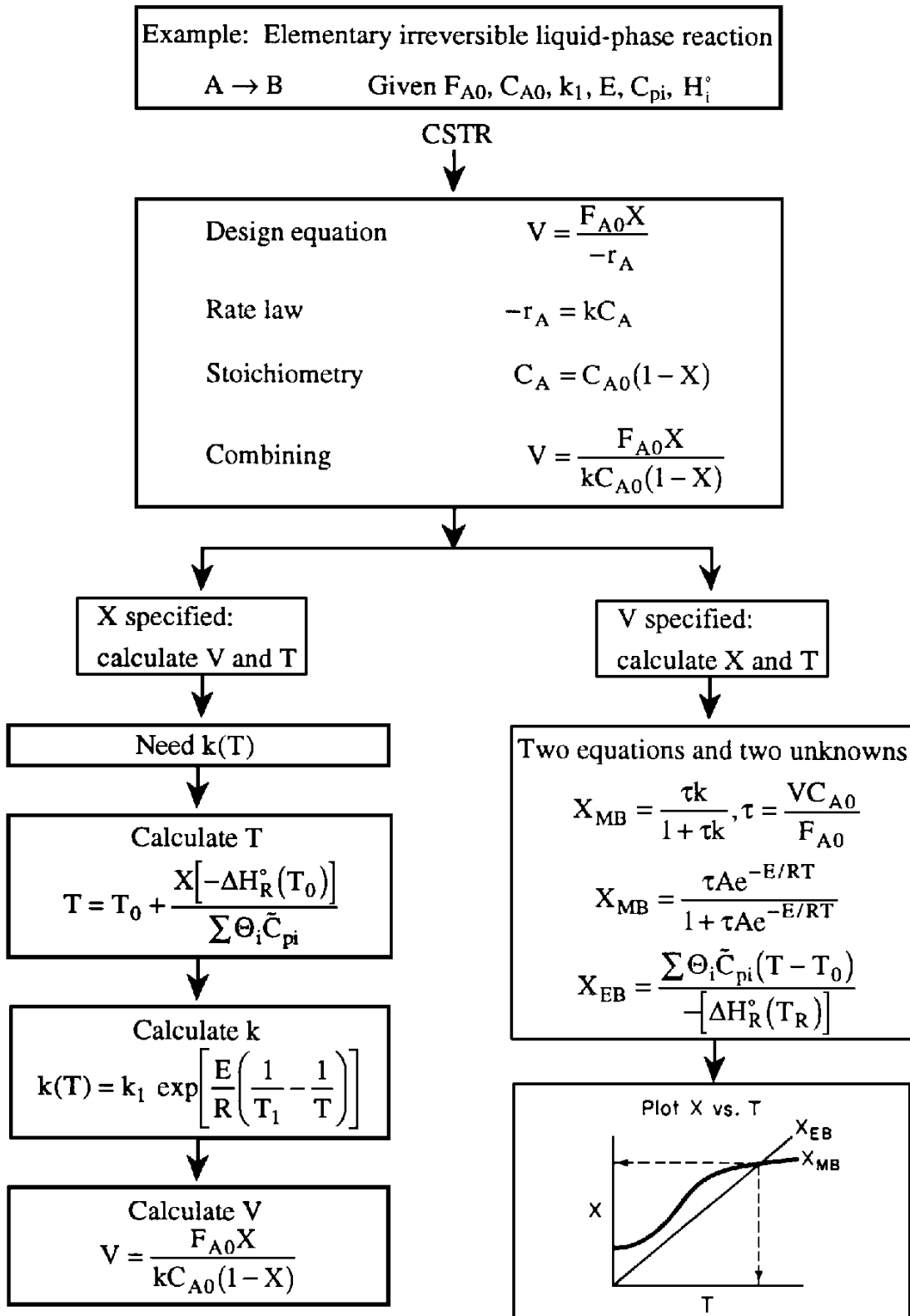
solution, given by equation (A) in Fig. 76.2, which gives reactor volume necessary to achieve a conversion  $X$  for a gas phase reaction carried out isothermally in a PFR. However, in the majority of situations, analytical solutions to the ordinary differential equations appearing in the combine step are not possible. By using this structure, one should be able to solve reactor engineering problems through reasoning rather than memorization of numerous equations together with the various restrictions and conditions under which each equation applies (i.e., whether there is a change in the total number of moles, etc.). In perhaps no other area of engineering is mere formula plugging more hazardous; the number of physical situations that can arise appears infinite, and the chances of a simple formula being sufficient for the adequate design of a real reactor are vanishingly small.

**Figure 76.2** Algorithm for isothermal reactors. (Source: Fogler, H. S. 1996. *Elements of Chemical Reaction Engineering*. 3rd ed. Prentice Hall, Englewood Cliffs, NJ.)

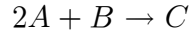


**Figure 76.3** Algorithm for nonisothermal CSTR design. (Source: Fogler, H. S. 1992. *The Elements of Chemical Reaction Engineering*, 2nd ed. Prentice Hall, Englewood Cliffs, NJ.)

**Algorithm**



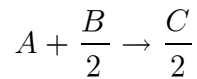
**Example.** The elementary gas phase reaction



$$-r_A = k_A C_A^2 C_B$$

is carried out at constant  $T$  (500 K) and  $P$  (16.4 atm) with  $k_A = 10 \text{ dm}^6/\text{mol}^2 \cdot \text{s}$ . Determine the CSTR reactor volume necessary to achieve 90% conversion when the feed is 50% mole  $A$  and 50%  $B$ .

**Solution.** The feed is equal molar in  $A$  and  $B$ ; therefore,  $A$  is the limiting reactor and taken as our basis of calculation:



Mole balance is given as:

$$V = \frac{F_{A0} X}{-r_A} \quad (76.27)$$

Rate law is given as:

$$-r_A = k_A C_A^2 C_B \quad (76.28)$$

Stoichiometry is found as follows:

$$C_A = C_{A0} \cdot \frac{(1 - X)}{(1 + \varepsilon X)} \frac{P}{P_0} \frac{T_0}{T} = C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)}$$

$$\varepsilon = y_{A0} \delta = 0.5 \left[ \frac{1}{2} - \frac{1}{2} - 1 \right] = -0.5 \quad (76.29)$$

$$C_A = C_{A0} (1 - X) / (1 - 0.5X)$$

$$C_{A0} = \frac{y_{A0} P_0}{RT_0} = \frac{(0.5)(16.4 \text{ atm})}{\frac{0.082 \text{ atm m}^3}{\text{kmol K}} \cdot 500 \text{ K}} = 0.2 \frac{\text{kmol}}{\text{m}^3} = 0.2 \frac{\text{mol}}{\text{dm}^3} \quad (76.30)$$

$$C_B = C_{A0} \frac{\Theta_B - \frac{1}{2}X}{(1 + \varepsilon X)} = C_{A0} \frac{(1 - 0.5X)}{(1 - 0.5X)} = C_{A0} \quad (76.31)$$

For the combine step,

$$\begin{aligned} -r_A &= k_A C_A^2 C_B = k_A C_{A0}^3 \frac{(1 - X)^2}{(1 - 0.5X)^2} \\ &= 0.08 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \frac{(1 - X)^2}{(1 - 0.5X)^2} \end{aligned} \quad (76.32)$$

For a CSTR,

$$\begin{aligned} V &= \frac{F_{A0} X}{-r_A} = \frac{(5 \text{ mol/s})(0.9)[1 - 0.5(0.9)]^2}{(0.08) \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} (1 - 0.9)^2} \\ &= 1701 \text{ dm}^3 \end{aligned} \quad (76.33)$$

## 76.2 Pressure Drop in Reactors

---

If pressure drop is not accounted for in gas phase reactions, significant underdesign of the reactor size can result. This variation is handled in the stoichiometry step, in which concentration is expressed as a function of conversion, temperature, and total pressure. The change in total pressure is given by the Ergun equation [Fogler, 1992]:

$$\frac{dP}{dL} = -\frac{G(1 - \phi)}{\rho g_C D_p \phi^3} \left[ \frac{150(1 - \phi)\mu}{D_p} + 1.75G \right] \quad (76.34)$$

For isothermal operation the density is (assuming ideal gas)

$$\rho = \frac{\rho_0}{(1 + \varepsilon X)} \frac{P}{P_0} \quad (76.35)$$

The catalyst weight,  $W$ , and length down the reactor,  $L$ , are related by the equation

$$W = LA_c(1 - \Phi)\rho_{\text{cat}}$$

Substituting back in the Ergun equation,

$$\frac{dP}{dW} = -\frac{\alpha_p}{2} \frac{(1 + \varepsilon X)}{\frac{1}{P_0} \left( \frac{P}{P_0} \right)} \quad (76.36)$$

where

$$\alpha_p = \frac{\frac{G(1 - \Phi)}{\rho_0 g_c D_p \Phi^3} \left[ \frac{150(1 - \Phi)\mu}{D_p} + 1.75G \right]}{A_c(1 - \Phi)\rho_{\text{cat}} P_0}$$

We now need to solve this differential equation to obtain the pressure as a function of the weight of catalyst the gas has passed over. We can obtain an analytical solution of  $\varepsilon = 0$ . Otherwise, we must solve the equation numerically and simultaneously with the mole balance. For an analytical solution,

$$\frac{d(P/P_0)^2}{dW} = -\alpha_p(1 + \varepsilon X) \quad (76.37)$$

For POLYMATH solution, letting  $y = P/P_0$ ,

$$\frac{dy}{dW} = -\frac{\alpha_p(1 + \varepsilon X)}{2y} \quad (76.38)$$

**Example.** To understand the effect pressure drop has on gas phase reaction in a packed bed, we analyze the reaction  $A \rightarrow B$  carried out in a packed bed reactor (PBR). Mole balance (PBR) is

$$F_{A0} \frac{dX}{dW} = -r'_A$$

Wherever pressure drop occurs in a PBR we must use the differential form of the mole balance to separate variables. Pressure drop only affects  $C_A$ ,  $C_B$ , and so on, as well as  $-r'_A$ .

Rate law is second order in A and irreversible, according to the formula  $-r'_A = kC_A^2$ .

Stoichiometry is given by

$$C_A = C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$

For  $\varepsilon = 0$  and isothermal operation,

$$\frac{P}{P_0} = (1 - \alpha_p W)^{1/2}$$

$$C_A = C_{A0}(1 - X) \frac{P}{P_0} = C_{A0}(1 - X)(1 - \alpha_p W)^{1/2}$$

Combining,

$$F_{A0} \frac{dX}{dW} = -r'_A = kC_{A0}^2(1 - X)^2(1 - \alpha_p W)$$

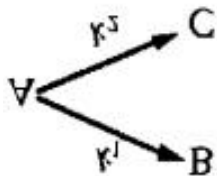
By integrating with limits  $W = 0, X = 0$  we obtain the desired relationship between conversion and catalyst weight.

$$\frac{X}{1 - X} = \frac{kC_{A0}^2}{F_{A0}} \left[ W - \frac{\alpha_p W^2}{2} \right]$$

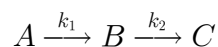
## 76.3 Multiple Reactions

---

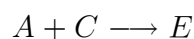
There are three basic types of multiple reactions: series, parallel, and independent. In *parallel reactions* (also called *competing reactions*) the reactant is consumed by two different reactions to form different products:



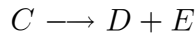
In *series reactions*, also called *consecutive reactions*, the reactant forms an intermediate product, which reacts further to form another product:



Multiple reactions involve a combination of both series and parallel reactions, such as

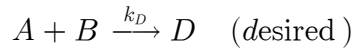


*Independent* reactions are of the type



and occur in feed stocks containing many reactants. The cracking of crude oil to form gasoline is an example of an independent reaction.

To describe selectivity and yield we consider the following competing reactions.



The rate laws are

$$r_D = k_D C_A^{\alpha_1} C_B^{\beta_1} \quad (76.39)$$

$$r_U = k_U C_A^{\alpha_2} C_B^{\beta_2} \quad (76.40)$$

We want the rate of  $D$ ,  $r_D$ , to be high with respect to the rate of formation  $U$ ,  $r_U$ . Taking the ratio of these rates, we obtain a rate *selectivity parameter*,  $S$ , which is to be maximized:

$$S_{DU} = \frac{r_D}{r_U} \quad (76.41)$$

Substituting Eqs. (76.39) and (76.40) into Eq. (76.41) and letting  $a = \alpha_1 - \alpha_2$  and  $b = \beta_2 - \beta_1$ , where  $a$  and  $b$  are both positive numbers, we have

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_A^a}{k_2 C_B^b}$$

To make  $S_{DU}$  as large as possible we want to make the concentration of  $A$  high and the concentration of  $B$  low. To achieve this result, use the following:

A semibatch reactor in which  $B$  is fed slowly into a large amount of  $A$

A tubular reactor with side streams of  $B$  continually fed to the reactor

A series of small CSTRs with  $A$  fed only to the first reactor and  $B$  fed to each reactor

Another definition of selectivity used in the current literature is given in terms of the flow rates leaving the reactor:

$$\tilde{S}_{DU} = \text{Selectivity} = \frac{F_D}{F_U} = \frac{\text{Exit molar flow rate of desired product}}{\text{Exit molar flow rate of undesired product}} \quad (76.42)$$

For a batch reactor the selectivity is given in terms of the number of moles of  $D$  and  $U$  at the

end of the reaction time:

$$\tilde{S}_{DU} = \frac{N_D}{N_U} \quad (76.43)$$

One also finds that the reaction yield, like the selectivity, has two definitions: one based on the ratio of reaction rates and one based on the ratio of molar flow rates. In the first case the yield at a point can be defined as the ratio of the reaction rate of a given product to the reaction rate of the key reactant A [Carbery, 1967]:

$$Y_D = \frac{r_D}{-r_A} \quad (76.44)$$

In the case of reaction yield based on molar flow rates, the yield is defined as the ratio of moles of product formed at the end of the reaction to the number of moles of the key reactant, A, that have been consumed. For a batch system,

$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A} \quad (76.45)$$

For a flow system,

$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A} \quad (76.46)$$

Because of the various definitions for selectivity and yield, when reading literature dealing with multiple reactions, check carefully to ascertain the definition intended by the author.

## 76.4 Heat Effects

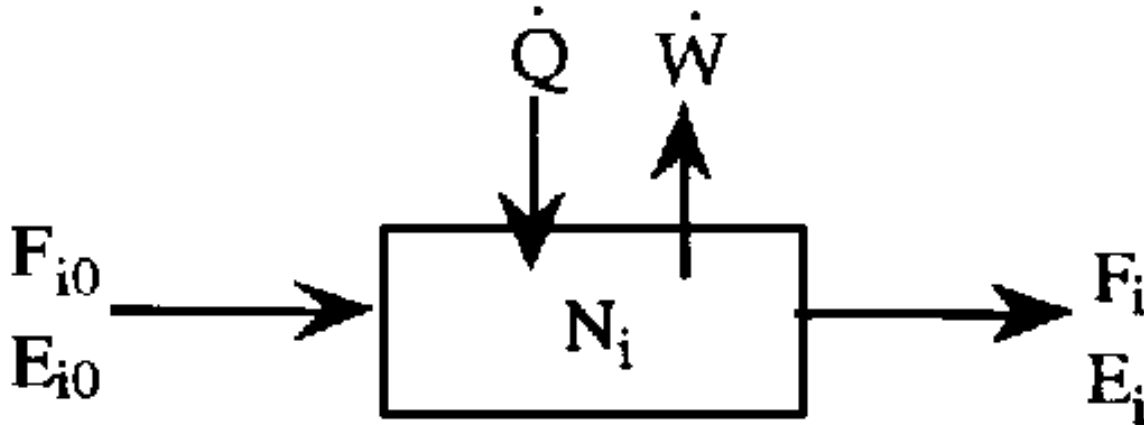
---

For nonisothermal reaction in CRE we must choose which form of the energy balance to use (e.g., PFR, CSTR) and which terms to eliminate (e.g.,  $Q = 0$  for adiabatic operation). The structure introduced to study these reactors builds on the isothermal algorithm by introducing the Arrhenius equation,  $k = Ae^{-E/RT}$  in the **rate law** step, which results in one equation with two unknowns,  $X$  and  $T$ , when we finish with the combine step. For example, using again the PFR mole balance and conditions in Fig. 76.2 [Eq. (A)], we have, for constant pressure,

$$\frac{dX}{dV} = \frac{k(1-X)}{v_0(1+\varepsilon X)} \frac{T_0}{T} \quad (76.47)$$

$$\frac{dX}{dV} = \frac{Ae^{-E/RT}(1-X)}{v_0(1+\varepsilon X)} \left(\frac{T_0}{T}\right) \quad (76.48)$$

We can now see the necessity of performing an energy balance on the reactor to obtain a second equation relating  $X$  and  $T$ . We will use energy balance to relate  $X$  and  $T$ .



$$\begin{aligned}
 \left[ \begin{array}{c} \text{Rate of} \\ \text{accumulation} \\ \text{of energy} \\ \text{within the} \\ \text{system} \end{array} \right] &= \left[ \begin{array}{c} \text{Rate of flow} \\ \text{of heat to} \\ \text{the system} \\ \text{from the} \\ \text{surroundings} \end{array} \right] - \left[ \begin{array}{c} \text{Rate of work} \\ \text{done by} \\ \text{the system} \\ \text{on the} \\ \text{surroundings} \end{array} \right] \\
 &+ \left[ \begin{array}{c} \text{Rate of energy} \\ \text{added to the} \\ \text{system by mass} \\ \text{flow into the} \\ \text{system} \end{array} \right] - \left[ \begin{array}{c} \text{Rate of} \\ \text{energy leaving} \\ \text{system by mass} \\ \text{flow out of} \\ \text{the system} \end{array} \right]
 \end{aligned}$$

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum F_{in} E_{in} - \sum F_{out} E_{out}$$

Neglecting potential and kinetic energy, the energy  $E_i$  is just the internal energy of species  $i$ , substituting for  $W$  in terms of the flow work and the shaft work,  $W_S$ , and using the definition of enthalpy gives for steady state operation

$$\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = 0 \quad (76.49)$$

For adiabatic operation, no work done on the system and constant heat capacity and  $\Delta C_p = 0$ , the energy balance reduces to

$$T = T_0 + \frac{(-\Delta H_R) X}{\sum \theta_i C_{pi} + \Delta C_p X} \quad (76.50)$$

We now use this relationship to solve adiabatic reactor design problems.

The procedure for nonisothermal reactor design can be illustrated by considering the first-order irreversible liquid-phase reaction  $A \rightarrow B$ . The CSTR design equation is

$$V = \frac{F_{A0} X}{-r_A}$$

Rate law is found by

$$-r_A = kC_A \quad (76.51)$$

with the Arrhenius equation:

$$k = Ae^{-E/RT}$$

Stoichiometry for the liquid phase (i.e.,  $v = v_0$ ) is given by

$$C_A = C_{A0}(1 - X)$$

Combining yields

$$V = \frac{v_0}{Ae^{-E/RT}} \left( \frac{X}{1 - X} \right) \quad (76.52)$$

Continuing from this point requires two distinct cases. For the first case, the variables  $X$ ,  $v_0$ ,  $C_{A0}$ , and  $F_{i0}$  are specified and the reactor volume,  $V$ , must be determined. The procedure is as follows:

1. Evaluate Eq. (76.50) to find the temperature,  $T$ , for the conditions specified.
2. Calculate  $k$  from the Arrhenius equation.
3. Calculate the reactor volume,  $V$ , from Eq. (76.52).

For the second case, the variables  $v_0$ ,  $C_{A0}$ ,  $V$ , and  $F_{i0}$  are specified and the exit temperature,  $T$ , and conversion,  $X$ , are unknown quantities. The procedure is as follows:

1. Solve the energy balance for  $X$  as a function of  $T$ . If adiabatic, Eq. (76.50) becomes

$$X_{EB} = \frac{\sum \Theta_i \tilde{C}_{pi} (T - T_0)}{-[\Delta H_R^\circ(T_R)]} \quad (76.53)$$

2. Solve the mole balance [Eq.(76.52)]for  $X$  as a function of  $T$ .

$$X_{MB} = \frac{\tau Ae^{-E/RT}}{1 + \tau Ae^{-E/RT}}$$

where  $\tau = V/v_0$

3. Plot the previous two steps on the same graph to determine the intersection. At this point the values of  $X$  and  $T$  satisfy both the energy balance and mole balance. As an alternative, one may equate the equations for  $X$  from the previous two steps and solve numerically.

An energy balance on a PFR with heat exchange yields the second equation we need relating our independent variables  $X$  and  $T$ :

$$\frac{dT}{dV} = \frac{[U A_c (T_a - T) + (r_A)(\Delta H_R)]}{F_{A0} C_{P_A}} \quad (76.54)$$

The differential equation describing the change of temperature with volume (i.e., distance) down the reactor,

$$\frac{dT}{dV} = g(X, T) \quad (76.55)$$

must be coupled with the mole balance, Eq. (76.5),

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} f(X, T) \quad (76.56)$$

and solved simultaneously. A variety of numerical integration schemes and ODE solvers can be used to solve these two equations simultaneously.

## SHELL'S HYCON PROCESS

As long ago as 1967, the laboratory of the Royal Dutch/Shell Group in Amsterdam headed the development of the HYCON process, by which even the heaviest oil fraction could be converted into premium products, such as gasoline, kerosene, and gasoil.

This had not really been necessary before the first oil crisis in 1973. Oil then was still cheap and in plentiful supply and there was a ready market for all products.

After the oil crises in 1973 and 1979, however, prices had risen to such a level as to provide a powerful incentive for producing the greatest amount of light products from the crude oil, which had, moreover, been getting gradually heavier.

Initially, this was no problem for complex refineries such as Shell Pernis. In contrast with other refineries, Shell Pernis was able to treat the heavy residue remaining after atmospheric distillation by redistilling it under high vacuum. In this way, valuable products such as gasoline, gasoil, and lubricating oil distillates could be manufactured.

But even after this conversion method, a black, viscous mass still remained, which could only be used as a component of heavy fuel oil after adding gasoil. Adding gasoil, however, was a costly solution for a product that was earning less and less. In the Shell laboratories, meanwhile, people were hard at work on a process with better economic prospects: HYCON.

This process is based on the fact that the vacuum residue contains much less hydrogen than the

lighter products. The aim, therefore, is to reduce the size of the molecules and to increase the ratio of hydrogen atoms to carbon atoms.

This ratio can be increased either by removing some carbon from the molecules or by attaching hydrogen to the atoms with the aid of a catalyst. Shell chose the latter approach and called its process HYCON (hydroconversion).

This all sounds much simpler than it actually is. Reducing the size (cracking) of the large molecules is only possible at high temperatures, but the problem with heating is that it produces a heavy deposit of carbon on the catalyst. This problem, and also the addition of hydrogen to the molecules, was solved by carrying out the process under high pressure. Another difficulty is that the asphaltenes (substances with a complex molecular structure) in the residue react very slowly. The reaction mixture therefore has to remain in the reactors for a long time. All in all, this means: several reactors in series, large amounts of catalyst, and high pressures and temperatures in the reactors.

There was another problem that had to be solved in the laboratories. The residue contains heavy metals, such as vanadium and nickel, which poison the catalyst. The solution for this is first of all to pass the residue through a number of reactors containing a specially developed catalyst which removes most of the metals. A technique was also developed to regenerate this catalyst during the process.

The HYCON process required the largest capital investment ever made by Shell in the Netherlands. HYCON in Pernis was put into operation at the beginning of 1989. (Courtesy of the Shell Group.)

## 76.5 Summary

---

By arranging chemical reaction engineering in a structure analogous to a French menu, we can study a multitude of reaction systems with very little effort. This structure is extremely compatible with a number of user-friendly ordinary differential equation (ODE) solvers. Using **ODE solvers** such as POLYMATH, the student is able to focus on exploring reaction engineering problems rather than crunching numbers. Thus, the teacher is able to assign problems that are more open ended and give students practice at developing their creativity. Practicing creativity is extremely important, not only in CRE, but in every course in the curriculum if students are to compete in the world arena and succeed in solving the relevant problems that they will be faced with in the future.

### Nomenclature

$A$	frequency factor (appropriate units)
$A_C$	cross-sectional area, $m^2$
$C_i$	concentration of species $i$ ( $i = A, B, C, D$ ), $mol/dm^3$
$C_{P_i}$	heat capacity of species $i$ , $J/g/K$

$D_P$	particle diameter, m
$E$	activation energy, J/mol
$F_i$	entering molar flow rate of species $i$ , mol/s
$G$	superficial gas velocity g/m <sup>2</sup> /s
$g_c$	conversion factor
$k$	specific reaction rate (constant), appropriate units
$K_A$	adsorption equilibrium constant (dm <sup>3</sup> /mol)
$K_e$	equilibrium constant, appropriate units
$L$	length down the reactor, m
$N_t$	number of moles of species $i$ , mol
$P$	pressure, kPa
$r_t$	rate of formation of species $i$ per unit volume, mol/s/dm <sup>3</sup>
$r_t'$	rate of formation of species $i$ per unit mass of catalyst, mol/s/g
$R$	ideal gas constant, J/mol/K
$t$	time, s
$T$	temperature, K
$U$	overall heat transfer coefficient, J/(dm <sup>3</sup> s K)
$V$	volume, dm <sup>3</sup>
$W$	catalyst weight, g
$X$	conversion
$y$	pressure drop parameter ( $P/P_0$ )
$y_A$	mole fraction of $A$
$a$	ambient temperature
$A$	refers to species $A$
cat	catalyst density kg/m <sup>3</sup>
EB	energy balance
MB	mole balance
$T$	total number of moles
$0$	entering or initial condition
$\alpha$	reaction order
$\alpha_P$	pressure drop parameter, g <sup>-1</sup>
$\beta$	reaction order
$\Delta H_R$	heat of reaction, J/mole $A$
$\delta$	change in the total number of moles per mole of $A$ reacted
$\epsilon$	volume change parameter = $y_{A0} \delta$
$\phi$	porosity
$\mu$	viscosity, cp
$\rho$	density, g/dm <sup>3</sup>
$\nu$	volumetric flow rate, dm <sup>3</sup> /s

$$\Theta_i \quad N_i/N_{A0}$$

## Defining Terms

**Batch reactor:** A closed vessel (tank) in which there is no flow in or out of the vessel during the time the reaction is taking place.

**Continuous stirred tank reactor (CSTR):** A reactor in which the reactant and products flow continuous into and out of (respectively) the tank. A reactor where the contents are well mixed.

**ODE solver:** A user-friendly software package that solves ordinary differential equations, for example, Mathematica, POLYMATH, Matlab.

**Packed bed reactor:** Usually a tubular reactor packed with solid catalyst pellets.

**Plug flow reactor:** Usually a tubular reactor used for gas phase reactions in which it is assumed there are no radial gradients in temperature or concentration as well as no dispersion of reactants.

**Semibatch reactor:** A reactor (vessel) in which one of the reactants is placed in the reactor and a second reactant is slowly added to the reactor.

## References

Fogler, H. S. 1992. *The Elements of Chemical Reaction Engineering*, 2nd ed. Prentice Hall, Englewood Cliffs, NJ.

Shacham, M. and Cutlip, M. B. 1988. Applications of a microcomputer computation package in chemical engineering. *Chemical Engineering Education*. 12(1):18

Carbery, J. J. 1967. Applied kinetics and chemical reaction engineering, *Chemical engineering education*, ed. R. L. Goring and V. W. Weekman, p.89. *American Chemical Society*, Washington, DC.

## Further Information

### Professional Organizations

The American Institute of Chemical Engineers (three national meetings per year), 345 E. 47th St., New York, NY 10017. Phone (212) 705-7322.

The American Chemical Society (several national meetings each year), 1155 16th St., Washington, DC 20036. Phone (202) 872-4600.

### Special Meetings and Conferences

The Engineering Foundation Conferences on Chemical Reaction Engineering, 345 E. 47th St., New York, NY 10017. Phone (212) 705-7835.

International Symposia on Chemical Reaction Engineering (even years), sponsored by American Institute of Chemical Engineers, American Chemical Society, Canadian Society for Chemical Engineering, and the European Federation of Chemical Engineering.

**Professional Journals**

*AICHE Journal*. Published monthly by the American Institute of Chemical Engineers, New York, NY.

*Chem. Eng. Sci.* Published semimonthly by Elsevier Science, Oxford, U.K.

# The Scaleup of Chemical Reaction Systems from Laboratory to Plant

---

## 77.1 General Considerations in the Rational Design of Chemical Reactors

Reaction Kinetics Models and Reactor Models

## 77.2 Protocol for the Rational Design of Chemical Reactors

Step 1: Select the Type of Reactor for the Commercial Process • Step 2: Design the Laboratory to Generate Reaction Kinetics Data • Step 3: Use Statistically-Valid Experimental Programs and Models • Step 4: Develop Computer Programs for Reactor Simulation and Design • Step 5: Develop the Economically Optimum Reactor Design • Step 6: Validate the Design in a Pilot Plant Reactor

### J. B. Cropley

*Union Carbide Corporate Fellow(Retired)*

*Scaleup* is one of those overworked terms that has come to mean almost anything and everything, depending on who is using it. In this article we will use it very little, and then only to indicate the generic process of commercializing new chemical technology. The alternative to scaleup is rational design, which utilizes mathematical relationships and computer simulation to develop the best design for the reactor. The mathematical relationships describe both the reaction kinetics and the attributes of the reactor and its associated auxiliary equipment.

Geometric scaleup was practiced routinely in the chemical industry as a design protocol until a few decades ago, but, today, rational design—based on laboratory data and correlations—has largely replaced it for most types of industrial chemical reaction systems. To understand why this is so, it is necessary to note how the chemical industry has changed over the years.

Forty or 50 years ago, merely producing a chemical on an industrial scale was usually sufficient to ensure a profit for the manufacturer. Chemical processes were labor intensive, but capital and energy were cheap and the selling price of a pound of finished product was typically several times the raw material cost. Furthermore, the environment had not yet been discovered either by industry or by the public at large.

It was really unnecessary to design reactors rationally for most kinds of processes in that era, because any questions about productive capacity could be addressed simply by making the reactor larger, raw material selectivities usually were not economically critical, and the large quantities of energy that were expended in complex distillation trains to remove by-products and impurities were both practicable and inexpensive.

In contrast, the petrochemical industry today utilizes chemical reactions that produce the desired products much more directly and cleanly, with as little waste as possible. Raw material cost is

frequently the largest component of the final product cost, and the crude product must not contain unexpected by-products that the refining system cannot remove adequately and efficiently. The failure to meet tight product specifications can produce chemicals that either cannot be sold at all without expensive reprocessing or can be sold only for little more than their value as fuel.

In any case, both today's marketplace and concerns for the environment demand that chemical reaction systems produce no more than extremely small amounts of waste or off-specification product per pound of refined salable product. Reactors must be accurately designed and operated because today's chemistry frequently is strongly dependent upon carrying out just the desired amount of reaction in order to avoid the production of unwanted by-products by over-reaction. The energy efficiencies of refining systems strongly depend upon their receiving crude product of uniform and predictable composition, because product specifications are usually tight and must be met at minimum cost. Simply put, today's chemical reaction systems must operate as intended.

## 77.1 General Considerations in the Rational Design of Chemical Reactors

---

### Reaction Kinetics Models and Reactor Models

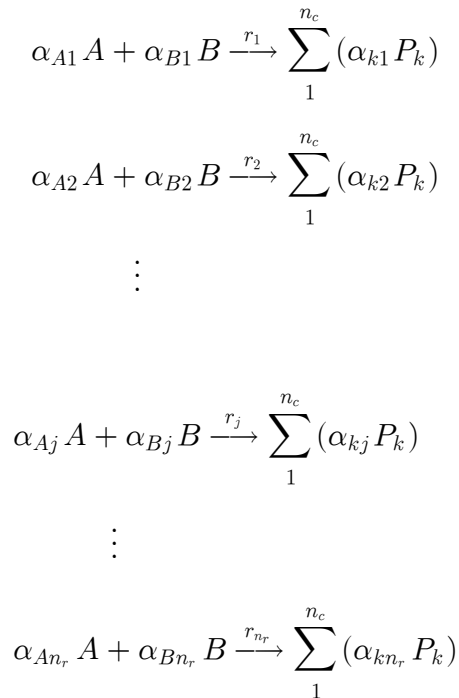
The rational design of any type of reactor involves the marriage of one or more reaction kinetics models and a reactor model. It is important to recognize exactly what these two kinds of models describe:

- *Reaction kinetics models* describe the response of reaction rates to the reaction environment—that is, to temperature and the concentrations of virtually everything in the system—reactants, products, by-products, catalysts, and contaminants. For design purposes, it is necessary and sufficient that the kinetic model reflect the reaction stoichiometry accurately and that it predict reaction rates accurately. It is not important that it reflect the actual reaction mechanism.
- *Reactor models* describe how the reaction environment is shaped by the geometry of the reactor, by physical processes like fluid dynamics and heat and mass transport, and by process variables and conditions such as mean reactor residence time and residence time distribution, flow rate, pressure, and temperature.

These distinctions are subtle, but important. It is sufficient to remember that kinetics models contain *only* temperature and concentration terms, whereas reactor models may contain these as well as everything else that influences the conduct of the reaction.

### Kinetics of a Simple Hypothetical System of Reactions

Real systems will have their own individual structures and characteristics and will reflect the particular stoichiometry of the reaction system at hand. In this chapter, we will use a general, somewhat simplified set of reactions and reactor equations for illustration. Consider the general group of  $n_r$  reactions presented below, in which chemical species  $A$  and  $B$  react to produce several products  $P_k$  according to the following scheme:



Kinetic models for the rational design of reaction systems will usually be of one of two basic mathematical forms, each given in moles/volume/time and describing the response of the reaction rates  $r_j$  to temperature and concentration. For exponential models,

$$r_j = K_{o_j} e^{-\frac{E_{a_j}}{RT}} C_A^{a_j} C_B^{b_j} C_{P_1}^{P_{1j}} \dots C_{P_n}^{p_{nj}} \quad (77.1)$$

For hyperbolic models,

$$r_j = \frac{K_{o_j} e^{-\frac{E_{a_j}}{RT}} C_A C_B}{1 + K_{A_j} C_A + K_{B_j} C_B + \sum_1^{n_c} (K_{P_{kj}} C_{P_k})} \quad (77.2)$$

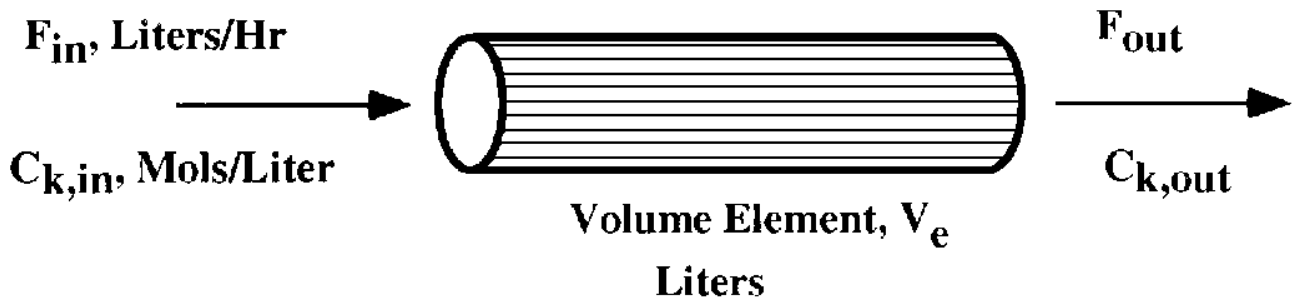
Each of these two types of kinetic models has its own preferred uses. Their development will be discussed in a later section of this chapter. For now, assume that either of these types is to be used in a combined kinetics and reactor model to predict reaction rates, as described in the following section.

### Combined Kinetics and Reactor Models: The General Continuity Equation

Virtually all combined reaction kinetics and reactor models utilize some form of the general continuity equation for flow and reaction in an element of volume of some kind of reactor, such as that shown in [Fig. 77.1](#). In its simplest form, this equation states that the quantity of each component  $k$  that enters the volume element of the reactor must either leave, react, or accumulate:

$$F_{e_{in}} C_{k_{in}} = F_{e_{out}} C_{k_{out}} - V_e \sum_1^{n_r} (\alpha_{kj} r_j) + \frac{d(V_e C_{k_e})}{dt} \text{ mol/time} \quad (77.3)$$

**Figure 77.1** Flow and concentration in a volume element of a chemical reactor.



Different types of idealized reactors can be represented by this equation, simply by noting what terms are not appropriate and eliminating them. Thus, a simple *batch reactor* has no flow in or out, and therefore terms containing  $F$  drop out. So, for a simple batch reactor,

$$\frac{d(V_e C_{k_e})}{dt} = \sum_1^{n_r} (\alpha_{kj} r_j) V_e \quad (77.4)$$

which may be further simplified by canceling the  $V_e$  terms as well if the reaction volume is constant. Note that the volume element in this case is simply the entire filled volume of the reactor, because the concentration is assumed to be uniform throughout.

A steady state *continuous stirred tank reactor (CSTR)* may have the same flow rate in and out, and the entire contents of the reactor comprise the volume element, as in the batch reactor. The time-derivative term is absent because the reactor is at steady state. The concentrations of all species in the reactor are the same as in the outlet. Thus we have, for the CSTR,

$$F C_{k_{in}} = F C_{k_{out}} - V \sum_1^{n_r} (\alpha_{kj} r_j) \quad (77.5)$$

which can be rearranged to

$$\sum_1^{n_r} \alpha_{kj} r_j = \frac{F(C_{k_{out}} - C_{k_{in}})}{V} \text{ mol/volume/time} \quad (77.6)$$

Weight of catalyst,  $W_c$ , replaces reactor volume,  $V$ , for a catalytic reaction:

$$\sum_1^{n_r} \alpha_{kj} r_j = \frac{F(C_{k_{out}} - C_{k_{in}})}{W_c} \text{ mol/wt. catalyst/time} \quad (77.7)$$

This simple relationship makes the CSTR the preferred type of reactor for many kinds of kinetics studies, in which the net rates of formation or disappearance [that is,  $\sum_1^{n_r} (\alpha_{kj} r_j)$ ] for each individual component can be observed directly.

For design purposes it is more convenient to integrate the unsteady state form of the general continuity equation for the CSTR until the steady state concentrations are attained. (The model will behave very much as the real reactor would in this respect.) This procedure avoids the need to use constrained nonlinear estimation to predict the reactor outlet concentrations. Again, assuming that flows in and out of the reactor are the same and that volume is constant,

$$\frac{d(C_k)}{dt} = \frac{F(C_{k_{in}} - C_{k_{out}})}{V} + \sum_1^{n_r} (\alpha_{kj} r_j) \text{ mol/h} \quad (77.8)$$

The reactor model will comprise an equation like Eq. (77.8) for each component  $k$  in the CSTR. Another advantage of the unsteady state model is that stoichiometry is automatically preserved without the need for any constraints. It may be used readily to simulate a system comprising a large number of components and reactions in a multistage system of CSTRs, which is otherwise mathematically intractable. And, of course, it may be used to study the dynamic behavior of the system as well. Therefore, it is the preferred design approach for multistage CSTR systems.

In the *ideal steady state plug flow reactor*, all elements of fluid that enter the reactor together travel down its length and exit together, having thus stayed in the reactor for identical lengths of time. The volume element will be only a differential slice of the reactor cross section, denoted by  $dV$ . There will be no accumulation term, since the reactor is at steady state. The differential concentration difference across the differential volume element will be denoted by  $dC$ . Thus, Eq. (77.3) is once again applicable and simplifies to

$$F_e dC_k = \sum_1^{n_r} (\alpha_{kj} r_j) dV_e \quad (77.9)$$

If  $F$  changes as the reaction proceeds (as with many gas-phase reactions), then this can be accommodated down the length of the plug flow reactor by modifying the above equation to

$$d(F_e C_k) = \sum_1^{n_r} (\alpha_{kj} r_j) dV_e$$

whence

$$F_e \frac{dC_k}{dV_e} + C_k \frac{dF_e}{dV_e} = \sum_1^{n_r} (\alpha_{kj} r_j) dV_e$$

$$\frac{dC_k}{dV_e} = \frac{\sum_1^{n_r} (\alpha_{kj} r_j)}{F_e} - \frac{C_k}{F_e} \frac{dF_e}{dV_e} \quad (77.10)$$

Equation (77.10) describes the rate of change of concentration  $C$  of species  $k$  with volume down a plug flow reactor as a function of the reaction rates, concentration, and flow. It also reflects the change in molar flow as the reaction proceeds.

A complete *isothermal* plug flow reactor model can readily be constructed using as many Eqs. (77.10) as there are components  $k$ , and as many kinetic models as there are reactions  $j$ . For *nonisothermal* reactors, differential equations that describe the temperature changes down the length of the reactor can be constructed in an analogous fashion, using the molar heat generation for each reaction  $j$  and its corresponding reaction rate  $r_j$  and heat transfer terms appropriate to the reactor type and geometry. For a multitube plug flow reactor with coolant on the outside of the tubes, the equation for reaction temperature (in degrees/volume) is as follows:

$$\frac{dT_r}{dV_e} = \frac{\sum_1^{n_r} (r_j \Delta H_j) - \frac{4U}{D_t} (T_r - T_c)}{F_e \rho_p c_p} \quad (77.11)$$

For coolant temperature,

$$\frac{dT_c}{dV_e} = \frac{\frac{4U}{D_t} (T_r - T_c) (\text{Mode})}{F_c \rho_c c_c} \quad (77.12)$$

Combined model equations like these are simplified in the sense that they do not account for departures from ideality because of nonideal mixing patterns in the case of stirred reactors, radial and axial diffusion effects in the case of tubular catalytic reactors, or the very specialized phenomena in fluidized beds and fixed-bed multiphase reactors. Yet they are surprisingly applicable in many industrial applications—and will certainly be preferred to geometric scaleup in almost all cases.

## **77.2 Protocol for the Rational Design of Chemical Reactors**

---

Given the distinctions between kinetics models and reactor models, as well as the characteristics of combined reaction and reactor models, we can now establish a general protocol for rational design that will apply to many types of chemical reactors in industrial situations. The protocol comprises several steps, each of which is discussed in the following sections.

### **Step 1: Select the Type of Reactor for the Commercial Process**

First, select one or more potentially useful types of reactors for the commercial process. In many instances, the preferred reactor type will be known from past experience with the same or similar reactions. Even so, the scaleup characteristics and requirements for two important types of reaction—batch reactions and solid-catalyzed reactions—merit special attention here. The reader is referred to the large open literature for additional information. Texts by Froment and Bischoff [1979], and Levenspiel [1972] are classic and are particularly recommended.

### **Scaleup of Laboratory Batch Reactions**

***Plant-Size Batch Reactors.*** Many reactions are conveniently studied in laboratory batch reactors, but batch reactors often are not preferred for full-scale operations, particularly if the reaction is rapid or if the planned plant will be quite large. Plant-size batch reactors are costly to operate, simply because they must be shut down, emptied, and recharged after a fairly short time—typically after only a few hours. This means that each reactor produces chemicals only on a part-time basis. As a consequence, batch reactors are usually preferred only for fairly high-priced specialty chemicals like pharmaceuticals that are produced at fairly low volumes—say, under 50 000 000 pounds per year—so that the required number and size of batch reactors are reasonable.

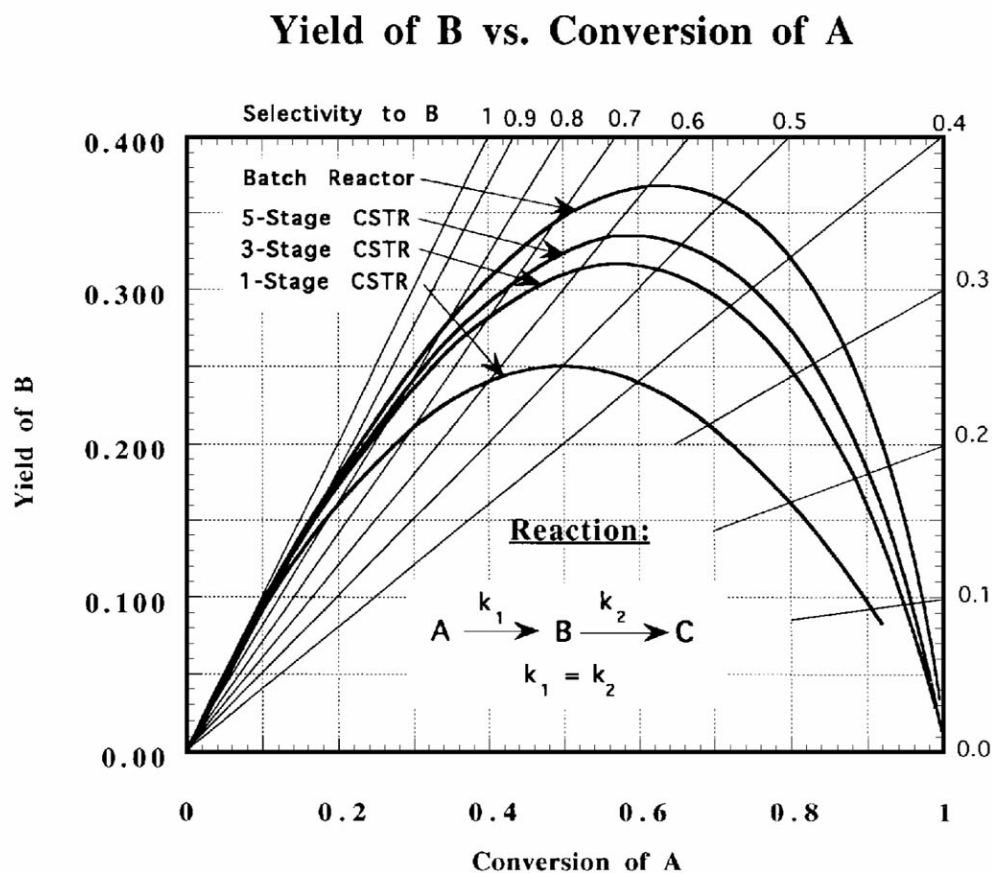
***Ideal Plug Flow Reactors (PFRs).*** PFRs have the same residence-time distribution as ideal batch reactors—that is, each element of feed is exposed to reaction conditions for exactly the same length of time. They are particularly useful for high-volume, low-priced commodity chemicals, for which the laboratory batch reactor is preferred. If the reaction time is short—say, under an hour—it may be practicable to use some type of large-scale plug flow reactor (PFR) for the plant. A baffled column is a common example. More often than not, however, batch times are at least several hours, and a plug flow continuous reactor would be too large and too costly for full-scale plant use. However, PFRs are routinely used in industry for solid-catalyzed reactions, as discussed later. The difference here is that the catalyst dramatically accelerates the reaction so that large-scale plug flow reactors are quite practicable.

***Single and Multistage CSTRs.*** The single-stage continuous stirred tank reactor (CSTR) is relatively inexpensive and provides good temperature control, but it has a broad residence-time distribution. This means that some of the feed may be under reaction for a very short time and some may be in the reactor for an extended time. Also, concentrations of reactants and products throughout a CSTR will be the same as their exit concentrations, so that the reactions are conducted at minimum reactant concentration and maximum product concentration. This will mean a relatively slow reaction rate with maximum exposure of products to further reaction, which may lead to relatively low production rates and relatively high by-product formation rates.

***Residence-Time Distribution and the Effects of Staging.*** To overcome some of the disadvantages of both the PFR and CSTR reactors for reactions that are ideally carried out by batch in the laboratory, several CSTRs are frequently connected in series. Their residence-time distributions will be intermediate between the very narrow distributions of the batch reactor or PFR and the very broad distributions of the CSTR. Such a multistage reactor may be a good compromise, but it will not operate identically to the laboratory batch reactor.

The effect of staging on a chemical reaction may be inferred from Fig. 77.2, in which a simple sequential reaction of  $A$  going to  $B$  (desired) and then to  $C$  (undesired) is assumed. The figure shows that the batch reactor has the highest conversion of  $A$  and the highest yield of  $B$ , and that the CSTR has the lowest. The three- and five-stage CSTRs are intermediate between the batch and CSTR reactors. In practice, multistage systems of two to five CSTRs are common. Froment and Bischoff [1979], Levenspiel [1972], and others have written extensively on residence-time distribution and its impact on product yields and selectivities. These concepts are important to the successful commercialization of batchwise laboratory reaction technology.

**Figure 77.2** Effects of residence-time distribution.



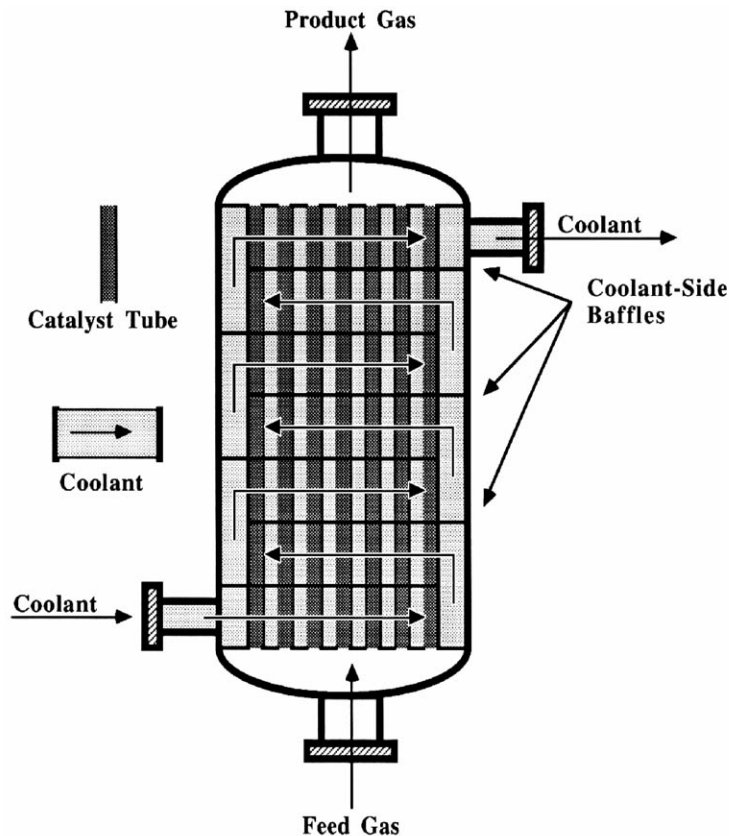
### Scaleup of Solid-Catalyzed Reactions

Solid catalysts are widely used in the chemical industry in several types of packed-bed reactors, slurry reactors, and fluidized bed reactors. Commercial processes frequently utilize solid-catalyzed gas-phase reactions, but it is not uncommon for them to use both gas and liquid streams, which greatly complicates the hydrodynamics. Reactors for solid-catalyzed reactions are all subject to scaleup problems because of differences in mass- and heat-transport in large-scale equipment and laboratory equipment.

*Packed-bed reactors* are probably used more than any other type for solid-catalyzed reactions. They tend to have residence-time distributions that closely approach plug flow, especially for plant-scale single-phase systems in which the bed length is at least 5 to 10 meters. Their narrow residence-time distribution makes them preferred from the standpoint of being able to control product distribution in systems of sequential reactions. Equations (77.10)–(77.12) are appropriate here.

*Shell-and-tube packed-bed reactors* have excellent heat removal characteristics, particularly if the tube diameters are fairly small—say, one to one-and-a-half inches. A schematic of a typical plant-scale shell-and-tube reactor is shown in Fig. 77.3. Although relatively expensive, such reactors can usually be designed rationally with confidence.

**Figure 77.3** Conceptual shell-and-tube fixed-bed reactor. (Source: Reproduced with permission of the American Institute of Chemical Engineers from Cropley, J. B. 1990. Development of optimal fixed bed catalytic reaction systems. *Chemical Engineering Progress* 86(2): 32–39. American Institute of Chemical Engineers, New York, February 1990. ©1990 AIChE. All rights reserved.)



*Adiabatic packed-bed reactors* are attractive because of their relatively low cost. (At their simplest, they can be little more than an empty tank filled with catalyst pellets.) However, they suffer from the effects of an uncontrolled reaction temperature and tend to drift towards the maximum possible attainable temperature, which usually means that the limiting reactant is completely consumed or that equilibrium has been reached. This is a desirable property for some reactions (e.g., hydrogenations), but usually the chemical selectivity suffers as a result. Unwanted

by-products may result, even in hydrogenation systems. The adiabatic reactor usually is not recommended where temperature control is important.

*Multiphase packed-bed reactors* (e.g., trickle beds) are widely used, but the transport of reactants and products between the flowing gas and liquid and the solid catalyst is a major uncertainty. A lot of work remains to be done before the rational design of these reactors can be undertaken with confidence. Instead, back-and-forth experimentation and mathematical analysis of the hydrodynamics is necessary. Suffice it to note here that the transport characteristics of multiphase reactors are different in each of the several hydrodynamic regimes that may be experienced (e.g., trickle flow, bubbling flow, pulsing flow, slug flow, mist flow). A priori calculations using relationships from the open literature can often predict whether reaction kinetics or mass transfer will limit the reactor's performance, and the preliminary design sometimes can be developed rationally thereafter. Pilot-scale experimental verification of the performance of the final design in the *same hydrodynamic region* as the plant reactor is nonetheless essential to avoid surprises. There is an abundant literature on this type of reactor, and the excellent text by Ramachandran and Chaudhari [1983] is a good place to obtain an introduction to this complex technology.

*Fluidized-bed reactors* are widely used in fluidized catalytic cracking, the manufacture of polyethylene and polypropylene, the manufacture of silicones from silicon, and some other commercial reactions. The fluid and solid dynamics of these systems are extremely complex, and available models are best described as learning models, rather than predictive models for reaction system design. Scaleup is typically done incrementally in a series of pilot-plant reactors. Despite the well-known advantages of these systems for some purposes (excellent temperature control, absence of diffusional and transport restrictions), the decision to use fluidized systems for new applications must not be taken lightly. Although the solid phase may usually be assumed to be well mixed, the residence-time distribution of the fluid phase is complex and largely unpredictable. It follows that the performance of a scaled-up reactor is also largely unpredictable if the fluid-phase residence-time distribution is important.

It is worth noting that, with few exceptions, all successful commercial fluidized bed reaction systems involve a solid phase that is always in some kind of rapid transition. Fluidized catalytic-cracking catalyst becomes coked and inactive in only 3 to 5 seconds and is continuously removed from the fluidized riser reactor and regenerated by burning in dilute oxygen. The solid phase is in fact the product polyolefin in fluidized systems like Union Carbide's Unipol™ polyolefins process. Dimethyldichloro silane (an intermediate in the manufacture of silicone oils and other products) is manufactured by reacting silicon metal and methyl chloride in a fluidized-bed reactor. Here, the silicon reactant is in the form of a fine metal powder that is continually consumed by the reaction and that comprises the solid phase in the reactor. An exception to the above observation is the Badger process for the manufacture of phthalic anhydride in a fluidized-bed reactor, in which the solid is a catalyst that is not undergoing any rapid change. It is carried out in a fluidized bed because the temperature control is important to the process.

The technology of fluidization has been studied in depth since before World War II and continues to be studied still because of its importance in those industries that depend upon it. AIChE has published several volumes on fluidization in its symposium series, and more appear

periodically. Some excellent texts exist on fluidization phenomena; that by Kunii and Levenspiel [1969] is considered a classic.

*Slurry reactors* are attractive for many gas-liquid systems that are catalyzed by solid catalysts, but their design is nearly as complicated as for fluidized-bed systems. There is an extensive open literature on this type of reactor. The Air Products Company has published a number of reports on work done under contract for the U.S. Department of Energy and has a large pilot plant at LaPorte, Texas, for the manufacture of methanol and higher alcohols from CO and hydrogen. These reports and the text on multiphase reactors by Ramachandran and Chaudhari [10] are recommended.

## Step 2: Design the Laboratory to Generate Reaction Kinetics Data

The second step in the protocol for rational design is to design the laboratory reaction system specifically to generate kinetics rate data. By now it should be clear that the kinetic model is the link between the laboratory operations and the large-scale plant design. The experimental reactor for kinetics studies will ordinarily not look at all like the final plant reactor. Rather, it will be designed to obtain the kinetic data necessary for kinetic model development. Three primary types of laboratory reactor are suitable for design-quality kinetics studies:

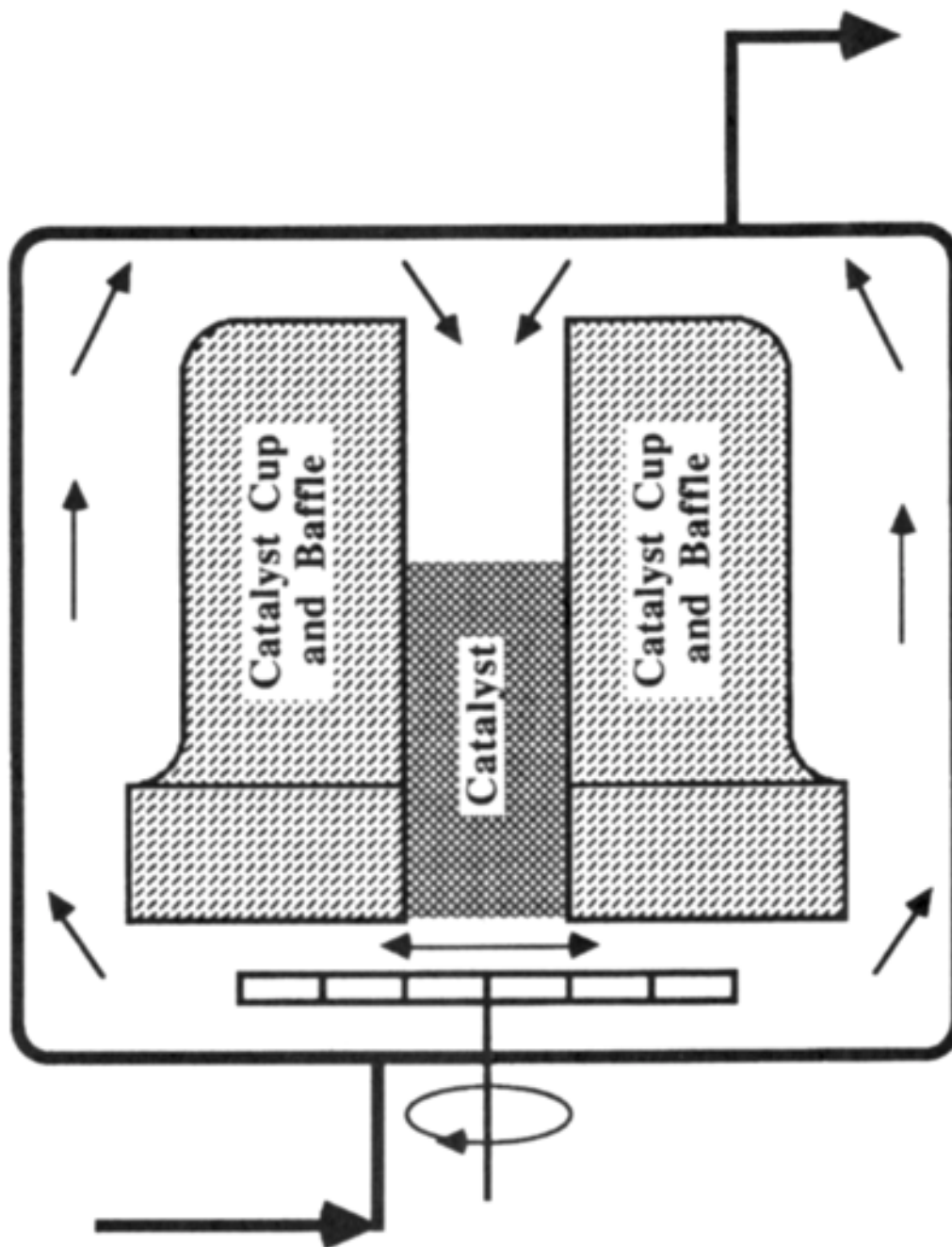
- The batch reactor
- The long-tube reactor with sample points along its length
- The continuous stirred tank reactor, or CSTR

The following paragraphs discuss each of these types, with the emphasis upon what kinds of reactions are suitable for each and any special considerations that may apply.

*Laboratory batch reactors* are found in virtually limitless variety in most industrial chemical laboratories. For kinetics studies it is imperative that chemical analyses be obtained at several times during the reaction period. This sometimes poses problems if the reaction starts before the desired reaction temperature has been reached or if the reaction proceeds so quickly that multiple samples are not practical. Likewise, the loss of reacting volume due to sampling may be important, particularly if a solid catalyst is involved. Both of these problems are best handled during mathematical analysis of the data by forcing the simulated time-temperature and time-reacting volume profiles to be the same as the observed ones.

Batch laboratory reactors are suitable for either uncatalyzed or catalyzed liquid-phase or gas-liquid reactions. In special situations they may be useful for gas-phase reactions as well. They are especially useful for slurry-catalyzed reactions, but they can also be used with pelleted catalysts, provided that provision is made to retain the pellets in a basket or container through which the fluid passes. Both the Berty reactor [see Fig. 77.4 and (Berty, 1974)] and the Carberry rotating basket reactor [Levenspiel, 1972] have been widely used for batchwise kinetic studies of catalytic reactions, although their best use is probably in continuous gas-phase kinetics studies.

**Figure 77.4** The Berty reactor for experimental catalyst testing and kinetics. (*Source:* Reproduced with permission of the American Institute of Chemical Engineers from Cropley, J. B. 1990. Development of optimal fixed bed catalytic reaction systems. *Chemical Engineering Progress* 86(2): 32–39. American



*Long-tube reactors* for kinetics studies will typically be of a length to promote both plug flow characteristics and good mass and heat transfer so that these physical processes do not mask the chemical reaction rates. Tube length per se is not critical, although it is highly desirable that the length-to-diameter ratio be at least 100:1 to avoid the effects of axial mixing and departure from plug flow behavior. Tube diameter is not particularly important, but should be small enough to ensure good heat transfer. If solid-catalyst pellets are to be used, the tube diameter should be no more than four or five pellet diameters to avoid radial temperature gradients. It is important that provision be made for samples to be taken at multiple points down the tube length. Reactors like these are particularly well suited for kinetics studies using plant-scale catalyst pellets and for the

study of the kinetics of sequential by-product formation, in which the desired product reacts to form unwanted by-products.

Perhaps the most difficult requirement from the standpoint of experimental reactor design is to provide for multiple sampling points down the length of the tube. It is relatively easy to make such a reactor using lengths of stainless steel tubing connected by tubing tees, which can then be used simultaneously as sample taps and for the insertion of thermocouples. Tubing diameter will typically be between 0.25 and 0.50 inches, and the length will be five to six feet. Sample taps at 12-inch intervals will provide good composition and temperature profiles. Excellent temperature control can be attained in such a reactor if it is immersed in a thermostated heat transfer fluid or fluidized sand-bath heater.

*Continuous stirred tank reactors (CSTRs)* are ideally suited for kinetics studies for many types of reactions, owing largely to the ease with which reaction rates can be measured directly. Kinetics models are readily developed from CSTR data, as discussed by Cropley [1978]. The Berty and Carberry reactors cited previously are especially useful for continuous studies of catalytic kinetics, using real catalyst pellets. There is an abundant literature on their use; Cropley [1990] describes an overall strategy for their use in catalytic reactor design.

### Step 3: Use Statistically-Valid Experimental Programs and Models

The third element of the protocol is to utilize statistically valid experimental programs and data analysis for kinetic model development. Usually, kinetic data should be generated from statistically designed experimental programs, such as the factorial or central composite design, for which an abundant literature is available. The writings of Hendrix [1979] are recommended. Cropley [1978] describes the heuristic development of both exponential and hyperbolic kinetic models from a statistically designed data set. Table I from that article is an example of a central composite statistical design for the study of the kinetics of a fictitious catalytic reaction (the oxidation of Dammitol to Valualdehyde). The experimental reactor was assumed to be a CSTR like the Berty reactor, which permitted kinetic rates to be observed directly, as in Eq. (77.7). The synthetic data in that table were developed from the following "true" model, with the incorporation of 20% normally distributed random error [reproduced with permission of the American Chemical Society from (Cropley, 1978)].

$$r_{\text{Val}} = \frac{4.67(10^{11})e^{-20000/RT} (P_{\text{O}_2})^{0.5} (P_{\text{Dam}})^{1.0}}{1 + 5.52(10^{-4})e^{5000/RT} (P_{\text{O}_2})^{0.5} + 7.64(10^{-4})e^{5000/RT} (P_{\text{Val}})^2} \text{ Gmols/Kgcat/H}$$

(77.13)

If a CSTR is used as the experimental reactor, the experimental design should include the independent control of any product species that might influence the reaction rates to avoid systematic bias in the kinetic parameters, as discussed by Cropley [1987].

In the heuristic study cited above, log-linear multiple regression was used for the development of exponential models, and the Nelder-Mead nonlinear search algorithm [Nelder and Mead,

1965] was used for estimation of the nonlinear parameters in the hyperbolic models. (Although Nelder-Mead tends to converge more slowly than some other algorithms, it is robust, stable, and reliable for nonlinear estimation and optimization studies.)

## **Step 4: Develop Computer Programs for Reactor Simulation and Design**

The fourth element of the protocol is to develop computer programs for reactor simulation and design. The typical reaction system design model will comprise several dozen differential equations and a number of nonlinear constraints as well. Consider very carefully just how complex the final models should be. The determination of the true economic optimum may require that the reactor be simulated iteratively many thousands of times, and the model at this point should be no more complex than necessary in order to minimize computer time. Therefore, simulation models for reactor design and optimization should in most cases be based primarily upon the kind of simple idealized reactors represented by Eqs. (77.3)–(77.12), as discussed earlier. Even so, simulation models can become unwieldy. For example, a five-stage CSTR model for a system of four chemical components and temperature will comprise 25 nonlinear differential equations similar to Eq. (77.8). Any of a number of numerical integration techniques may be used for the solution of the differential equations; the fourth-order Runge-Kutta algorithm is perhaps the most common.

## **Step 5: Develop the Economically Optimum Reactor Design**

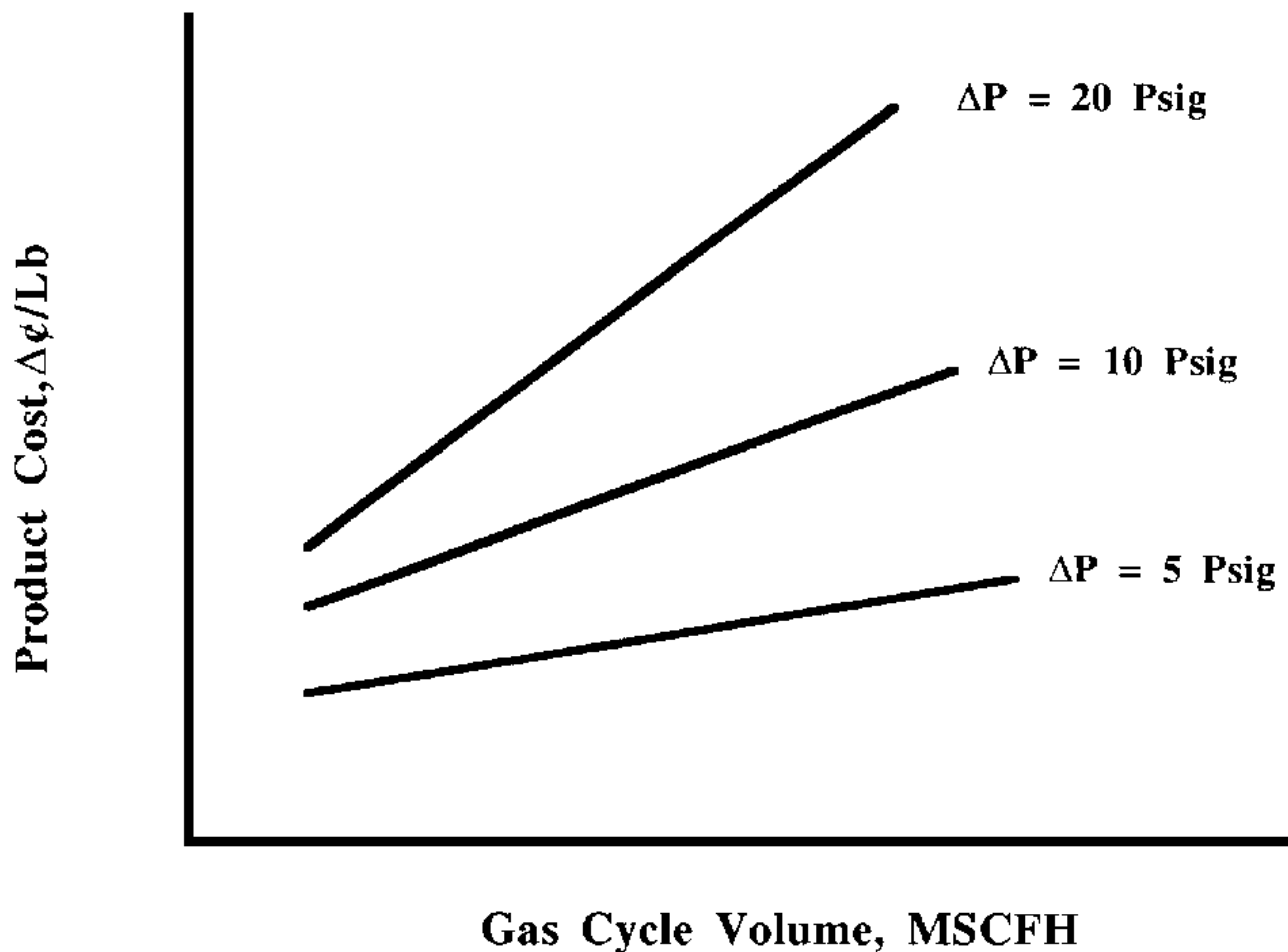
The fifth protocol for rational design is to develop economically optimum reactor designs. The potentially useful reactor types should be compared to one another at their individual economic optimum design and operating conditions. Arrive at these for each type by varying the simulated reactor size and geometry (e.g., diameter, length and number of tubes, or agitator horsepower and vessel diameter and height) and operating conditions (like pressure, flow rate, reactant concentration, coolant temperature, and so on). A suitable optimization procedure, such as the Nelder-Mead algorithm cited previously [Nelder and Mead, 1965], should be used.

### **The Objective Function for Optimization**

The design process will include the computation of objective economic or reactor performance criteria for the comparison of optimized design alternatives. This objective function must be reasonably accurate, yet simple enough to be evaluated easily and quickly for each iteration. It is convenient and quite accurate to use simple linear relationships for optimization criteria like that in Fig. 77.5, which illustrates the dependence of incremental product cost on cycle gas flow rate and catalyst bed pressure drop for a hypothetical process. Several similar relationships can comprise an easily used objective function for optimization. Relationships like this can be developed easily from detailed economic analyses of a small number of base case designs. Their development was discussed by Cropley [1990].

**Figure 77.5** Elements of product cost. (Source: Reproduced with permission of the American Institute of Chemical Engineers from Cropley, J. B. 1990. Development of optimal fixed bed catalytic reaction systems. *Chemical Engineering Progress* 86(2): 32–39. American Institute of Chemical Engineers, New York, February 1990. ©1990 AIChE. All rights reserved.)

### Incremental Product Cost vs. Gas Cycle Volume



#### Explicit and Implicit Constraints

The optimization package will normally utilize both explicit and implicit constraints to relate the reactor to the rest of the process. In a typical design, for example, reactor inlet pressure and reactor gas flow rate might be *explicitly* constrained to reasonable ranges. Likewise, the maximum reactor temperature might be *implicitly* constrained not to exceed a stipulated maximum. Constraints like these are at the very heart of the optimization process. At the same time, their formulation is both esoteric and beyond the scope of this article, and they are not extensively treated in the open literature. It is recommended that an optimization or numerical analysis specialist be consulted in their development.

## Step 6: Validate the Design in a Pilot Plant Reactor

The final step in the protocol for rational design is to validate the overall optimum design by operation of a pilot reactor system. This is the *only time* that scaleup, per se, will be considered in the design. Here again, this may not necessarily involve a pilot reactor that is geometrically similar to the final plant design, although it may be in some cases. It will be important to design the pilot reactor to be able to confirm the predicted reaction yields and selectivities under design conditions. It is vital that all important recycle streams be incorporated into the pilot plant system—which will then be, to the extent possible, a scaled-down version of the integrated commercial process. Typically, recycle streams include previously unreacted raw materials, by-products that can be reverted to useful product, or potential pollutants that can simply be destroyed by further reaction in the reactor. But trace components and minor species can build up in recycle systems to many times their single-pass concentrations, and they may have adverse effects on catalyst life, equilibrium conversion, crude product quality, and so on. It is important that the effects of recycled species be incorporated into the kinetics model for operational monitoring and control. Unanticipated effects of recycle streams probably account for a significant fraction of scaleup problems in commercial systems.

Finally, please note that this chapter has not discussed the *size* of the pilot plant reactor—size per se really is not an issue. What *is* important is that it function in such a way as to test the rational design before it is built. More discussion of process optimization and validation can be found in Cropley [1990].

## Nomenclature

### Uppercase Symbols

$A, B$	Reactants
$C_k$	Concentration of $k$ th chemical component, in mols/volume units
$D_t$	Tube diameter, in linear units
Dam	Fictitious component Dammitol
$F_e, F_c$	Flow rate of process fluid ( $e$ ) or of coolant ( $c$ ) through the volume element, in volume/time units
$\Delta H_j$	Heat of reaction of $j$ th reaction in heat/mol units
$K_{oj}, E_{aj}$	Arrhenius kinetic parameters for reaction $j$
$K_{Aj},$ $K_{Bj},$ $K_{Pkj}$	Kinetic parameters associated with reactants $A$ and $B$ and products $P_k$ for reaction $j$
Mode	(-1) if coolant flows countercurrent to process stream flow (+1) if flows are cocurrent (0) if coolant is isothermal (infinite flow, boiling, etc.)

$P_k$	Reaction products
$R$	Gas constant, typically 1.987 cal/Gmol/K for kinetics models
$T_r, T_c$	Reaction and coolant temperature, respectively
$U$	Overall heat transfer coefficient, in heat/area/time/temperature units
Val	Fictitious component Valualdehyde
$V_e$	An element of volume of any reactor
$W_c$	Weight of catalyst in the reactor, in weight units

## Lowercase and Greek Symbols

$\alpha_{kj}$	Stoichiometric coefficient for species $k$ in reaction $j$
$c_c$	Heat Capacity of coolant stream, in heat/mass/temperature units
$c_p$	Heat capacity of flowing process stream, in heat/mass/temperature units
$n_c$	Total number of products $k$ in the kinetic model
$n_r$	Number of reactions $j$ in the kinetic model
$n_t$	Number of tubes in a tubular reactor
$\rho_p, \rho_c$	Density of process stream ( $p$ ) or coolant ( $c$ ), in mass/volume units
$r$	Kinetic reaction rate, mols/volume/time (or mols/wt. catalyst/time for catalytic reactions)
$t$	Time, in units consistent with $F, r, U$

## Defining Terms

**Chemical reaction:** The chemical transformation of one or more reactant species into one or more chemical products, usually with the evolution or absorption of heat.

**Chemical reactor:** The vessel in which a chemical reaction is conducted.

**Continuous stirred tank reactor:** A well-mixed continuous reactor, characterized by a broad residence time distribution.

**Conversion:** The fraction of a feed component that undergoes chemical transformation in the reactor.

**Plug flow reactor:** A type of reactor in which all entering elements of fluid have the same residence time. The residence time distribution is thus extremely narrow.

**Residence time:** The amount of time that a reactive mixture spends in a chemical reactor.

**Residence-time distribution (RTD):** The spread of residence times that different elements entering a reactor spend in it. RTD is one of the distinguishing characteristics of different reactor types.

**Selectivity:** The fraction of all of a feed component that is converted to form a specified product.

**Yield:** The fraction of all of a feed component entering a reactor that is converted to a specified product. Yield = (Selectivity)(Conversion).

## References

- Berty, J. M. 1974. Reactor for vapor-phase catalytic studies. *Chem. Eng. Prog.* 70: 57–584.
- Cropley, J. B. 1978. Heuristic approach to complex kinetics. In *Chemical Reaction Engineering*  $\frac{3}{4}$ Houston, D. Luss and V. Weekman, eds. ACS Symposium Series 65. Paper 24.
- Cropley, J. B. 1987. Systematic errors in recycle reactor kinetics studies. *Chemical Engineering Pro*

- 50. American Institute of Chemical Engineers, New York.
- Cropley, J. B. 1990. Development of optimal fixed bed catalytic reaction systems. *Chemical Engine*
- 39. American Institute of Chemical Engineers, New York.
- Froment, G. F. and Bischoff, K. B. 1979. *Chemical Reactor Analysis and Design*. John Wiley & Sons, New York.
- Hendrix, C. D. 1979. What every technologist should know about experimental design. *Chemtech*. 1
- 174. American Chemical Society, Washington, DC.
- Kunii, D. and Levenspiel, O. 1969. *Fluidization Engineering*. John Wiley & Sons, New York.
- Levenspiel, O. 1972. *Chemical Reaction Engineering*, 2nd ed. John Wiley & Sons, New York.
- Nelder, J. A. and Mead, J. R. 1965. A simplex method for function minimization. *Computer Journal*.
- 313.
- Ramachandran, P. A. and Chaudhari, R. V. 1983. *Three-Phase Catalytic Reactors*. Gordon and Breach Science, New York.

## **Further Information**

### **Professional Organizations**

- The American Institute of Chemical Engineers (three national meetings per year). 345 E. 47th St., New York, NY 10017. Phone (212) 705-7322.
- The American Chemical Society (several national/regional meetings each year). 1155 16th St., N.W., Washington, DC, 20036. Phone (202) 872-4600.

### **Special Meetings and Conferences**

- The Engineering Foundation Conferences on Chemical Reaction Engineering. 345 East 47th Street, New York, NY 10017. Phone (212) 705-7835.
- International Symposia on Chemical Reaction Engineering (even years). Sponsored by American Institute of Chemical Engineers, American Chemical Society, Canadian Society for Chemical Engineering, and the European Federation of Chemical Engineering.

# Senthil Kumar's eBooks Collection - 2007



SD. Senthil Kumar,  
Process Engineer.