PRINCIPLES OF CHEMICAL REACTOR ANALYSIS AND DESIGN

New Tools for Industrial Chemical Reactor Operations

Second Edition

UZI MANN
Texas Tech University

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In memory of my sister, Meira Lavie

To Helen, and to David, Amy, and Joel

"Discovery consists of looking at the same thing as everyone else and thinking something different."

Albert Szent-Györgyi
Nobel Laureate, 1937

CONTENTS

PREFACE

I decided to write this book because I was not pleased with the way current textbooks present the subject of chemical reactor analysis and design. In my opinion, there are several deficiencies, both contextual and pedagogical, to the way this subject is now being taught. Here are the main ones:

- Reactor design is confined to simple reactions. Most textbooks focus on the design of chemical reactors with single reactions; only a brief discussion is devoted to reactors with multiple reactions. In practice, of course, engineers rarely encounter chemical reactors with single reactions.
- Two design formulations are presented; one for reactors with single reactions (where the design is expressed in terms of the conversion of a reactant), and one for reactors with multiple reactions (where the design formulation is based on writing the species balance equations for all the species that participate in the reactions). A unified design methodology that applies to all reactor operations is lacking.
- The operations of chemical reactors are expressed in terms of extensive, system-specific parameters (i.e., reactor volume, molar flow rates). In contrast, the common approach used in the design of most operations in chemical engineering is based on describing the operation in terms of dimensionless quantities. Dimensionless formulations provide an insight into the underlining phenomena that affect the operation, which are lost when the analysis is case specific.
- The analysis of chemical reactor operations is limited to simple reactor configurations (i.e., batch, tubular, CSTR), with little, if any analysis, of other configurations (i.e., semibatch, tubular with side injection, distillation reactor),

which are commonly used in industry to improve the yield and selectivity of the desirable product. These reactor configurations are discussed qualitatively in some textbooks, but no design equations are derived or provided.

- Most examples cover isothermal reactor operations; nonisothermal operations are sparsely discussed. In the few nonisothermal examples that are presented, usually single reactions are considered, and the dependency of the heat capacity of the reacting fluid on the temperature and composition is usually ignored. Consequently, the effect of the most important factor that affect the rates of the chemical reactions—the temperature—is not described in the most comprehensive way possible.

- In all solved examples, the heat-transfer coefficient is usually specified. But, what is not mentioned is the fact that the heat transfer can be determined only after the reactor size and geometry are specified, and the flow conditions are known. Those, of course, are not known in the initial steps of reactor design. What is needed is a method to estimate, a priori, the range of heat-transfer coefficient and then determine what reactor configuration and size provide them.

Considering those points, the current pedagogy of chemical reactor analysis and design falls short of providing students with the needed methodology and tools to address the actual technical challenges they will face in practice.

This book presents a different approach to the analysis of chemical reactor operations—reaction-based design formulation rather than the common species-based design formulation. This volume describes a unified methodology that applies to both single and multiple reactions (reactors with single reactions are merely simple special cases). The methodology is applicable to any type of chemical reactions (homogeneous, heterogeneous, catalytic) and any form of rate expression. Reactor operations are described in terms of *dimensionless* design equations that generate dimensionless *operating curves* that describe the progress of the individual chemical reactions, the composition of species, and the temperature. All parameters that affect the heat transfer are combined into a single dimensionless number that can be estimated a priori. Variations in the heat capacity of the reacting fluid are fully accounted. The methodology is applied readily to all reactor configurations (including semibatch, recycle, etc.), and it also provides a convenient framework for *economic-based* optimization of reactor operations.

One of the most difficult decisions that a textbook writer has to make is to select what material to cover and what topics to leave out. This is especially difficult in chemical reaction engineering because of the wide scope of the field and the diversity of topics that it covers. As the title indicates, this book focuses on the analysis and design of chemical reactors. The objective of the book is to present a comprehensive, unified methodology to analyze and design chemical reactors that overcomes the deficiencies of the current pedagogy. To concentrate on this objective, some topics that are commonly covered in chemical reaction engineering textbooks (chemical kinetics, catalysis, effect of diffusion, mass-transfer limitation, etc.) are

not covered here. Those topics are discussed in detail in many excellent textbooks, and the reader is expected to be familiar with them. Also, advanced topics related to special reactor types (fluidized bed, trickle bed, etc.) are not covered in the text.

Students require knowledge of solving (numerically) simultaneous first-order differential equations (initial value problems) and multiple nonlinear algebraic equations. The use of mathematical software that provides numerical solutions to those types of equations (e.g., Matlab, Mathematica, Maple, Mathcad, Polymath, HiQ, etc.) is required. Numerical solutions of all the examples in the text are posted on the book web page.

The problems at the end of each chapter are categorized by their level of difficulty, indicated by a subscript next to the problem number. Subscript 1 indicates simple problems that require application of equations provided in the text. Subscript 2 indicates problems whose solutions require some more in-depth analysis and modifications of given equations. Subscript 3 indicates problems whose solutions require more comprehensive analysis and involve application of several concepts. Subscript 4 indicates problems that require the use of a mathematical software or the writing of a computer code to obtain numerical solutions.

I am indebted to many people for their encouragement and help during the development of this text. M. D. Morris was the driving force in developing this book from early conception of the idea to its completion. Stan Emets assisted in solving and checking the examples, and provided constructive criticism. My wife, Helen Mann, typed and retyped the text, in which she put not only her skills, but also her heart.

Uzi Mann

NOTATION

All quantities are defined in their generic dimensions (length, time, mass or mole, energy, etc.). Symbols that appear in only one section are not listed. Numbers in parentheses indicate the equations where the symbol is defined or appears for the first time.

A	Cross-section area, area
a	Species activity coefficient
C	Molar concentration, mole/volume
CF	Correction factor of heat capacity, dimensionless (Eq. 5.2.19)
c_p	Mass-based heat capacity at constant pressure, energy/mass K
$\hat{c}_p$	Molar-based heat capacity at constant pressure, energy/mole K
D	Reactor (tube) diameter, length
DHR	Dimensionless heat of reaction, dimensionless (Eq. 5.2.23)
d_p	Particle diameter, length
E	Total energy, energy
E_a	Activation energy, energy/mole extent
e	Specific energy, energy/mass
F	Molar flow, mole/time
f	Conversion of a reactant, dimensionless (Eqs. 2.6.1a and 2.6.1b)
f	Friction factor, dimensionless
G	Mass velocity, mass/time area
G_j	Generation rate of species j in a flow reactor, moles j/time
g	Gravitational acceleration, length/time^2
H	Enthalpy, energy
$\hat{H}$	Molar-based specific enthalpy, energy/mole
ΔH_R	Heat of reaction, energy/mole extent

h	Mass-based specific enthalpy, energy/mass
HTN	Dimensionless heat-transfer number, dimensionless (Eq. 5.2.22)
$\mathbf{J}_j$	Molar flux of species j, mole j/(time area)
J	Total number of species
K	Equilibrium constant
KE	Kinetic energy, energy
$k, k(T)$	Reaction rate constant
k	Index of dependent reactions
L	Length, length
M	Mass, mass
MW	Molecular weight, mass/mole
m	Index of independent reactions
$\dot{m}$	Mass flow rate, mass/time
$N, N(t)$	Molar content in a reactor, moles
n	Index for chemical reactions
$\mathbf{n}$	Unit outward vector
$(n_j - n_{j_0})_i$	Moles of species j formed by the ith reaction, moles of species j
OC	Operating cost
P	Total pressure, force/area
PE	Potential energy, energy
$Q(t)$	Heat added to the reactor in time t, energy
$\dot{Q}$	Rate heat added to the reactor, energy/time
R	Gas constant, energy/temperature mole
R	Recycle ratio (Eq. 9.4.9) dimensionless
r	Volume-based rate of a chemical reaction, mole extent/time volume
(r_j)	Volume-based rate of formation of species j, mole j/time volume
$(r_j)_s$	Surface-based rate of formation of species j, mole j/time surface area of catalyst
$(r_j)_w$	Mass-based rate of formation of species j, mole j/time catalyst mass
S	Surface area, area
s_j	Stoichiometric coefficient of species j, mole j/mole extent
SC	Separation cost
T	Temperature, K or $^\circ$R
t	Time, time
t_{cr}	Characteristic reaction time, time (Eq. 3.5.1)
U	Internal energy, energy
U	Heat-transfer coefficient, energy/time area K
u	Mass-based specific internal energy, energy/mass
u	Velocity, length/time
V	Volume, volume
V_R	Reactor volume, volume

Val$_j$	Value of species j, \$/mole
v	Volumetric flow rate, volume/time
W	Work, energy
X, $X(t)$	Extent of a chemical reaction, mole extent (Eq. 2.3.1)
$\dot{X}$	Reaction extent per unit time, mole extent/time (Eq. 2.3.10)
y	Molar fraction, dimensionless
Z	Dimensionless extent, dimensionless (Eqs. 2.7.1 and 2.7.2)
z	Vertical location, length

Greek Symbols

α	Order of the reaction with respect to species A, dimensionless
α_{km}	Multiplier factor of mth independent reaction for kth dependent reaction (Eq. 2.4.9)
β	Order of the reaction with respect to component B, dimensionless
γ	Dimensionless activation energy, $E_a/R \cdot T_0$, dimensionless (Eq. 3.3.5)
Δ	Change in the number of moles per unit extent, mole (Eq. 2.2.5)
ε	Void of packed bed, dimensionless
η	Yield, dimensionless (Eqs. 2.6.12 and 2.6.14)
θ	Dimensionless temperature, T/T_0, dimensionless
μ	Viscosity, mass/length time
ρ	Density, mass/volume
σ	Selectivity, dimensionless (Eqs. 2.6.16 and 2.6.18)
τ	Dimensionless operating time, t/t_{cr}, or space time, $V_R/v_0 t_{cr}$, dimensionless (Eqs. 4.4.3 and 4.4.8)
Φ	Particle sphericity, dimensionless

Subscripts

0	Reference state or stream
A	Limiting reactant
all	All
cr	Characteristic reaction
D	Dependent reaction
dep	Dependent
eq	Equilibrium
F	Heating (or cooling) fluid
gas	Gas phase
I	Inert
I	Independent reaction
i	The ith reaction
in	Inlet, inlet stream
inj	Injected stream

j	The jth species
k	Index number for dependent reactions
liq	Liquid phase
m	Index number for independent reactions
op	Operation
out	Outlet
R	Reactor
S	Surface
sh	Shaft work (mechanical work)
sp	Space
sys	System
tot	Total
V	Volume basis
vis	Viscous
W	Mass basis

1

OVERVIEW OF CHEMICAL REACTION ENGINEERING*

Chemical reaction engineering (CRE) is the branch of engineering that encompasses the selection, design, and operation of chemical reactors. Because of the diversity of chemical reactor applications, the wide spectrum of operating conditions, and the multitude of factors that affect reactor operations, CRE encompasses many diverse concepts, principles, and methods that cannot be covered adequately in a single volume. This chapter provides a brief overview of the phenomena encountered in the operation of chemical reactors and of the concepts and methods used to describe them.

A chemical reactor is an equipment unit in a chemical process (plant) where chemical transformations (reactions) take place to generate a desirable product at a specified production rate, using a given chemistry. The reactor configuration and its operating conditions are selected to achieve certain objectives such as maximizing the profit of the process, and minimizing the generation of pollutants, while satisfying several design and operating constraints (safety, controllability, availability of raw materials, etc.). Usually, the performance of the chemical reactor plays a pivotal role in the operation and economics of the entire process since its operation affects most other units in the process (separation units, utilities, etc.).

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*This chapter is adopted from *Kirk-Othmer's Encyclopedia of Chemical Technology, 7th ed*, Wiley Interscience, NY (2007).

Chemical reactors should fulfill three main requirements:

1. Provide appropriate contacting of the reactants.
2. Provide the necessary reaction time for the formation of the desirable product.
3. Provide the heat-transfer capability required to maintain the specified temperature range.

In many instances these three requirements are not complimentary, and achieving one of them comes at the expense of another. Chemical reaction engineering is concerned with achieving these requirements for a wide range of operating conditions—different reacting phases (liquid, gas, solid), different reaction mechanisms (catalytic, noncatalytic), and different operating temperature and pressure (low temperature for biological reaction, high temperature for many reactions in hydrocarbon processing).

1.1   CLASSIFICATION OF CHEMICAL REACTIONS

For convenience, chemical reactions are classified in two groups:

- Homogeneous reactions—Reactions that occur in a single phase
- Heterogeneous reactions—Reactions that involve species (reactants or products) that exist in more than one phase. Heterogeneous reactions are categorized further as:
  - Fluid–fluid reactions—Chemical reactions between reactants that are in two immiscible phases (gas–liquid or liquid–liquid). The reaction occurs either at the interface or when one reactant dissolves in the other phase (which also contains the products). In many instances, the overall reaction rate depends on the interface area available, the miscibility of the reactant, and the transfer rates (e.g., diffusion) of the reactants to the interface and in the reacting phase.
  - Noncatalytic gas–solid reactions (e.g., combustion and gasification of coal, roasting of pyrites). These reactions occur on the surface of the solid. The gaseous reactant is transported to the interface, where it reacts with the solid reactant. Gaseous products are transported to the gas phase, and solid products (e.g., ash) remain in the solid. The overall reaction rate depends on the surface area available and the rate of transfer of the gaseous reactant to the solid surface.
  - Catalytic gas–solid reactions in which the reactants and products are gaseous, but the reaction takes place at the solid surface where a catalytic reagent is present. To facilitate the reaction, a large surface area is required; hence, porous particles are commonly used. The reaction takes place on the surface of the pores in the interior of the particle.

In many instances, the overall reaction rate is determined by the diffusion rate of reactants into the interior of the pore, and the diffusion of the product out of the pore.
  • Catalytic gas–liquid–solid reactions—Reactants are gases and liquids, and the reaction takes place at a solid surface where a catalytic reagent is deposited (e.g., hydrogenation reactions). Normally, the liquid reactant covers the solid surface and the gaseous reactant is transferred (by diffusion) to the catalytic site.

Each of these reaction categories has its features and characteristics that should be described quantitatively.

1.2 CLASSIFICATION OF CHEMICAL REACTORS

Chemical reactors are commonly classified by the three main charateristics:

1. Mode of operation (e.g., batch, continuous, semibatch)
2. Geometric configuration (e.g., tubular, agitated tank, radial flow)
3. Contacting patterns between phases (e.g., packed bed, fluidized bed, bubble column)

In addition, reactor operations are also classified by the way their temperature (or heat transfer) is controlled. Three operational conditions are commonly used: (i) isothermal operation—the same temperatures exist throughout the reactor, (ii) adiabatic operation—no heat is transferred into or out of the reactor, and (iii) non-isothermal operation—the operation is neither isothermal nor adiabatic.

The following terms are commonly used:

  • Batch reactors (Fig. 1.1a)—Reactants are charged into a vessel at the beginning of the operation, and products are discharged at the end of the operation. The chemical reactions take place over time. The vessel is usually agitated to provide good contacting between the reactants and to create uniform conditions (concentrations and temperature) throughout the vessel.
  • Semibatch reactor (Fig. 1.1b)—A tank in which one reactant is charged initially and another reactant is added continuously during the operation. This mode of operation is used when it is desirable to maintain one reactant (the injected reactant) at low concentration to improve the selectivity of the desirable product and to supply (or remove) heat.
  • Distillation reactor (Fig. 1.1c)—A batch reactor where volatile products are removed continuously from the reactor during the operation.
  • Continuous reactor (flow reactors)—A vessel into which reactants are fed continuously and products are withdrawn continuously from it. The chemical
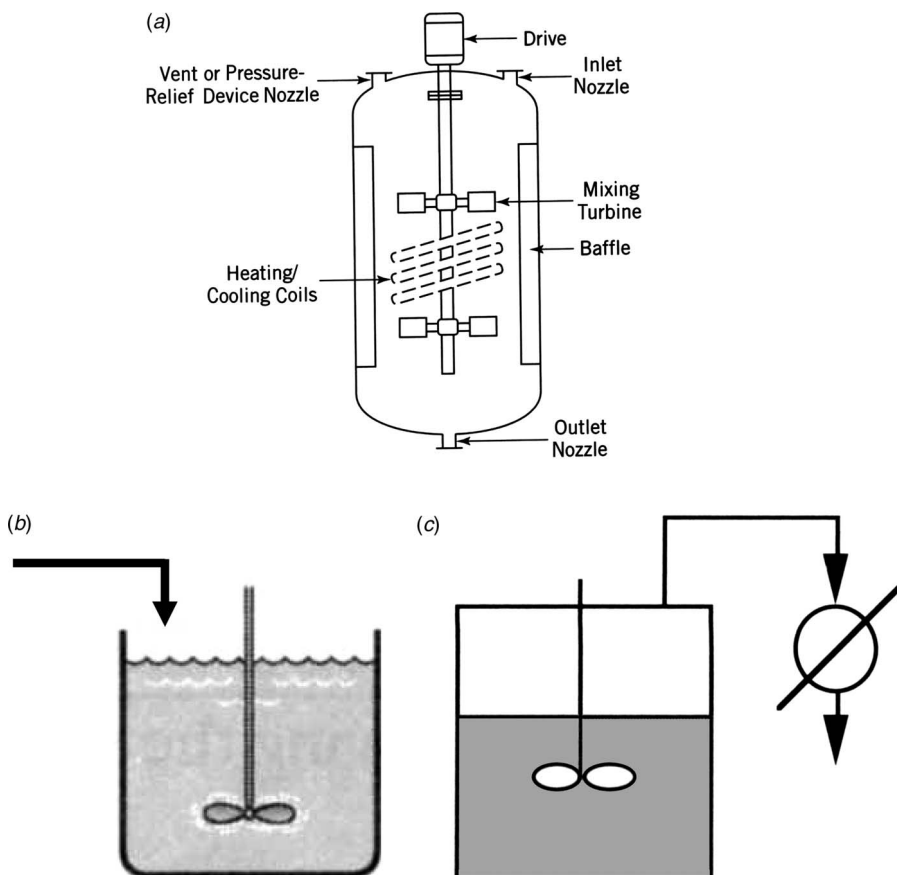
Figure 1.1 Batch operations: (*a*) batch reactor, (*b*) semibatch reactor, and (*c*) distillation reactor.

reactions take place over space (the reactor volume), and the residence time of the reacting fluid in the reactor provides the required reaction time. Common configurations of continuous reactors:

- Tubular reactor (Fig. 1.2*a*)
- Continuous stirred-tank reactor (CSTR) (Fig. 1.2*b*)
- Cascade of CSTRs (Fig. 1.2*c*)
- For multiphase reactions, the contacting patterns are used as a basis for classifying the reactors. Common configurations include:
  - Packed-bed reactor (Fig. 1.3*a*)—A vessel filled with catalytic pellets and the reacting fluid passing through the void space between them. Relatively large pellets (e.g., larger than 1 cm) are used to avoid excessive pressure drop and higher operating cost. In general, heat transfer to/from large-scale packed-bed reactors is a challenge.
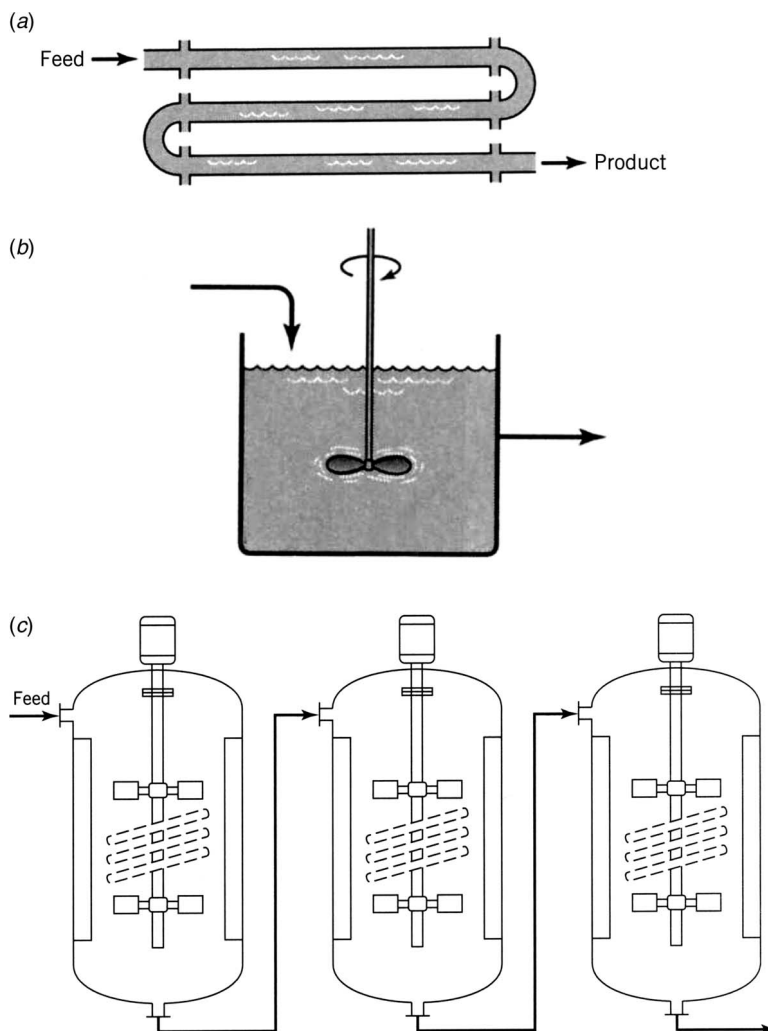
Figure 1.2   Continuous reactors: (*a*) tubular reactor, (*b*) continuous stirred-tank reactor (CSTR), and (*c*) cascade of CSTRs.

- Moving-bed reactor (Fig. 1.3*b*)—A vessel where solid particles (either reactant or catalyst) are continuously fed and withdrawn. The gas flow is maintained to allow the downward movement of the particles.
- Fluidized-bed reactor (Fig. 1.3*c*)—A vessel filled with fine particles (e.g., smaller than 500 μm) that are suspended by the upward flowing fluid. The fluidized bed provides good mixing of the particles and, consequently, a uniform temperature.
- Trickle-bed reactor—A packed bed where a liquid reactant is fed from the top, wetting catalytic pellets and a gas reactant, fed either from the top or

(a)

Packed Bed

Coolant in

Gas in

(b)

Gas out

Side Stream to Regenerator

Bucket Elevator or Hydraulic Lift to Raise Catalyst to Top of Reactor

Moving Bed of Solids

Reactant Gas in

(c)

Gas
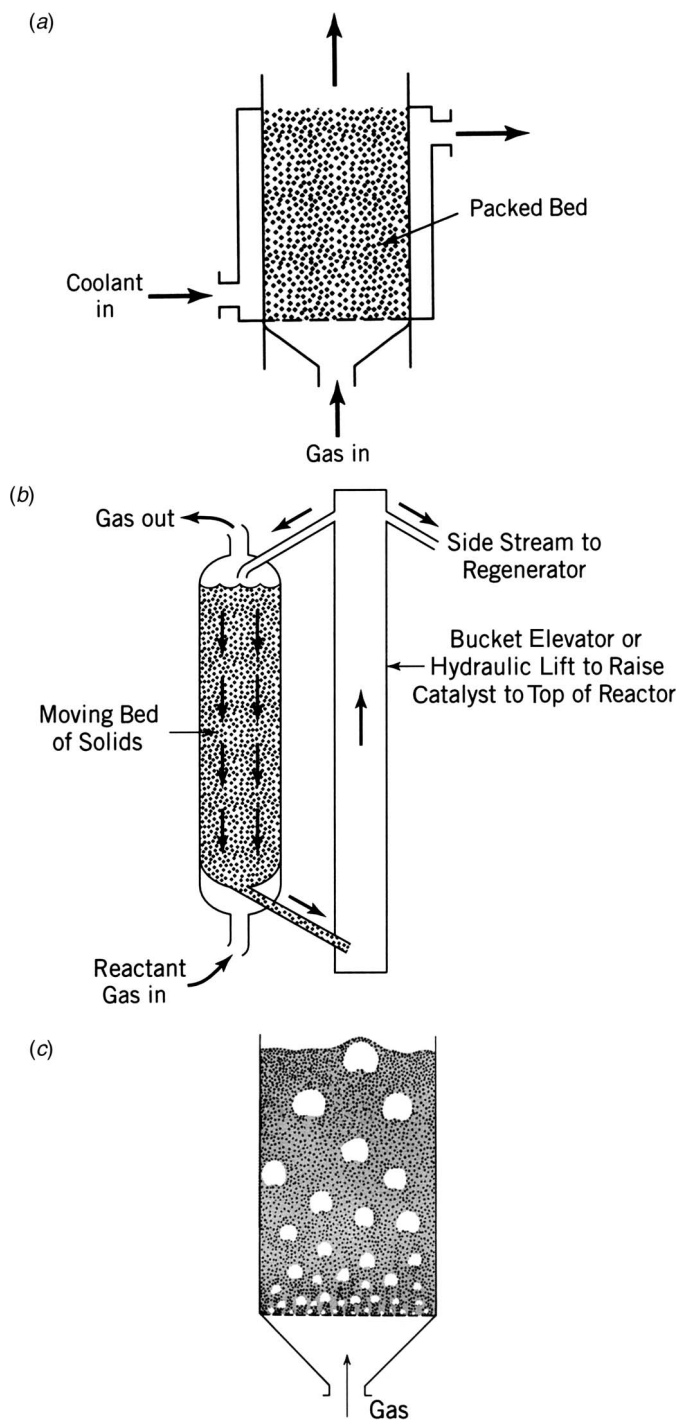
Figure 1.3   Multiphase reactors: (*a*) packed-bed reactor, (*b*) moving-bed reactor, (*c*) fluidized-bed reactor, (*d*) bubbling column reactor, (*e*) spray reactor, and (*f*) kiln reactor.
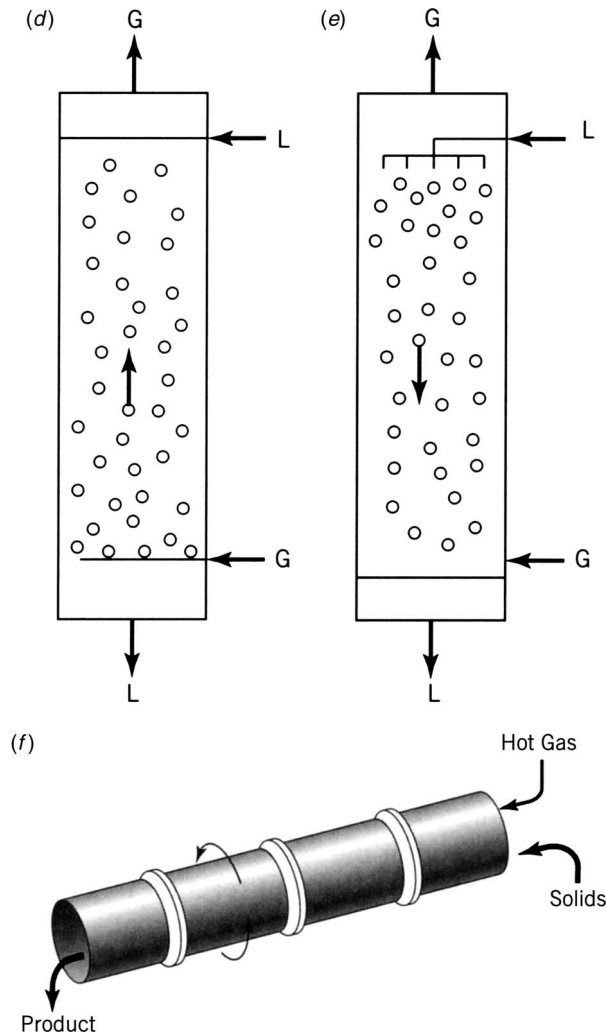
Figure 1.3 (*Continued*).

the bottom, flows through the void spaces between the pellets. The gaseous reactant must be absorbed and transported across the liquid film to the catalytic sites at the surface of the pellets.

- Bubbling column reactor (Fig. 1.3*d*)—A vessel filled with a liquid reactant and a gas reactant, fed from the bottom, moves upward in the form of bubbles. The liquid reactant is fed from the top and withdrawn from the bottom. The gaseous reactant is absorbed in the liquid reactant, and the reaction takes place in the liquid phase.
- Others [e.g., spray reactor (Fig. 1.3*e*), slurry reactor, kiln reactor (Fig. 1.3*f*), membrane reactor, etc.].

Due to the diverse applications and numerous configurations of chemical reactors, no generic design procedure exists to describe reactor operations. Rather, in each case it is necessary to identify the characteristics of the chemical reaction and the main features that the reactor should provide. Once these are identified, the appropriate physical and chemical concepts are applied to describe the selected reactor operation.

1.3   PHENOMENA AND CONCEPTS

The operation of a chemical reactor is affected by a multitude of diverse factors. In order to select, design, and operate a chemical reactor, it is necessary to identify the phenomena involved, to understand how they affect the reactor operation, and to express these effects mathematically. This section provides a brief review of the phenomena encountered in chemical reactor operations as well as the fundamental and engineering concepts that are used to describe them. Figure 1.4 shows schematically how various fundamental and engineering concepts are combined in formulating the reactor design equations.

1.3.1   Stoichiometry

Stoichiometry is an accounting system used to keep track of what species are formed (or consumed) and to calculate the composition of chemical reactors. Chapter 2 covers in detail the stoichiometric concepts and definitions used in reactor analysis.
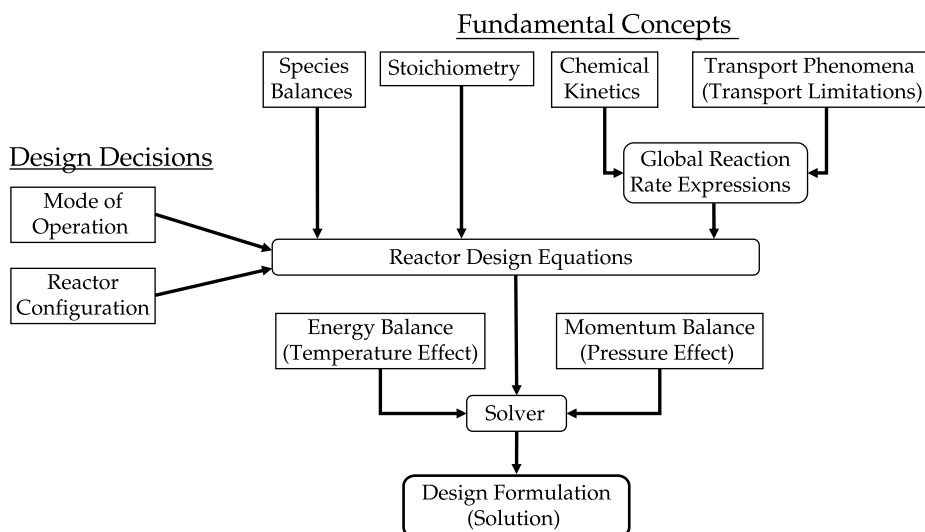

Figure 1.4   Schematic diagram of reactor design formulation.

1.3.2   Chemical Kinetics

Chemical kinetics is the branch of chemistry concerned with the rates of chemical reactions [3, 14, 19, 36–41]. Many chemical reactions involve the formation of unstable intermediate species (e.g., free radicals). Chemical kinetics is the study of the mechanisms involved in obtaining a rate expression for the chemical reaction (the reaction pathway). In most instances, the reaction rate expression is not available and should be determined experimentally. Chapter 3 covers the definitions and relations used in reactor analysis and design.

1.3.3   Transport Effects

The rate expressions obtained by chemical kinetics describe the dependency of the reaction rate on kinetic parameters related to the chemical reactions. These rate expressions are commonly referred to as the "intrinsic" rate expressions of the chemical reactions (or intrinsic kinetics). However, in many instances, the local species concentrations depend also on the rate that the species are transported in the reacting medium. Consequently, the actual reaction rate (also referred to as the *global reaction rate*) is affected by the transport rates of the reactants and products.

   The effects of transport phenomena on the global reaction rate are prevalent in three general cases:

   1. Fluid–solid catalytic reactions
   2. Noncatalytic fluid–solid reactions
   3. Fluid–fluid (liquid–liquid, gas–liquid) reactions

Incorporating the effects of species transport rates to obtain the global rates of the chemical reactions is a difficult task since it requires knowledge of the local temperature and flow patterns (hydrodynamics) and numerous physical and chemical properties (porosity, pore size and size distribution, viscosity, diffusion coefficients, thermal conductivity, etc.).

   The species transfer flux to/from an interface is often described by a product of a mass-transfer coefficient, k_M, and a concentration difference between the bulk and the interface. The mass-transfer coefficient is correlated to the local flow conditions [13, 21, 26–29]. For example, in a packed bed the mass-transfer coefficient from the bulk of the fluid to the surface of a particle is obtained from a correlation of the form

$$\mathrm{Sh} = \frac{k_M d_p}{D} = C\,\mathrm{Re}^{0.5}\,\mathrm{Sc}^{0.33}, \tag{1.3.1}$$

where Sh is the Sherwood number, Re is the Reynolds number (based on the particle diameter and the superficial fluid velocity—the velocity the fluid would have if there were no particle packing), Sc is the Schmidt number, D is the diffusivity of the

fluid, and C is a dimensionless constant. Similar correlations are available for mass transfer between two immiscible fluids.

In *catalytic gas–solid reactions*, the reaction takes place at catalytic sites on the surface of the solid. To obtain appreciable reaction rates, porous solids are used and the reactions take place on the surface of the pores in the interior of the particle. Hence, catalytic gas–solid reactions involve seven steps: (1) transport of the reactant from the fluid bulk to the mouth of the pore, (2) diffusion of the reactant to the interior of the pore, (3) adsorption of the reactant to the surface of the solid, (4) surface reaction at the catalytic site, (5) desorption of the product from the surface, (6) diffusion of the products to the mouth of the pore, and (7) transport of the products from the mouth of the pore to the bulk of the fluid. Steps 3–5 represent the kinetic mechanism of heterogeneous catalytic reactions. The rate of the reaction depends on the rates of these individual steps and the interactions between the catalytic site and the species, and the adsorption equilibrium constants of the various species present. A procedure, known as the Langmuir–Hishelwood–Hougen–Watson (LHHW) formulation, is used to derive and verify the reaction rate expressions for catalytic reactions [1, 3, 5, 7, 8, 14–18]. In many instances, one step is much slower than the other two steps and it determines the overall rate. This step is referred to as *the rate-limiting step.*

Often the global reaction rate of heterogeneous catalytic reactions is affected by the diffusion in the pore and the external mass-transfer rate of the reactants and the products. When the diffusion in the pores is not fast, a reactant concentration profile develops in the interior of the particle, resulting in a different reaction rate at different radial locations inside the catalytic pelet. To relate the global reaction rate to various concentration profiles that may develop, a kinetic effectiveness factor is defined [1, 3, 4, 7, 8] by

$$\begin{pmatrix} \text{Effectiveness} \\ \text{factor} \end{pmatrix} \equiv \frac{\text{Actual reaction rate}}{\text{Reaction rate at the bulk condition}} \qquad (1.3.2)$$

Hence, to express the actual reaction rate, we have to multiply the reaction rate based on the bulk condition by a correction factor, which accounts for the diffusion effects. The effectiveness factor depends on the ratio between the reaction rate and the diffusion rate and is expressed in terms of a modulus (Thiele modulus), ϕ, defined by

$$\phi^2 = \frac{\text{Characteristic reaction rate}}{\text{Characteristic diffusion rate}} \qquad (1.3.3)$$

The function expressing the Thiele modulus in terms of kinetic parameters and the catalyst properties depends on the intrinsic reaction rate. For first-order reactions, the modulus is

$$\phi = L\sqrt{\frac{k}{D_{\text{eff}}}} \qquad (1.3.4)$$