

# **FUNDAMENTALS OF CHEMICAL REACTION ENGINEERING**

**SECOND EDITION**

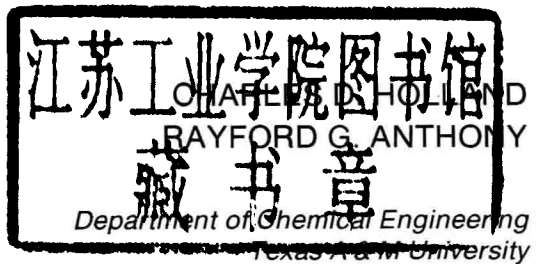


**Prentice-Hall International Editions**

**CHARLES D. HOLLAND  
RAYFORD G. ANTHONY**

SECOND EDITION

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***FUNDAMENTALS OF  
CHEMICAL REACTION  
ENGINEERING***

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*Dedicated to*

FRED J. BENSON

*Dean Emeritus of the College of Engineering*

*and in memory of*

JAMES DONALD LINDSAY

*Professor Emeritus and former Head of the  
Department of Chemical Engineering  
Texas A & M University*

# *Preface*

This book is written for the beginning student and practicing engineer in chemical kinetics and chemical reaction engineering. All topics are initiated by commencing with first principles. Derivations are complete, rigorous, and easily followed. The chapters are ordered with respect to the increasing difficulty of the subject matter. For example, Chapter 12, Theory of Reaction Rates, could have been included in Chapter 1 but was deferred because the level of that subject matter is higher than that needed by the student in order to master the material presented in subsequent chapters.

In this edition, the first four chapters present the design and analysis of data for isothermal reactors for irreversible, reversible, parallel, series, and complex reactions. New problems have been introduced which in many cases require use of numerical methods to obtain the solutions. Chapter 5 presents a rigorous review of thermodynamics required in the analysis and design of chemical reactions for ideal and nonideal systems. These principles are used in Chapters 6, 7, 8, and 9 in the design and analysis of tubular reactors, thermal and catalytic, with plug flow and for convective or dispersive fluxes in three dimensions, batch and perfectly mixed flow reactors. The terms for ideal and non-ideal contributions to the enthalpy of the solution are clearly presented. Several new design problems representing actual case studies were added to the problems.

The book is divided into three sections, fundamental principles of chemical kinetics and reactor engineering, design of thermal and catalytic reactors, and advanced topics on polymerization reactions, mixing effects, and theory of reaction rates. Since tracer techniques are important in the diagnosis of mixing

and flow problems in reactors, Chapter 11, Use of Tracer Techniques to Determine Mixing Effects, was added in this edition. Chapters 1 through 7 and part of Chapter 8 are covered in an undergraduate course, and Chapters 8 through 12 serve as a basis for a graduate course at Texas A & M University.

Helpful suggestions from Professors A. Akgerman, J. Bullin, P. T. Eubank, A. Gadalla, R. White, and D. T. Hanson of the Department of Chemical Engineering are appreciated. The authors also wish to thank D. L. Tanner of Dow Chemical Company for his assistance in the solution of examples in Chapter 7, and T. Helton, H. Ghaeli, P. Moore, Y-T. Chen, and L. Czarnecki for their assistance on some of the problems requiring computer solutions.



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# *Reaction Rates and Batch Reactors*

1

## **I. INTRODUCTION**

*Chemical kinetics* is the branch of physical chemistry that is concerned with the rates and mechanisms of chemical reactions. The first quantitative data on rates of reaction were reported in 1777 by Wenzel [1], who investigated the effect of acid concentration on the rate of dissolution of copper and zinc metals in acid solutions. The law of mass action for homogeneous reactions was formulated by Guldberg and Waage in 1867, and Van't Hoff extended it for heterogeneous reactions in 1877. The concept of the reaction velocity constant and the classification of reactions according to molecularity were introduced in 1884 by Van't Hoff [2]. In 1889, Arrhenius [3] suggested that only those molecules having an energy equal to or greater than a given level had the potential for reaction.

Van Narum appears to have been among the first to recognize catalysis when he observed in 1796 the effect of the surface catalysis in the dehydrogenation of alcohol. In 1902, Ostwald [4] defined a catalyst as "any substance which alters the velocity of a chemical reaction without appearing in the end products."

The beginning of the use of reaction kinetics in the design of reactors is marked by a paper published in 1923 by Lewis and Ries [5] on the catalytic oxidation of sulfur dioxide. Hougen [6] has given major credit for the early development of the theory and applications of chemical kinetics to process design, particularly in catalytic processes, to Kenneth M. Watson. A text

written by Hougen and Watson [7] led to the further development and acceptance of the subject of reactor design.

Reactions may be classified in a variety of useful ways. Some of the methods of classification are enumerated. Reactions may be classified according to the number of phases involved in the reactions:

1. Homogeneous
2. Heterogeneous or multiphase

They may be classified according to the manner in which the reaction is carried out:

3. Thermal or uncatalyzed
4. Catalyzed

Sometimes reactions are classified according to the nature of the reaction, such as:

5. Unidirectional or irreversible
6. Reversible
7. Isothermal or nonisothermal
8. Biological

Sometimes reactions are classified according to the type of equipment used to carry out the reactions:

9. Batch reactors
10. Flow reactors
  - (a) tubular
  - (b) continuous stirred tank
  - (c) trickle bed
  - (d) bubble column
  - (e) slurry
  - (f) ebullating flow
11. Catalytic reactors with fixed or fluidized beds

Batch reactors were no doubt the first type of reactor to be devised. They consist of well-stirred pots or kettles in which the reactants are mixed by stirring and allowed to react over a period of time. Provisions are generally made for heating or cooling the reacting mixture. Batch reactors are still used in the modern petrochemical industry. Figure 1-1 shows a reactor that may be used in either a batch or a continuous process.

The use of batch reactors in the manufacture of soap has been known for centuries and was recorded by early historians. During the excavation of Pompeii, a soap factory was discovered, complete with boiling pans and a quantity of soap which had been buried under volcanic ash for nearly 2000 years [8]. Batch-type reactors are still in use in the manufacture of soap by the "kettle or full-boiled method." This method consists of the saponification of

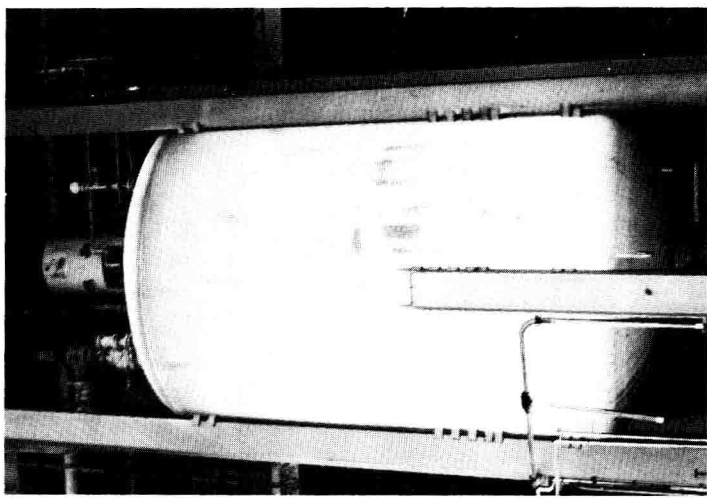
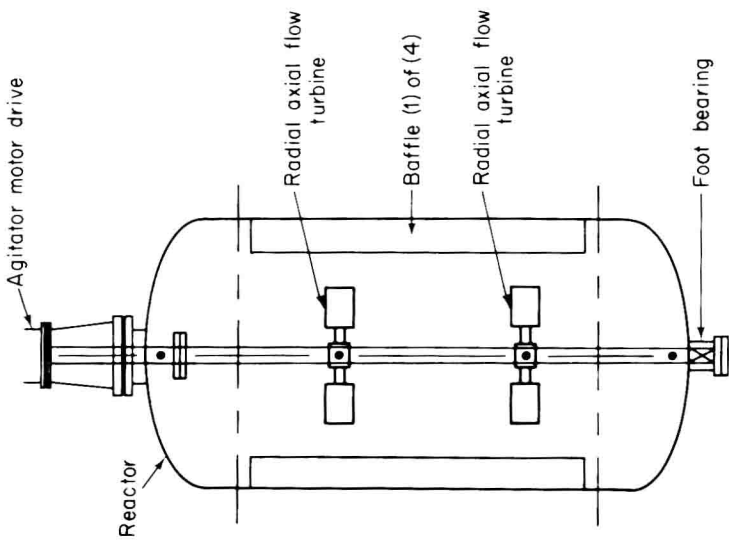
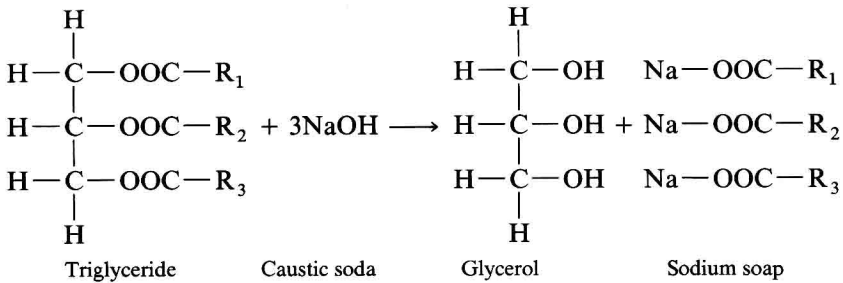


Figure 1-1. Reactor used in the production of synthetic rubber (Courtesy of Goodyear Tire and Rubber Company).

neutral fats and oils (triglycerides) with caustic soda as follows:



High-grade toilet soaps as well as low-grade industrial soaps with a high glycerol recovery efficiency may be made by this method [9].

The fundamental principles upon which the field of chemical reaction engineering is based are introduced in Parts II and III of this chapter. The rate of reaction, introduced in Part II, is shown to depend on the manner in which the molecules participate in a chemical reaction. After the development of the material-balance equations for batch reactors has been presented in Part III, expressions are developed for the variation of the moles reacted as a function of time.

## II. FUNDAMENTAL KINETIC AND THERMODYNAMIC RELATIONSHIPS

Rate expressions for various types of reactions are formulated in this section. A summary of the fundamental principles of the theory of reaction rates which are needed in these formulations are also presented. (A comprehensive treatment of the theory of reaction rates is presented for the benefit of the advanced student in Chapter 12.) Also presented in this section is the relationship between reaction kinetics and thermodynamics, as well as other relationships which are needed in subsequent chapters.

### A. Definition of the Rate of Reaction

The following definition for the rate of reaction leads to rate expressions, based on experimental results, which are valid over wide ranges of operating conditions. The net rate of disappearance (or appearance) of component  $A$  in a reacting mixture is defined as follows:

$$r_A = \frac{\text{moles of } A \text{ disappearing (or appearing)}}{(\text{unit time})(\text{unit of reactor volume})} \quad (1-1)$$

Suppose that the reacting mixture consists of components  $A$ ,  $B$ ,  $C$ , and  $D$  at a given temperature and pressure. Then the rate of reaction may be expected to



depend on the temperature, pressure, and concentrations of the reacting species; that is,

$$r_A = f(T, P, C_A, C_B, C_C, C_D) \quad (1-2)$$

The precise form of this functional relationship has been deduced for molecular or elementary reactions by use of the kinetic theory of gases and the transition state theory, but for most complex reactions encountered in chemical engineering practice, the functional form must be determined experimentally. Hereafter, this functional relationship is referred to as simply the *rate expression*. The form of the rate expression depends on *how* the molecules participate in the reaction, and if properly determined it is independent of the type of reactor used to carry out the reaction.

### B. Principles of the Kinetic Theory of Bimolecular Reactions

While the values of the rate constants predicted by the kinetic theory are generally highly inaccurate, many concepts of the kinetic theory carry over to subsequent theories used to describe chemical reactions. Thus, a summary of the results of the theory developed in Chapter 12 is presented next. The two principal postulates of this theory are (1) before two molecules *A* and *B* can react, they must collide, and (2) of the molecules which collide, only those react which have a kinetic energy equal to or greater than  $\epsilon$  along the line of centers of the molecules at the moment of contact, provided that they are properly orientated.

On the basis of these postulates, it is shown in Chapter 12 that the rate of reaction, based on the kinetic theory of gases, for two unlike molecules *A* and *B* is given by

$$r_A \left( \frac{\text{g mol}}{\text{s cm}^3} \right) = r_B = k_c C_A C_B \quad (1-3)$$

and the rate constant  $k_c$  is given by

$$k_c = p \sigma_{AB}^2 \sqrt{\frac{8\pi RT}{\mu}} e^{-E_A/RT} \quad (1-4)$$

where  $C_A, C_B$  = concentrations of *A* and *B*, g mol/cm<sup>3</sup>

$E_A$  = energy of activation, cal/g mol

$p$  = fraction of the molecules that collide that have the proper orientation

$R$  = gas constant, cal/(g mol)(K)