JOHN B. BUTT

REACTION KINETICS AND REACTOR DESIGN

PRENTICE-HALL INTERNATIONAL SERIES
in the PHYSICAL and CHEMICAL ENGINEERING SCIENCES

A clearly written, complete and modern introduction to the principles and practical implications of chemical kinetics and chemical reactor engineering.

REACTION KINETICS AND REACTOR DESIGN

JOHN B. BUTT

Department of Chemical Engineering
Northwestern University
Evanston, Illinois

PRENTICE-HALL, INC.,
Englewood Cliffs, New Jersey 07632

Library of Congress Cataloging in Publication Data

Butt, John B date
Reaction kinetics and reactor design.

Includes index.
1. Chemical reaction, Rate of. 2. Chemical reactors. I. Title.
QD502.B87 1980 541'.39 79-16115
ISBN 0-13-753335-7

Editorial/production supervision and interior design
by *Virginia Huebner*
Cover design by Edsal Enterprises
Manufacturing buyer: *Gordon Osbourne*

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

Prentice-Hall International, Inc., *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall of Canada, Ltd., *Toronto*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Prentice-Hall of Southeast Asia Pte. Ltd., *Singapore*
Whitehall Books Limited, *Wellington, New Zealand*

REACTION
KINETICS
AND
REACTOR DESIGN

PRENTICE-HALL INTERNATIONAL SERIES IN THE PHYSICAL AND CHEMICAL ENGINEERING SCIENCES

AMUNDSON *Mathematical Methods in Chemical Engineering: Matrices and Their Application*
ARIS *Introduction to the Analysis of Chemical Reactors*
BALZHISER, SAMUELS, AND ELIASSEN *Chemical Engineering Thermodynamics*
BRIAN *Staged Cascades in Chemical Processing*
BUTT *Reaction Kinetics and Reactor Design*
DENN *Process Fluid Mechanics*
DENN *Stability of Reaction and Transport Processes*
DOUGLAS *Process Dynamics and Control: Vol. 1, Analysis of Dynamic Systems*
DOUGLAS *Process Dynamics and Control: Vol. 2, Control System Synthesis*
FOGLER *The Elements of Chemical Kinetics and Reactor Calculations: A Self-Paced Approach*
FREDRICKSON *Principles and Applications of Rheology*
FRIEDLY *Dynamic Behavior of Processes*
HIMMELBLAU *Basic Principles and Calculations in Chemical Engineering*, 3rd edition
HOLLAND *Fundamentals and Modeling of Separation Processes: Absorption, Distillation, Evaporation, and Extraction*
HOLLAND *Multicomponent Distillation*
HOLLAND *Unsteady State Processes with Applications in Multicomponent Distillation*
HOLLAND AND ANTHONY *Fundamentals of Chemical Reaction Engineering*
LEVICH *Physicochemical Hydrodynamics*
MEISSNER *Processes and Systems in Industrial Chemistry*
MODELL AND REID *Thermodynamics and its Applications*
MYERS AND SEIDER *Introduction to Chemical Engineering and Computer Calculations*
NEWMAN *Electrochemical Systems*
PERLMUTTER *Stability of Chemical Reactors*
PRAUSNITZ *Molecular Thermodynamics of Fluid-Phase Equilibria*

PRAUSNITZ, ECKERT, ORYE, AND O'CONNELL *Computer Calculations for Multicomponent Vapor-Liquid Equilibria*
RUDD ET AL. *Process Synthesis*
SCHULTZ *Polymer Materials Science*
SEINFELD AND LAPIDUS *Mathematical Methods in Chemical Engineering: Vol. 3, Process Modeling, Estimation and Identification*
VILLADSEN AND MICHELSEN *Solution of Differential Equation Models by Polynomial Approximation*
WILLIAMS *Polymer Science and Engineering*
WOODS *Financial Decision Making in the Process Industry*

To all my students
who, over the years,
have taught me at least
as much as I have taught them.

> All I know is just what I read in the papers.
>
> *Will Rogers*

Preface

It is probably obvious even to the beginning student that much of chemical engineering is centered about problems involving chemical transformation, that is, chemical reaction. It is probably not so obvious, at least in the beginning, that the rate at which such transformations occur is the determining factor in a great number of the processes that have been developed over the years to produce that vast array of goods that we consider an integral part of contemporary life. The study, analysis, and interpretation of the rates of chemical reactions is, itself, a legitimate field of endeavor. It ranges in scope from those problems concerned with the fundamentals of detailed mechanisms of chemical transformation and the associated rates to problems that arise during the development and implementation of procedures for chemical reactor and process design on a large scale. If we must give names to these two extremes, we might call the first "chemical kinetics", and the second "chemical reaction engineering".

In the following we shall range from one limit to the other, although our primary objective is the understanding of kinetic principles and their application to engineering problems. What will we find? For one thing, we will find that chemical reactions are not simple things; those fine, balanced equations which everyone has used in solving stoichiometry problems ordinarily represent only the sum of many individual steps. We will find that the rates of chemical transformation, particularly in engineering application, are often affected by the rates of other processes, such as the transport of mass or heat, and cannot be isolated from the physical enviroment. We will find that the normal dependence of reaction rate on temperature is one of the most intractable of nonlinearities in nature, providing at the same time many of the difficulties and many of the challenges in the analysis of chemical rates. We will find that often it is not the absolute rate of a single reaction but the relative rates of two or more reactions that will be important in determining a design. We will find that space as well as time plays an important role in reaction engineering, and in the treatment of such problems it will be necessary to develop some facility in the use of rational mathematical models. Finally, we will find that the artful compromise is as important, if not more so, in our applications of reaction kinetics as it is in all the other areas of chemical engineering practice.

This may seem like a very short list of what is to be found if the topic is truly as important as we have indicated. It is intentionally short, because the essence should not be submerged in detail quite so soon, or, to paraphrase Thomas a Kempis, it is better not to speak a word at all than to speak more words than we should.

The material of this text is intended primarily to provide instruction at the undergraduate level in both chemical kinetics and reactor design. Of particular concern has been the detailing of reaction kinetics beyond phenomonological description. The rationale for the Arrhenius equation was a personal mystery to the author in earlier years, who hopes an appropriate solution is revealed in Chapter 2. Numerous other aspects of classical theories of chemical kinetics are assembled Chapter 2 and Chapter 3 to give some perception of the origin of phenomological rate laws and an understanding of the differing types of elementary reaction steps. In Chapter 4 we swap the beret of the theoretician for the hard hat of the engineer, in pursuit of means for developing rational chemical reactor design and analysis models. A parallelism between mixing models and reactor models has been maintained in order to demonstrate clearly how reaction kinetic laws fit into reactor design. Chapters 4 through 6 are based on homogeneous models, and proceed from standard plug flow and stirred tank analysis to description of nonideal behavior via dispersion, segregated flow, mixing cell and combined model approaches. Phenomena associated with reaction in more than one phase are treated in Chapter 7 but no attempt is made to develop multiphase reactor models. The fact that reaction selectivity as well as reaction rate is an important and often determining factor in chemical reaction or reactor analysis is kept before the eyes of the reader throughout the text.

The exercises are an intentionally well-mixed bag. They range from simple application of equations and concepts developed in the text to relatively open-ended situations which may require arbitarary judgement and, in some instances, have no unique answer. The units employed are equally well mixed. Historically, multiple systems of measure have been a curse of the engineering profession and such is the case here particularly, where we range from the scientific purity of Planck's constant to the ultimate practicality of a barrel of oil. The SI system will eventually provide standarization, it is to be hoped, but this is not a short term proposition. Because both author and reader must continue to cope with diverse sets of units, no attempt at standarization has been made here.

Symbols are listed in alphabetical order by the section of the chapter in which they appear. Only symbols which have not been previously listed or which are used in a different sense from previous listings are included for each section. Symbols used in equations for simplification of the form are generally defined immediately thereafter and are not listed in Notation.

Each chapter is divided into more or less self-contained modules dealing with a unified concept or a group of related concepts. Similarly, the exercises and notation are keyed to the individual modules, so that a variety of possibilities exist for pursuit of the material presented.

Acknowledgment must be made to teachers and colleagues who, over the years, have had influence in what is to be found in this text. I am grateful to the late Charles E. Littlejohn and R. Harding Bliss, to Professors C. A. Walker, H. M. Hulburt, and R. L. Burwell, Jr., and especially to Professor C. O. Bennett, who offered many constructive and undoubtedly kind comments during preparation of this manuscript. Tanks also to R. Mendelsohn, D. Casleberry and J. Pherson for typing various sections of the manuscript, and to the Northwestern chemical engineering students for detecting unworkable problems, inconsistent equations, and all the other gremlins waiting to smite the unwary author.

JOHN B. BUTT

Evanston, Illinois

Contents

Gather ye rosebuds while ye may
Old time is still a-flying
Robert Herrick

Apparent Reaction Kinetics in Homogeneous Systems

1

1.1 Mass Conservation and Chemical Reaction

Certainly, the most fundamental of laws governing the chemical transformations and separations with which chemical engineering is involved is that of the *conservation of mass*. Consider the steady-state separation process depicted on Figure 1.1. A stream, L, mass/time, containing two components, A and B, is fed to a separation process of some sort which divides in into two product streams, V and W, mass/time, also containing components A and B. We can define the mass fractions of components A and B in L, V, and W as x_A, x_B, y_A, y_B, and z_A, z_B, respectively. Mass is conserved in this separation; we may express this mathematically with the following simple relations:

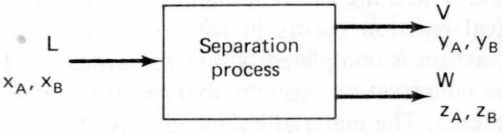

Figure 1.1 Simple separation

$$L = V + W \tag{1-1}$$

$$Lx_A = Vy_A + Wz_A \tag{1-2}$$

$$Lx_B = Vy_B + Wz_B \tag{1-3}$$

Now, since we know also that each stream consists of the sum of its parts, then

$$x_A + x_B = 1 \tag{1-4}$$

$$y_A + y_B = 1 \tag{1-5}$$

$$z_A + z_B = 1 \tag{1-6}$$

This, in turn, means that only two of the three mass-balance relationships (1-1) to (1-3) are independent and can be used to express the law of conservation of mass for the separation. We are then left with a system of five equations and nine potential unknowns such that if any four are specified, the remaining five may be determined. Of course, all we have done is to say:

$$\text{total mass in/time} = \text{total mass out/time}$$
$$\text{mass A in/time} = \text{mass A out/time}$$
$$\text{mass B in/time} = \text{mass B out/time}$$

Since the uniform time dimension divides out of each term of these equation, our result is the direct mass-conservation law.

Now let us consider a slightly different situation in which the process involved is not a separation but a chemical transformation. In fact, we shall simplify the situation to a single input and output stream as in Figure 1.2, with a feed stream consisting of component A alone. However, within the process a chemical reaction occurs in which B is formed by the reaction A ⟶ B. If the reaction is completed within the process, all the A reacts to form B and mass conservation requires that the mass of B produced equal the mass of A reacted. The material balance is trivial:

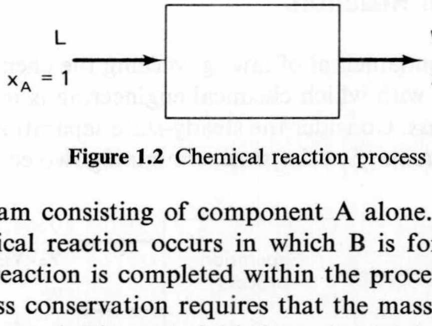

Figure 1.2 Chemical reaction process

$$L = W \qquad (x_A = 1, z_B = 1) \tag{1-7}$$

What happens, though, if not all of the A reacts to form B in the process? Then, obviously, the mass of B leaving is not equal to the mass of A entering, but rather

$$L = Wz_A + Wz_B \tag{1-8}$$

This chemical reaction process illustrates in a simplistic way the general concerns of this text, which are to determine z_A and z_B given a certain type and size of reaction process, or to determine the type and size of reaction process needed to produce a specified z_A and z_B.

Two factors enter into this problem. The first is the *stoichiometry* of the reaction transforming A to B. Chemical equations as normally written express the relationship between molal quantities of reactants and products, and it is necessary to transform these to the mass relationship in problems of mass conservation involving chemical reaction. The details of this are clear from the familiar combustion/mass balance problems, which seem so vexing the first time they are encountered. In our simple example reaction, the stoichiometric relationship is 1:1, so mass conservation requires the molecular weight of B to equal that of A, and thus the mass of B produced equal the mass of A reacted. This particular type of reaction is called an *isomerization reaction* and is a common and important reaction in industrial application.

The second factor is the *rate* at which A reacts to form B. Consider the problem in which we wish to determine z_A and z_B, given the type and size of process used in Figure 1.2. For the mass balance on component A, we want to write

$$\text{mass A in/time} = \text{mass A out/time} + \text{mass A reacted/time} \tag{1-9}$$

and for B (recalling that there is no B in the feed)

$$\left(\frac{\text{mass B out}}{\text{time}}\right) = \left(\frac{\text{mass B formed}}{\text{time}}\right) = \left(\frac{\text{mass A reacted}}{\text{time}}\right) \tag{1-10}$$

The last two terms of equation (1-10) incorporate the information concerning the stoichiometric relationship involved in the chemical reaction, since we have already seen that the mass relationship as well as the molal relationship in this particular example is 1:1. We can also paraphrase the statement of equation (1-10) to say that the *rate* at which B passes out of the system is equal to the *rate* at which it is formed, which is also equal to the *rate* at which A reacts. Thus, the rate of reaction is closely involved in this mass-balance relationship—exactly how is what we are to learn—so for the moment our simple example must remain unsolved.

The most important matter is to define properly a rate of reaction. One undesirable property exhibited by the rate involved in equation (1-10) is that its magnitude depends on the magnitude of the process; and we could have an infinity of processes, as in Figure 1.2, of differing sizes under identical conditions of operation, each producing the same z_A and z_B, yet each having a different reaction rate. *Volume* is the measure of the size of a system, so if we define a reaction rate with respect to unit volume of reaction mixture, the size dependency will be removed. Further, we must be sure to define the rate of reaction such that it will properly reflect the influence of state variables such as composition and temperature but will not be dependent on the particular process or reactor in which the reaction takes place. In accord with this, we can write

$$r' = \text{rate of reaction} = \frac{\text{change in mass of reactant or product}}{\text{time–volume reaction mixture}} = \frac{1}{V}\frac{dM}{dt} \tag{1-11a}$$

or, in molal quantities,

$$r = \text{rate of reaction} = \frac{\text{change in moles of reactant or product}}{\text{time–volume reaction mixture}} = \frac{1}{V}\frac{dN}{dt} \tag{1-11b}$$

where V is the volume of the reaction mixture and M and N are mass and moles, respectively. The rate is positive for change in product and negative for change in reactant.

There are a number of traps involved even in this simple definition. The use of the reference volume as that of the reaction mixture is necessary to account for the fact that in some cases the total volume will change in proportion to the molal balance between reactants and products. If the reaction were, for example, A → 2B and involved ideal gases with no change in temperature or total pressure, the volume of product at the completion of reaction would be twice that of initial reactant. To conserve our definition of reaction rate independent of the size of the system, the volume change must be accounted for. This is not difficult to do, as we shall show a little later. The problem is that one often sees reaction rates written in the following form:

$$r = \frac{dC}{dt} = \frac{d(N/V)}{dt} \tag{1-12}$$

where concentration C (in moles/volume) is used in the rate definition. As the last term in equation (1-12) shows, such a simplification is possible only when the volume of the reaction mixture does not change as the reaction progresses. In most cases it is convenient to use concentration units, however, so one can avoid problems with changes in reference volume if the rate is written

$$r = \frac{1}{V}\frac{d(CV)}{dt} \tag{1-13}$$

where $N = CV$,

A second and not so obvious trap involved in the rate definition is the use of the time derivative, (dM/dt) or (dN/dt). This implies that things are changing with time and may tempt one to associate the appearance of reaction-rate terms in mass conservation equations with unsteady-state processes. This is not necessarily true; in general, one must make a distinction between the ongoing time of operation of some process (i.e., that measured by an observer) and individual phenomena such as chemical reactions which occur at a *steady* rate in an operation that does not vary with time (i.e., steady state). Later we will encounter both steady- and unsteady-state types of processes involving chemical reaction, to be sure, but this depends on the process itself; the reaction-rate definition has been made without regard to a particular process.

Returning for a moment to the mass-conservation equation (1-9), we may now restate it in terms of the definition of the rate of reaction. We use