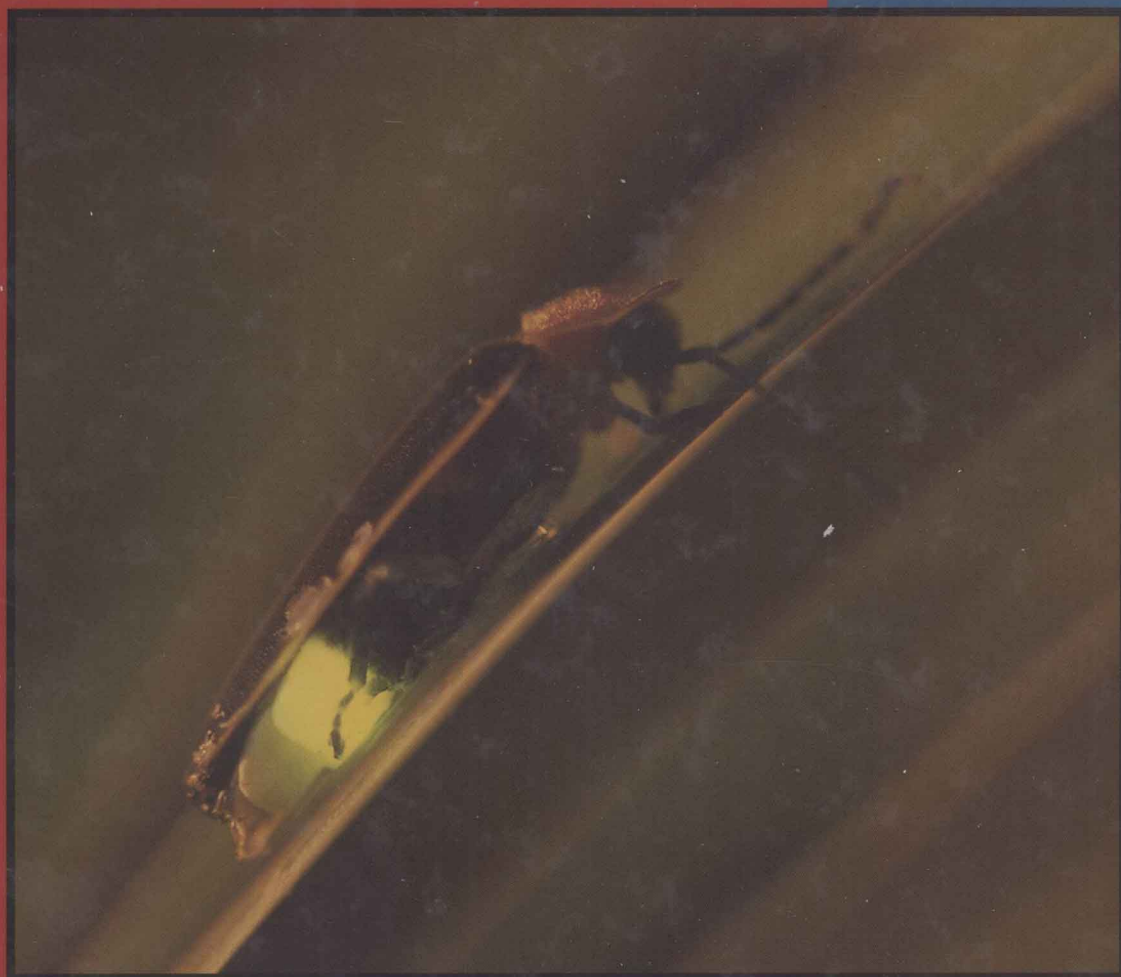


Chemical Reactions and Chemical Reactors



George W. Roberts

Chemical Reactions and Chemical Reactors

George W. Roberts

North Carolina State University

Department of Chemical and Biomolecular Engineering



WILEY

John Wiley & Sons, Inc.

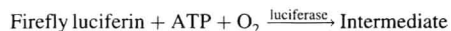
VICE PRESIDENT AND EXECUTIVE PUBLISHER
ASSOCIATE PUBLISHER
ACQUISITIONS EDITOR
VICE PRESIDENT AND DIRECTOR OF MARKETING
EXECUTIVE MARKETING MANAGER
SENIOR PRODUCTION EDITOR
DESIGNER
PRODUCTION MANAGEMENT SERVICES
EDITORIAL ASSISTANT
MARKETING ASSISTANT
MEDIA EDITOR
COVER PHOTO

Don Fowley
Dan Sayre
Jenny Welter
Susan Elbe
Chris Ruel
Trish McFadden
Michael St. Martine
Thomson Digital Limited
Mark Owens
Chelsee Pengal
Lauren Sapira
© Taylor Kennedy/NG Image Collection

Cover Description:

The firefly on the cover is demonstrating the phenomenon of “bioluminescence”, the production of light within an organism (the *reactor*) by means of a chemical *reaction*. In addition to fireflies, certain marine animals also exhibit bioluminescence.

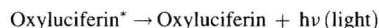
In the firefly, a reactant or substrate known as “firefly luciferin” reacts with O₂ and adenosine triphosphate (ATP) in the presence of an enzyme catalyst, luciferase, to produce a reactive intermediate (a four-member cyclic perester).



The intermediate then loses CO₂ spontaneously to form a heterocyclic intermediate known as “oxyluciferin”. As formed, the oxyluciferin is in an excited state, i.e., there is an electron in an anti-bonding orbital.



Finally, oxyluciferin decays to its ground state with the emission of light when the excited electron drops into a bonding orbital.



This series of reactions is of practical significance to both fireflies and humans. It appears that firefly larvae use bioluminescence to discourage potential predators. Some adult fireflies use the phenomenon to attract members of the opposite sex.

In the human world, the reaction is used to assay for ATP, a very important biological molecule. Concentrations of ATP as low as 10⁻¹¹ M can be detected by measuring the quantity of light emitted. Moreover, medical researchers have implanted the firefly’s light-producing gene into cells inside other animals and used the resulting bioluminescence to track those cells in the animal’s body. This technique can be extended to cancer cells, where the intensity of the bioluminescence can signal the effectiveness of a treatment. Finally, the energy released by the bioluminescence-producing reactions is almost quantitatively converted into light. In contrast, only about 10% of the energy that goes into a conventional incandescent light bulb is converted into light.

This book was set in Times New Roman by Thomson Digital Limited and printed and bound by Hamilton Printing. The cover was printed by Phoenix Color.

This book is printed on acid free paper. ∞

Copyright © 2009 John Wiley & Sons, Inc. All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc. 222 Rosewood Drive, Danvers, MA 01923, website www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030-5774, (201)748-6011, fax (201)748-6008, website <http://www.wiley.com/go/permissions>.

To order books or for customer service please, call 1-800-CALL WILEY (225-5945).

ISBN-13 978-0471-742203

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Chemical Reactions and Chemical Reactors

Preface

Intended Audience

This text covers the topics that are treated in a typical, one-semester undergraduate course in chemical reaction engineering. Such a course is taught in almost every chemical engineering curriculum, internationally. The last three chapters of the book extend into topics that may also be suitable for graduate-level courses.

Goals

Every engineering text that is intended for use by undergraduates must address two needs. First, it must prepare students to function effectively in industry with only the B.S. degree. Second, it must prepare those students that go to graduate school for advanced coursework in reaction kinetics and reactor analysis. Most of the available textbooks fall short of meeting one or both of these requirements. “Chemical Reactions and Chemical Reactors” addresses both objectives. In particular:

Focus on Fundamentals: The text contains much more on the fundamentals of chemical kinetics than current books with a similar target audience. The present material on kinetics provides an important foundation for advanced courses in chemical kinetics. Other books combine fundamentals and advanced kinetics in one book, making it difficult for students to know what’s important in their first course.

Emphasis on Numerical Methods: The book emphasizes the use of numerical methods to solve reaction engineering problems. This emphasis prepares the student for graduate coursework in reactor design and analysis, coursework that is more mathematical in nature.

Analysis of Kinetic Data: Material on the analysis of kinetic data prepares students for the research that is a major component of graduate study. Simultaneously, it prepares students who will work in plants and pilot plants for a very important aspect of their job. These features are discussed in more detail below.

“Chemical Reactions and Chemical Reactors” is intended as a text from which to teach. Its objective is to help the student master the material that is presented. The following characteristics aid in this goal:

Conversational Tone: The tone of the book is conversational, rather than scholarly.

Emphasis on Solving Problems: The emphasis is on the solution of problems, and the text contains many example problems, questions for discussion, and appendices. Very few derivations and proofs are required of the student. The approach to problem-solving is to start each new problem from first principles. No attempt is made to train the student to use pre-prepared charts and graphs.

Use of Real Chemistry: Real chemistry is used in many of the examples and problems. Generally, there is a brief discussion of the practical significance of each reaction that is introduced. Thus, the book tries to teach a little industrial chemistry along with chemical kinetics and chemical reactor analysis. Unfortunately, it is difficult to find real-life examples to illustrate all of the important concepts. This is particularly true in a discussion of reactors in which only one reaction takes place. There are several important principles that must be illustrated in such a discussion, including how to handle reactions with different stoichiometries and how to handle changes in the mass density as the reaction takes place. It was not efficient to deal with all of these variations through real

examples, in part because rate equations are not openly available. Therefore, in some cases, it has been necessary to revert to generalized reactions.

Motivation and Differentiating Features

Why is a new text necessary, or even desirable? After all, the type of course described in the first paragraph has been taught for decades, and a dozen or so textbooks are available to support such courses. “Chemical Reactions and Chemical Reactors” differs substantially in many important respects from the books that are presently available. On a conceptual level, this text might be regarded as a fusion of two of the most influential (at least for this author) books of the past fifty years: Octave Levenspiel’s “Chemical Reaction Engineering” and Michel Boudart’s “Kinetics of Chemical Processes.” As suggested by these two titles, one of the objectives of this text is to integrate a fundamental understanding of reaction kinetics with the application of the principles of kinetics to the design and analysis of chemical reactors. However, this text goes well beyond either of these earlier books, both of which first appeared more than forty years ago, at the dawn of the computer era.

This text is differentiated from the reaction engineering books that currently are available in one or more of the following respects:

1. The field of chemical kinetics is treated in some depth, *in an integrated fashion* that emphasizes the fundamental tools of kinetic analysis, and challenges the student to apply these common tools to problems in many different areas of chemistry and biochemistry.
2. Heterogeneous catalysis is introduced early in the book. The student can then solve reaction engineering problems involving heterogeneous catalysts, in parallel with problems involving homogeneous reactions.
3. The subject of transport effects in heterogeneous catalysis is treated in significantly greater depth.
4. The analysis of experimental data to develop rate equations receives substantial attention; a whole chapter is devoted to this topic.
5. The text contains many problems and examples that require the use of numerical techniques.

The integration of these five elements into the text is outlined below.

Topical Organization

Chapter 1 begins with a review of the stoichiometry of chemical reactions, which leads into a discussion of various definitions of the reaction rate. Both homogeneous and heterogeneous systems are treated. The material in this chapter recurs throughout the book, and is particularly useful in Chapter 7, which deals with multiple reactions.

Chapter 2 is an “overview” of rate equations. At this point in the text, the subject of reaction kinetics is approached primarily from an empirical standpoint, with emphasis on power-law rate equations, the Arrhenius relationship, and reversible reactions (thermodynamic consistency). However, there is some discussion of collision theory and transition-state theory, to put the empiricism into a more fundamental context. The intent of this chapter is to provide enough information about rate equations to allow the student to understand the derivations of the “design equations” for ideal reactors, and to solve some problems in reactor design and analysis. A more fundamental treatment of reaction kinetics is deferred until Chapter 5. The discussion of thermodynamic consistency

includes a “disguised” review of the parts of chemical thermodynamics that will be required later in the book to analyze the behavior of reversible reactions.

The definitions of the three ideal reactors, and the fundamentals of ideal reactor sizing and analysis are covered in Chapters 3 and 4. Graphical interpretation of the “design equations” (the “Levenspiel plot”) is used to compare the behavior of the two ideal continuous reactors, the plug flow and continuous stirred-tank reactors. This follows the pattern of earlier texts. However, in this book, graphical interpretation is also used extensively in the discussion of ideal reactors in series and parallel, and its use leads to new insights into the behavior of *systems* of reactors.

In most undergraduate reaction engineering texts, the derivation of the “design equations” for the three ideal reactors, and the subsequent discussion of ideal reactor analysis and sizing, is based exclusively on *homogeneous* reactions. This is very unfortunate, since about 90 percent of the reactions carried out industrially involve *heterogeneous catalysis*. In many texts, the discussion of heterogeneous catalysis, and heterogeneous catalytic reactors, is deferred until late in the book because of the complexities associated with transport effects. An instructor who uses such a text can wind up either not covering heterogeneous catalysis, or covering it very superficially in the last few meetings of the course.

“Chemical Reactions and Chemical Reactors” takes a different approach. The design equations are derived in Chapter 3 for *both* catalytic and non-catalytic reactions. In Chapter 4, which deals with the use of the design equations to size and analyze ideal reactors, transport effects are discussed qualitatively and conceptually. The student is then able to size and analyze ideal, heterogeneous catalytic reactors, *for situations where transport effects are not important*. This builds an important conceptual base for the detailed treatment of transport effects in Chapter 9.

As noted previously, one major differentiating feature of “Chemical Reactions and Chemical Reactors” is its emphasis on the fundamentals of reaction kinetics. As more and more undergraduate students find employment in “non-traditional” areas, such as electronic materials and biochemical engineering, a strong grasp of the fundamentals of reaction kinetics becomes increasingly important. Chapter 5 contains a unified development of the basic concepts of kinetic analysis: elementary reactions, the steady-state approximation, the rate-limiting step approximation, and catalyst/site balances. These four “tools” then are applied to problems from a number of areas of science and engineering: biochemistry, heterogeneous catalysis, electronic materials, etc. In existing texts, these fundamental tools of reaction kinetics either are not covered, or are covered superficially, or are covered in a fragmented, topical fashion. The emphasis in “Chemical Reactions and Chemical Reactors” is on helping the student to understand and apply the *fundamental* concepts of kinetic analysis, so that he/she can use them to solve problems from a wide range of technical areas.

Chapter 6 deals with the analysis of kinetic data, another subject that receives scant attention in most existing texts. First, various techniques to test the suitability of a given rate equation are developed. This is followed by a discussion of how to estimate values of the unknown parameters in the rate equation. Initially, graphical techniques are used in order to provide a visual basis for the process of data analysis, and to demystify the subject for “visual learners”. Then, the results of the graphical process are used as a starting point for statistical analysis. The use of non-linear regression to fit kinetic data and to obtain the “best” values of the unknown kinetic parameters is illustrated. The text explains how non-linear regression can be carried out with a spreadsheet.

Multiple reactions are covered in Chapter 7. This chapter begins with a qualitative, conceptual discussion of systems of multiple reactions, and progresses into the

quantitative solution of problems involving the sizing and analysis of isothermal reactors in which more than one reaction takes place. The numerical solution of ordinary differential equations, and systems of ordinary differential equations, is discussed and illustrated. The solution of non-linear systems of algebraic equations also is illustrated.

Chapter 8 is devoted to the use of the energy balance in reactor sizing and analysis. Adiabatic batch and plug-flow reactors are discussed first. Once again, numerical techniques for solving differential equations are used to obtain solutions to problems involving these two reactors. Then, the CSTR is treated, and the concepts of stability and multiple steady states are introduced. The chapter closes with a treatment of feed/product heat exchangers, leading to a further discussion of multiplicity and stability.

The topic of transport effects in catalysis is revisited in Chapter 9. The structure of porous catalysts is discussed, and the internal and external resistances to heat and mass transfer are quantified. Special attention is devoted to helping the student understand the influence of transport effects on overall reaction behavior, including reaction selectivity. Experimental and computational methods for predicting the presence or absence of transport effects are discussed in some detail. The chapter contains examples of reactor sizing and analysis in the presence of transport effects.

The final chapter, Chapter 10, is a basic discussion of non-ideal reactors, including tracer techniques, residence-time distributions, and models for non-ideal reactors. In most cases, the instructor will be challenged to cover this material, even superficially, in a one-semester course. Nevertheless, this chapter should help to make the text a valuable starting point for students that encounter non-ideal reactors after they have completed their formal course of study.

Numerical Methods

“Chemical Reactions and Chemical Reactors” contains problems and examples that require the solution of algebraic and differential equations by numerical methods. By the time students take the course for which this text is intended, a majority of them will have developed some ability to use one or more of the common mathematical packages, e.g., Mathcad, Matlab, etc. This text does not rely on a specific mathematical package, nor does it attempt to teach the student to use a specific package. The problems and examples in the book can be solved with any suitable package(s) that the student may have learned in previous coursework. This approach is intended to free the instructor from having to master and teach a new mathematical package, and to reinforce the students’ ability to use the applications they have already learned. Many of the numerical solutions that are presented in the text were developed and solved on a personal computer using a spreadsheet. Appendices are included to illustrate how the necessary mathematics can be carried out with a spreadsheet. This approach gives students a “tool” that they eventually might need in an environment where a specific mathematical package was not available. The spreadsheet approach also familiarizes the student with some of the mathematics that underlies the popular computer packages for solving differential equations.

In the Classroom

“Chemical Reactions and Chemical Reactors” is written to provide the instructor with flexibility to choose the order in which topics are covered. Some options include:

Applications Up Front: Lately, I have been covering the chapters in order, from Chapter 1 through Chapter 9. This approach might be labeled the “mixed up” approach because it switches back and forth between kinetics and reactor sizing/analysis. Chapter 2 provides just enough information about chemical kinetics to allow the student to understand ideal

reactors, to size ideal reactors, and to analyze the behavior of ideal reactors, in Chapters 3 and 4. Chapters 5 and 6 then return to kinetics, and treat it in more detail, and from a more fundamental point of view. I use this approach because some students do not have the patience to work through Chapters 2 and 5 unless they can see the eventual application of the material.

Kinetics Up Front: Chapter 5 has been written so that it can be taught immediately after Chapter 2, before starting Chapter 3. The order of coverage then would be Chapters 1, 2, 5, 3, 4, 6, 7, 8, and 9. This might be referred to as the “kinetics up front” approach.

Reactors Up Front: A third alternative is the “reactors up front” approach, in which the order of the chapters would be either: 1, 2, 3, 4, 7, 8, 9, 5, 6 or 1, 2, 3, 4, 7, 8, 5, 6, 9. The various chapters have been written to enable any of these approaches. The final choice is strictly a matter of instructor preference.

Some important topics are not covered in the first version of this text. Two unfortunate examples are transition-state theory and reactors involving two fluid phases. An instructor that wished to introduce some additional material on transition-state theory could easily do so as an extension of either Chapter 2 or Chapter 5. Supplementary material on multiphase reactors fits well into Chapter 9.

Based on my personal experience in teaching from various versions of this text, I found it difficult to cover even the first nine chapters, in a way that was understandable to the majority of students. I seldom, if ever, got to Chapter 10. A student that masters the material in the first nine chapters should be very well prepared to learn advanced material “on the job,” or to function effectively in graduate courses in chemical kinetics or chemical reaction engineering.

Instructor Resources

The following resources are available on the book website at www.wiley.com/college/roberts. These resources are available only to adopting instructors. Please visit the Instructor section of the website to register for a password:

Solutions Manual: Complete solutions to all homework exercises in the text.

Image Gallery: Figures from the text in electronic format, suitable for use in lecture slides.

Instructor’s Manual: Contains the answers to all of the “Exercises” in the book.

Acknowledgements

This book is the culmination of a long journey through a subject that always held an enormous fascination for me. The trip has been tortuous, but never lonely. I have been accompanied by a number of fellow travelers, each of who helped me to understand the complexities of the subject, and to appreciate its beauty and importance. Some were teachers, who shared their accumulated wisdom and stimulated my interest in the subject. Many were collaborators, both industrial and academic, who worked with me to solve a variety of interesting and challenging problems. Most recently, my fellow travelers have been students, both undergraduate and graduate. They have challenged me to communicate my own knowledge in a clear and understandable manner, and have forced me to expand my comprehension of the subject. I hope that I can express the debt that I owe to all of these many individuals.

A summer internship started my journey through catalysis, reaction kinetics, and reactor design and analysis, before the term “chemical reaction engineering” came into popular use. For three months, with what was then the California Research Corporation, I tackled a very exciting set of problems in catalytic reaction kinetics. Two exceptional industrial practitioners, Drs. John Scott and Harry Mason, took an interest in my work, made the importance of catalysis in industrial practice clear to me, and had a great influence on the direction of my career.

I returned to Cornell University that fall to take my first course in “kinetics” under Professor Peter Harriott. That course nourished my developing interest in reaction kinetics and reactor design/analysis, and provided a solid foundation for my subsequent pursuits in the area.

In graduate school at the Massachusetts Institute of Technology, I had the privilege of studying catalysis with Professor Charles Satterfield, who became my thesis advisor. Professor Satterfield had a profound influence on my interest in, and understanding of, catalysts and catalytic reactors. My years with Professor Satterfield at MIT were one of the high points of my journey.

I began my professional career with the Rohm and Haas Company, working in the area of polymerization. In that environment, I had the opportunity to interact with a number of world-class chemists, including Dr. Newman Bortnick. I also had the opportunity to work with a contemporary, Dr. James White, in the mathematical modeling of polymerization reactors. My recent work in polymerization at North Carolina State University is an extension of what I learned at Rohm and Haas.

Next, at Washington University (Saint Louis), I had the opportunity to work and teach with Drs. Jim Fair and Ken Robinson. Jim Fair encouraged my study of gas/liquid/solid reactors, and Ken Robinson brought some valuable perspectives on catalysis to my teaching and research efforts.

The next stop in my travels was at what was then Engelhard Minerals and Chemicals Corporation, where I worked in a very dynamic environment that was focused on heterogeneous catalysts and catalytic processes. Four of my co-workers, Drs. John Bonacci, Larry Campbell, Bob Farrauto, and Ron Heck, deserve special mention for their contributions to my appreciation and understanding of catalysis. The five of us, in various combinations, spent many exciting (and occasionally frustrating) hours discussing various projects in which we were involved. I have continued to draw upon the

knowledge and experience of this exceptional group throughout the almost four decades that have passed since our relationships began. I must also mention Drs. Gunther Cohn and Carl Keith, both extremely creative and insightful scientists, who helped me immeasurably and had the patience to tolerate some of my streaks of naivety.

I then spent more than a decade with Air Products and Chemicals, Inc. Although the primary focus of my efforts lay outside the area of chemical reaction engineering, there were some notable exceptions. These exceptions gave me the opportunity to work with another set of talented individuals, including Drs. Denis Brown and Ed Givens.

The last and longest stop in my travels has been my present position in the Department of Chemical Engineering (now Chemical and Biomolecular Engineering) at North Carolina State University. This phase of the journey led to four important collaborations that extended and deepened my experience in chemical reaction engineering. I have benefited greatly from stimulating interactions with Professors Eduardo Sáez, now at the University of Arizona, James (Jerry) Spivey, now at Louisiana State University, Ruben Carbonell, and Joseph DeSimone.

This book would not have been possible without the contributions of the Teaching Assistants that have helped me over the years, in both undergraduate and graduate courses in chemical reaction engineering. These include: Collins Appaw, Lisa Barrow, Diane (Bauer) Beaudoin, Chinmay Bhatt, Matt Burke, Kathy Burns, Joan (Biales) Frankel, Nathaniel Cain, “Rusty” Cantrell, Naresh Chennamsetty, Sushil Dhoot, Laura Beth Dong, Kevin Epting, Amit Goyal, Shalini Gupta, Surendra Jain, Concepcion Jimenez, April (Morris) Kloxin, Steve Kozup, Shawn McCutchen, Jared Morris, Jodee Moss, Hung Nguyen, Joan Patterson, Nirupama Ramamurthy, Manish Saraf, George Serad, Fei Shen, Anuraag Singh, Eric Shreiber, Ken Walsh, Dawei Xu, and Jian Zhou. Three graduate students: Tonya Klein, Jorge Pikunic, and Angelica Sanchez, worked with me as part of university-sponsored mentoring programs. Two undergraduates who contributed to portions of the book, Ms. Amanda (Burris) Ashcraft and Mr. David Erel, also deserve my special thanks.

I am indebted to Professors David Ollis and Richard Felder, who offered both advice and encouragement during the darker days of writing this book. I am also grateful to Professors David Bruce of Clemson University, Tracy Gardner and Anthony Dean of Colorado School of Mines, Christopher Williams of the University of South Carolina, and Henry Lamb and Baliji Rao of North Carolina State University for insightful comments and/or for “piloting” various drafts of the book in their classes. Professor Robert Kelly, also of North Carolina State University, contributed significantly to the “shape” of this book.

I would like to thank the following instructors who reviewed drafts of the manuscript, as well as those reviewers who wished to remain anonymous:

Pradeep K. Agrawal, Georgia Institute of Technology
 Dragomir B. Bukur, Texas A&M University
 Lloyd R. Hile, California State University, Long Beach
 Thuan K. Nguyen, California State University, Pomona
 Jose M. Pinto, Polytechnic University
 David A. Rockstraw, New Mexico State University
 Walter P. Walawender, Kansas State University

I fear that I may have omitted one or more important companions on my journey through reaction kinetics, reactor design and analysis, and heterogeneous catalysis. I offer my sincere apologies to those who deserve mention, but are the victims of the long span of my career and the randomness of my memory.

Dedication:

I am intensely grateful for the support of my family. I now realize that my wife, Mary, and my children, Claire and Bill, were the innocent victims of the time and effort that went into the preparation for, and the writing of, this book. Thank you, Mary, Claire, and Bill. This book is dedicated to the three of you, collectively and individually.

Contents

1. Reactions and Reaction Rates	1
1.1 Introduction	1
1.1.1 The Role of Chemical Reactions	1
1.1.2 Chemical Kinetics	2
1.1.3 Chemical Reactors	2
1.2 Stoichiometric Notation	3
1.3 Extent of Reaction and the Law of Definite Proportions	4
1.3.1 Stoichiometric Notation—Multiple Reactions	6
1.4 Definitions of Reaction Rate	8
1.4.1 Species-Dependent Definition	8
1.4.1.1 Single Fluid Phase	9
1.4.1.2 Multiple Phases	9
Heterogeneous Catalysis	9
Other Cases	10
1.4.1.3 Relationship between Reaction Rates of Various Species (Single Reaction)	10
1.4.1.4 Multiple Reactions	11
1.4.2 Species-Independent Definition	11
Summary of Important Concepts	12
Problems	12
2. Reaction Rates—Some Generalizations	16
2.1 Rate Equations	16
2.2 Five Generalizations	17
2.3 An Important Exception	33
Summary of Important Concepts	33
Problems	33
3. Ideal Reactors	36
3.1 Generalized Material Balance	36
3.2 Ideal Batch Reactor	38
3.3 Continuous Reactors	43
3.3.1 Ideal Continuous Stirred-Tank Reactor (CSTR)	45
3.3.2 Ideal Continuous Plug-Flow Reactor (PFR)	49
3.3.2.1 The Easy Way—Choose a Different Control Volume	51
3.3.2.2 The Hard Way—Do the Triple Integration	54
3.4 Graphical Interpretation of the Design Equations	54
Summary of Important Concepts	57
Problems	57
Appendix 3 Summary of Design Equations	60
4. Sizing and Analysis of Ideal Reactors	63
4.1 Homogeneous Reactions	63
4.1.1 Batch Reactors	63
4.1.1.1 Jumping Right In	63
4.1.1.2 General Discussion: Constant-Volume Systems	68
Describing the Progress of a Reaction	68
Solving the Design Equation	71

4.1.1.3	General Discussion: Variable-Volume Systems	74
4.1.2	Continuous Reactors	77
4.1.2.1	Continuous Stirred-Tank Reactors (CSTRs)	78
	Constant-Density Systems	78
	Variable-Density (Variable-Volume) Systems	80
4.1.2.2	Plug-Flow Reactors	82
	Constant-Density (Constant-Volume) Systems	82
	Variable-Density (Variable-Volume) Systems	84
4.1.2.3	Graphical Solution of the CSTR Design Equation	86
4.1.2.4	Biochemical Engineering Nomenclature	90
4.2	Heterogeneous Catalytic Reactions (Introduction to Transport Effects)	91
4.3	Systems of Continuous Reactors	97
4.3.1	Reactors in Series	98
4.3.1.1	CSTRs in Series	98
4.3.1.2	PFRs in Series	103
4.3.1.3	PFRs and CSTRs in Series	103
4.3.2	Reactors in Parallel	107
4.3.2.1	CSTRs in Parallel	107
4.3.2.2	PFRs in Parallel	109
4.3.3	Generalizations	110
4.4	Recycle	111
	Summary of Important Concepts	114
	Problems	114
	Appendix 4 Solution to Example 4-10: Three Equal-Volume CSTRs in Series	122
5.	Reaction Rate Fundamentals (Chemical Kinetics)	123
5.1	Elementary Reactions	123
5.1.1	Significance	123
5.1.2	Definition	125
5.1.3	Screening Criteria	126
5.2	Sequences of Elementary Reactions	129
5.2.1	Open Sequences	130
5.2.2	Closed Sequences	130
5.3	The Steady-State Approximation (SSA)	131
5.4	Use of the Steady-State Approximation	133
5.4.1	Kinetics and Mechanism	136
5.4.2	The Long-Chain Approximation	137
5.5	Closed Sequences with a Catalyst	138
5.6	The Rate-Limiting Step (RLS) Approximation	140
5.6.1	Vector Representation	141
5.6.2	Use of the RLS Approximation	142
5.6.3	Physical Interpretation of the Rate Equation	143
5.6.4	Irreversibility	145
5.7	Closing Comments	147
	Summary of Important Concepts	147
	Problems	148
6.	Analysis of Experimental Kinetic Data	154
6.1	Experimental Data from Ideal Reactors	154
6.1.1	Stirred-Tank Reactors (CSTRs)	155
6.1.2	Plug-Flow Reactors	156
6.1.2.1	Differential Plug-Flow Reactors	156

6.1.2.2	Integral Plug-Flow Reactors	157
6.1.3	Batch Reactors	158
6.1.4	Differentiation of Data: An Illustration	159
6.2	The Differential Method of Data Analysis	162
6.2.1	Rate Equations Containing Only One Concentration	162
6.2.1.1	Testing a Rate Equation	162
6.2.1.2	Linearization of Langmuir–Hinshelwood/Michaelis–Menten Rate Equations	165
6.2.2	Rate Equations Containing More Than One Concentration	166
6.2.3	Testing the Arrhenius Relationship	169
6.2.4	Nonlinear Regression	171
6.3	The Integral Method of Data Analysis	173
6.3.1	Using the Integral Method	173
6.3.2	Linearization	176
6.3.3	Comparison of Methods for Data Analysis	177
6.4	Elementary Statistical Methods	178
6.4.1	Fructose Isomerization	178
6.4.1.1	First Hypothesis: First-Order Rate Equation	179
	Residual Plots	179
	Parity Plots	180
6.4.1.2	Second Hypothesis: Michaelis–Menten Rate Equation	181
	Constants in the Rate Equation: Error Analysis	184
	Non-Linear Least Squares	186
6.4.2	Rate Equations Containing More Than One Concentration (Reprise)	186
	Summary of Important Concepts	187
	Problems	188
	Appendix 6-A Nonlinear Regression for AIBN Decomposition	197
	Appendix 6-B Nonlinear Regression for AIBN Decomposition	198
	Appendix 6-C Analysis of Michaelis–Menten Rate Equation via Lineweaver–Burke Plot Basic Calculations	199

7. Multiple Reactions 201

7.1	Introduction	201
7.2	Conversion, Selectivity, and Yield	203
7.3	Classification of Reactions	208
7.3.1	Parallel Reactions	208
7.3.2	Independent Reactions	208
7.3.3	Series (Consecutive) Reactions	209
7.3.4	Mixed Series and Parallel Reactions	209
7.4	Reactor Design and Analysis	211
7.4.1	Overview	211
7.4.2	Series (Consecutive) Reactions	212
7.4.2.1	Qualitative Analysis	212
7.4.2.2	Time-Independent Analysis	214
7.4.2.3	Quantitative Analysis	215
7.4.2.4	Series Reactions in a CSTR	218
	Material Balance on A	219
	Material Balance on R	219
7.4.3	Parallel and Independent Reactions	220
7.4.3.1	Qualitative Analysis	220
	Effect of Temperature	221

	Effect of Reactant Concentrations	222
7.4.3.2	Quantitative Analysis	224
7.4.4	Mixed Series/Parallel Reactions	230
7.4.4.1	Qualitative Analysis	230
7.4.4.2	Quantitative Analysis	231
	Summary of Important Concepts	232
	Problems	232
Appendix 7-A	Numerical Solution of Ordinary Differential Equations	241
7-A.1	Single, First-Order Ordinary Differential Equation	241
7-A.2	Simultaneous, First-Order, Ordinary Differential Equations	245
8.	Use of the Energy Balance in Reactor Sizing and Analysis	251
8.1	Introduction	251
8.2	Macroscopic Energy Balances	252
8.2.1	Generalized Macroscopic Energy Balance	252
8.2.1.1	Single Reactors	252
8.2.1.2	Reactors in Series	254
8.2.2	Macroscopic Energy Balance for Flow Reactors (PFRs and CSTRs)	255
8.2.3	Macroscopic Energy Balance for Batch Reactors	255
8.3	Isothermal Reactors	257
8.4	Adiabatic Reactors	261
8.4.1	Exothermic Reactions	261
8.4.2	Endothermic Reactions	262
8.4.3	Adiabatic Temperature Change	264
8.4.4	Graphical Analysis of Equilibrium-Limited Adiabatic Reactors	266
8.4.5	Kinetically Limited Adiabatic Reactors (Batch and Plug Flow)	268
8.5	Continuous Stirred-Tank Reactors (General Treatment)	271
8.5.1	Simultaneous Solution of the Design Equation and the Energy Balance	272
8.5.2	Multiple Steady States	276
8.5.3	Reactor Stability	277
8.5.4	Blowout and Hysteresis	279
8.5.4.1	Blowout	279
	Extension	281
	Discussion	282
8.5.4.2	Feed-Temperature Hysteresis	282
8.6	Nonisothermal, Nonadiabatic Batch, and Plug-Flow Reactors	284
8.6.1	General Remarks	284
8.6.2	Nonadiabatic Batch Reactors	284
8.7	Feed/Product (F/P) Heat Exchangers	285
8.7.1	Qualitative Considerations	285
8.7.2	Quantitative Analysis	286
8.7.2.1	Energy Balance—Reactor	288
8.7.2.2	Design Equation	288
8.7.2.3	Energy Balance—F/P Heat Exchanger	289
8.7.2.4	Overall Solution	291
8.7.2.5	Adjusting the Outlet Conversion	291
8.7.2.6	Multiple Steady States	292
8.8	Concluding Remarks	294
	Summary of Important Concepts	295

Problems	296
Appendix 8-A Numerical Solution to Equation (8-26)	302
Appendix 8-B Calculation of $G(T)$ and $R(T)$ for “Blowout” Example	304
9. Heterogeneous Catalysis Revisited	305
9.1 Introduction	305
9.2 The Structure of Heterogeneous Catalysts	306
9.2.1 Overview	306
9.2.2 Characterization of Catalyst Structure	310
9.2.2.1 Basic Definitions	310
9.2.2.2 Model of Catalyst Structure	311
9.3 Internal Transport	311
9.3.1 General Approach—Single Reaction	311
9.3.2 An Illustration: First-Order, Irreversible Reaction in an Isothermal, Spherical Catalyst Particle	314
9.3.3 Extension to Other Reaction Orders and Particle Geometries	315
9.3.4 The Effective Diffusion Coefficient	318
9.3.4.1 Overview	318
9.3.4.2 Mechanisms of Diffusion	319
Configurational (Restricted) Diffusion	319
Knudsen Diffusion (Gases)	320
Bulk (Molecular) Diffusion	321
The Transition Region	323
Concentration Dependence	323
9.3.4.3 The Effect of Pore Size	325
Narrow Pore-Size Distribution	325
Broad Pore-Size Distribution	326
9.3.5 Use of the Effectiveness Factor in Reactor Design and Analysis	326
9.3.6 Diagnosing Internal Transport Limitations in Experimental Studies	328
9.3.6.1 Disguised Kinetics	328
Effect of Concentration	329
Effect of Temperature	329
Effect of Particle Size	330
9.3.6.2 The Weisz Modulus	331
9.3.6.3 Diagnostic Experiments	333
9.3.7 Internal Temperature Gradients	335
9.3.8 Reaction Selectivity	340
9.3.8.1 Parallel Reactions	340
9.3.8.2 Independent Reactions	342
9.3.8.3 Series Reactions	344
9.4 External Transport	346
9.4.1 General Analysis—Single Reaction	346
9.4.1.1 Quantitative Descriptions of Mass and Heat Transport	347
Mass Transfer	347
Heat Transfer	347
9.4.1.2 First-Order, Reaction in an Isothermal Catalyst Particle—The Concept of a Controlling Step	348
$\eta k_v l_c / k_c \ll 1$	349
$\eta k_v l_c / k_c \gg 1$	350
9.4.1.3 Effect of Temperature	353
9.4.1.4 Temperature Difference Between Bulk Fluid and Catalyst Surface	354