Chemical Reactions and Chemical Reactors

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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 O_2 and adenosine triphosphate (ATP) in the presence of an enzyme catalyst, luciferase, to produce a reactive intermediate (a four-member cyclic perester).

$$\text{Firefly luciferin} + \text{ATP} + O_2 \xrightarrow{\text{luciferase}} \text{Intermediate}$$

The intermediate then loses CO_2 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.

$$\text{Intermediate} \rightarrow \text{Oxyluciferin}^* + CO_2$$

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

$$\text{Oxyluciferin}^* \rightarrow \text{Oxyluciferin} + h\nu\,(\text{light})$$

This series of reactions is of practical significance to both fireflies and humans. It appears that firefly larvae use bioluminescense 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 bioluminescense to track those cells in the animal's body. This technique can be extended to cancer cells, where the intensity of the bioluminescense can signal the effectiveness of a treatment. Finally, the energy released by the bioluminescense-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.

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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

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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.

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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.

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