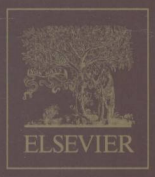

COMPREHENSIVE CHEMICAL KINETICS

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N.J.B. GREEN

VOLUME 42

MODELING OF CHEMICAL REACTIONS

R.W. CARR

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CHEMICAL KINETICS

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MODELING OF CHEMICAL REACTIONS

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E2008000915

AMSTERDAM - BOSTON - HEIDELBERG - LONDON - NEW YORK - OXFORD - PARIS
SAN DIEGO - SAN FRANCISCO - SINGAPORE - SYDNEY - TOKYO

附光盘壹张

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2007

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Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-444-51366-3
ISSN: 0069-8040 (Series)

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Printed and bound in Italy

07 08 09 10 11 10 9 8 7 6 5 4 3 2 1

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Preface

The overall chemical transformations that occur in nature and in many processes designed by chemists and engineers can be very complex. They frequently consist of hundreds, or even thousands, of different kinds of molecular reactions through which the overall chemical transformation occurs. These are called elementary chemical reactions, and they are the fundamental quantities governing the molecular pathways by which chemical compounds are converted during overall chemical transformations. Elementary chemical reactions are the basis for a detailed understanding of how complex chemical reactions occur, and at what rate they occur.

The historical development of chemical kinetics, which is the study of the rates of chemical reactions, started with empirical observations of the overall rates at which chemical compounds are converted into final reaction products, because knowledge of the underlying elementary chemical reactions was very meager. Consequently, the chemical process industries developed empirical models to describe process chemistry, a practice which still comprises a significant part of chemical engineering. Generations of chemical engineers have learned and developed these methods, frequently to a high degree of sophistication. Textbooks of chemical reaction engineering amply describe this branch of applied chemical kinetics. The empirical models, however, have limitations. They are limited to the range of experimental variables over which they were developed, and should not be used outside that range. They do not have predictive ability. And they do not incorporate detailed chemistry, making it very difficult to see how process improvements can be made.

The twentieth century saw an enormous amount of experimental and theoretical research on elementary chemical reactions, an effort which continues today. The fruits of this work are extensive kinetics databases, and molecular theories from which to make estimates when experimental data are not available. Equally important are parallel developments in thermochemistry. All of this information makes possible the development of detailed chemical kinetics models of overall chemical reactions. Models have been constructed and applied to such diverse topics as atmospheric chemistry, combustion, low temperature oxidation, chemical vapor deposition, and reactions in traditional chemical process industries. The rate of each elementary reaction in a model is expressed as

an ordinary differential equation, so the models are dynamical systems. Furthermore, the rates vary by many orders of magnitude, and the models are very stiff. Advances in the speed and memory of digital computers, along with the development of methods for handling stiffness, are the final piece of the puzzle, making facile numerical computations possible.

This book covers several topics that are essential for the construction of detailed chemical kinetics models. I hope that it will be useful to chemists and chemical engineers who are just starting to delve into this subject, and to others whose technical training lies outside kinetics, even outside chemistry, and who wish to undertake the construction of a detailed chemical kinetics model for their own purposes. Complex chemical reactions are not solely the purview of chemists any more. The subject of chemical kinetics has been important to chemical engineers since the inception of the discipline over 100 years ago. Mechanical engineers have for a long time been interested in combustion, the chemical aspects of microelectronics processing has involved electrical engineers, and civil engineers are becoming ever more involved with environmental chemistry. Researchers in all of these disciplines, and perhaps in others as well, may come up against chemical reactions that need to be modeled for understanding.

The coverage is restricted to gas phase chemical reactions because this is the most highly developed area, and the one permitting the most accurate and predictive models at the present time. Reactions in the liquid phase and at solid interfaces present difficulties, although progress is being made. Reactions in solids are the most undeveloped currently. Chapter 1 is a brief introduction to the subject. One of the most important advances in recent years is the improvement in quantum chemistry methods for the computation of molecular structure and energetics. Methods capable of computing energies to "chemical accuracy" (a few kilojoules per mole) are now available, although some judgment is needed to assess the results. Chapter 2 discusses these methods and shows how to use the results to obtain thermochemical quantities for stable molecules. Part of Chapter 5 shows how to extend these methods to transition states. Chapter 3 is titled "Elements of Chemical Kinetics." It is a summary of some basic principles of kinetics, and of theories of bimolecular reactions. Its usefulness will be primarily for those who have very little background in kinetics. Chapter 4 treats pressure dependent reactions. These are unimolecular reactions and certain bimolecular reactions. Many detailed chemical kinetics models in the past have not included the pressure dependence of these reactions, although they are not rare, and should be included in models when appropriate. Chapter 4

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provides the theoretical basis for the pressure dependence, and presents practical methods for estimating rate parameters. One of the most time consuming and laborious tasks in detailed modeling is putting together the list of elementary reactions, called the reaction mechanism. It is also one of the most crucial tasks. Chapter 5 deals with this subject, and goes beyond the ordinary to show how to proceed when there are few experimental data on which to rely. Chapter 6 addresses the very important issue of building predictive reaction models. The data used in constructing a reaction model have uncertainty, whether they are obtained from experiment, quantum chemistry, or estimation methods, and the individual errors are propagated in the model. This chapter examines mathematical approaches to incorporate the uncertainty into the model, and thus provide information on the predictive reliability of the model.

Robert Carr
Minneapolis
December, 2006

Contents

Chapter 1

Introduction

Robert W. Carr

Chemical reactions abound in nature. They are essential for life, in both living organisms and systems that support life. Chemical reactions occur in all states of matter—gas, liquid, and solid. For example, gas phase reactions occur in interplanetary space, planetary atmospheres (those in Earth's atmosphere are of particular interest to us), flames and combustion, microelectronics processing, and many industrial processes. In the case of Earth's atmosphere, the chemical details of urban air pollution and stratospheric ozone depletion must be described by large numbers of gas phase chemical reactions involving man-made pollutants. These reactions account for the formation of harmful substances, and in the case of the stratosphere account for depletion of Earth's protective ozone shield by man-made chlorofluorocarbons. Understanding the chemical details is essential for undertaking policies to mitigate the effects of pollution. Liquid phase reactions include biological reactions, such as enzyme catalysis and cellular processes, and a large number of industrial applications from the manufacture of polymers to organic and inorganic chemicals. Examples of solid state reactions may be found in Earth's crust, cooking, and detonation of explosives. Many more examples of reactions in all three states of matter could be cited. Chemical reactions are also of great commercial importance. In the majority of chemical processes the chemical industry depends on chemical reactions to convert raw materials or other feedstocks into higher value substances. For example, ethylene, the largest volume industrial organic substance produced in the world today, is produced by the gas phase thermal decomposition of ethane.

Describing the rates at which chemical reactions occur is the subject of chemical kinetics. It is the study of the rates at which chemical compounds interact with one another to produce new chemical species, and the insight into factors governing chemical reactivity that derives therefrom. The rates of chemical change span an enormous range of time

Comprehensive Chemical Kinetics, Volume 42, 1–6
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ISSN: 0069-8040/doi:10.1016/S0069-8040(07)42001-5

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