



Chemical Kinetics — And — Dynamics

Jeffrey I. Steinfeld
Joseph S. Francisco
William L. Hase

Library of Congress Cataloging-in-Publication Data

Steinfeld, Jeffrey I.
Chemical kinetics and dynamics / Jeffrey Steinfeld, Joseph
Francisco, William Hase.
p. cm.
Bibliography.
Includes index.
ISBN 0-13-129479-2
1. Chemical reaction, Rate of. 2. Molecular dynamics.
I. Francisco, Joseph II. Hase, William. III. Title.
QD502.S74 1989 88-21842
541.3'94--dc19 CIP

Editorial/production supervision: Karen Winget/Wordcrafters
Cover design: Joel Mitnick Design, Inc.
Manufacturing buyer: Paula Massenaro



© 1989 by Prentice-Hall, Inc.
A Division of Simon & Schuster
Englewood Cliffs, New Jersey 07632

All rights reserved. No part of this book may be
reproduced, in any form or by any means,
without permission in writing from the publisher.

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

ISBN 0-13-129479-2

PRENTICE-HALL INTERNATIONAL (UK) LIMITED, *London*
PRENTICE-HALL OF AUSTRALIA PTY. LIMITED, *Sydney*
PRENTICE-HALL CANADA INC., *Toronto*
PRENTICE-HALL HISPANOAMERICANA, S.A., *Mexico*
PRENTICE-HALL OF INDIA PRIVATE LIMITED, *New Delhi*
PRENTICE-HALL OF JAPAN, INC., *Tokyo*
SIMON & SCHUSTER ASIA PTE. LTD., *Singapore*
EDITORA PRENTICE-HALL DO BRASIL, LTDA., *Rio de Janeiro*

Contents

PREFACE xi

Chapter 1

BASIC CONCEPTS OF KINETICS 1

- 1.1 Definition of the Rate of a Chemical Reaction, 1
 - 1.2 Order and Molecularity of a Reaction, 3
 - 1.3 Elementary Reaction Rate Laws, 6
 - 1.4 Determination of Reaction Order: Reaction Half Lives, 13
 - 1.5 Temperature Dependence of Rate Constants: The Arrhenius Equation, 14
 - 1.6 Reaction Mechanisms, Molecular Dynamics, and the Road Ahead, 16
- References, 17
Bibliography, 17
Problems, 18

Chapter 2

COMPLEX REACTIONS 21

- 2.1 Exact Analytic Solutions for Complex Reactions, 21
- 2.2 Approximation Methods, 38
- 2.3 Example of a Complex Reaction Mechanism: The Hydrogen + Halogen Reaction, 41
- 2.4 Laplace Transform Method, 48

2.5	Determinant (Matrix) Methods, 54
2.6	Numerical Methods, 56
2.7	Stochastic Method, 67
	References, 73
	Bibliography, 74
Appendix 2.1	The Laplace Transform, 75
Appendix 2.2	Numerical Algorithms for Differential Equations, 92
Appendix 2.3	Stochastic Numerical Simulation of Chemical Reactions, 97
	Problems, 103

Chapter 3

KINETIC MEASUREMENTS 109

3.1	Introduction, 109
3.2	Techniques for Kinetic Measurements, 111
3.3	Treatment of Kinetic Data, 133
	References, 150
Appendix 3.1	Least Square Method in Matrix Form, 152
	Problems, 154

Chapter 4

REACTIONS IN SOLUTION 156

4.1	General Properties of Reactions in Solution, 156
4.2	Phenomenological Theory of Reaction Rates, 157
4.3	Diffusion-Limited Rate Constant, 161
4.4	Slow Reactions, 163
4.5	Effect of Ionic Strength on Reactions Between Ions, 164
4.6	Linear Free-Energy Relationships, 169
4.7	Relaxation Methods for Fast Reactions, 171
	References, 174
	Bibliography, 175
	Problems, 175

Chapter 5

CATALYSIS 178

5.1	Catalysis and Equilibrium, 178
5.2	Homogeneous Catalysis, 180
5.3	Autocatalysis and Oscillating Reactions, 182
5.4	Enzyme-Catalyzed Reactions, 190
5.5	Heterogeneous Catalysis and Gas-Surface Reactions, 194
	References, 198
	Problems, 199

Chapter 6
**THE TRANSITION FROM THE MACROSCOPIC
TO THE MICROSCOPIC LEVEL 202**

- 6.1 Relation Between Cross Section and Rate Coefficient, 202
 - 6.2 Microscopic Reversibility and Detailed Balancing, 205
 - 6.3 The Microscopic-Macroscopic Connection, 206
- References, 208

Chapter 7
POTENTIAL ENERGY SURFACES 209

- 7.1 Long-Range Potentials, 210
 - 7.2 Empirical Intermolecular Potentials, 213
 - 7.3 Molecular Bonding Potentials, 216
 - 7.4 Internal Coordinates and Normal Modes of Vibration, 217
 - 7.5 Potential Energy Surfaces, 220
 - 7.6 Ab Initio Calculation of Potential Energy Surfaces, 225
 - 7.7 Analytic Potential Energy Functions, 231
 - 7.8 Experimental Determination of Potential Energy Surface Properties, 235
 - 7.9 Details of the Reaction Path, 236
 - 7.10 Potential Energy Surfaces of Electronically Excited Molecules, 237
- References, 240
- Bibliography, 242
- Problems, 244

Chapter 8
DYNAMICS OF BIMOLECULAR COLLISIONS 246

- 8.1 Simple Collision Models, 246
 - 8.2 Two-Body Classical Scattering, 251
 - 8.3 Complex Scattering Processes, 261
- References, 276
- Problems, 277

Chapter 9
**EXPERIMENTAL DETERMINATION OF NEW
KINETIC PARAMETERS 282**

- 9.1 Molecular Beam Scattering, 282
- 9.2 State-Resolved Spectroscopic Techniques, 290
- 9.3 An Example of State-to-State Kinetics: The F + H₂ Reaction, 293
- 9.4 Some General Principles Concerning Energy Disposition in Chemical Reactions, 297
- 9.5 Detailed Balance Revisited, 299

Contents

vii

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.