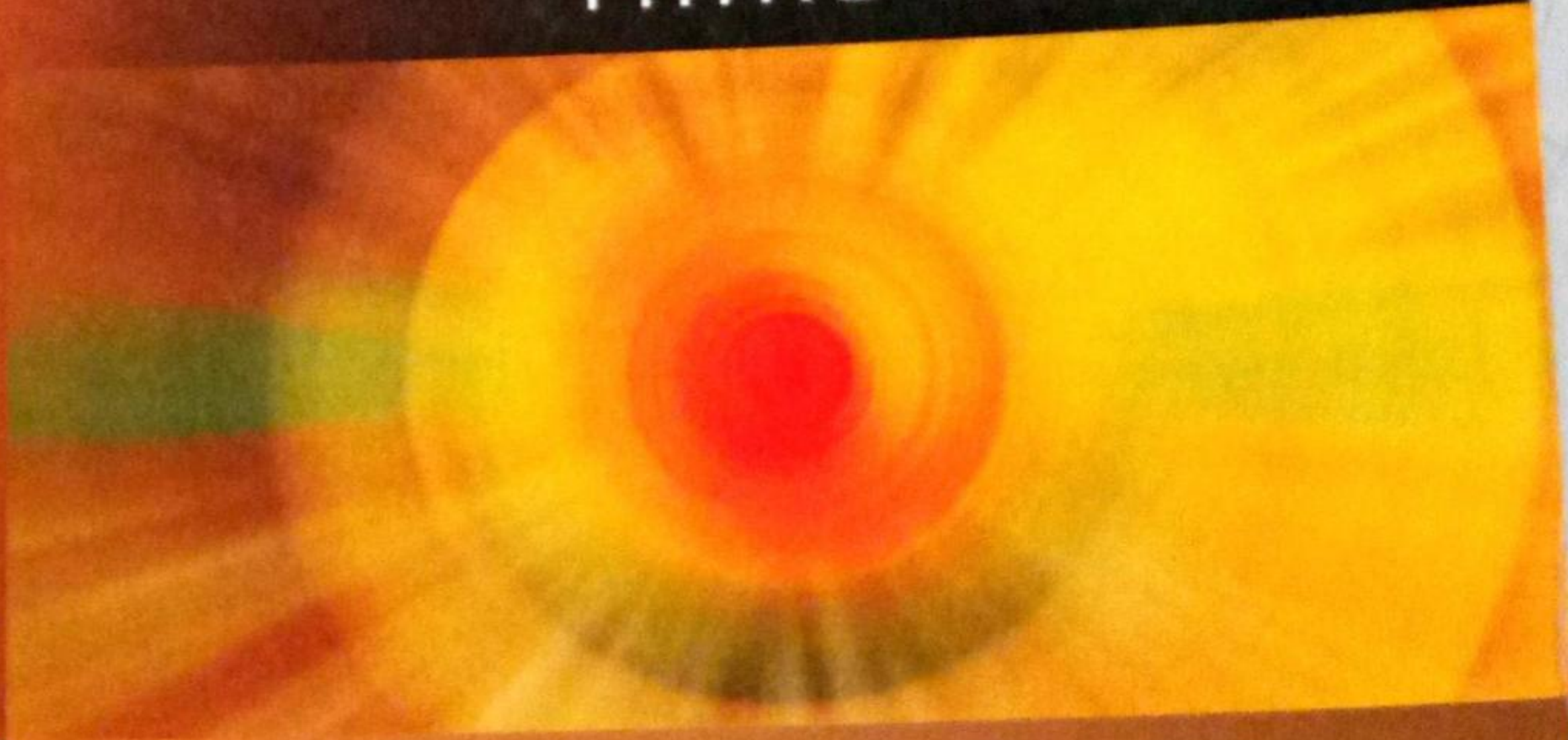



Copyright © 2005  
All rights reserved. No  
part of this publication may be  
reproduced, stored in a retrieval  
system, or transmitted, in any  
form or by any means, electronic,  
mechanical, photocopying, recording,  
or by any information storage and  
retrieval system, without permission  
in writing from Pearson Education, Inc.  
UNAUTHORIZED

# Chemical Kinetics

THIRD EDITION



Keith J. Laidler

 Pearson

# CONTENTS

---

Preface xi

## Chapter 1 BASIC KINETIC CONCEPTS 1

- 1.1 Scope of Chemical Kinetics 2
  - 1.1.1 Macroscopic and Microscopic Kinetics 3
- 1.2 Reaction Stoichiometry 4
- 1.3 Rates of Consumption and Formation 6
- 1.4 Extent of Reaction 7
- 1.5 Rate of Reaction 8
- 1.6 Volume Change During Reaction 9
- 1.7 Empirical Rate Equations 10
  - 1.7.1 Order of Reaction 10
  - 1.7.2 Rate Constants 11
  - 1.7.3 Reactions Having No Order 12
- 1.8 Elementary, Composite, and Chain Reactions 13
  - 1.8.1 Chain Reactions 14
- 1.9 Catalysis and Inhibition 14
- Problems 15
- References 16
- Bibliography 17

## Chapter 2 ANALYSIS OF KINETIC RESULTS 18

- 2.1 Differential Method 18
- 2.2 Method of Integration 21
  - 2.2.1 First-Order Reactions 21
  - 2.2.2 Second-Order Reactions 23
  - 2.2.3 Reactions of the  $n$ th Order 25
- 2.3 Isolation Method 26
- 2.4 Half-Life 26
- 2.5 Comparison of Methods 28
- 2.6 Opposing Reactions 29
- 2.7 Reactions in Flow Systems 31

2.8	Techniques for Very Fast Reactions	33
2.8.1	Stopped-Flow Method	34
2.8.2	Relaxation Methods	35
2.8.3	Shock-Tube Methods	39
2.8.4	Flash Photolysis	39
2.9	Influence of Temperature on Reaction Rates	39
2.9.1	Survey of Empirical Equations for Temperature Dependence	40
2.9.2	Arrhenius Equation	44
2.9.3	Improved Treatments of Temperature Dependence	45
2.9.4	Temperature Dependence of the Pre-exponential Factor	46
	Problems	48
	References	50
	Bibliography	51

### Chapter 3 ENERGY OF ACTIVATION 54

3.1	Statistical Distribution of Molecular Energies	55
3.1.1	Simple Statistical Expressions	55
3.1.2	Tolman's Theorem	56
3.2	Potential-Energy Surfaces	59
3.3	Ab Initio Calculations of Potential-Energy Surfaces	64
3.3.1	Treatments Based on the London Equation	64
3.3.2	Variational Calculations	64
3.4	Semiempirical Calculations of Potential-Energy Surfaces	67
3.4.1	London-Eyring-Polanyi (LEP) Method	68
3.4.2	Sato Method	69
3.4.3	Modified LEP Methods	70
3.4.4	Bond-Energy-Bond-Order (BEBO) Method	70
3.5	Empirical Treatments of Activation Energy	71
	Appendix: Statistical Distribution of Molecular Energies	74
	Motion in Two Dimensions	74
	Motion in Three Dimensions	75
	Motion in Many Degrees of Freedom	76
	Problems	77
	References	78
	Bibliography	79

### Chapter 4 THEORIES OF REACTION RATES 80

4.1	Kinetic Theory of Collisions	81
4.1.1	Generalized Kinetic Theory	84
4.1.2	Extensions of Collision Theory	87
4.2	Rate Theories Based on Thermodynamics	87
4.3	Rate Theories Based on Statistical Mechanics	88
4.4	Early Dynamical Theories of Rates	88

4.5	Conventional Transition-State Theory	89
4.5.1	Equilibrium Hypothesis	90
4.5.2	Statistical Mechanics and Chemical Equilibrium	93
4.5.3	Derivations of the Rate Equation	94
4.5.4	Symmetry Numbers and Statistical Factors	98
4.6	Some Applications of Conventional Transition-State Theory	106
4.6.1	Reactions between Atoms	106
4.6.2	Reactions between Molecules	107
4.6.3	An Example: The Reaction $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$	109
4.7	Thermodynamic Formulation of Conventional Transition-State Theory	112
4.8	Assumptions and Limitations of Conventional Transition-State Theory	115
4.8.1	Multiple Crossings and the Equilibrium Hypothesis	116
4.8.2	Separability of the Reaction Coordinate	119
4.8.3	Quantum Effects	121
4.9	Extensions of Transition-State Theory	123
4.9.1	Variational Transition-State Theory	124
4.9.2	Quantum-Mechanical Transition-State Theory	127
4.9.3	Muonium Kinetics	129
4.10	Microscopic Reversibility and Detailed Balance	129
	Problems	131
	References	132
	Bibliography	135

## Chapter 5 ELEMENTARY GAS-PHASE REACTIONS 137

5.1	Bimolecular Reactions	138
5.1.1	Reactions of the Type $\text{H} + \text{H}_2$	138
5.1.2	Other Atom and Free-Radical Reactions	140
5.1.3	Temperature Dependence of Pre-exponential Factors	145
5.1.4	Ion-Molecule Reactions	146
5.2	Trimolecular Reactions	147
5.3	Unimolecular Reactions	150
5.3.1	Lindemann-Christiansen Hypothesis	152
5.3.2	Hinshelwood's Treatment	155
5.3.3	Rice-Ramsperger-Kassel (RRK) Treatment	157
5.3.4	Slater's Treatment	163
5.3.5	Marcus's Extension of the RRK Treatment (RRKM)	164
5.3.6	Influence of Foreign Gases	167
5.3.7	Intermolecular Energy Transfer	168
5.3.8	Intramolecular Energy Transfer	168
5.3.9	Laser-Induced Unimolecular Reactions	170
5.3.10	Decomposition of Ions	171
5.4	Combination and Disproportionation Reactions	171
5.4.1	Mechanisms of Atom and Radical Combinations	173
	Problems	176
	References	177
	Bibliography	180

**Chapter 6**  
**ELEMENTARY REACTIONS IN SOLUTION 183**

- 6.1 Solvent Effects on Reaction Rates 183
  - 6.1.1 Comparison between Gas-Phase and Solution Reactions 184
  - 6.1.2 Comparison between Different Solvents 184
- 6.2 Factors Determining Reaction Rates in Solution 185
  - 6.2.1 Collisions in Solution 186
  - 6.2.2 Transition-State Theory 188
  - 6.2.3 Influence of Internal Pressure 189
  - 6.2.4 Influence of Solvation 190
- 6.3 Reactions between Ions 191
  - 6.3.1 Influence of Solvent Dielectric Constant 191
  - 6.3.2 Pre-exponential Factors 194
  - 6.3.3 Single-Sphere Activated Complex 195
  - 6.3.4 Influence of Ionic Strength 197
  - 6.3.5 More Advanced Treatments 201
- 6.4 Ion-Dipole and Dipole-Dipole Reactions 203
  - 6.4.1 Pre-exponential Factors 204
  - 6.4.2 Influence of Ionic Strength 205
- 6.5 Influence of Hydrostatic Pressure 206
  - 6.5.1 Van't Hoff's Equation 206
  - 6.5.2 Volumes of Activation 207
- 6.6 Substituent and Correlation Effects 209
  - 6.6.1 Hammett Equation 209
  - 6.6.2 Compensation Effects 211
- 6.7 Diffusion-Controlled Reactions 212
  - 6.7.1 Full Microscopic Diffusion Control 212
  - 6.7.2 Partial Microscopic Diffusion Control 216
  - 6.7.3 Ionic Reactions 217
- Problems 222
- References 224
- Bibliography 226

**Chapter 7**  
**REACTIONS ON SURFACES 229**

- 7.1 Adsorption 230
- 7.2 Adsorption Isotherms 230
  - 7.2.1 Simple Langmuir Isotherm 231
  - 7.2.2 Adsorption with Dissociation 232
  - 7.2.3 Competitive Adsorption 233
  - 7.2.4 Nonideal Adsorption 234
  - 7.2.5 Thermodynamics and Statistical Mechanics of Adsorption 235
- 7.3 Structures of Solid Surfaces and Adsorbed Layers 237
  - 7.3.1 Detailed Structural Studies 238
  - 7.3.2 Induced Heterogeneity 241
- 7.4 Mechanisms of Surface Reactions 241
  - 7.4.1 Kinetic Effects of Surface Heterogeneity 243
  - 7.4.2 Kinetic Effects of Interactions 244

7.5	Unimolecular Surface Reactions	244
7.5.1	Inhibition	246
7.5.2	Activation Energies	246
7.6	Bimolecular Surface Reactions	248
7.6.1	Reaction between Two Adsorbed Molecules	249
7.6.2	Reaction between a Gas Molecule and an Adsorbed Molecule	250
7.6.3	Adsorption of Two Gases without Mutual Displacement	250
7.6.4	Inhibition	251
7.6.5	Activation Energies	251
7.6.6	Parahydrogen Conversion	252
7.6.7	Combination and Formation of Atoms at Surfaces	252
7.6.8	Exchange Reactions	253
7.6.9	Addition of Hydrogen to Ethylene	257
7.7	Transition-State Theory of Surface Reactions	258
7.7.1	Rates of Chemisorption	259
7.7.2	Rates of Desorption	261
7.7.3	Unimolecular Surface Reactions	262
7.7.4	Bimolecular Surface Reactions	264
7.7.5	Comparison of Homogeneous and Heterogeneous Reaction Rates	266
	Problems	268
	References	270
	Bibliography	273

## Chapter 8 COMPOSITE REACTIONS 276

8.1	Types of Composite Mechanism	278
8.2	Rate Equations for Composite Mechanisms	278
8.2.1	Simultaneous and Consecutive Reactions	279
8.2.2	Steady-State Treatment	282
8.2.3	Rate-Determining (Rate-Controlling) Steps	283
8.2.4	Microscopic Reversibility and Detailed Balance	285
8.3	Chain Reactions	288
8.3.1	Chain Initiation Processes	290
8.4	Some Inorganic Mechanisms	291
8.4.1	Hydrogen-Bromine Reaction	291
8.4.2	Hydrogen-Chlorine Reaction	295
8.4.3	Hydrogen-Iodine Reaction	298
8.4.4	Comparison of the Hydrogen-Halogen Reactions	300
8.4.5	Formation and Decomposition of Phosgene	301
8.4.6	Decomposition of Nitrogen Pentoxide	303
8.4.7	Decomposition of Ozone	305
8.4.8	Thermal Para-Ortho Hydrogen Conversion	307
8.5	Organic Decompositions	307
8.5.1	Goldfinger-Letort-Niclause Rules	311
8.5.2	Molecular Processes	314
8.5.3	Decomposition of Ethane	316
8.5.4	Decomposition of Acetaldehyde	319
8.5.5	Inhibition Mechanisms	321

8.6	Gas-Phase Combustion	322
8.6.1	Hydrogen-Oxygen Reaction	323
8.6.2	Combustion of Hydrocarbons	328
8.7	Polymerization Reactions	330
8.7.1	Molecular Mechanisms	330
8.7.2	Free-Radical Mechanisms	332
8.7.3	Cationic Polymerization	335
8.7.4	Anionic Polymerization	338
8.7.5	Emulsion Polymerization	339
	Problems	340
	References	342
	Bibliography	346

## **Chapter 9** **PHOTOCHEMICAL AND RADIATION-CHEMICAL REACTIONS** **348**

9.1	Photochemical Reactions	349
9.1.1	Photochemical Primary Process	349
9.1.2	Reactions of Electronically Excited Species	353
9.1.3	Photochemical Thresholds	355
9.1.4	Law of Photochemical Equivalence	355
9.1.5	Rotating-Sector Technique	356
9.1.6	Flash Photolysis	359
9.2	Laser Photochemistry	360
9.2.1	Pulsed Lasers	361
9.2.2	Multiphoton Excitation	362
9.3	Photosensitization	362
9.4	Radiation-Chemical Reactions	365
9.4.1	Radiation-Chemical Primary Process	366
9.4.2	Pulse Radiolysis	370
9.4.3	Hydrated Electrons	370
9.5	Chemiluminescence	371
	Problems	372
	References	373
	Bibliography	374

## **Chapter 10** **HOMOGENEOUS CATALYSIS** **377**

10.1	General Catalytic Mechanisms	379
10.1.1	Equilibrium Treatment: Arrhenius Intermediates	380
10.1.2	Steady-State Treatment: van't Hoff Intermediates	382
10.1.3	Activation Energies for Catalyzed Reactions	383
10.2	Acid-Base Catalysis	384
10.2.1	General Acid-Base Catalysis	387
10.2.2	Mechanisms of Acid-Base Catalysis	388
10.2.3	Catalytic Activity and Acid-Base Strength	394

- 10.2.4 Salt Effects in Acid-Base Catalysis 396
- 10.2.5 Acidity Functions 397
- 10.3 Catalysis by Enzymes 399
  - 10.3.1 Influence of Substrate Concentration 400
  - 10.3.2 Influence of pH 406
  - 10.3.3 Influence of Temperature 409
  - 10.3.4 Transient-Phase Kinetics 410
  - 10.3.5 Enzyme Mechanisms 412
- 10.4 Catalysis in Gaseous Systems 412
- 10.5 Chain Mechanisms 413
- 10.6 Catalysis by Ions of Variable Valency 414
- 10.7 Activation of Molecular Hydrogen 415
- Problems 418
- References 421
- Bibliography 424

## Chapter 11 ISOTOPE EFFECTS 427

- 11.1 Equilibrium Isotope Effects 428
  - 11.1.1 Equilibria in Solution 432
- 11.2 Primary Kinetic Isotope Effects 433
  - 11.2.1 Semiclassical Treatments 434
  - 11.2.2 Quantum-Mechanical Tunneling 437
  - 11.2.3 Reactions of the Type  $H + H_2$  438
  - 11.2.4 Transfer of  $H^+$ ,  $H$ , and  $H^-$  442
  - 11.2.5 Reactions of Muonium 442
  - 11.2.6 Isotope Effects with Heavier Atoms 444
- 11.3 Secondary Kinetic Isotope Effects 446
  - References 447
  - Bibliography 448

## Chapter 12 REACTION DYNAMICS 449

- 12.1 Molecular-Dynamical Calculations 451
  - 12.1.1 The Reaction  $H + H_2$  454
  - 12.1.2 The Reaction  $Br + H_2$  457
  - 12.1.3 More Complex Reactions 458
- 12.2 Chemiluminescence 459
  - 12.2.1 Highly Dilute Flames 459
  - 12.2.2 Diffusion Flames 460
- 12.3 Features of Potential-Energy Surfaces 460
  - 12.3.1 Attractive Surfaces for Exothermic Reactions 461
  - 12.3.2 Repulsive Surfaces for Exothermic Reactions 462
  - 12.3.3 Surfaces of Intermediate Types for Exothermic Reactions 462
  - 12.3.4 Selective Enhancement of Reaction 466



x

12.3.5	Disposal of Excess Energy	469
12.3.6	Gradual and Sudden Surfaces	469
12.3.7	Influence of Rotational Energy	471
12.4	Molecular Beams	472
12.4.1	Stripping and Rebound Mechanisms	475
12.5	State-to-State Kinetics	476
12.5.1	Influence of Reactant Vibrational Energy	477
12.5.2	Influence of Reactant Rotational Energy	481
12.6	Spectroscopy of Transition Species	483
	References	485
	Bibliography	488

**Biographical Sketches 491**

**Answers to Problems 523**

**Index 525**