
CHEMICAL KINETICS AND REACTION MECHANISMS

Second Edition

James H. Espenson

*Distinguished Professor of Chemistry
Iowa State University*

McGraw-Hill, Inc.

New York St. Louis San Francisco Auckland Bogotá Caracas
Lisbon London Madrid Mexico City Milan Montreal New Delhi
San Juan Singapore Sydney Tokyo Toronto

CONTENTS

Preface	xi
1 Reactions and Reaction Rates	1
1.1 Reaction Mechanisms	1
1.2 Net Reactions and Reaction Rates	2
1.3 Elementary Reactions and Reaction Mechanisms	4
1.4 The Order of a Rate Law	5
1.5 Factors Influencing Reaction Rates	9
1.6 Practical Kinetics	10
1.7 Pitfalls	11
1.8 Stoichiometric Equations, Elementary Reactions, Mechanisms, and Molecularity	12
Problems	13
References	14
Bibliography	14
2 Reactions with a Simple Kinetic Form	15
2.1 First-Order Reactions	15
2.2 Second-Order Kinetics, $v = k[A]^2$	18
2.3 Second-Order Kinetics, $v = k[A][B]$	19
2.4 Use of Physical Properties with Kinetic Data	22
2.5 Methods When the Infinity Reading ("End Point") is Unknown	25
2.6 Reactions that are Zeroth-Order or a Fractional Order with Respect to a Single Concentration	28
2.7 Rate Expressions and the Method of Flooding	30
2.8 The Experimental Determination of Reaction Orders	31
2.9 Reactions with a Complex Dependence on a Single Concentration Variable	34

2.10	Product-Catalyzed Reactions	36
2.11	Methods of Data Analysis	37
	Problems	40
	References	44
3	Reversible and Concurrent Reactions	46
3.1	Reversible First-Order Reactions	46
3.2	Opposing Reactions of Higher Order	49
3.3	Concentration-Jump Methods for Opposing Reactions	52
3.4	Exchange Reactions	55
3.5	Parallel and Concurrent Reactions	58
3.6	Concurrent Reactions of Mixtures	62
	Problems	64
	References	69
4	Consecutive Reactions; the Steady-State and Other Approximations	70
4.1	Consecutive First-Order Reactions	71
4.2	Dual Solutions in Consecutive Reactions	75
4.3	A Series Reaction with a Reversible Step	77
4.4	The Steady-State Approximation	77
4.5	The Rate-Controlling Step	82
4.6	The Prior-Equilibrium and Improved Steady-State Approximations	86
4.7	Catalyzed and Enzyme-Catalyzed Reactions	90
4.8	Racemization and Reaction	95
	Problems	95
	References	100
5	Complex Mechanisms—Intermediates and Numerical Solutions	101
5.1	Identification of the Intermediate	101
5.2	The Reactivity of Intermediates	103
5.3	Kinetic Probes and Radical Clocks	107
5.4	Other Tests for Reaction Intermediates	110
5.5	Numerical Simulations	112
	Problems	119
	References	123
6	Deduction of Reaction Mechanisms	125
6.1	The Transition State	126
6.2	Mechanistic Interpretation of Rate Laws	127
6.3	Equivalent Kinetic Expressions	133
6.4	Kinetically Indistinguishable Schemes	135
6.5	pH-Rate Profiles and Downward Bends	139
6.6	pH-Rate Profiles and Upward Bends	142
6.7	Complexation Equilibria	145
	Problems	148
	References	153

7	Transition State Theory and Microscopic Reversibility	155
7.1	Temperature Effects	156
7.2	The Heat Capacity of Activation	160
7.3	Composite Rate Constants	161
7.4	The Isokinetic Relationship	164
7.5	Pressure Effects and the Volume of Activation	166
7.6	The Chemical Interpretation of Activation Parameters	168
7.7	Transition State Theory	169
7.8	Forward and Reverse Rate Constants and the Principle of Microscopic Reversibility	172
	Problems	176
	References	180
8	Chain Reactions and Oscillating Reactions	181
8.1	Characteristics of Chain Reactions	181
8.2	The Decomposition of Acetaldehyde	182
8.3	Autoxidation of an Organochromium Complex	184
8.4	Oxidation of Phosphorous Acid by Peroxodisulfate Ions	186
8.5	Well-Behaved Chain Reactions	187
8.6	Further Features of Chain Mechanisms	187
8.7	Branching Chain Reactions	189
8.8	Oscillating Reactions	190
	Problems	192
	References	195
9	Reactions in Solution	197
9.1	The Nature of Reactions in a Solvent	197
9.2	Diffusion-Controlled Reactions	199
9.3	Applications of Transition State Theory	203
9.4	Solvent Effects on Polar and Ionic Reactions	204
9.5	Salt Effects on Second-Order Ionic Reactions	206
9.6	Salt Effects on Other Reaction Orders	210
9.7	Salt Effects and Reaction Mechanisms	211
9.8	Kinetic Isotope Effects	214
	Problems	220
	References	222
10	Extrakinetic Probes of Mechanism	223
10.1	Linear Free Energy Relations (LFER)	223
10.2	The Hammett Correlation	225
10.3	The Taft Equation	229
10.4	The Swain-Scott and Edwards Equations	230
10.5	Acid-Base Catalysis	232
10.6	The Brønsted Catalysis Law	233
10.7	Mechanisms of Acid-Base Catalyzed Reactions	237
10.8	The Reactivity-Selectivity Principle and the Isoselectivity Rule	238
10.9	The Intrinsic Barrier and Hammond's Postulate	239

10.10	The Marcus Equations for Electron Transfer	243
10.11	Applications of the Marcus Equation	247
	Problems	249
	References	251
11	Reactions at Extreme Rates	252
11.1	Survey of Methods for Very Fast Reactions	252
11.2	Flow Methods for Rapid Reactions	253
11.3	Chemical Relaxation Methods	255
11.4	Kinetic Equations for Chemical Relaxation	257
11.5	NMR Line Shape Analysis	260
11.6	Flash and Laser Photolysis	263
11.7	Picosecond and Femtosecond Methods	266
11.8	Pulse Radiolysis	266
	Problems	268
	References	270
	A Concluding Assignment	272
	Answers to Numerical Problems	273
	Index	277