CONTENTS

QUANTUM THEORIES OF CHEMICAL KINETICS 1
By John C. Light

A REVIEW OF ION-MOLECULE REACTIONS 33
By Lewis Friedman and Bryan G. Reuben

ION CYCLOTRON RESONANCE 141
By George A. Gray

STABILITY AND DISSIPATIVE STRUCTURES IN OPEN SYSTEMS FAR FROM EQUILIBRIUM 209
By G. Nicolis

STATISTICAL-MECHANICAL THEORIES IN BIOLOGY 325
By Edward H. Kerner

PHOTOCHEMICAL REACTION CENTERS AND PHOTOSYNTHETIC MEMBRANES 353
By Roderick K. Clayton

AUTHOR INDEX 379

SUBJECT INDEX 389

QUANTUM THEORIES OF CHEMICAL KINETICS

JOHN C. LIGHT

James Franck Institute and the Department of Chemistry
The University of Chicago, Chicago, Illinois

CONTENTS

I. Introduction 1
II. Model Potentials and Perturbation Theory 4
A. Perturbation Theory 6
B. Model Potentials 7
III. Numerical Calculations for Collinear Collisions 8
A. Finite Difference Methods 9
B. Reaction Coordinates and Coupled Channel Calculations . . . 11
C. Quantum Tunneling in Reactive Collisions 23
IV. Alternative Approaches 25
References 30

A REVIEW OF ION-MOLECULE REACTIONS*

LEWIS FRIEDMAN AND BRYAN G. REUBEN†

Department of Chemistry, Brookhaven National Laboratory, Upton, New York

CONTENTS

I. Introduction 35
II. Historical Background 37
A. The Single Source Technique 37
B. Further Development of the Single Source 41
C. The Development of the Tandem Mass Spectrometer 46
1. Lindholm 46
2. Cermak and Herman 51
3. Giese and Maier 52
III. Thermochemistry of Ions 56
A. Introduction 56
B. Ionization and Appearance Potentials 57
C. Kinetic Approach to Thermochemistry 59
1. Proton Affinity of Hydrogen 59
2. Proton Affinity of Water 64
3. Proton Affinity of Ammonia 67
4. Proton Affinities of Other Molecules 68
5. Threshold for the Reaction $C^+ + D_2 \rightarrow CD^+ + D$ . . . 69
6. N_3^+, C_2O^+, O_3^+ 70
7. Attenuation Data and the Identification of Excited States in Beams . 71
D. Equilibrium Approach to Ion Thermochemistry 73
E. Discussion 80
IV. Kinetics of Ion-Molecule Reactions 82
A. Introduction 82
B. Complex Formation versus Stripping 83
1. Stripping Mechanisms 83
2. Development of Angular and Velocity Distribution Measurements . 85
3. Ion Intensity Maps 86
4. Crossed Beam Experiments 89
5. Evidence for Complex Formation 90

* Work supported by the U.S. Atomic Energy Commission.

† On leave from: Department of Chemistry, University of Surrey, Guildford, Surrey, England.

6. Transition from Stripping to Complex Formation . . . 92
7. Discussion 95
C. Isotope Effects 97
1. Simple Systems 97
2. Complex Systems 99
D. Long-Lived Collision Complexes 102
1. Introduction 102
2. Polymerization Reactions 103
3. Addition Reactions 105
4. Clustering Reactions 109
5. Determination of Rate Constants in High Pressure Systems . . 109
E. State Selection of Reactants 111
1. Introduction 111
2. Pulsed Source Techniques 112
3. Flowing Afterglow 114
4. Photoionization 118
F. Channels of Reaction 123
1. Introduction 123
2. Single Source and Tandem Mass Spectrometer Techniques . . 123
3. High Pressure Mass Spectrometry 125
4. Ion Cyclotron Resonance Spectroscopy 126
5. "Exotic" Channels of Reaction 129
References 132

ION CYCLOTRON RESONANCE

GEORGE A. GRAY

Oregon Graduate Center for Study and Research, Portland, Oregon

CONTENTS

I. Introduction 141
II. Experimental 143
A. Single and Double Resonance 143
B. Pulse Experiments 147
C. Scattering Experiments 151
D. Transient ICR 152
III. Collision-broadened ICR 153
IV. Energy Dependence of Ion Molecule Reactions 157
A. Bimolecular Rate Constants 157
B. Interaction Potential 159
V. ICR of Small Molecules 161
VI. Systems of Chemical Interest 171
A. Rate Constants 171
B. Methane-Hydrogen 172
C. Olefins 177
D. Reactions of Hydrocarbon Derivatives 182
E. Thermochemical Considerations 191
F. Applications of ICR to Ionic Structure 195
VII. Conclusion 203
References 204

STABILITY AND DISSIPATIVE STRUCTURES IN OPEN SYSTEMS FAR FROM EQUILIBRIUM

G. NICOLIS,

Faculté des Sciences de l'Université Libre de Bruxelles, Belgium

CONTENTS

I. Introduction 210
II. Thermodynamics of Irreversible Processes 211
A. General Theory and the Linear Region 211
B. Nonlinear Thermodynamics 217
III. Open Systems at Mechanical Equilibrium 220
A. General Comments 220
B. Evolution Criterion 221
C. Stability Theory 224
D. Stability Theory and Irreversible Thermodynamics 228
E. Dissipative Structures 234
IV. Chemical Oscillations—General Theory and Conservative Systems . 237
A. Introduction 237
B. Two Independent Variables—Singular Points and Variational Equations 239
C. Thermodynamic Interpretation 244
D. The Volterra–Lotka Model 247
E. Thermodynamic Properties of the Volterra–Lotka System . . 252
V. Limit Cycles 255
A. Introduction 255
B. Chemical Instabilities—A Simple Example 258
C. Thermodynamic Analysis of Limit Cycles 265
D. Temporal Organization Beyond Instability—Comparison with the Volterra–Lotka Model 269
E. Experimental Evidence and Further Examples of Chemical Instabilities 275
VI. Symmetry-breaking Instabilities 277
A. General Comments 277
B. Examples of Symmetry-breaking Instabilities 278
C. Dissipative Structures Beyond Symmetry-breaking Instabilities . 283
D. Stability of time-dependent States and Interference Effects . . 284
VII. Multistationary States 287
A. Introduction 287

B. Examples of Multiple Steady States 288
C. Thermodynamic Properties 294
VIII. Fluctuations 295
A. Introduction 295
B. The Markovian Stochastic Approximation 296
C. Fluctuations Around Nonequilibrium States—General Ideas and a Simple Application 298
D. Evolution of Large Fluctuations—The Volterra–Lotka Model . . 305
IX. Applications in Biology 314
A. Introduction 314
B. Oscillatory Processes in Biology 315
C. Symmetry-breaking Instabilities and Interference Effects . . . 317
D. Multiple steady States. 318
X. General Conclusions 319
Acknowledgments 321
References 321

STATISTICAL–MECHANICAL THEORIES IN BIOLOGY

EDWARD H. KERNER

Physics Department, University of Delaware, Newark, Delaware

CONTENTS

I. Introduction 325
II. Generalities on Ensembles 328
III. Ecodynamics 333
IV. Neural Networks 339
V. Biochemical Kinetics 342
VI. Mathematical Overview 346
References 351