

A TEXTBOOK OF PHYSICAL CHEMISTRY

ARTHUR W. ADAMSON

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PREFACE

It might seem that there are only a limited number of ways in which the contents of the first course in physical chemistry can be presented to the student, and that all have already been tried. The pedagogical problem is a complex one, however; it is also one that shifts with time. We have seen the appearance of a **great** deal of traditional first year physical chemistry in 'beginning general chemistry texts, usually in curtailed form. At the same time, material which in the past was more commonly found in graduate courses is now appropriate for the undergraduate. The problem is that it is very easy to add new material to a course, and very difficult to avoid making it just an addition.

The older physical chemistry texts gradually evolved a coherent, integrated presentation in which the student progressed steadily through an accepted sequence of material, with each subject building on the previous one. The attempt here has been to achieve something comparable in the contemporary vein.

The traditional physical chemistry course performed a second function—one with which I think we **dare** not dispense. This was the function of indoctrinating the student, by practice as well as by precept, in scientific thinking. The student was asked to develop at least the beginnings of a critical understanding of the principle and of the approximations that go into each physical chemical relationship. He could be expected to know something about the limitations of a treatment and thus to have a real appreciation of its scope. The better student would acquire the ability to vary the principle or the assumptions to produce modified derivations. I have felt it to be essential that the newer material that is added be presented in reasonable depth so that the same demands can be made on the student as with the traditional topics. The effort has been to avoid letting physical chemistry become a descriptive course in which the student is asked to accept the results of advanced treatments but is not afforded the basis for being critical of them.

Preface

The order as well as the philosophy of presentation of material in this text deserves some explanation. An immediate problem is that which arises from the presence of two aspects of modern physical chemistry. One aspect is macroscopic and phenomenological in nature; it is exemplified by the topics of thermodynamics, phase equilibria, and electrochemistry. This is the classical aspect; the traditional textbook devoted itself almost exclusively to it. The second aspect is molecular and theoretical, exemplified by statistical thermodynamics and wave mechanics. The contemporary course gives about equal emphasis to these two main streams of physical chemistry, but there are differences of opinion as to their best order of presentation and the various existing texts differ noticeably in this respect. To be blunt, the choice has seemed to be whether to cover wave mechanics in the first or in the second half of the book. On the one hand, the theoretical approach provides great insight and it may therefore seem proper that it precede the classical material. On the other hand, phenomenology comprises that which we know as scientific, that is, experimental truth. It seems logical, for example, that the great concepts of thermodynamics precede theories about molecular details. An important practical point is that the macroscopic approach provides an entrée to physical chemistry which is easier on the student than is an initial burst of wave mechanics. The scientific maturity of students increases noticeably during the year course in physical chemistry and wave mechanics is a difficult subject.

I have adopted an order of presentation which attempts to be responsive to each of the above considerations. The first half of the book follows the general macroscopic stream, but with a great deal of the molecular approach presented at the same time. Thus Chapter 2 on kinetic molecular theory follows the opening one on gases; and Chapter 2 introduces the Boltzmann principle. Chapter 3 continues the emphasis of the molecular level with a discussion of polarizability, and of dipole and magnetic moments; it applies the Boltzmann principle to the treatment of molar polarization. (Chapter 3 includes the phenomenology of light absorption since this topic is too useful as a tool to be deferred to the much later chapter on molecular spectroscopy; the chapter also provides an early opportunity to discuss systems of units.)

The next group of chapters takes up thermodynamics. Classical and statistical thermodynamics are given almost equal emphasis—the two aspects *should* be together. The pedagogical problem of an early introduction of statistical thermodynamics is met as follows. First, the repeated use of the Boltzmann principle in the preceding chapters prepares the student for the formal development of partition functions. It is assumed that the modern student enters his physical chemistry course well aware that molecules have translational, rotational, and vibrational energy states, and it is straightforward to then derive the detailed statistical expressions for the various thermodynamic properties of ideal gases. The wave mechanical equations for the spacings of energy states must, of course, be used; however, their derivation (which comes later in the text) is not essential to the understanding of the thermodynamic concepts.

Chapters 7–13 complete the traditional sequence of chemical and phase equi-

Preface

libria, and electro-chemistry. The early introduction of statistical thermodynamics allows a good deal of reference to the molecular point of view.

Chapters 14 and 15 are innovative in that they divide chemical kinetics between gas phase and solution phase aspects. It seems to me that quite different emphases are involved and that such division is overdue. In gas kinetics, theory is concerned with the kinetic molecular treatment of collisions or, alternatively, with the statistical thermodynamics of the transition state (treated as an ideal gas). Solution kinetics seem better understood in terms of diffusional encounters, with the encounter complex generally requiring activation energy if reaction is to occur. The role of the solvent cannot be ignored. Also, of course, the mechanisms proposed for gas phase and for solution phase reactions often draw on rather different chemistries.

Surface chemistry is too often relegated to a dispensable chapter in the physical chemistry text. It seems better to spread surface chemical topics among various chapters, according to where their inclusion is most appropriate. For the same reason, the methods of colloid chemistry for molecular weight determination have been included in the chapter on colligative properties.

Chapters 16-18 carry the student through wave mechanics and its applications. The subject presents the problem that all but the very simplest results require so extensive a mathematical approach that their presentation could easily transform the course into one on mathematical methods. Fortunately, these simpler results do in fact provide the basis for the great majority of applications outside of serious chemical physics. Thus the solutions for the hydrogen atom supply the language of chemical bonding as well as the basis functions for many first order calculations. Hydrogen-like wave functions are, accordingly, discussed in considerable quantitative detail. Further, the treatment of chemical bonding rests to a high degree on the use of the symmetry properties of molecules. The central role that group theory plays in this respect makes it an appropriate and again overdue subject in the physical chemistry course. I have found that group theory used in conjunction with hydrogen-like wave functions provides students with a better appreciation of chemical bonding than does the usual approach. Knowledge of some formal group theory is also necessary to the treatment of electronic and vibrational excited states. Finally, much time is lost in certain senior courses if the student is not reasonably well acquainted with group theoretical methods. For these various reasons, the topic receives the attention of a full chapter.

The chapter on molecular spectroscopy and photochemistry takes a somewhat broader view than is usual. The excited state is presented as a chemical species which differs from the ground state in structure as well as in energy, and which can undergo various chemical and physical processes. Vibrational spectra can be discussed in terms of normal modes because of the group theoretical background supplied by the preceding chapter.

Crystal structure, colloid and polymer chemistry, and radio and nuclear chemistry are placed at the end. The material is not terminal with respect to any pedagogical scheme, of course. The situation is simply that these three subjects are not

Preface

prerequisite to any others in the text and therefore have no unique logical positioning.

An explanation should also be given of the manner in which the text is structured. As usual, there is more material than can be covered in the normal year course in physical chemistry. I have felt that some distinction is needed between that which is essential, that which is important, and that which is interesting but merely descriptive. To assist both the instructor and the student in making such distinction, each chapter is divided into three parts.

The first portion of every chapter is deemed essential to the topic; collectively, these portions comprise a coherent core. The second part of each chapter is called Commentary and Notes. In this section we look back over the chapter in terms of commentaries on one aspect or another; also, additional material may be presented, but generally without detailed derivation. The Commentary and Notes sections are intended to be descriptive in nature and to be helpful, rather than a burden to the student. With a few exceptions, no problems are written on these sections.

The last part of each chapter is called Special Topics. As the name suggests, various specific topics are presented; these are given in the same detail as is material in the core. Certain topics are placed in this section because, although they are standard, they are judged to be of lower priority than core material, and not to be prerequisite to it. Examples are: magnetochemistry, the Joule-Thomson effect, the Hittorf method in transference measurements, heterogeneous catalysis, and blackbody radiation. Other special topics cover advanced material whose study should be valuable, time permitting. Examples are: use of the Lennard-Jones potential function in the treatment of nonideal gases, the statistical thermodynamic treatment of equilibrium constants, first order perturbation theory, ligand field theory, the Hückel method. The core does not draw appreciably on any special topic; assignment of a special topic is therefore entirely optional (occasionally a special topic will refer to a preceding one).

The problems at the end of each chapter consist of Exercises (with answers given), Problems, and Special Topics Problems. Some are in the style of those in my study-aid book, "Understanding Physical Chemistry," Benjamin, 1969; others are of the longer, calculational type. Especially long ones are marked as requiring the use of a calculator or desk type computer. I do feel that many aspects of physical chemistry cannot properly be appreciated unless the relevant calculations are actually made in detail.

Some acknowledgments are in order. Much of this book was written while the author was a guest at the University of Western Australia. I am greatly indebted to the hospitality extended by Professor N. Bayliss as Chairman of the Department of Chemistry, and by all members of the department individually. My thanks go to D. W. Watts both as a friendly critic and for his many special efforts on our behalf. I sincerely appreciate the assistance of E. Leffler, whose proofreading included reworking many problems, and the efforts of colleagues at the University of Southern California and elsewhere, who helped greatly in their reviewing of various chapters. I should mention J. Aklonis, R. Bau, T. Dunn, and G. Segal,

Preface

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I know from experience that errors and maladroit passages inevitably remain in spite of all efforts. I sincerely hope that readers will freely call such to my attention.

A Note to the Reader

Many of the topics are sufficiently involved that I have used a spiral approach to them. By this I mean that the initial presentations sometimes are made on the most direct basis, with certain sidelights or elegancies deferred until later in the chapter. I suggest that the core portion of each chapter be read in its entirety before detailed study is undertaken. Because of this aspect and also because of the structuring of the chapters into divisions, I have tried to make the Index unusually complete. It is intended to be used routinely.

CONTENTS

Preface

xvii

1 IDEAL AND NONIDEAL GASES

1-1	<i>Introduction</i>	1
1-2	<i>Equations of State</i>	2
1-3	<i>Development of the Concept of an Ideal Gas; the Absolute Temperature Scale</i>	3
1-4	<i>The Ideal Gas Law and Related Equations</i>	6
1-5	<i>Mixtures of Ideal Gases; Partial Pressures</i>	7
1-6	<i>Partial Volumes; Amagat's Law</i>	10
1-7	<i>The Barometric Equation</i>	10
1-8	<i>Deviations from Ideality—Critical Behavior</i>	14
1-9	<i>Semiempirical Equations of State. The van der Waals Equation</i>	21
1-10	<i>The van der Waals Equation, Critical Phenomena, and the Principle of Corresponding States</i>	27
	Commentary and Notes	29
	Special Topics	32
	<i>General References</i>	37
	<i>Cited References</i>	38
	<i>Exercises and Problems</i>	38
	<i>Exercises</i>	38
	<i>Problems</i>	39
	<i>Special Topics Problems</i>	42

2 KINETIC MOLECULAR THEORY OF GASES

2-1	<i>Introduction</i>	44
2-2	<i>The Boltzmann Distribution Law</i>	46
2-3	<i>The Distribution of Molecular Velocities</i>	49
2-4	<i>Average Quantities from the Distribution Laws</i>	54

vii

Contents

2-5	<i>Some Applications of Simple Kinetic Molecular Theory. Collision Frequency on a Plane Surface and Graham's Law</i>	56
2-6	<i>Bimolecular Collision Frequency and Mean Free Path</i>	59
2-7	<i>Transport Phenomena; Viscosity, Diffusion, and Thermal Conductivity</i>	63
2-8	<i>Summary of Kinetic Molecular Theory Quantities</i>	69
Commentary and Notes		
2-CN-1	<i>Some Further Comments on the Various Distribution Laws</i>	72
2-CN-2	<i>Verification of the Distribution Laws</i>	73
2-CN-3	<i>Molecular Diameters; Avogadro's Number</i>	74
2-CN-4	<i>Transport Phenomena; Phenomenological Equations</i>	75
2-CN-5	<i>Verification of the Kinetic Molecular Theory</i>	76
Special Topics		
2-ST-1	<i>Use of a Lennard-Jones Potential Function</i>	77
<i>General References</i>		80
<i>Cited References</i>		80
<i>Exercises</i>		81
<i>Problems</i>		82
<i>Special Topics Problems</i>		84

3 SOME ADDITIVE PHYSICAL PROPERTIES OF MATTER

3-1	<i>Introduction</i>	85
3-2	<i>Absorption of Light</i>	86
3-3	<i>Molar Refraction</i>	88
3-4	<i>Molar Polarization; Dipole Moments</i>	91
3-5	<i>Dipole Moments and Molecular Properties</i>	96
Commentary and Notes		
3-CN-1	<i>Additive Properties</i>	99
3-CN-2	<i>Systems of Units</i>	100
Special Topics		
3-ST-1	<i>The Charge Distribution of a Molecule</i>	103
3-ST-2	<i>Magnetic Properties of Matter</i>	106
<i>General References</i>		109
<i>Cited References</i>		110
<i>Exercises</i>		110
<i>Problems</i>		111
<i>Special Topics Problems</i>		114

4 CHEMICAL THERMODYNAMICS. THE FIRST LAW OF THERMODYNAMICS

4-1	<i>Introduction</i>	115
4-2	<i>The Story of a Man</i>	117
4-3	<i>Energy and the First Law of Thermodynamics</i>	119
4-4	<i>Mathematical Properties of State Functions. Exact and Path-Dependent Differentials</i>	122
4-5	<i>Heat and Work for Various Processes</i>	127
4-6	<i>Enthalpy. An Alternative Form of the First Law</i>	130
4-7	<i>Applications of the First Law to Ideal Gases</i>	131
4-8	<i>Molecular Basis for Heat Capacities. The Equipartition Principle</i>	139
4-9	<i>Statistical Mechanical Treatment of First Law Quantities</i>	141

Contents

4-10	<i>Translational Partition Function for an Ideal Gas</i>	144
4-11	<i>The Rotational Partition Function</i>	146
4-12	<i>The Vibrational Partition Function</i>	148
Commentary and Notes		
4-CN-1	<i>Internal Pressure</i>	151
4-CN-2	<i>Additional Aspects of Statistical Mechanical Treatments</i>	152
Special Topics		
4-ST-1	<i>The Joule-Thomson Effect</i>	154
4-ST-2	<i>The Heat Capacity of a Solid</i>	157
<i>General References</i>		159
<i>Exercises</i>		160
<i>Problems</i>		161
<i>Special Topics Problems</i>		163

5 THERMOCHEMISTRY

5-1	<i>Introduction</i>	165
5-2	<i>Measurement of Heats of Reaction: Relationship between ΔE and ΔH</i>	167
5-3	<i>Some Enthalpies of Combustion, Hydrogenation, and Solution</i>	170
5-4	<i>Combining ΔH or ΔE Quantities</i>	172
5-5	<i>Enthalpies of Formation</i>	174
5-6	<i>Dependence of ΔH and ΔE on Temperature</i>	177
Commentary and Notes		
5-CN-1	<i>Explosions, Flames, and Rockets</i>	181
Special Topics		
5-ST-1	<i>Chemical Bond Strengths</i>	183
5-ST-2	<i>Internal Energy and Enthalpy Functions</i>	187
<i>General References</i>		191
<i>Cited References</i>		191
<i>Exercises</i>		191
<i>Problems</i>		192
<i>Special Topics Problems</i>		194

6 THE SECOND AND THIRD LAWS OF THERMODYNAMICS

6-1	<i>Introduction</i>	195
6-2	<i>The Carnot Cycle—Heat Machines</i>	200
6-3	<i>Generalization of the Carnot Cycle—the Entropy Function</i>	204
6-4	<i>Calculations of ΔS for Various Reversible Processes</i>	207
6-5	<i>Calculation of ΔS for Various Irreversible Processes</i>	210
6-6	<i>Free Energy. Criteria for Equilibrium</i>	214
6-7	<i>Second Law Relationships</i>	218
6-8	<i>The Third Law of Thermodynamics</i>	219
6-9	<i>Statistical Mechanical Treatment of Second Law Quantities</i>	223
Commentary and Notes		
6-CN-1	<i>Summary of the Statements of the Laws of Thermodynamics</i>	232
6-CN-2	<i>Statistical Thermodynamics—Ensembles—and J. Willard Gibbs</i>	233
6-CN-3	<i>Additional Comments on the Third Law of Thermodynamics and on the Attainment of 0°K</i>	235

Contents

Special Topics	
6-ST-1 <i>Thermodynamic Relationships</i>	238
6-ST-2 <i>Thermodynamic Treatment of a Nonideal Gas—Fugacity</i>	241
6-ST-3 <i>The Free Energy Function</i>	243
<i>General References</i>	246
<i>Cited References</i>	246
<i>Exercises</i>	247
<i>Problems</i>	249
<i>Special Topics Problems</i>	252

7 CHEMICAL EQUILIBRIUM

7-1 <i>Introduction</i>	254
7-2 <i>The Thermodynamic Equilibrium Constant</i>	256
7-3 <i>The Determination of Experimental Equilibrium Constants</i>	258
7-4 <i>The Variation of K_p with Temperature</i>	263
7-5 <i>Gas-Solid Equilibria</i>	266
7-6 <i>Le Châtelier's Principle</i>	268
7-7 <i>Free Energy and Entropy of Formation</i>	269
7-8 <i>Application of Statistical Thermodynamics to Chemical Equilibrium</i>	270
Commentary and Notes	
7-CN-1 <i>Chemical Equilibrium and the Second Law of Thermodynamics</i>	272
7-CN-2 <i>Some Important Gas Equilibria</i>	274
Special Topics	
7-ST-1 <i>Effect of Pressure on Chemical Equilibria Involving Gases</i>	275
<i>General References</i>	278
<i>Cited References</i>	278
<i>Exercises</i>	278
<i>Problems</i>	280
<i>Special Topics Problems</i>	283

8 LIQUIDS AND THEIR SIMPLE PHASE EQUILIBRIA

8-1 <i>Introduction</i>	284
8-2 <i>The Vapor Pressure of Liquids (and Solids)</i>	286
8-3 <i>Enthalpy and Entropy of Vaporization; Trouton's Rule</i>	292
8-4 <i>Liquid-Solid and Solid-Solid Equilibria. Phase Maps</i>	298
8-5 <i>The Free Energy of a Liquid and Its Vapor</i>	302
8-6 <i>The Surface Tension of Liquids. Surface Tension as a Thermodynamic Quantity</i>	304
8-7 <i>Measurement of Surface Tension</i>	308
8-8 <i>Results of Surface Tension Measurements</i>	313
8-9 <i>The Kelvin Equation. Nucleation</i>	315
8-10 <i>Viscosity of Liquids</i>	316
Commentary and Notes	
8-CN-1 <i>Additional Thermodynamic Properties of Liquids</i>	319
8-CN-2 <i>The Structure of Water</i>	321
Special Topics	
8-ST-1 <i>Intermolecular Forces</i>	323
8-ST-2 <i>The Viscosity of Liquids</i>	328

Contents

<i>General References</i>	331
<i>Cited References</i>	331
<i>Exercises</i>	332
<i>Problems</i>	333
<i>Special Topics Problems</i>	338

9 SOLUTIONS OF NONELECTROLYTES

9-1 <i>Introduction</i>	339
9-2 <i>The Vapor Pressure of Solutions. Raoult's and Henry's Laws</i>	341
9-3 <i>The Thermodynamics of Multicomponent Systems</i>	353
9-4 <i>Ideal Gas Mixtures</i>	357
9-5 <i>Ideal and Nonideal Solutions. Activities and Activity Coefficients</i>	358
9-6 <i>The Temperature Dependence of Vapor Pressures</i>	364
9-7 <i>Boiling Point Diagrams</i>	365
9-8 <i>Partial Miscibility</i>	372
Commentary and Notes	
9-CN-1 <i>Other Properties of Solutions</i>	375
9-CN-2 <i>Ideal, Regular, and Athermal Solutions</i>	378
9-CN-3 <i>Statistical Thermodynamics of Solutions</i>	379
Special Topics	
9-ST-1 <i>Partial Molal Quantities</i>	381
9-ST-2 <i>The Surface Tension of Solutions. The Gibbs Equation</i>	387
<i>General References</i>	391
<i>Cited References</i>	391
<i>Exercises</i>	392
<i>Problems</i>	394
<i>Special Topics Problems</i>	396

10 DILUTE SOLUTIONS OF NONELECTROLYTES. COLLIGATIVE PROPERTIES

10-1 <i>Vapor Pressure Lowering</i>	399
10-2 <i>Boiling Point Elevation</i>	400
10-3 <i>Freezing Point Depression</i>	401
10-4 <i>Summary of the First Three Colligative Properties</i>	402
10-5 <i>Osmotic Equilibrium</i>	405
10-6 <i>Activities and Activity Coefficients for Dilute Solutions</i>	409
10-7 <i>Other Methods of Molecular Weight Determination</i>	410
Commentary and Notes	
10-CN-1 <i>Colligative Properties and Deviations from Ideality</i>	419
10-CN-2 <i>Relationship between Freezing Point Depression and Solubility</i>	421
10-CN-3 <i>Water Desalination</i>	422
10-CN-4 <i>Molecular Weight Determination</i>	424
Special Topics	
10-ST-1 <i>Dilute Solution Conventions for Activities and Activity Coefficients</i>	425
10-ST-2 <i>Theoretical Treatment of Diffusion</i>	432
<i>General References</i>	433
<i>Cited References</i>	434
<i>Exercises</i>	434
<i>Problems</i>	435
<i>Special Topics Problems</i>	438

Contents

11 HETEROGENEOUS EQUILIBRIUM

11-1	<i>The Gibbs Phase Rule</i>	439
11-2	<i>One-Component Systems</i>	443
11-3	<i>Two-Component Systems</i>	444
11-4	<i>Sodium Sulfate-Water and Other Systems</i>	453
11-5	<i>Three-Component Systems</i>	457
11-6	<i>Three-Component Solubility Diagrams</i>	462
Commentary and Notes		
11-CN-1	<i>Definitions of the Terms Component and Phase</i>	466
Special Topics		
11-ST-1	<i>Two-Component Freezing Point Diagrams. Partial Miscibility</i>	468
11-ST-2	<i>Partial Miscibility in Three-Component Systems</i>	474
<i>General References</i>		478
<i>Cited Reference</i>		478
<i>Exercises</i>		478
<i>Problems</i>		479
<i>Special Topics Problems</i>		485

12 SOLUTIONS OF ELECTROLYTES

12-1	<i>Introduction</i>	486
12-2	<i>Conductivity—Experimental Definitions and Procedures</i>	489
12-3	<i>Results of Conductance Measurements</i>	493
12-4	<i>Some Sample Calculations</i>	498
12-5	<i>Ionic Mobilities</i>	502
12-6	<i>Transference Numbers—Ionic Equivalent Conductivities</i>	510
12-7	<i>Activities and Activity Coefficients of Electrolytes</i>	513
12-8	<i>The Debye-Hückel Theory</i>	522
12-9	<i>Ionic Equilibria</i>	527
Commentary and Notes		
12-CN-1	<i>Electrolytic Dissociation</i>	537
12-CN-2	<i>Activity Coefficients for Other than Dilute Aqueous Solutions</i>	539
12-CN-3	<i>Acids and Bases</i>	542
Special Topics		
12-ST-1	<i>Ionic Diffusion Coefficients</i>	545
12-ST-2	<i>The Hittorf Method</i>	547
12-ST-3	<i>Treatment of Complex Ionic Equilibria</i>	551
<i>General References</i>		557
<i>Exercises</i>		557
<i>Problems</i>		559
<i>Special Topics Problems</i>		563

13 ELECTROCHEMICAL CELLS

13-1	<i>Definitions and Fundamental Relationships</i>	565
13-2	<i>Experimental Procedures</i>	572
13-3	<i>Determination of \mathcal{E}^0 Values and Activity Coefficients</i>	575
13-4	<i>Additivity Rules for Emf's. Standard Oxidation Potentials</i>	576
13-5	<i>Emf and Chemical Equilibria</i>	579

Contents

13-6	Concentration Cells	583
13-7	Oxidation-Reduction Reactions	584
13-8	Determination of pH	587
13-9	Irreversible Electrode Processes	589
	Commentary and Notes	
13-CN-1	Standard Oxidation Potential E° and Standard Electrode Potential \mathcal{V}°	592
13-CN-2	Storage Batteries	593
13-CN-3	Thermodynamic Quantities for Aqueous Ions	594
13-CN-4	Electrocapillarity. Absolute Electrode Potentials	596
	Special Topics	
13-ST-1	Liquid Junctions	599
13-ST-2	Polarization at Electrodes. Polarography	602
	General References	609
	Cited References	609
	Exercises	609
	Problems	611
	Special Topics Problems	614

14 KINETICS OF GAS-PHASE REACTIONS

14-1	Introduction	615
14-2	Rate Laws and Simple Mechanisms	617
14-3	Experimental Methods and Rate Law Calculations	625
14-4	Rate Laws and Reaction Mechanisms	632
14-5	Temperature Dependence of Rate Constants	637
14-6	Collision Theory of Gas Reactions	642
14-7	Unimolecular Reactions	645
14-8	Absolute Rate Theory. The Activated Complex	649
	Commentary and Notes	
14-CN-1	Termolecular Reactions	656
14-CN-2	Collision versus Transition-State Theory	658
14-CN-3	Molecular Beam and Related Studies	660
14-CN-4	Chemical Estimation of Arrhenius Parameters	661
14-CN-5	Explosions	662
14-CN-6	Free Radicals	663
	Special Topics	
14-ST-1	Heterogeneous Catalysis. Chemisorption of Gases	664
14-ST-2	Statistical Thermodynamic Treatment of Transition-State Theory	672
	General References	675
	Cited References	675
	Exercises	675
	Problems	678
	Special Topics Problems	680

15 KINETICS OF REACTIONS IN SOLUTION

15-1	Additional Comments on Rate Laws. Reversible Reactions	683
15-2	Experimental Methods	688
15-3	Kinetic-Molecular Picture of Reactions in Solution	691
15-4	Diffusion-Controlled Reactions	698
15-5	Transition-State Theory	700

Contents

15-6	Linear Free Energy Relationships. Reactions Involving an Acid or a Base	701
15-7	Ionic Reactions. Role of Activity Coefficients	708
	Commentary and Notes	
15-CN-1	Comparison of Collision-Encounter and Transition-State Theories	712
15-CN-2	Relationship between the Equilibrium Constant for a Reaction and Its Rate Constants	714
15-CN-3	The Composition of the Encounter or Activated Complex	717
	Special Topics	
15-ST-1	Integrated Forms for Some Additional Rate Laws	718
15-ST-2	Enzyme Catalysis	729
15-ST-3	Effect of Mechanical Pressure on Reaction Rates	731
	General References	732
	Cited References	732
	Exercises	733
	Problems	733
	Special Topics Problems	737

16 WAVE MECHANICS

16-1	Introduction	739
16-2	Energy Units	745
16-3	Hydrogen and Hydrogen-Like Atoms	746
16-4	The Schrödinger Wave Equation	749
16-5	Some Simple Choices for the Potential Function V	754
16-6	The Harmonic Oscillator	759
16-7	Solutions of the Wave Equation for the Hydrogen Atom	764
16-8	The Graphical Appearance of Hydrogen-Like Orbitals	770
16-9	Graphical Appearance of the Electron Density around a Hydrogen-Like Atom	779
16-10	Hybrid Orbitals	782
	Commentary and Notes	
16-CN-1	Albert Einstein	784
16-CN-2	Steps beyond Hydrogen-Like Wave Functions	787
16-CN-3	Chemical Bonding from the Atomic Orbital Point of View. The Variation Method	789
	Special Topics	
16-ST-1	Quantum Theory of Blackbody Radiation	791
16-ST-2	The Rigid Rotator	795
16-ST-3	Domain Representation of Hydrogen-Like Orbitals	796
16-ST-4	First-Order Perturbation Theory	797
	General References	799
	Cited References	800
	Exercises	800
	Problems	801
	Special Topics Problems	803

17 MOLECULAR SYMMETRY AND BONDING

17-1	Introduction	804
17-2	Symmetry and Symmetry Operations	805
17-3	A Set of Symmetry Operations as Constituting a Group	814
17-4	Representations of Groups	818
17-5	Atomic Orbitals as Bases for Representations	825