CHEMISTRY EXPERIMENT AND THEORY

SECOND EDITION

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PREFACE

The world about us presents to our senses an endless variety of natural phenomena, and there is little to suggest to the casual observer any sort of underlying unity. Careful observations, combined with the processes of rational thought, have shown that all these phenomena result from the behavior of different combinations of a few kinds of very small particles, which are present in enormous numbers and which obey certain natural laws. The science of chemistry includes the study of these particles and their combinations with one another, the laws governing their behavior, and the natural phenomena resulting therefrom. This is, indeed, a large order, for at one extreme it includes the phenomena occurring within our own bodies and at another extreme the phenomena occurring in the most distant celestial bodies.

Experiment and theory are the twin pillars on which modern science is founded. In the ensuing pages we shall stress the importance of each in reaching an understanding of chemical phenomena. It is within an experimental setting that the meaning of a theoretical concept is revealed, and it is within the context of theory that an experiment acquires purpose and significance. Thus each illuminates the other, and together they show the path toward understanding.

We have written this book to present the science of chemistry as a full-year course at the beginning university or college level. The approach taken here assumes that the student is interested in one of the physical or biological sciences or in an applied field such as agriculture, engineering, or medicine, but is not necessarily interested in a career in chemistry itself. Most students who study chemistry at this level are still assessing and reassessing their interests and goals. This process will be enlightened by acquiring a good overview

of chemistry. The student who is already inclined toward a career in chemistry will also benefit from this approach.

In principle and practice, chemistry is a quantitative science. At various points its expression requires a certain amount of mathematics, mainly arithmetic and elementary algebra. Nevertheless, in discussing quantitative relationships the emphasis here is on their physical significance rather than on their mathematical aspects. To the practicing chemist, even one engaged in areas seemingly dominated by sophisticated mathematics, the chemistry comes first—mathematics is only a tool, albeit an essential one.

Subject to the limitation that more advanced mathematics (including calculus) is avoided, we have followed a course designed to present chemistry in a form acceptable to the serious student—chemistry the way it really is. In our view, this approach is the most practical in the long run, for it will most quickly bring the student to an understanding of modern chemistry.

The introductory chapters of this book emphasize macroscopic phenomena. Topics introduced in this section include the different forms of matter (Chapter 1), stoichiometry (Chapter 2), and the physical properties of gases (Chapter 3). The kinetic theory of gases is then developed (Chapter 4) both as a model explaining the behavior of gases and as an introduction to the study of individual molecules. Energy and related topics, including the first law of thermodynamics and thermochemistry, are introduced in Chapter 5. In addition to the inherent importance of all these subjects, they provide the basis for understanding the behavior of individual particles, and they are a necessary foundation for beginning laboratory work.

We then turn to the microscopic world. Following introductory chapters on electrons and nuclei (Chapter 6) and the modern interpretation of their behavior (Chapter 7), we take up atomic structure (Chapter 8), molecular structure (Chapter 9), and the interactions of molecules in liquids and solutions (Chapter 10).

The remaining chapters include a study of chemical equilibria (Chapters 12 and 13), equilibria in redox systems (Chapter 14), and the second and third laws of thermodynamics (Chapter 15). The topic of chemical kinetics is explored in Chapter 16; the solid state is covered in Chapter 17.

Descriptive chemistry is extensively developed in six chapters including a general introduction (Chapter 11), which provides a change of pace partway through the chapters on chemical principles, the inorganic chemistry of the main group elements (Chapters 18 and 19) and the transition metals (Chapters 20 and 21), and organic chemistry (Chapter 22). It should also be mentioned that a substantial amount of descriptive chemistry is woven into the preceding chapters on chemical principles in examples of their applications. We conclude with biological chemistry (Chapter 23) and nuclear chemistry (Chapter 24). Appendixes include reference materials, basic mathematics, and concepts from elementary physics.

A word of explanation is in order regarding the treatment of thermodynamics. We believe that a solid grounding in the concept of energy is an im-

portant prelude to the study of atomic and molecular structure, and therefore we have placed the relatively easy first-law topics in an early chapter. The concept of entropy, however, is more difficult for most students, and we find that second- and third-law topics are most easily grasped when the student has first developed an understanding of chemical equilibria.

NEW TO THIS EDITION

Our principal goals in revising this text have been to maintain its accuracy and clarity of exposition, and to bring the material up to date. Although the second edition is comprehensive, covering all important topics in general chemistry in sufficient depth for the student to acquire a working understanding, the book has been kept to a reasonable length so that all the material can be covered at a comfortable pace in a single academic year.

For the most part, only SI units are used, but we also include certain other units that are still widely used in chemistry: the liter and milliliter are used for volume, the atmosphere and torr are most often used as pressure units, and length at the molecular level is typically expressed in ångströms.

In general, the organization of the first edition, which we have found to be a successful one, has been retained. Material on solution stoichiometry has been added to Chapter 2 as an aid to the early use of solutions in laboratory work. The discussion of hybrid orbitals in Chapter 9 has been expanded by including material on hydrocarbons formerly in Chapter 22. The materials of Chapters 10 and 11 have been interchanged so that the introduction to descriptive chemistry can make use of the discussion of liquids and liquid solutions, particularly the concept of electrolytes. In Chapter 16, the sections on rate laws and mechanisms have been expanded substantially. An extensive table of thermodynamic properties of chemical substances is included as a new Appendix F. The more important equations in each chapter are marked in color for emphasis.

The number of problems has been increased by over 60 percent, and the more difficult problems are now marked in color. Brief answers to all problems not requiring a discussion or other extensive material are listed in Appendix H.

SUPPLEMENTARY MATERIALS

A complete *Solutions Manual* is available, showing in detail how to work each problem and answer each question. Of course, students are encouraged to attempt each problem on their own, but this supplement is designed to provide step-by-step assistance where it is needed. An *Instructor's Manual* is also provided, with discussions of the pedagogy of each chapter and sample examination problems.

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to the many persons who have assisted in various ways in shaping this book. The ideas on which the book is based and their manner of presentation have been developed through many discussions with our colleagues and with the students whom we have been privileged to teach.

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Thomas L. Allen
Raymond M. Keefer

PERIODIC TABLE OF THE ELEMENTS

Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII		
1	1.008 H 1									
2	6.941 Li 3	9.012 Be 4								
3	22.99 Na 11	24.31 Mg 12								
4	39.10 K 19	40.08 Ca 20	44.96 Sc 21	47.90 Ti 22	50.94 V 23	52.00 Cr 24	54.94 Mn 25	55.85 Fe 26	58.93 Co 27	58.71 Ni 28
5	85.47 Rb 37	87.62 Sr 38	88.91 Y 39	91.22 Zr 40	92.91 Nb 41	95.94 Mo 42	[97] Tc 43	101.1 Ru 44	102.9 Rh 45	106.4 Pd 46
6	132.9 Cs 55	137.3 Ba 56	* 57-71	178.5 Hf 72	180.9 Ta 73	183.9 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77	195.1 Pt 78
7	[223] Fr 87	226.0 Ra 88	† 89-103	[261] Rf 104	[262] Ha 105	[263] 106				

*	138.9 La 57	140.1 Ce 58	140.9 Pr 59	144.2 Nd 60	[145] Pm 61	150.4 Sm 62	152.0 Eu 63	157.3 Gd 64
†	[227] Ac 89	232.0 Th 90	231.0 Pa 91	238.0 U 92	237.0 Np 93	[244] Pu 94	[243] Am 95	[247] Cm 96

							0
		IIIA	IVA	VA	VIA	VIIA	4.003 He 2
		10.81 B 5	12.01 C 6	14.01 N 7	16.00 O 8	19.00 F 9	20.18 Ne 10
		26.98 Al 13	28.09 Si 14	30.97 P 15	32.06 S 16	35.45 Cl 17	39.95 Ar 18
IB	IIB						
63.54 Cu 29	65.37 Zn 30	69.72 Ga 31	72.59 Ge 32	74.92 As 33	78.96 Se 34	79.90 Br 35	83.80 Kr 36
107.9 Ag 47	112.4 Cd 48	114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54
197.0 Au 79	200.6 Hg 80	204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	[209] Po 84	[210] At 85	[222] Rn 86

158.9 Tb 65	162.5 Dy 66	164.9 Ho 67	167.3 Er 68	168.9 Tm 69	173.0 Yb 70	175.0 Lu 71
[247] Bk 97	[251] Cf 98	[254] Es 99	[257] Fm 100	[258] Md 101	[255] No 102	[256] Lr 103

Atomic Masses

Expressed to four significant figures

Based on the atomic mass of $^{12}C = 12$ exactly

Number in brackets denotes isotope of longest known half-life

Name	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	[227]
Aluminum	Al	13	26.98
Americium	Am	95	[243]
Antimony	Sb	51	121.8
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	[210]
Barium	Ba	56	137.3
Berkelium	Bk	97	[247]
Beryllium	Be	4	9.012
Bismuth	Bi	83	209.0
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.08
Californium	Cf	98	[251]
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	[247]
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	[254]
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	[257]
Fluorine	F	9	19.00
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Hahnium	Ha	105	[262]
Helium	He	2	4.003
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9
Lawrencium	Lr	103	[256]
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	175.0

Name	Symbol	Atomic Number	Atomic Mass
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Mendelevium	Md	101	[258]
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.2
Neon	Ne	10	20.18
Neptunium	Np	93	237.0
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	[255]
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.1
Plutonium	Pu	94	[244]
Polonium	Po	84	[209]
Potassium	K	19	39.10
Praseodymium	Pr	59	140.9
Promethium	Pm	61	[145]
Protactinium	Pa	91	231.0
Radium	Ra	88	226.0
Radon	Rn	86	[222]
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.1
Rutherfordium	Rf	104	[261]
Samarium	Sm	62	150.4
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.9
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.9
Technetium	Tc	43	[97]
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.90
Tungsten	W	74	183.9
Uranium	U	92	238.0
Vanadium	V	23	50.94
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22
(not named as yet)		106	[263]

CONTENTS

Preface xvii

CHAPTER 1 CHEMISTRY AS A SCIENCE 1

1.1 The Study of Chemistry 2
1.2 Heterogeneous Systems and Homogeneous Systems 3
1.3 Substances and Solutions 5
1.4 Compounds and Elements 9
1.5 Isotopes 10
1.6 Macroscopic Forms of Matter 11
1.7 Observation and Interpretation 11
1.8 The Law of Conservation of Mass and the Law of Definite Proportions 12
1.9 The Atomic-Molecular Theory 13
1.10 Induction and Deduction 14
1.11 The Dynamic Character of Chemistry 15
1.12 Measurement and Units 15

CHAPTER 2 ATOMS AND MOLECULES 21

2.1 Atoms and Atomic Masses 22
2.2 The Mole and Avogadro's Number 23
2.3 Molecules, Molecular Masses, and Moles 26
2.4 Composition, Atomic Masses, and Simplest Formulas 30
2.5 Simultaneous Determination of the Simplest Formula and Atomic Masses 32

2.6 Chemical Reactions and Chemical Equations 32
2.7 Nonequivalent Amounts in Chemical Reactions 34
2.8 Solutions and Molarity 37

CHAPTER 3 EXPERIMENTAL STUDIES OF GASES 43

3.1 Physical Properties of Gases 44
3.2 Dependence of Volume on Amount at Constant Temperature and Pressure 45
3.3 Pressure Measurements 46
3.4 Dependence of Volume on Pressure at Constant Temperature and Amount 48
3.5 Gaseous Solutions 50
3.6 Dependence of Volume on Temperature at Constant Pressure and Amount 52
3.7 Volume Relations of Reacting Gases 53
3.8 Simultaneous Determination of Atomic Masses and Molecular Formulas 55
3.9 Experimental Determination of Molecular Masses from Gas Densities 57
3.10 The Ideal or Perfect Gas Equation 58
3.11 Real Gases 61
3.12 Equations of State for Real Gases 61

CHAPTER 4 THE KINETIC MOLECULAR THEORY OF GASES 69

4.1 Pressure Exerted by Molecules Having Speed u 70
4.2 Correction for Molecules Having Different Speeds 73
4.3 Temperature and Average Translational Kinetic Energy 74
4.4 RMS Speed and Graham's Law of Diffusion 76
4.5 Distribution of Molecular Speeds 78
4.6 Real Gases 81

CHAPTER 5 ENERGY CHANGES IN CHEMICAL SYSTEMS 87

5.1 The Concept of Energy 88
5.2 The First Law of Thermodynamics 91
5.3 Heat Capacity 96
5.4 Heat Capacities of Pure Substances 98

5.5 Explanation of Thermodynamic Properties 100
5.6 Enthalpies of Fusion and Enthalpies of Vaporization 103
5.7 Enthalpies of Reaction 104
5.8 Standard Enthalpies of Formation 107
5.9 Calorimetry 110

CHAPTER 6 ELECTRONS AND NUCLEI 117

6.1 General Features of Atomic Structure 118
6.2 Discovery of the Electron 119
6.3 Measurement of the Electronic Charge 124
6.4 Discovery of the Nucleus 127
6.5 Nuclear Charge 130
6.6 Isotopic Mass 134

CHAPTER 7 PARTICLES AND WAVES 141

7.1 Wave Motion 142
7.2 Light Waves 144
7.3 Energy Quanta 147
7.4 Photons 152
7.5 Wave Properties of Electrons 154
7.6 Standing de Broglie Waves for a Particle in a Box 156
7.7 The Heisenberg Uncertainty Principle 158
7.8 Wave Functions and Probability Densities 161

CHAPTER 8 ATOMIC STRUCTURE 165

8.1 Atomic Spectra 166
8.2 The Spectrum of Atomic Hydrogen 168
8.3 Quantum Numbers for the Hydrogen Atom 171
8.4 Description of Hydrogen Atom Orbitals 174
8.5 Electron Spin 178
8.6 The Pauli Exclusion Principle 180
8.7 The Shielding Effect for Many-Electron Atoms 181
8.8 Electron Configurations 184
8.9 The Building-up Principle and the Periodic Law 185
8.10 Electron Correlation 190
8.11 Electron Densities and Atomic Radii 192
8.12 Ionization Potentials and Electron Affinities 194
8.13 Electron-Dot Symbols 196

CHAPTER 9 MOLECULAR STRUCTURE AND CHEMICAL BONDING 201

9.1 Molecular Properties 202
9.2 Simple Ionic Bonding Theory 204
9.3 Internuclear Distances in Ionic Crystals 206
9.4 Bond Energies of Ionic Molecules 207
9.5 Covalent Bonding—Lewis Structures 210
9.6 Violations of the Octet Rule 213
9.7 Donor-Acceptor Bonds and Formal Charge 214
9.8 Covalent Bond Angles and the VSEPR Theory 216
9.9 Covalent Bond Radii 222
9.10 Resonance 223
9.11 Polar Bonds and Electronegativity 224
9.12 Molecules in Electric Fields 230
9.13 Dipole Moments 231
9.14 Molecular Orbitals and Chemical Bonding 235
9.15 Molecular Orbitals in Diatomic Molecules Formed by Like Atoms 238
9.16 Molecular Orbital Description of Diatomic Molecules Formed by Like Atoms 240
9.17 Molecular Orbitals in Diatomic Molecules Formed by Unlike Atoms 244
9.18 Valence Bond Theory 246
9.19 Linear Molecules and *sp* Hybrid Orbitals 246
9.20 Triangular Molecules and sp^2 Hybrid Orbitals 249
9.21 Tetrahedral Molecules and sp^3 Hybrid Orbitals 251

CHAPTER 10 LIQUIDS AND LIQUID SOLUTIONS 259

10.1 Vapor Pressure 260
10.2 Phase Diagrams 263
10.3 Kinetic Molecular Theory of Liquids 265
10.4 Intermolecular Forces 267
10.5 Concentration 271
10.6 Vapor Pressure Lowering 273
10.7 Boiling Point Elevation and Freezing Point Depression 279
10.8 Osmotic Pressure 282
10.9 Solubility of Nonelectrolytes 285
10.10 Electrolytes 286
10.11 Solubility of Electrolytes in Water 290
10.12 Chemical Reactions and Net Reactions 290

CHAPTER 11 THE CHEMICAL ELEMENTS AND THEIR COMPOUNDS 299

11.1 Metals, Metalloids, and Nonmetals 300
11.2 Hydrogen 301
11.3 Acids, Bases, and Salts 306
11.4 The Noble Gases 309
11.5 The Alkali Metals 310
11.6 The Alkaline Earth Metals 311
11.7 The Group IIIA Elements 312
11.8 Carbon—Organic Chemistry 313
11.9 Isomerism 317
11.10 Silicon, Germanium, Tin, and Lead 319
11.11 The Group VA Elements 320
11.12 The Group VIA Elements 322
11.13 The Halogens 324
11.14 The Transition Metals 326

CHAPTER 12 CHEMICAL EQUILIBRIA 333

12.1 Gas Phase Equilibria 334
12.2 Calculation of Equilibrium Concentrations 339
12.3 Conventions Used for Equilibrium Constants 340
12.4 Le Châtelier's Principle 342
12.5 Dissociation of Weak Electrolytes 345
12.6 Heterogeneous Equilibria 348

CHAPTER 13 SIMULTANEOUS EQUILIBRIA 359

13.1 Generalized Systems of Acids and Bases 360
13.2 The Dissociation of Water; Solutions of Strong Acids and Strong Bases 363
13.3 The Concept of pH 365
13.4 Relative Strengths of Acids and Bases 366
13.5 Weak Acids and Bases; Exact Solutions of Equilibrium Problems 368
13.6 Approximations 370
13.7 Salt Solutions 374
13.8 Buffers 377
13.9 Acid-Base Indicators 380
13.10 Acid-Base Titrations 381
13.11 Polyprotic Acids 386
13.12 Sulfide Precipitations 391

13.13 Complex Ions 393
13.14 Use of Acids or Ligands to Dissolve Slightly Soluble Electrolytes 396

CHAPTER 14 ELECTRON-TRANSFER REACTIONS 405

14.1 Oxidation and Reduction 406
14.2 Oxidation States 407
14.3 The Concept of Half-Reactions 410
14.4 Balancing Electron-Transfer Reactions 413
14.5 The Standard Potential of an Electrochemical Cell 418
14.6 Standard Electrode Potentials 421
14.7 The Relative Strength of Oxidizing Agents and Reducing Agents 425
14.8 Effect of Concentration and Pressure on Cell Voltage; Determination of Equilibrium Constants 426
14.9 Primary Cells, Storage Cells, and Fuel Cells 430

CHAPTER 15 THERMODYNAMICS AND CHEMICAL EQUILIBRIA 439

15.1 Temperature Dependence of Vapor Pressures and Equilibrium Constants 440
15.2 Entropy 446
15.3 Entropies of Chemical Substances 447
15.4 Entropy Changes in Spontaneous Irreversible Processes 451
15.5 Heat Engines 454
15.6 Entropy and Probability 456
15.7 The Gibbs Free Energy 458
15.8 Standard Free-Energy Changes 462

CHAPTER 16 CHEMICAL KINETICS 471

16.1 Rate of Reaction 472
16.2 Rate Laws 475
16.3 Method of Initial Rates 477
16.4 Integrated Form of the First-Order Rate Law 478
16.5 Integrated Form of the Second-Order Rate Law 480
16.6 Reaction Rates and Equilibrium 483
16.7 *Effect of Temperature on the Rate Constant* 484
16.8 The Collision Theory of Reaction Rates 488
16.9 The Transition-State Theory 493

16.10 Reaction Mechanisms 494
16.11 Catalysts and Enzymes 501

CHAPTER 17 THE SOLID STATE 509

17.1 Macroscopic Properties of Solids 510
17.2 The Seven Systems of Crystals 513
17.3 X-ray Diffraction 513
17.4 Metallic Crystal Structures 518
17.5 The Metallic Bond 520
17.6 Ionic Crystal Structures 521
17.7 The Born-Haber Cycle 529
17.8 Covalent Network Crystals 531
17.9 Molecular Crystals 531
17.10 Hydrogen-Bonded Crystals 533
17.11 The Free-Electron Theory of Metals 534
17.12 The Electronic Band Theory 539
17.13 Magnetic Properties 540
17.14 Crystal Defects 543

CHAPTER 18 THE ELEMENTS OF GROUPS IA–IVA 549

18.1 The Group IA Elements 551
18.2 The Group IIA Elements 557
18.3 The Group IIIA Elements 562
18.4 The Group IVA Elements 567

CHAPTER 19 THE ELEMENTS OF GROUPS VA–VIIA AND THE NOBLE GASES 577

19.1 The Group VA Elements 578
19.2 The Group VIA Elements 588
19.3 The Group VIIA Elements 598
19.4 The Noble Gases 602

CHAPTER 20 THE TRANSITION METALS—GENERAL ASPECTS 607

20.1 General Features 608
20.2 Natural Occurrence and Separation 610
20.3 Metals 613