general chemistry

principles and modern applications second edition ralph h. petrucçi

COLLIER MACMILLAN INTERNATIONAL EDITIONS

chemistry chemistry chemistry chemistry

AND MODERN APPLICATIONS

SECOND EDITION

MACMILLAN PUBLISHING CO., INC.

New York

COLLIER MACMILLAN PUBLISHERS

London

Copyright © 1977, Ralph H. Petrucci Printed in the United States of America

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the Publisher.

Earlier edition copyright © 1972 by Ralph H. Petrucci.

Macmillan Publishing Co., Inc. 866 Third Avenue, New York, New York 10022

Collier Macmillan Canada, Ltd.

Library of Congress Cataloging in Publication Data

Petrucci, Ralph H
General chemistry: principles and modern applications.

Includes index.

1. Chemistry. I. Title.

QD31.2.P48 1977

540

76-10412

ISBN 0-02-394980-5

Printing: 1 2 3 4 5 6 7 8 9 Year: 7 8 9 0 1 2 3

The first edition of this text was based on certain assumptions about the students who study general chemistry and the courses that have been designed to serve them. These assumptions were apparently shared by many users of the first edition, and they have been adopted again, with some modifications, as the pedagogical basis of the current edition. The modifications are two or three in number.

To me it seems still that most students are interested in the practical applications, social significance, and historical roots of the subject areas they study, as well as in conceptual frameworks and bodies of facts and theories. Of these several aspects, probably the historical background of a subject is the most difficult to pursue successfully in an introductory text of necessarily limited length and scope. The idea that the patterns of thought that underlie modern theory can be traced through their historical development has not been abandoned in this edition, but historical aspects of chemistry have been deemphasized.

Although the typical student of this text is not likely ever to be called upon to pursue the quantitative aspects of chemistry to the extent that current theory permits, additional emphasis has been placed on quantitative subject matter. It is probably still true that students learn best by doing, and this edition provides more opportunities for "doing chemistry." The number of worked-out examples in the text has been more than doubled, as has the number of end-of-chapter exercises. In addition, each of the text examples is keyed to several similar end-of-chapter exercises, and the exercises are grouped according to the major concept illustrated. Answers to more than half of the exercises are provided in Appendix 6, and complete solutions of all exercises are available in a separate *Solutions Manual*. As in the first edition, exercises that are either more difficult



or that require an extension of concepts presented in the text are designated by a bold star *. Also as in the first edition, marginal notes are employed to provide additional background, clarification, or elaboration of ideas introduced in the text.

Despite the fact that chemistry is among the most highly organized and formal of academic disciplines, the approaches to teaching chemistry can be quite varied. I believe that instructors who prefer an approach different from mine will be able to adjust the order in which topics are considered to suit their own preferences. The general format is that of the first edition: consideration first of a number of basic ideas, particularly those related to stoichiometry, followed by a discussion of the structure of matter, and then chemical reactions. Practical applications are given throughout the text, but primary emphasis on

applications is deferred to the later chapters.

Some of the topics that were introduced in the opening chapters of the first edition have been deferred in this edition to later chapters where they can be discussed in full; for example, solution stoichiometry is considered with other topics in solution chemistry instead of with the stoichiometry of chemical reactions, and oxidation-reduction concepts are similarly deferred. The discussion of states of matter has been divided into two chapters—one on gases and one on liquids and solids—and these have been moved forward (Chapters 5 and 6) to provide some background on the observable macroscopic behavior of matter prior to a study of the microscopic structure of matter. Properties of solutions (Chapter 12) are considered after the structure of matter because the theoretical approach involves intermolecular forces. However, some may prefer to consider solutions after the states of matter and before the structure of matter, and this can easily be done. Chemical bonding is covered in two chapters instead of one. The first of the two (Chapter 9) emphasizes Lewis structures, oxidation states, and valence-shell electron-pair repulsion theory; the second (Chapter 10) deals with atomic and molecular orbital theory. Selective study of topics in Chapter 10 should be possible in courses where molecular structure is not strongly emphasized. Another change in organization from the first edition is the inclusion of separate chapters on nuclear chemistry and on coordination chemistry. SI units are introduced in the text but are not used exclusively. Many fields related to chemistry continue to use different systems of units, and it will probably be necessary for students to become familiar with a variety of units for some time to come.

I wish to thank students and instructors alike who used the first edition and offered helpful suggestions. Whatever improvements are to be found in this edition are largely the result of these suggestions. In particular I am grateful to the several individuals who provided critiques of the first edition and/or read parts or all of the manuscript of the second edition: Professors Geoffrey Davies and William E. Cass (Northeastern University); Captain Walter P. Menzies, Jr. (United States Air Force Academy); Professor Michael F. Farona (University of Akron); Professor Gardiner H. Myers (University of Florida); Professor Galen L. Ober (Clarion State College); Professor Kay O. Watkins (Adams State College). I am especially indebted to Professor Davies for his very careful reading of the entire manuscript of this edition and his detailed suggestions for

its improvement, and to my colleague Professor James D. Crum for his continuing counsel. Finally, I am happy to have had the opportunity to work with James L. Smith and Leo Malek of Macmillan Publishing Company; their efforts in the production of this text have been tireless.

The professional assistance of the aforementioned individuals has been invaluable in the preparation of this edition; but the encouragement, forbearance, and sacrifice that have made possible both editions of this text are those of my wife and family. To them I owe the most gratitude of all.

Ralph H. Petrucci

1	Matter—Its Properties and Measurement	1
2	Development of the Atomic Theory	21
3	Chemical Arithmetic I. Elements and Compounds	50
4	Chemical Arithmetic II. Chemical Reactions	68
5	Gases	88
6	Liquids and Solids	123
7	Electrons in Atoms	148
8	Atomic Properties and the Periodic Table	180
9	Chemical Bonding	205
10	Additional Aspects of Covalent Bonding	235
11	Intermolecular Forces and Crystal Structures	253
12	Mixtures	281
13	Thermodynamics and Chemistry	318
14	Chemical Kinetics	345
15	Principles of Chemical Equilibrium	371
16	Acids, Bases, and Ionic Equilibria	391
	·	

contents

			426
1	7	Oxidation-Reduction and Electrochemistry	
11	18 The Chemistry of Selected Representative Elements		456
1	9	The Chemistry of Transition Elements	499
2	0	Complex Ions and Coordination Compounds	518
2	21	Nuclear Chemistry	539
2	2	Organic Structures and Reactions	562
2	3	Chemistry of the Living State	
2	4	The Chemistry of Natural Resources and Man-Made Materials	643
2	5	Chemistry and the Environment	691
appendix	1	Mathematical Operations	719
appendix	2	Some Basic Physical Concepts	725
appendix	3	SI Units	730
appendix	4	On Thermodynamic Calculations	733
appendix	5	Electron Configurations of the Elements	737
appendix	6	Answers to Selected Exercises	740
		Index	755

	1-1	Properties of Matter	2	
	1-2	Classification of Matter	2	
	1-3	The Scientific Method	3	
	1-4	The Need for Measurement	4	
	1-5	The English and Metric Systems of		
		Measurement	5	
	1-6	Density	7	
		Temperature	8	
	1-8	Problem Solving—The Conversion Factor	O	
		Method	10	
	1-9	Significant Figures	14	
		SI Units	16	
		Exercises	17	
	_	language of the Atomic Theory	0.4	
	Deve	lopment of the Atomic Theory	21	
	Deve		21	1.0.20
2		Dalton's Atomic Theory		holictoh
2	2-1	Dalton's Atomic Theory Cathode Rays	21	helisteh
2	2-1 2-2	Dalton's Atomic Theory Cathode Rays Canal Rays (Positive Rays)	21 27	detailed
_	2-1 2-2 2-3	Dalton's Atomic Theory Cathode Rays Canal Rays (Positive Rays) X Rays	21 27 31	
~	2-1 2-2 2-3 2-4 2-5	Dalton's Atomic Theory Cathode Rays Canal Rays (Positive Rays)	21 27 31 33 34	
2	2-1 2-2 2-3 2-4 2-5	Dalton's Atomic Theory Cathode Rays Canal Rays (Positive Rays) X Rays Radioactivity The Nuclear Atom	21 27 31 33 34 35	
2	2-1 2-2 2-3 2-4 2-5 2-6	Dalton's Atomic Theory Cathode Rays Canal Rays (Positive Rays) X Rays Radioactivity	21 27 31 33 34	detailed contents

1

1 Matter—Its Properties and Measurement

	2_0	A Summary of the Proportion of Fundamental	
	2-9	A Summary of the Properties of Fundamental Particles	39
	2-10	Chemical Elements	40
		Atomic Weights	41
		Epilog: Do Atoms Exist?	44
		Exercises	45
3	Cher	mical Arithmetic I: Elements and	
	100	pounds	50
	3-1	Avogadro's Number and the Concept of the Mole	
	3-2	Some Illustrative Examples Using the Mole Concept	50 52
	3-3		54
		Composition of Chemical Compounds	57
	3-5	Formulas and Nomenclature	61
		Exercises	64
4	Chen	nical Arithmetic II: Chemical Reactions	68
	4-1	Experimental Evidence for Chemical Reactions	69
		The Chemical Equation	69
	4-3	8	
	4.4	Equation	74
	4-4	Some Complexities in the Stoichiometry of Chemical Reactions	
		Exercises	77
		LACICISES	82
5	Gase	s	88
		Properties of a Gas	88
		Gas Pressure	89
		The Simple Gas Laws	94
	5-4	The Gas Laws and Development of the Atomic Theory	0.0
	5-5	The Ideal Gas Equation	98
		Molecular Weight Determination	101 105
	5-7	Gases in Chemical Reactions	103
		Mixtures of Gases	108
		The Kinetic Theory of Gases	112
		Nonideal Gases	117
		Exercises	118
6	Liqui	ds and Solids	123
	6-1	Comparison of the States of Matter	123
		Surface Tension	124
	6-3	Specific Heat Capacity and Molar Heat Capacity	127

	6-4	Vaporization	129
	6-5		
		Related Concepts	135
	6-6		137
	6-7	Phase Diagrams	140
		Exercises	143
7	Elect	rons in Atoms	148
	7-1	Electromagnetic Radiation	148
	7-2	Atomic Spectra	153
	7-3	The Photoelectric Effect	155
	7-4	The Quantum Theory	156
	7-5	The Bohr Atom	159
	7-6	Wave-Particle Duality	163
	7-7	The Uncertainty Principle	164
		Wave Mechanics	165
	7-9	Electron Orbitals and Quantum Numbers	168
		Electron "Spin"	170
	7-11	Electron Configurations	171
	7-12	Electron Configurations of the Elements	173
		Exercises	176
8	Aton	nic Properties and the Periodic Table	180
	8-1	On the Idea of Order	180
		Early Attempts to Classify the Elements	181
		Periodic Law and the Periodic Table	182
		A Modern Periodic Table—The Long Form	185
		Electron Configurations and the Periodic Table	187
		Metals and Nonmetals	189
		Atomic Sizes	191
	8-8	Ionization Energy (Ionization Potential)	196
		Electron Affinity	199
		Electronegativity	199
		Magnetic Properties	200
		Exercises	201
9	Cher	mical Bonding	205
	9-1	The Importance of Electrons in Chemical	
	-	Bonding	205
	9-2	Ionic Bonding	208
		Covalent Bonding	211
		Covalent Lewis Structures—Some Examples	212
		Covalent Carbon Compounds	215
		Resonance	216
		Egilure of the Octat Pula	218

Detailed Contents

	9-8	Oxidation States	219
	9-9	Molecular Shapes	222
		Bond Energies and Bond Distances	226
	9-11	Partial Ionic Character of Covalent Bonds	227
		Exercises	231
10	Addi	tional Aspects of Covalent Bonding	235
	10-1	Formation of the Covalent Bond	235
	10-2	The Valence-Bond Method	237
		Hybridization of Orbitals	240
		Multiple Covalent Bonds	244
	10-5	Molecular Orbital Theory	247
		Exercises	251
11	Inter	molecular Forces and Crystal	
	Struc	ctures	253
	11-1	Condensed States of the Noble Gases	253
	11-2	van der Waals Forces	254
	11-3	Hydrogen Bonds	257
		Network Covalent Solids	259
		The Ionic Bond as an Intermolecular Force	261
		Bonding in Metals	263
		Crystal Structures	266 272
	11-8	Ionic Crystal Structures Exercises	277
12	Mixt		281
			281
		Homogeneous and Heterogeneous Mixtures	285
		Solution Concentration Some Illustrative Examples Utilizing Solution	203
	12-3	Concentrations	287
	12-4	Solubility Equilibrium	294
		Colligative Properties	297
		Theory of Electrolytic Dissociation	304
		Interionic Attractions	308
	12-8	Colloidal Mixtures	309
		Exercises	313
13	Ther	modynamics and Chemistry	318
	13-1	Some Terminology	318
	13-2		319
	13-3		321
	13-4	1 0	324
	13-5		325
	13-6	Bond Energies and Heats of Reactions	327

	13-7	Failure of the First Law of Thermodynamics as	
		a Criterion for Spontaneous Change	328
	13-8	IIIIII da / IIIIII do	330
	13-9	Applications of the Second Law	332
	13-1	0 Free Energy	335
	13-1	1 The Third Law of Thermodynamics	340
		Exercises	340
14	Che	mical Kinetics	345
	14-1		345
	14-2	The Rates of Chemical Reactions	348
	14-3	The Rate Law for Chemical Reactions	354
	14-4	More on the Collision Theory	360
		Catalysis More on Brentine M. I.	363
	14-0	More on Reaction Mechanisms Exercises	366
		Exercises	367
15	Prin	ciples of Chemical Equilibrium	371
	15-1	The Condition of Chemical Equilibrium	371
		Illustrative Examples	374
	15-3	8 1 Et Chatcher's	
	15-4	Principle Some Equilibria of Landau	378
	15-5	The state of the s	381
	13-3	Some Theoretical Aspects of Equilibrium Exercises	383
_		DACT CISES	386
16	Acid	s, Bases, and Ionic Equilibria	391
		Acid-Base Theories	391
	16-2	or water	394
	16-3	8	395
	16-4	I amount I amount I	396
		Weak Acids and Bases Hydrolysis	399
		Neutralization Reactions	406
	16-8	Solubility Equilibrium of Slightly Soluble Solids	408
		Precipitation of Metal Sulfides	413
		Predicting Ionic Reactions in Solution	417 419
		Exercises Exercises	419
17	Oxida	ation-Reduction and Electrochemistry	426
	17-1	Oxidation-Reduction: Some Definitions	
	17-2	Measurement of Oxidation and Reduction	426
		Tendencies	428
	17-3	A New Criterion for Spontaneous Change	431

	17-4 17-5 17-6 17-7 17-8 17-9	Electrical Work and Free Energy Change	434 437 441 444 445 446 451
18		Chemistry of Selected Representative	450
	Elem	nents	456
	18-1	The Alkali (IA) and Alkaline Earth (IIA) Metals	456
	18-2	Boron and Aluminum	462
	18-3	The Halogen Elements (VIIA)	466
	18-4	Oxygen	472
	18-5 18-6	Sulfur Silicon	476
	18-7		482 485
	18-8	Additional Aspects of Nitrogen Chemistry	488
	18-9	Additional Aspects of Phosphorus Chemistry	490
		Exercises	495
19	The	Chemistry of Transition Elements	499
	19-1	Some Properties of the Transition Elements	499
	19-2	Some Aspects of the Chemistry of Chromium	501
	19-3	Some Aspects of the Chemistry of the Iron Triad Elements	
	19-4		504 510
		The Lanthanide Elements	510
	19-6	The Actinide Elements	515
		Exercises	516
20	Com	plex Ions and Coordination Compounds	518
	20-1	Werner's Theory	518
		Bonding in Complex Ions—Valence Bond Theory	519
	20-3	The Coordination Number	520
	20-4	Ligands	521
	20-5	Nomenclature	522
	20-6	Geometrical Isomerism in Complex Ions	523
	20-7	Inner- and Outer-Orbital Complexes	524
	20-8 20-9	Bonding in Complex Ions—Crystal Field Theory	525
		Color of Complex Ions Equilibria Involving Complex Ions	527
		Equilibria Involving Complex Ions Applications of Coordination Chemistry	528
	4 0-11	Exercises	531 536

21	Nucl	ear Chemistry	539
	21-3 21-4 21-5 21-6 21-7 21-8 21-9	Nuclear Stability Naturally Occurring Radioactive Nuclides Nuclear Reactions and Artificial Radioactivity Transuranium Elements Rate of Radioactive Decay Effect of Radiation on Matter Energetics of Nuclear Reactions Nuclear Fission Nuclear Fusion Applications of Radioisotopes Exercises	539 541 542 543 545 547 551 552 556 557 559
22	Orga	nic Structures and Reactions	562
	22-4 22-5 22-6 22-7 22-8 22-9	The Nature of Organic Compounds and Structures Alkanes Alkenes and Alkynes Aromatic Hydrocarbons Alcohols, Phenols, and Ethers Aldehydes and Ketones Carboxylic Acids and Their Derivatives Amines Heterocyclic Compounds The Synthesis of Organic Compounds Exercises	563 569 575 580 585 588 590 593 594 596 597
23	Chen	nistry of the Living State	602
	23-3 23-4	Structure and Composition of the Cell Principal Constituents of the Cell Biochemical Reactivity Some Additional Natural Products of Interest The Nucleic Acids Exercises	602 604 623 632 633 640
24		Chemistry of Natural Resources and	643
	24-1 24-2 24-3 24-4 24-5 24-6 24-7 24-8	Occurrence of the Elements The Atmosphere as a Natural Resource The Oceans as a Natural Resource Metals Some Raw Materials for the Inorganic Chemical Industry Raw Materials for the Organic Chemical Industry Polymers Energy as a Natural Resource Exercises	644 645 649 651 663 670 676 680 686

25	Chem	nistry and the Environment	691
	25-4	The Atmosphere and Its Pollution The Water Environment Water Pollution Solid Wastes Pesticides Exercises	692 700 705 712 713 715
Ap	per	ndixes	
1	Math	nematical Operations	719
	A1-3	Exponential Arithmetic Logarithms Algebraic Operations Graphs	719 720 721 722
2	Som	e Basic Physical Concepts	725
	A2-2 A2-3 A2-4 A2-5 A2-6	Velocity and Acceleration Force and Work Energy Magnetism Static Electricity Current Electricity Electromagnetism	725 726 726 727 727 728 729
3	SI U	nits	730
	A3-2 A3-3 A3-4	SI Base Units SI Prefixes Derived SI Units Units to Be Discouraged or Abandoned Fundamental Constants	730 731 731 732 732
4	On T	Thermodynamic Calculations	733
5	Elec	tron Configurations of the Elements	737
6	Ansv	wers to Selected Exercises	740
Ind	ex		755

matter—its properties and measurement

Interaction with the environment is crucial to human existence. At the most elementary level this means breathing air and consuming food to maintain metabolism, a process in which one set of materials is transformed into another. The most basic and all-inclusive definition of chemistry is the study of the transformations of matter. Principles of chemistry are fundamental to an understanding of all processes of the living state, as we shall discover in due course.

A powerful agent for effecting chemical transformations discovered in ancient times was fire, which made possible the cooking of food, the baking of pottery, the manufacture of glass, and the smelting of ores to produce metals—first copper, and then lead, tin, and iron. Among other chemical processes discovered long ago were the making of butter, cheese, wine, beer, and soap; the tanning of hides; and the dyeing of fabrics.

Despite these many early applications, an understanding of the principles of chemistry has developed only in recent times, principally in the nineteenth and twentieth centuries. And it is from this theoretical base that the profound changes we are now able to effect on the environment have arisen. For example, as basic knowledge of the field of organic chemistry has grown, more and more ways have been found to exploit the natural resource, petroleum, not only as a source of fuels but also for the production of plastics, drugs, and pesticides.